Historical and Philosophical Remarks on Ziegler-Natta Catalysts

A Discourse on Industrial Catalysis

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Abstract: Part 1 outlines the complex, parallel historical evolution of Ziegler-Natta catalysts and related problems. In Part 2, as a general method of inquiry, chemical language and discourse are analyzed, at first to clarify chemists' epistemic views and the ontological status of catalysts. After analyzing contrasting definitions of 'catalyst' and the chemical properties of catalysts, a suitable metaphor is suggested for catalytic activity, and then 'applied' to different cases of industrial catalysis (incl. Ziegler-Natta). The last two sections deal with intellectual attitudes to industrial catalysis and the makeup of industrial catalysis as academic discipline. In conclusion, I suggest that references to the economic level of reality (the industrial production) serve both a better understanding of the microscopic level of reality (the chemical process), and a higher status at the social level of reality (the chemical community).

Keywords: *Ziegler-Natta catalysts, industrial catalysis, chemical discourse*

Introduction

Without any doubt, the works on the polymerization of olefins by Karl Ziegler in Germany and by Giulio Natta in Italy had a striking impact on the academic and scientific role of macromolecular chemistry as discipline, and on the great development of polymer industry. On their own, since 1955 Ziegler-Natta catalysts have been the object of an enormous quantity of chemical studies, both of basic and applied research. The case of Ziegler-Natta catalysts is almost perfect for a study of many philosophical aspects of industrial catalysis. The quasi-perfection of the case derives from the long-term perspective offered by their industrial application; from their intrinsic complication; from the exceptional features of the products; and finally from their economic and scientific relevance, testified by the continuous flow of research on their constitution and mode of action. At any rate, the following historical sketch and philosophical remarks will be focused only on stereospecific polymerization, because in this case the performance of catalysts is at the highest degree of complexity.

In the first part of the present essay, the history of Ziegler-Natta catalysts will be presented in a minimal form, with a choice of topics and argumentation aimed to give an acceptable description of the complex, parallel evolution of the catalysts themselves, and of the problems connected to them. In the second part of the essay, the discourse will proceed with a more philosophical *allure*. As a general method of inquiry, I will analyze chemical language and chemical discourse,[1] in order to make clear which actual epistemology is used by chemists, and what is the ontological status of catalysts. I may add that my philosophical inquiry does not need any sophisticated preliminary notion, because it is almost a common sense reflection on chemistry. Anyway, after a discussion of several contrasting definitions of 'catalyst'[2], and an analysis of the catalysts chemical properties, I will venture to propose a suitable metaphor for the catalytic activity of a material. Afterwards, the metaphor will be 'applied' to different reactions of the olefins, in order to illustrate some critical features of industrial catalysts (including the Ziegler-Natta catalysts). In the last two sections, I will regard

intellectual attitudes to industrial catalysis, and, eventually, conclude with a glance on the makeup of industrial catalysis as an academic discipline.

1. Historical Sketch

1.1 Cameo portraits

It is impossible in few lines to give realistic portraits of two scientists as Karl Ziegler [3] and Giulio Natta [4], so I will outline only the essential traits which permits a better understanding of their role in the history of stereospecific polymerization [5]. Table 1 shows the principal dates of the academic careers of Ziegler and Natta, whose similar cadence has yet been stressed (McMillan 1979, pp. 50-52). At the end of the Second World War, both researchers had an impressive record of achievements.

Before 1945 Ziegler had obtained important results in several connected fields: free-radicals chemistry (1923-35); polymerization of butadiene by alkali metals (1928-34); new synthesis of organolithium compounds (1930); large-ring compounds, dilution principle (1933); synthesis of cantharidine and ascaridole (1942-4). The last theme of research (developed during the war!) was originated by his interest in many-members rings; not only synthesized Ziegler the two natural compounds, he also developed two reactions of broad utility, allylic bromination with N-bromosuccinimide and 1,4-addition of oxygen to 1,3-dienes (Elsch 1983, p. 1011). The obvious comment on this type of scientific interests is that Ziegler was fundamentally an organic chemist of the classical German school. It can be added that, as a German professor, his Institute was practically an extension of himself (McMillan 1979, p. 62).

| Karl Ziegler (1898-1973)		Giulio Natta (1903-1979)	
1898	Birth near Kassel, Germany	1903	Birth in Porto Maurizio, Liguria, Italy
1920	Doctorate in chemistry, Marburg	1924	*Laurea in chemical engineering, Milan Polytechnic*
1923	*Privatdocent, appointment as a lecturer*	1925	Appointed as lecturer (*professore incaricato*)
1927	Professor of chemistry, Heidelberg	1927	*Libero docente*
		1932	Grant for studying the techniques of electron interference (H. Seemann, Freiburg); acquaintance with H. Staudinger
		1933	Chair of General Chemistry, Pavia
		1935	Professor of Physical Chemistry, Rome
1936	Head of the Department of Chemistry, Halle	1937	Professor of Industrial Chemistry, Turin
		1939	Professor of Industrial Chemistry, Milan
1943	Successor of Franz Fischer as director of K.-W.-Institut für Kohlenforschung, Mülheim		
1963	Nobel prize	1963	Nobel prize
1973	Death, Mülheim	1979	Death, Milan

If we follow an analogous 'biographical' scheme for Natta, we see that his principal achievements until 1945 were essentially in industrial catalysis: industrial synthesis of methanol (1928, with Montecatini); industrial synthesis of formaldehyde and its polymerization (1932, with Montecatini); synthesis of butadiene from alcohol and its separation from butenes (1942, with Pirelli); oxosynthesis (1945, with BDP). A couple of comments may be useful. In his researches as student, Natta worked on X-ray structure determination, and his first industrial synthesis was the result of a careful study of the relationship between the crystal structure of the catalytic oxides and their activity. The second noteworthy point is Natta's continuous connection with the most important Italian chemical companies. His success as industrial chemist was so evident that already in 1938 he was considered the most important Italian chemist, at least concerning the autarchy research policy. From that point of view, the contrast between the research fields Ziegler and Natta during the war is strident; while Ziegler worked on an antihelminthic (ascaridole), Natta worked on the intermediates of the synthesis of Buna.

1.2 A meeting in Frankfurt, and its consequences

As it is well known, the way that led to stereopolymers has its starting point in the field of metallorganic chemistry studied by Ziegler. Here I give only a cursory narrative of the most noteworthy events of the six years running from 1949 until 1954. In 1949, Ziegler and Gellert found that 1-butene was formed from ethylene in contact with ethyllithium. The crucial observation was actually made during attempts at purifying ethyllithium. Purification was unsuccessful because the compound decomposed into lithium hydride, ethylene, and higher α-olefins. This observation led the two chemists to discover the "stepwise organometallic synthesis" (*stufenweise metallorganische Synthese*), occurring when ethyllithium or its homologous were heated with ethylene under pressure:

$$C_nH_{2n+1}–Li + C_2H_4 \rightarrow C_nH_{2n+1}–CH_2–CH_2–Li \qquad (1)$$
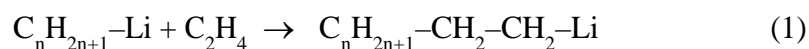
In addition, the decomposition of lithium alkyls into olefins and lithium hydride was interesting. Given the reaction:

$$C_nH_{2n+1}–Li \rightarrow C_nH_{2n} + LiH$$
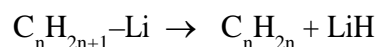
"[N]othing more was necessary but to write the arrow […] as a double arrow of an equilibrium in order to come to the conclusion that the predicted catalysis of the oligomerization of ethylene by lithium hydride should exist". However, the high-melting LiH was too stable; a new starting substance was looked for, and it was found in $LiAlH_4$ (discovered in 1947). With this compound "the whole thing worked quite nicely", but Ziegler was astonished when discovering 'growth' reactions (1) also in the field of aluminum chemistry (Ziegler 1968, p. 6).

Ziegler considered the so-called *Aufbau* reaction an important discovery, and he was diligent in publishing and patenting the results. The international chemical community was not at all excited, however. Eventually something happened when Ziegler gave a lecture at a meeting of the Gesellschaft Deutscher Chemiker in Frankfurt (19 May 1952). Among the audience, there were Natta and his assistant, Piero Pino, an organic chemist. While the lecture did not cause any general stir, Natta and Pino were stirred. Since Natta's research budget was tight, he convinced Giustiniani, an important Montecatini manager, to invite Ziegler to Milan. At the Milan meeting an agreement was signed, whereby Montecatini purchased rights for industrial developments of Ziegler's discoveries in Italy, and Natta obtained access to Ziegler's studies, in a field badly defined as "transformation of olefins" (McMillan 1979, p. 54). As a consequence of the agreement, Italian chemists would work in Mülheim, so that in February 1953 three young researchers arrived at Ziegler's institute.

Since the end of 1952, a doctoral candidate, Holzkamp, has been working on growth reaction with ethylene and ethylaluminum in a steel pressure vessel (100°C, 100 atm). In a routine experiment he was surprised to get almost only 1-butene very fast. After a "strenuous investigation" (Ziegler 1968, p. 11) Holzkamp discovered that the catalytic effect was due to nickel present in the reaction vessel. A systematic search for substances having effects similar to nickel began. In June 1953, they investigated chromium, whose compounds gave some butene but also a small amount of material with high molecular weight. This result was encouraging. At the end of October, Breil, another of Ziegler's collaborators, came to zirconium: a rapid and complete polymerization occurred. Moreover, the infrared spectra demonstrated that the polymer was *linear*. When the turn of titanium came up, the result was again striking. The

reaction was so fast that the vessel became hot, and the product was partially decomposed. Thus, the problem was passed to Heinz Martin, who was looking for the mildest possible conditions of polymerization. Since it was apparent that the system Ti/Al-alkyl was very active, Martin tried the simplest possible conditions: no higher pressure at all and no external heating (Ziegler *et al.* 1955b, 543-544). The result of the trial was that Martin burst in Ziegler's office waving a glass flask and crying: "*Es geht in Glass!"* (McMillan 1979, p. 67).[6]

In Milan, Natta was constantly informed about Ziegler's progress by his young researchers, but he and his principal collaborator, Piero Pino, were more interested in synthetic rubber than in plastic, so propylene was the monomer of election. On 11 March 1954, Paolo Chini fractionated the reaction product by boiling solvent extraction. He obtained three fractions, the last of which was a highly crystalline, high melting, white powder. The very next day Paolo Corradini obtained a diffraction pattern from a sample stretched to five times its length, and the pattern confirmed a high degree of crystallinity (Pino & Moretti 1987, p. 689; McMillan 1979, p. 96). The most extraordinary aspect of the new polymer went to light when "the X-ray diffraction spectra were satisfactorily interpreted assuming that all the asymmetric carbon atoms of the main chain had, at least for long chain sections, the same steric configuration" (Pino & Moretti, *loc. cit.*).

In Mülheim laboratory, the attention remained concentrated for a while on ethylene polymerization (a topic of enormous economic relevance), and in Milan laboratory the research was focused on the polymerization of various monomers, including styrene. In the following months Natta's laboratory was very busy, as we can read in a personal account by Pino (*ibid.*). Since June many patents were filed, and in December 1954, Natta presented the principal results at the Accademia dei Lincei in Rome, and sent a short letter to the *Journal of the American Chemical Society*. The letter was published in the 20 March 1955 issue of the American journal; the unexpected result of stereoregularity was stressed and a new, relevant term was coined: "We propose to designate as 'isotactical chains' […] the polymer chains having such exceptionally regular structure, containing series of asymmetric carbon atoms with the same steric configuration" (Natta *et al.* 1955, p. 1709). However, a few scientists had yet received the pre-print from Milan. P. Flory wrote Natta a letter (dated 21 January 1955) in which we can read: "The results disclosed in your manuscript are of extraordinary interest; perhaps one should call them revolutionary in significance. The possibilities opened up by such asymmetric polymerizations are of the utmost importance, I am sure" (Pino & Moretti 1987, p. 683).

Probably Ziegler was shocked and hurt by the flow of discoveries, papers and patents from Milan, but his reaction was slow (Ziegler *et al.* 1955a; arrived at the *Angewandte Chemie* on 21 July 1955), and only in September 1955 the new process of polyethylene synthesis was fully described (Ziegler *et al.* 1955b).

1.3 Four or more generations of catalysts for α-olefins polymerization

The history of industrial Ziegler-Natta catalysts covers more than four decades, and since many years it is usual to speak about their evolution in terms of 'generations': three for Tait (1986), Goodall (1986), Whiteley *et al.* (1992, p. 520), five for Galli (1995, p. 25), six for Schlüter (1999, p. 130). I have adopted the same scheme (see Table 2), with the obvious reservation that the dates reported for the beginning of each generation are only approximate, and that there is usually a more or less extended overlap between the generations.[7]

		Innovation			Result			Disciplinary Makeup[8]
		Catalyst	Cocatalyst	Support	Activity	Stereo selectivity	Morphology	
First generation	1957	TiCl$_3$ purple phases	AlEt$_2$Cl			+		Crystal structure analysis
Third component	1964		Lewis bases added		–	+		Co-ordination chemistry

Second generation	1973	TiCl$_3$ purple phases at lower temperature			+				Solid state
Third generation	1980			Activated MgCl$_2$	++		+		Solid state Materials science
Fourth generation	1991	Al-oxane activated metallocene complexes		Silica gel		+	(−)		Co-ordination chemistry

Table 2: Four generations of catalysts for α -olefins polymerization

The first commercial catalysts resulted from the industrial extension of Natta's pioneering work on the relationship between the crystal structure of titanium chlorides and the overall activity and selectivity of the catalysts. Natta and his collaborators discovered that TiCl$_3$ was more stereoselective and that only three structural modifications, out of the four possible ones for TiCl$_3$, were highly stereoselective. The active modifications (named α, γ, δ) had a deep purple color and a layer lattice structure, whereas β-TiCl$_3$ was brown and had a chain like structure. It is to be stressed that Natta had on the TiCl$_4$/TiCl$_3$problem the same epistemological position, which had led him to study the crystal structure of methanol catalysts thirty years before. Another important feature of the first generation catalysts was the use of diethylaluminum as cocatalyst. In Table 3, I have emphasized the contrast between activity and stereoselectivity for the three ethylaluminum derivatives, which could be present in the catalytic material.

Cocatalyst	Activity	Stereoselectivity
AlEt$_3$	++	+
AlEt$_2$Cl	+	++
AlEtCl$_2$	Inert	

Table 3: Micro-dialectics between activity and stereoselectivity

Since 1964 a Lewis base was added to the catalyst, essentially in order to improve the stereoregularity of polymers. Probably Montecatini took the first patent for a catalytic system composed of TiCl$_3$/AlEt$_3$ and pyridine (Tait 1986, p. 218). The addition of a Lewis base was a typical 'chemical move', based on knowledge from coordination chemistry. However, the higher stereospecificity did not correspond to a similar increase in activity (Crespi & Luciani 1981, p. 459). Thus, a variety of complexing agents have been tried, and "most commercial companies have their own particular *recipe* for catalyst modification with Lewis bases" (Tait 1986, p. 216; my italics [9]). A real progress was obtained only later, when Solvay introduced the second-generation catalysts. In this case, the crucial move towards increasing activity was made following a solid state chemistry procedure: the transformation of the brown β-TiCl$_3$ into the stereoselective δ-TiCl$_3$ at low temperature (<100 °C) in presence of TiCl$_4$, which acts as a catalyst (!) for the change of phase. The lowering of temperature from 160-200 to 65 °C prevented the catalyst particles from growing (Goodall 1986, p. 194). This type of innovation increased the activity of catalysts by a factor of 5, and its stereospecificity too, so that the removal of the atactic fraction from the final product was spared. It is important to stress that the success of the catalyst of the second generation was due to the new *morphology* of the catalyst particles. They were smaller, and because of a pre-treatment with ether (for extracting AlCl$_3$), they had a porous and weakly bonded matrix.

The morphology of the Ziegler-Natta catalyst particles is a very sensitive topic from the industrial point of view (as well as from the philosophical one [10]). In fact, the morphological properties of the resulting polymer particles depend on those of the catalyst particles. It is a real process of *replica*: a spherical catalyst particle provides a (much larger) spherical polymer particle (Galli *et al.* 1981).

The prehistory of the third generation began in 1960, when Shell patented a catalyst for propylene polymerization that used $TiCl_4$ supported on $MgCl_2$. A decisive progress was achieved in 1968, when Montecatini and Mitsui independently patented catalysts prepared from $TiCl_4$, $MgCl_2$ and an electron donor, and activated by a mixture of trialkyl-Al with another electron donor. Industrial plants based on this type of catalysts went on stream at the beginning of the 1980s. The actual preparation of the catalysts is complex, and the same use of a support gives a decisive role to materials science, a role enhanced by the crucial discovery of the process of replica by Galli. The third generation of catalysts brought a 50-fold increase of activity, so that the *removal* of the residual catalyst from the final product was no more necessary.

The fourth generation of catalysts, based on metallocene compounds, is now evolving towards an industrial success. Their origin is very interesting, because it was 'accidental'. Kaminsky has described the incident with these words: "An accident in our laboratory in 1976 brought about equimolecular amounts of water into the system compared to the trimethylaluminum, and, surprisingly, an unusual high polymerization activity of ethylene was observed" (Kaminsky 1986, p. 257). Kaminsky and Sinn suspected the formation of methyl aluminoxane (MAO), and, on following their conjecture, they discovered that MAO-activated *homogeneous* metallocene catalysts were capable of polymerizing propene and higher olefins (Brintzinger *et al.* 1995, p. 1146). In a review on the most promising developments of chiral metallocene catalysts, an important group of researchers wrote: "In the evolution of Ziegler-Natta catalysts, an *empirical* approach has proven highly successful", but they (and many other scientists) felt that the discovery by Kaminsky and Sinn offered a unique occasion in the search for a single-site catalyst.[11] Additionally it requires the "application of *rational* conceptual models to the design of new metallocene structures and catalyst activators".[12] However, just the morphology of the polymeric product had demanded a deviation from this completely 'rational' route. In fact "[p]ractical application of metallocene catalysts requires their preadsorption on solid supports such as alumina or silica gels", so "[d]etailed guidelines have been developed for the selection of supports", and "advanced *protocols*" have been proposed (Brintzinger *et al.* 1995, pp. 1143, 1163; my italics). It seems to me that these 'protocols' are not too far from the preceding 'recipes', as it may be read in the same above quoted text.[13]

I conclude the historical profile of the evolution of Ziegler-Natta catalysts with a note on the development of the reactor granule technology. In the words of one of the creators of this technology, the new catalysts "have disclosed a **new dimension** in catalysis: the domain of the polymer's shape and morphology. It is this control of the **architecture** or three dimensional structure of the catalyst that has enabled the polymerization reaction not only to reproduce the shape of the catalyst […], but also to generate a solid particle with a controlled reproducible porosity" (Galli 1995, p. 19; bold type in the original text). The metaphor of the *reactor granule* is revealing a new understanding and will-to-control of the polymerization reaction, whose practical result is "opening the way to the creation of new and completely revolutionary families of materials" (*ibid.*, p. 25). Other important authors have spoken of "*microreactors* […] *fabricated* by immobilizing different types of single-site metallocene catalysts" (Brintzinger *et al.* 1995, p. 1164; my italics), or have described "*molecularly engineered* mordenite that acts as a shape-constraining '*molecular reactor*'" (Cusumano 1995, p. 962). Thus, it is not surprising that this type of "catalyst particle *microreactor*" has been studied in considerable details, because "each particle can be regarded as an expanding microreactor *with its own energy and material balance*" (Tait *et al.* 1995, pp. 133-4; my italics).[14] The metaphor of the reactor granule 'moves' the 'chemical reactor' reference from the macroscopic world of engineers to the meso-world of materials scientists.

2. Philosophical Remarks

2.1 Classical chemistry, increasing complexity

The history of the discovery of Ziegler-Natta catalysts shows a remarkable mixing of classical chemical procedures and new physical techniques. It was an attempted *purification* of ethyllithium, which led Ziegler and Gellert to the discovery of the *stufenweise metallorganische Synthese*, or growth reaction. The high activity of $LiAlH_4$ rouse Ziegler's curiosity, whether the active metal is lithium or aluminum; this led him to prepare and test aluminum alkyls, and this was the first real breakthrough. It followed the most

classical event of classical chemistry: the *fortuitous encounter* with the unexpected chemical activity of a substance (the *Nickeleffekt*). At this point, Ziegler applied the strategy of Alwin Mittasch' seminal research on ammonia catalysts, *i.e.* the work is continued by methodical inspection of the periodical system ("*mit der systematischen Durchmusterung*[15] *des Periodensystem*", Ziegler *et al.* 1955b, p. 543). However, in this classical chemistry context, it was a *spectroscopic property* of the product that inflated the excitation in Mülheim laboratory: the linearity of the new polymer recognized because the methyl absorption band was missing ("*die Methyl-Spitze fehlt!*", Ziegler *et al.* 1955b, p. 545).

In Natta's laboratory, a similar mixture of attitudes was at work. On the one hand the first sample of crystalline polypropylene was obtained by *extraction* with boiling solvents, "a fractionation method little used in Polymer Science at that time as it is not efficient in fractionating polymers having similar structure, according to their molecular weight", but which "was adopted in Natta's laboratory from 1953 to separate the low molecular weight products from the solid hydrocarbons in the mixtures obtained on polymerizing ethylene with aluminum alkyls" (Pino & Moretti 1987, p. 689). In his personal account Pino speaks also of "some fortuitous events", *e.g.* "the solvent chosen for the fractionation of the polymers happened to be extremely selective" (*ibid.*, 689-690). On the other hand, since his original training as chemical engineer Natta had used the most advanced physical techniques, and it was the *X-ray structure determination* by Corradini which gave a firm foundation to the discovery of stereopolymers, "revolutionary in significance" in Flory's words.

Reaction	Product	Catalyst	Cocatalyst	Researcher
Growth reaction	Oligomers	$AlEt_3$	–	Ziegler
Ethylene polymerization	Linear polymers	$AlEt_3$	Transition metal compounds	Ziegler
Propylene polymerization	Stereopolymers	Transition metal compounds	$AlEt_3$	Natta

Table 4: Increasing complexity

When we consider the long history of Ziegler-Natta catalysts, probably the most important remark is that it is the narrative of an increasing complexity of the catalytic material. Table 4 refers again to the laboratory context; there I have collected the essential features of the three 'steps' from the discovery of the growth reaction to that of the propylene polymerization. We see two parallel processes of increasing complexity, one of the products and the other of the catalysts. The *linear* and *stereo*-polymers were a completely new type of molecules, and a result of unusual catalysts. It is to be noted that, while Ziegler referred to the nickel and titanium compounds as cocatalyst, Natta considered the transition metal compounds as catalysts, and the organometal compounds as cocatalyst. This lexical and semantic shift was not at all casual, if we look at the scientific background of the two scientists.

Let us now change the context from laboratory to industrial plant, and regard again the long industrial evolution of Ziegler-Natta catalysts in Table 2. The innovations of the first generation, the introduction of the third component, and the second generation principally aimed at the *control* of the process in order to improve the molecular quality of the product, *i.e.* its stereoregularity, with a bonus for catalyst activity in the second generation. The catalysts of the third generation gained in complexity with the use of *activated* $MgCl_2$, and the control of the process was extended to the non-molecular realm of the *polymer morphology*. By then the catalytic system included a catalyst, a cocatalyst, additional internal and external electron donors, and an active support. The laboratory development of chiral metallocene catalysts originated the hope of a 'simplified' industrial application of the fourth generation catalysts, but the meso-world of polymer morphology has demanded the use of a support, with the ensuing entanglement.

Finally, from the epistemological viewpoint, the developments towards the 'reactor granule' appear exciting, because they seem to be the consequence of a new holistic approach to catalysis. However, these 'fabricated microreactors' would deserve an additional analysis, which probably should consider the parallel developments in supramolecular chemistry.

2.2 Catalysts – substances or materials?

Philosophy is essentially a language game, so it may be opportune to analyze the meaning attributed to 'catalyst', the most important (or frequent) term in the present paper. We may begin with a formal, dictionary definition of 'catalyst': "Catalyst: any substance of which a small proportion notably affects the rate of a chemical reaction without itself being consumed or undergoing a chemical change" (Lewis 1993, p. 231). This is essentially Ostwald's famous definition, and the (linguistic) theme of the proposition suggests that a catalyst is a *substance*, a term which in modern chemistry has a precise meaning: "Substance: any chemical element or compound. All substances are characterized by a unique and identical constitution and are homogeneous" (*ibid.*, p. 1098).

Considering the authors whom I read for the present paper, a small list of similar, more or less formal definitions may be presented in chronological order. Benson (1976, p. 6) wrote, "Catalysts may be looked upon as substances that perturb the populations of chemical intermediates"[16]. Mills & Cusumano (1979, p. 16) wrote about "an unusual class of substances known as catalysts"; in the context of a book for chemical engineers Satterfield (1980, p. 8) emphasized the term: "A catalyst is defined as a *substance*; the acceleration of a rate by an energy-transfer is not regarded as catalysis by this definition". A few years later, in a volume of the *Ullmann's Encyclopedia*, Farkas (1986, p. 314) stated that: "Catalysis is the acceleration of a chemical reaction by a small quantity of substance, the catalyst, the amount and nature of which remain essentially unchanged during the reaction".

At that time, in my small collection of definitions the key term for 'catalyst' shifted from *substance* to *material*, *i.e.* from a term that has a precise meaning to another term, which is a "nonspecific term used with various shades of meanings in the technical literature". Obviously there are many 'intermediate' definitions; I report only one of this type, which will be recalled in the following discussion on *catalyticity [17]: "A catalyst is a substance, or a *mixture* of substances, which increases the rate of a chemical reaction by providing an alternative, quicker reaction path, without modifying the thermodynamic factors" (Cavani & Trifirò 1994, p. 11, my italics). Anyway, later in their text, Cavani and Trifirò write: "A catalyst used in heterogeneous catalysis is a composite material" (*ibid.*, p. 13). A few other quotations may give an idea of the new linguistic fashion.

Rabo (1993, p. 2) defines 'catalyst' in these terms: "a foreign material [which] can greatly accelerate chemical reactions without itself change (ultimately) in the process". According to Cusumano (1994, p. 962) certain "selective oxidation catalysts" are "materials [which] can now be used for the peroxide oxidative conversion of large and bulky organic molecules", and in the same page he discusses several examples taken out from "a new arsenal of safe, selective materials for acid catalysis". Maxwell (1996, pp. 2, 5) speaks of "new catalytic processes in the refining area based on novel shape selective microporous materials", and states that "new materials are also finding application in the area of catalysis related to the chemical industry". Maxwell was speaking at the 11th International Congress of Catalysis, and in the same official, public and highly professional context Burwell (1996, p. 63) adopted the 'new' term in a conscious and explicit manner: "Adequate descriptions of many catalysts will require a large number of bits of data since they are usually rather complicated materials rather than single chemicals".

It is possible that I have observed a bias that depends on my reading of certain (few) sources. However, the linguistic shift goes simultaneously with the rise in prestige of materials science.[18] In the context of our philosophical inquiry, that is important because it shows a more explicit attention towards the industrial practice. To be sure, in organic laboratory practice many catalysts are in use for preparative or synthetic aims. However, papers on catalysis rarely contain a single reference to the laboratory use. Overall, the large community of scientists working on catalysis seems to be committed to understand, improve or discover only industrial catalysts.

The actual connotation of the term 'catalyst' is much more complex than conveyed by single terms like 'substance' or 'material', plus a couple of chemical properties (changing the reaction rate; being unchanged at the end of reaction). In order to appreciate some traits of the connotation of 'catalyst' in an explicit industrial context we may refer to Table 5, where the principal properties of catalysts are reported, as they have been explicitly listed by representative authors.

Mills & Cusumano 1979	Farkas 1986	Cavani & Trifirò 1994
Selectivity	Activity	Activity
Activity	Selectivity	Selectivity
Stability	Stability	Lifetime

Physical suitability	Ease of regeneration
Regenerability	Toxicity
Cost	Price

Table 5: Principal properties of catalysts

The three lists agree in giving the greatest evidence to the fundamental characteristics of activity, selectivity, and stability. Farkas (1986, p. 322) closes his list at this point, even if in the course of the article he treats many other properties. The other authors list the remaining "factors" (Mills & Cusumano 1979, p. 20) or "properties" (Cavani & Trifirò 1994, p. 12) as elements which determine the *choice* of a particular catalyst. In this modal and pragmatic context, the *cost* of a catalyst becomes a significant property: it is also significant that these authors agree on the regenerability of catalysts, in spite of the usual definition, which denies any chemical change. [19] Cavani and Trifirò, the most recent authors quoted in Table 5, list also "toxicity" – a homage to the environmental correctness. Mills and Cusumano explicitly list the "physical suitability", however the Italian authors treat this and other important properties in the text following their first list, and I will examine the content and the structure of their text because it presents a meaningful hierarchy of concepts/properties.

The paper of Cavani and Trifirò is dedicated to the *classification* of industrial catalysts. Hence, it is extremely rich of implicit suggestions about the different *industrial* relevance of catalysts. They catalogue these relevant characteristics of a "composite material" used in heterogeneous catalysis: "i) the relative amount of several components, ii) its shape, iii) its size, iv) its pore distribution and v) its surface area". This list is impressive if one reads it having in mind the distinction between 'primary' and 'secondary properties' (Schummer 1998, p. 132), because terms such as 'shape', 'size', 'pore', 'area', seem to point in no way at chemical properties. In fact in the industrial context, they often pertain to a meso-world, somewhere in between the micro- and macro-worlds. [20] If we return to the article of the Italian authors, we see that they use the rhetoric device of successive expansion of the text (Cavani & Trifirò 1994, pp. 13-14), an expansion which may be summarized in this way:

"several components"

↓

Four different classes of components, including "supports"

↓

Seven "main roles of the support"

Their emphasis of the role of supports is noteworthy. On the one hand, they confirm the nature of materials for catalysts; on the other hand, they stress the fact that the catalyticity of a material results not only from the active species and from the chemical promoters, but also from the many co-operative functions of the support. In the following parts of the article, I will use the principal results of this section: the nature of materials of catalysts, the role of their secondary qualities, the functional meaning of the support.

2.3 A suitable metaphor

All scientific dialects are full of metaphors and of metaphoric terms. Since long, according to chemists, certain substances are *poisons* for certain catalysts. More recently, chemists observed that certain species – albeit on a surface during a catalytic reaction – were only *spectators* (Baiker 1996, p. 51); in certain other cases they found that active centers may became *dormant*, that is they do not contribute to polymer growth (Busico & Cipullo 1995, 278)[21]. In this section, I will look for a suitable metaphor for catalyticity, in order to gain a suitable pictorial description of the material work of the catalyst *and* of the correlate chemist's research work on catalysis.

I agree with Mills and Cusumano (1979) in judging selectivity as the first and essential property of a working catalyst. The metaphor which I will 'construct' is principally aimed for a description of this particular property. However, before proposing the metaphor it is

necessary to look closer at the meaning of the phrase 'chemical property'. Schummer has proposed a typology of scientific material properties, and he has given the following definition: *A material property is reproducible behavior within certain reproducible contextual conditions* (Schummer 1998, p. 133; emphasis in the original text). The context which the property is referred to has in Schummer's (and my) opinion the crucial role of distinguishing several types of properties, and in this way of permitting a classification of properties. In this vein, the contextual factors, which characterize the chemical properties of a certain substance, are other chemical substances. A slightly different way of exploring some shades of the pragmatic field [22] of 'chemical property' may be the analysis of the properties, which we usually attribute just to a *chemical substance*.

Only certain properties of a chemical substance are intrinsic, *i.e.* properties of a system made up only by this particular substance. Many physical properties of the substance of properties belong to this class, as well as a crucial chemical property: *stability*, in respect to a more or less canonical structure of its molecules. From this point of view, the concept of stability is tightly connected on one side with that of purity, with all its fascinating difficulties (Schummer 1998, pp. 136-143), on the other side with the physical conditions of the system (temperature, pressure, and electromagnetic fields). It has to be noted that specific electromagnetic fields may induce electronic excitation of the molecular system to states with features (geometry, electronic densities, reactivity) greatly different from the corresponding ones of the ground state. An important consequence is that "when the reaction is taking place on an excited electronic potential energy surface[, t]he topology of the excited surface can be completely different from the ground-state one" (Levine & Bernstein 1987, p. 121), and unusual reaction paths become accessible. A whole discipline, photochemistry, is concerned with the particular reactivity of excited molecules. The same use of the fundamental unity of measure of quantity of substance, the mole, for photons as well as for chemical substances, testifies to the fact that in a photochemical system the photons are the particles of a very special chemical substance, the light. Thus, at least some spectroscopic properties of a substance are at the border between physical and chemical (reactive) properties.

In particular circumstances, the molecules of a substance may react with themselves through the process of self-ionization; *e.g.*, in 'pure' water different molecular species exist, which may behave as Brønsted acid and base. In other circumstances the molecules of a substance may tautomerize, isomerize, simply decompose, or – as we have seen at length in this paper – the molecules of certain substances may polymerize. It is obvious that at the beginning of a chemical reaction, by definition (Schummer 1998, p. 134), at least two different chemical substances are present in the system; thus, the 'solitariness' of the substance disappears, and with it, the concept of 'intrinsic' properties fades. But a point important for my argument is that almost all the intrinsic properties are *virtual*, *i.e.* they need a particular context in order to become 'explicit', 'active', *etc.* A simple example is just that of spectroscopic properties which became 'actual' through the interaction of molecules of the substance with suitable electromagnetic fields.

The *virtuality* of most chemical properties is evident when we describe its *reactivity*. Here it is appropriate to refer to the detailed protocols, which have to be followed in order to use correctly a substance as a *reagent*. In the protocols, we find the instructions for (re)creating the right *context* for the *use* of the reagent. In many cases the immediately available information is less detailed and specialized. However the simple fact that a substance is, for example, a ketone suggests that in the appropriate conditions we could make sense of its 'ketonicity' by realizing any of those many reactions which qualify the assignment of that particular ketonic substance to a specific position inside the complex network of chemical relations (Schummer 1998, p. 135).

Following this train of thought we see that the property of being a catalyst is exceedingly virtual. Certain cases of catalytic activity seem almost scandalous. I think of the Orito reaction in which platinum, modified by the presence of preadsorbed cinchonidine, becomes active for the stereoselective hydrogenation of a α-ketoester. Since 1989 several groups have studied this type of reactions; *e.g.* Thomas (1994, p. 922) explored by computer graphics the way in which this stereoselective process might proceed; since 1991 another group of researchers worked on the cinchona-Pt question using quantum chemistry and molecular mechanics (Baiker 1996, pp. 55-59). Baiker's group was able to gain the knowledge necessary to identify new, simpler and more stereoselective (commercial) substances, but overall a crucial aspect of the problem remained unsolved, just the source of the catalytic activity. On this topic the words of Burwell (1996, p. 68) at the 11th International Congress of Catalysis are illuminating: "Presumably, adsorption of cinchonidine on Pt generates an optical active catalyst, but why should the rate be 30x that of the same catalyst without cinchonidine?" Anyway, also in less exotic cases than stereoselective modification, the catalyticity of a substance/material is a property, which (by definition) needs the context of other reacting substances in order to be expressed. This statement is useful because it draws our attention to the context of reacting substances, which are necessary in order that an (in general)[23] extraneous substance may act as catalyst; consequently we have to choose an appropriate general way to consider reacting systems.

In 1981, G.M. Schwab, in a note on the history of concepts in catalysis stressed that during several decades many authors had proposed a more or less generally valid 'theory of catalysis', but that "with time their concepts have gone astray more and more, and have grown rather in number than in validity". He added that "an older concept had seldom been totally replaced or refuted by a newer

one, but that usually an older concept [had] been represented in new or modern scientific language". Schwab regarded this last fact as a proof "that the mechanisms of catalysis are so manifold that many fields of thought must be employed – although the notion of catalysis is very unitary from the viewpoint of thermodynamics and kinetics" (Schwab 1981, p. 11). It is exactly from this point of view that I intend to discuss the catalytic activity and selectivity of a substance/material.

We can consider a closed *chemical system* consisting of a set of chemical substances each with a certain number of moles. At any value of temperature and pressure, the evolution of the system *must* obey the laws of thermodynamics. However, in many actual chemical systems the variation of the Gibbs free energy may be negative for a large set of reactions. Thus, we may set a *thermodynamic framework* given by all the $\Delta G < 0$ corresponding to possible reactions inside the system, such that the substances are connected through the usual stoichiometric equations. Nevertheless, as we know, the evolution of the system does not necessarily evolve towards the lowest value of the Gibbs energy, principally because of the kinetic aspect of the reactions. Speaking in terms of activation energy, at the given temperature the molecules of the virtually reacting system may or may not have enough energy to climb the energy passes which separates/unites the states before and after the permitted reactions. When the temperature rises, the number of different molecular species in the system may boost, because of the increasing probability of successful attacks on molecular stability. At a given temperature and pressure the most evident feature of the thermodynamic framework is built up by the minima corresponding to all the possible mixtures of products. These minima are connected by the relative maxima corresponding to the ambiguous substances named 'activated complexes'. On this supporting structure of the classical thermodynamic framework, chemical kinetics introduces/reproduces an essentially kinetic feature, the reaction rates, with their empirically determinate, non-stoichiometric, orders of reaction, and their reference to the macroscopic world of chemical substances. At this point, statistical thermodynamics and quantum chemistry try to describe, qualitatively and quantitatively, the molecular dynamics, which rules the transformation of molecular systems at the microscopic level of reality. We may say that classical and statistical thermodynamics and quantum chemistry give us a vantage point from which we enjoy a good view on the valleys, passes, and saddles of the potential energy surface. These valleys and passes constitute the 'natural' *kinetic landscape* of any chemical system. The metaphor I am proposing is to consider *a catalyst as a contrivance to modify the kinetic landscape of a chemical system*. In Sect. 2.4 I will 'apply' this metaphor to three cases of industrial catalysis, but before I support the choice of the word 'landscape' with a brief comment.

2.3.1 A gloss on 'landscape' and landscapes

There are several reasons in favor of the suggested metaphorical use of the word 'landscape'. First, it is clearly evoked by many illustrations of the calculated energy surfaces; moreover the same disciplinary language uses descriptive terms whose semantic content have evident overlaps with 'landscape'. In the preceding subsection I quoted the use of 'topology' by Levine and Bernstein, but much more frequently they do not use this mathematical term, and prefer to discuss "the dynamics arising from different topographical features of the [potential energy] surface" with geographical terms: "a low-energy mountain pass between the reactants' and the products' valleys", "the coll in the entrance valley", "a hollow along the reaction path", (Levine & Bernstein 1987, pp. 149, 126, 146, 155). Second, the connotation of 'landscape' in our culture is rich in semantic traits of aesthetic and emotional resonance,[24] and this type of traits can lend some strength to the metaphorical use of 'landscape'. Third, I point out other and new semantic traits, which are expressed in many disciplines interested in the evolution of the actual, terrestrial landscapes. A few years ago, the *Landscape Sensitivity* has been focused in a book of this title; in the introductory essay, we find several passages that are pertinent to our own inquiry:

> Understanding change within the natural environment frequently requires a fragmentation of natural systems for the sake of simplification. Individual components are studied, rather than adopting a holistic approach. […] Understanding and predicting change is not, however, merely a matter of understanding the mechanics of the change process. It requires the recognition and comprehension of the nature of the links between individual system components. […] One area still requiring much attention is the sensitivity of landscapes to change. Sensitivity can be defined in various ways. […] Ecologists frequently use the term to define the susceptibility of a system to disturbance. In other words, the use implies *fragility*. [Allison & Thomas 1993, pp. 1-2; my italics]

An holistic approach seems even more necessary in many disciplines in order to understand the behavior of complex systems; in this sense environmental science and catalysis make no exceptions (on catalysis as discipline *vide infra*). In addition, the last word of the quotations, *fragility*, is precious for the present inquiry because both the macroscopic terrestrial landscapes and the microscopic kinetic landscapes are fragile.
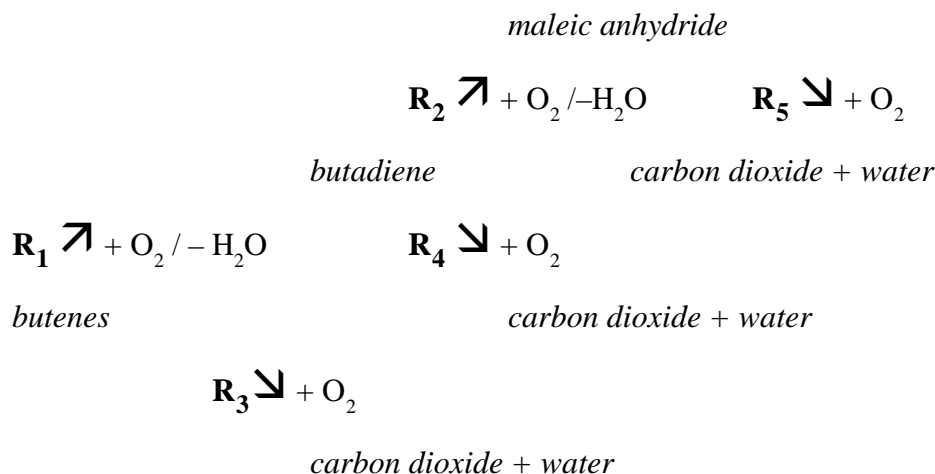
2.4 Kinetic landscaping

A useful feature of English is the attested use of 'landscape' as noun as well as verb. A current definition of the verb is "improve (a piece of land) by landscape gardening" (Hawkins & Allen 1991, p. 806). In this section, three cases of kinetic landscaping by catalysts will be treated, in order to throw light on different aspects of the improving functions of industrial catalysts. The first two cases are connected with the general problem of selective oxidation, in order to give a glimpse on "the formidable complexity of mechanism for any selective oxidation reactions" (Schlögl 1994, p. 312). The field is extremely interesting for industrial catalysis because, as Burwell stressed, "[t]here are myriads of possible oxidation for which ΔG is negative but which are unknown non-catalytically" (Burwell 1996, p. 67). The last case regards – not unexpectedly – the stereospecific polymerization of α-olefins.

2.4.1 Burning butenes

The first case of kinetic landscaping which I consider in some formal kinetic details is the selective oxidation of butens. 1-butene, cis- and trans-2-butene and 2-methylpropenes (isobutene) are the four isomers which correspond to the brute formula C_4H_8. In the chemical-industrial jargon, the designation 'n-butenes' refers to mixtures of the first three isomers. The four isomers show differences in their chemical behavior, and, mostly, their reactivity can be ordered in this way:

isobutene >> 1-butene > 2-butenes

Their main reactions are addition reactions, isomerization and polymerization, but here I am interested in considering the catalytic oxidative dehydrogenation of butenes to maleic anhydride. A simplified reaction scheme may be the following (Santacesaria *et al.* 1994, p. 199):

maleic anhydride

R_2 ↗ $+ O_2 / -H_2O$ R_5 ↘ $+ O_2$

butadiene   *carbon dioxide + water*

R_1 ↗ $+ O_2 / - H_2O$ R_4 ↘ $+ O_2$

butenes   *carbon dioxide + water*

R_3 ↘ $+ O_2$

carbon dioxide + water

Products and reagents are involved in more than one reaction, each occurring with its own rate and stoichiometry; thus, we can describe the rate of any appearing and disappearing substance in this form:
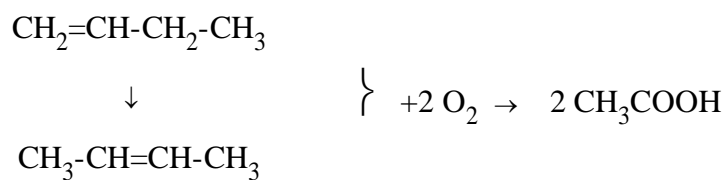
$r_i = \Sigma_j \alpha_{ij} r_j$ $i = 1,\dots 6; \; j = 1,\dots 5$

where i refers to a substance and j to a reaction rate. α_{ij} is the matrix of the stoichiometric coefficient which permits the description of the evolution of any single species, if the kinetic equations R_1 to R_5 are known. The scheme is extremely simplified; for example, any isobutene molecule present in the system is quickly oxidized to carbon oxide, carbon dioxide, and water, and any partial, destructive oxidation leads to the presence of carbon oxide. With carbon oxide and water, the water gas shift reaction becomes possible; with the
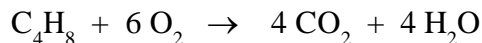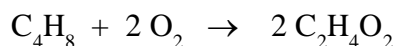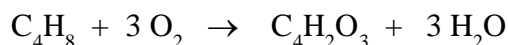
resulting hydrogen and other carbon oxide, the oxo-process becomes possible, or, in a way completely independent from the presence of olefins, it could start a Fischer-Tropsch reaction. In a sense, it is difficult to see the borders of the kinetic landscape corresponding to a gaseous mixture of butenes and oxygen, at the temperatures between 350 and 450 °C used in industry.

It is to be appreciated that in this vast kinetic landscape the most crowded resorts could be the minima of free energy corresponding to the combustion end products, carbon dioxide, and water. As a matter of fact, the ignition temperatures of the four butene isomers (listed at the beginning of this sub-section) are 384, 325, 325, and 465 °C, respectively. However, in 1985 there were three plants on stream, in Germany and in Japan, in which n-butenes and mixed butenes were oxidized to maleic anhydride over V_2O_5/P_2O_5 catalyst, with selectivity of about 50-60 mol % (Obenaus *et al.* 1985, p. 486).

A similar kinetic landscape (at a lower temperature) may be modified by catalyst containing vanadium pentoxide, along with a variety of other oxides (titanium, zinc, aluminum or antimony oxides). At 200-320 °C, it is possible to control the oxidation of n-butenes to form acetic acid in this way :

$$
\left.\begin{array}{c}
CH_2{=}CH\text{-}CH_2\text{-}CH_3 \\
\downarrow \\
CH_3\text{-}CH{=}CH\text{-}CH_3
\end{array}\right\} \ +2\,O_2 \ \rightarrow \ 2\,CH_3COOH
$$

If we now write three overall oxidation reactions of butenes in the simplest stoichiometric way, we see at a glance the *permanent identity of reagents* and the *enormous difference of products* in the making of maleic anhydride, the production of acetic acid, and the simple combustion:

$$C_4H_8 \ + \ 3\,O_2 \ \rightarrow \ C_4H_2O_3 \ + \ 3\,H_2O$$

$$C_4H_8 \ + \ 2\,O_2 \ \rightarrow \ 2\,C_2H_4O_2$$

$$C_4H_8 \ + \ 6\,O_2 \ \rightarrow \ 4\,CO_2 \ + \ 4\,H_2O$$

Returning now to the industrial process for obtaining maleic anhydride, the feedstock was the C_4 product from a steam cracker, consisting essentially of butenes and butadiene plus smaller amounts of butanes. Under optimum operating conditions butanes remained without reaction, isobutene burnt to carbon oxides and water, and the n-butenes and butadiene were converted to maleic anhydride (Satterfield 1980, p. 204). I conclude this point stressing that the C_4 components followed three very different paths: no reaction, completely oxidized, and partially oxidized (in the wanted measure and structural position).

2.4.2 Making nitriles

Propylene, ammonia, and air can react to give acrylonitrile and water:

$$CH_2{=}CH\text{-}CH_3 \ + \ NH_3 \ + \ 1\tfrac{1}{2}\,O_2 \ \rightarrow \ CH_2{=}CH\text{-}CN \ + \ H_2O$$
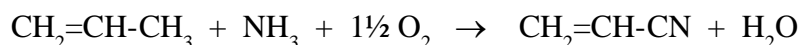
In the late 1950s several companies, including Sohio (USA), Distillers Ltd. (United Kingdom), Montecatini (Italy), and O.S.W. (Austria), developed routes for the ammoxidation of propylene with air and ammonia. Working with the Badger Company, Sohio ended up with the best process, which it commercialized in 1960 (Spitz 1988, p. 297). Over the following decade, Sohio introduced

several new generations of catalysts. Since 1970, Sohio used multicomponent catalysts containing mixed-metal molybdates, antimonates, and tellurates (Grasselli 1986, p. 217).

The process of ammoxidation is obviously connected with the previously discussed processes of oxydehydrogenation and oxidation. It is to be expected that ammoxidation which is a 6 electrons oxidation is more difficult and demanding process than oxidation *strictu sensu* (4 electrons) and oxydehydrogenation (2 electrons). As it was pointed out by Grasselli (1986, p. 217), "effective ammoxidation catalysts are multifunctional in nature. They must perform a complex sequence of [thirty-two] bond-breaking and bond-making processes […] and must provide a facile pathway to the desired intermediates since, thermodynamically, undesirable waste and by-product formation (*i.e.*, CO, CO_2, HCN) is more favorable than the formation of the desired product". The sequence of thirty-two microscopic processes discussed by Grasselli is a good example of the (tentative) mechanistic understanding of heterogeneous catalytic reactions. Nevertheless, I have mentioned Grasselli's knowledge exploit also for other reasons.

The first reason is that Grasselli's results let us look closer at the relationship between the chemical reaction and its description in terms of pathways on the free energy surface. The acts of the molecular drama of ammoxidation are actually played on particular sites of the catalyst surface. Our description in terms of quantum chemistry and statistical thermodynamics tries to reproduce the drama on the free energy surface, where any pass or saddle of the reaction path corresponds to an activated complex. Grasselli's scheme proposed only one type of active site of Bi_2MoO_6 (a model catalyst). This site (rather complicated) is the chemical stage of the thirty-two electronic acts. Our quantum mechanical description should reproduce the sequence on the energy surface, but there (probably) many of the thirty-two bond changes should happen on a different pass or on a different point of a saddle. At any point of interest, a transition state complex may be bigger and looser than the preceding one, or more compact and stiffer, and these different conditions change the frequency of the normal mode which correspond to a passage across the energy barrier (the pass, the saddle) (Benson 1976, pp. 86, 82). Grasselli describes π and σ allyl intermediates, and states that "the position of the equilibrium between the π and the σ allyl intermediates varies greatly depending on the nature of the catalyst" (molibdate or antimonate) (Grasselli 1986, p. 219). Thus, we see that any catalytic contrivance not only changes the height of the energy barriers, but also modifies the constitution of the activated complexes. The landscaping of the energy surface can (or must) became a more delicate gardening on the top of the energy barriers. As Benson (1976, p. 6) stated: "Catalysts may be looked upon as substances that perturb the populations of chemical intermediates".

A second aspect of the Sohio ammoxidation process is of interest, but not from an epistemological point of view. In the British process, developed by Distillers Ltd., propylene was converted first to acrolein, and then, without any actual treatment of the acrolein, it was converted to acrylonitrile. In the Sohio process, the whole reaction was carried out in a single step. There was a patent suit in the early 1960s between the British firm and the Standard Oil of Ohio, a suit which hinged on whether the Ohio one stage process was an infringement of Distillers' patents on the two-stage process. The essential question was 'simple': was acrolein an intermediate in the one-stage process? Thus the understanding of the reaction mechanism was of more than academic importance; unfortunately the case was settled out of the court, and we cannot read a sentence about the right, actual, pathway from propylene to acrylonitrile (Reuben & Burstall 1973, p. 300).

2.4.3 Assembling polymers

In the two preceding cases, we have seen how the kinetic landscaping by catalyst controls the oxidation of butenes and the ammoxidation of propylene. In both cases the product, maleic anhydride or acrylonitrile, were well known, but in the case of the Ziegler-Natta catalysts, the products were completely unknown before their production in Mülheim and in Milan. The linearity of the molecules of Ziegler's HDPE and the stereoregularity of the molecules of Natta's polypropylene were the results of the unique activity of the catalysts.

The landscaping of the Ziegler-Natta catalysts is very particular. The kinetic landscapes corresponding to the polymerization of ethylene or of propylene have thousands of valleys separated by passes of very similar relative height. In this case, the function of the catalyst seems to select a unique pathway, whose crucial feature is not the overall increase of the reaction rate, but the compulsory repetition of the same (microscopic) action, exactly as it happens in a (macroscopic) assembly line.[25] From this point of view, the Ziegler-Natta catalysts are extraordinary contrivances.

2.5 Intellectual attitudes to industrial catalysis

2.5.0 Industrial catalysis for the less intelligent?

The title given to this introductory subsection of my essay is an *ad hoc* modification of a phrase written in 1955 by Wigglesworth, a biologist,[26] who was telling the efforts of pure scientists during the war in order to get something which were sensibly applicable. They experienced new and tight constraints to their problem-solving activity, so that it was impossible to shift from the unsolved and perhaps insoluble problem *A* to a more promising problem *B*; "now they must find a solution to problem *A*, and problem *A* alone, and there was no escape".

> Furthermore [in applied science] there proved to be tiresome and unexpected rules which made the game unnecessary difficult: some solution were barred because there was not enough of the raw material available; others were barred because the materials required were too costly; and yet others were excluded because they might constitute a danger to human life or health. In short, they made the discovery that applied biology is not 'biology for the less intelligent', it is a totally different subject requiring a totally different attitude of mind [Polanyi 1983, p. 178].

The ironic mood of Wigglesworth does not veil the dramatic fact that during war time *there was no escape*, but the same connotation in various measure pertains to any applied research. While a fertile and useful research probably has no end (*vide infra*), it must have had a beginning: at a certain moment people find a way, leading to results rich of consequences (fertile), and to promising applications (useful). In academic research the beginning may be (and frequently is) accidental, as it happened in Ziegler's laboratory. If research is obliged to obtain certain results, the academic situation is often reversed: it is the starting point then, which has to be found, before *there is no engagement*.

Polanyi – through Wigglesworth's words – suggests two other themes connected with the opposition basic/applied science: in applied research, a *different attitude of mind* is necessary, and *unexpected rules* have to be followed. In the next subsections I will treat these two points, in order to get a better comprehension of industrial catalysis, as both discipline and subject matter.

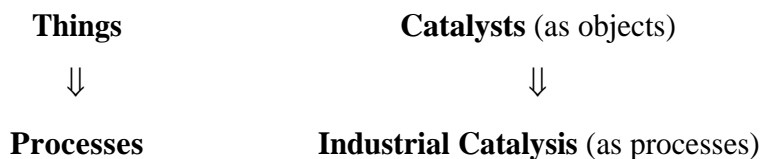## 2.5.1 A different attitude of mind, hints from philosophy of technology

Philosophy of technology gives us many hints on the mental switch necessary when a researcher passes from fundamental to applied research. Stanley Carpenter has considered technology as a form of knowledge with its own epistemic procedures, and has proposed epistemological differences between science and technology whose discussion can be useful in our inquiry on the epistemology of industrial catalysis. The first distinction is between laws and rules. In the scientific sense, *laws are descriptive of reality*, while the technological *rules are prescriptive of action*. Carpenter affirms that technological descriptive laws assume the form '*If A, then B*', and have an implicit, but definite, reference to concrete experience. They are empirical laws generalized on the basis of experience, from which we can infer technological rules. Technological rules are guides for practical, actual action, and assume the form: '*To get B, do A'*. That first distinction of Carpenter is (for me) completely acceptable. The second distinction is interesting too, but it contains also a value judgement (of dubious value) on scientific and technological laws. Technological laws "are like scientific laws in being explicitly descriptive and only implicitly prescriptive of action, but they are *not yet* scientific in that the theoretical framework which could explain the law is *not yet* explicit" (Carpenter 1974, p. 165; quoted from Mitcham 1984, p. 313, my italics). Carpenter erects a grammatical, spurious barrier between technology and science. By means of two cutting 'not yet' he outlines a precise fate for the technological endeavor: it has no autonomous life in respect to science. As a girl is not yet a woman, technology is not yet science. Moreover, Carpenter denies that technological laws have an explicit theoretical framework.

Sometimes technicians seem to share the same idea, or, better, the same ideology. The reading of a technical paper can help me to explain myself. In 1994, in the final part of a six-day seminar of catalysis, an Italian author was treating the distressing problem of the scale-up of catalyst production. In the published text of the lesson, he wrote, "Procedures for catalyst manufacturing are usually developed in an *empirical way*, through time-consuming and costly work, though some attempts of a *scientific approach* begin to appear in the literature". A few lines later he added, "the preparation of catalysts having good industrial performance can show insurmountable difficulties even for catalytic researchers, if not skilled in manufacturing practice. This mainly because even *small changes* in manufacturing procedure may have *large effects* on catalytic properties" (Pernicone 1994, p. 388, my italics). There is obviously a derogatory overtone attributed to 'empirical'. In this text (as well as in many other technical texts) the word 'empirical' is used as an antonym of 'scientific', while the syntactic and semantic context could bear quite a different couple of epistemic terms: 'experimental' vs. 'theoretical'. The ideology behind this attitude is apparent in the same quoted text, where the author explains that

"an empirical way" is time- and money consuming. The pressure towards a more 'scientific' industrial catalysis (as academic discipline) has its origin and justification in the high cost of the 'empirical' industrial catalysis (as the processes on stream). However, Pernicone gives us a clue for the correct understanding of his own work as a skilled manufacturer of catalyst. In fact, his couple of phrases "*small changes"–"large effects"* is indicative of the *complex* nature of industrial catalysis.

A last aspect of Pernicone's highly technical discourse is pertinent to our inquiry. The quantity of structured/organized knowledge available to a 'skilled manufacturer' is enormous. Pernicone quotes in particular 24 different unit operations in catalyst manufacturing (Pernicone 1994, p. 403), each of which has its own rules [27], and more or less approximate laws.[28] Frankly, I think that technology at large, and chemical technology in particular have that explicit theoretical framework required by Carpenter – though not always with a pedigree certified by mathematical physics.

From philosophy of technology, we might draw several other suggestions useful for the present inquiry. For sake of brevity (and, I hope, of clarity) I will mention only one more, which demands of the analyst of technology a shift of attention: from *things*, made and used, to *processes*, making and using. Introducing this point of view Mitcham states that "[t]o take process or activity as the fundamental category of technology is characteristic of two different professional groups, engineers and social scientists. Engineers, in focusing on process, place stress on the *making* aspect, social scientists on *using*" (Mitcham 1984, p. 308; italics in the original text). The 'making' point of view emphasizes the creative technological practices of invention and design; the' using' perspective regards the social, economic aspects of production and utilization. Both viewpoints have been used in the preceding parts of this essay, the first one mostly in the historical Part 1, the second one mostly in the present Part 2. The opposition thing/process is actually somewhat blurred when we consider the contextual meaning of the properties which define a thing (*cf.* Sects. 2.2 and 2.3); however an epistemologically meaningful parallel shift of focus remains:

<div align="center">

Things   **Catalysts** (as objects)

⇓   ⇓

Processes   **Industrial Catalysis** (as processes)

</div>

Mitcham states that "Cybernetics claims to reduce objects to processes; what is important is not what a thing is but how a thing behaves" (Mitcham 1984, p. 316). Probably, as in many other cases, the reductionism of cybernetics is too strong; anyway, in industrial catalysis *knowing how* a catalytic process runs (at the appropriate scale) is perhaps more important as *knowing that* a catalyst is such-and-such a thing.

2.5.2 Working rules and unexpected rules, hints from a Methodenstreit

The polemics published by scientists against one another provide suitable text material for an epistemological analysis; at least because only in extremely rare cases the positions expressed on the two sides are personal ones. In general, the clashing terms of the polemics represent the common opinion of one of the conflicting parties of the scientific community. In this subsection I will use the two oppositions gained from philosophy of technology in order to interpret a recent polemics between Sir John Thomas, the well-known British scientist, and Professor Robert Schlögl, then at the Institut für Anorganische Chemie in Frankfurt.

In the title of the article that caused Thomas' indignation, Schlögl rose a simple question: "Heterogeneous Catalysis – Still Magic or Already Science?", which he plainly answers in the conclusion: "if we try to answer the question asked in the title the realistic reply must be – still magic" (Schlögl 1993, p. 383). The three-page essay discusses the relationships between the "catalytic performance" of a solid catalyst and four groups of determining factors (formal kinetics, chemisorptions processes, microkinetics, and microstructure of the catalyst), whose quantitative relations between each other and the mode of catalyst operation must be determined. At the core of the analysis, there is the *catalytic reaction*.[29] Schlögl's principal points are:

a. The optimizing of industrial heterogeneous catalysis needs to understand "the operation of a catalytic system at an atomic level", but "it is not adequate to have only a model", because "[e]xtrapolations from the data obtained from the simplified model to the

actual catalytic reaction may endanger the relevance of a whole mechanistic reconstruction".

    b. "Industrial chemists tend to be rather skeptical towards inductive-scientific strategies in heterogeneous catalysis, since it is evident that our understanding of the relationships between structure and reactivity is inadequate".

    c. "[T]he long history of catalyst characterization should have taught the lesson that all analysis should be done *in situ*", *i.e.*, "a property of a catalyst [has to be] investigated as function of reaction conditions characteristic of the practical application under simultaneous observation of the reaction kinetics".

Catalysis researchers largely accepted the point (c), even if the methodological requirement of a simultaneous observation of the kinetic parameters of conversion and selectivity is really severe, and not all the published *in situ* analyses correspond to Schlögl's definition. On this point, there was no quarrel, but on the other two points Thomas disagreed. After a while *Angewandte Chemie* published a reply to Schlögl's article, with the full flagged title "Rationally Designed Inorganic Catalysts".

In the article, written by Sir John Thomas and Kyril I. Zamaraev, the answer to point (b) was oblique, if not devious: "If Schlögl's claims were true, future employers and boardroom protagonists could well underestimate or misjudge the contributions that the research chemist could make to the future of their industry, and employment prospects for numerous highly trained physical scientists would be bleak" (Thomas & Zamaraev 1994, p. 308). On the crucial point (a), the rebuttals by the two anglo-russian authors were numerous, distributed among "four distinct categories of catalysts". In many cases these were simply statements on the present state of the art concerning the characterization of catalyst by solid-state chemical research: "so well understood is the correlation between crystal structure and selectivity among acidic shape-selective catalysts that computational chemistry has already contributed significantly to the evolution of superior catalyst for a given task" (*ibid.*, p. 309). In at least one case the appeal to a 'new rationality' was somewhat whimsical: "The fourth category of catalyst research encompasses advances in the application of *rationalized* new ideas relating to the design and mode of operation of catalytic reactors" (*ibid.*, p. 310; my italics). In think that it is sufficient to open a textbook on chemical reactors for seeing that chemical engineers have not waited for Thomas' and Zamaraev's advice in order to use rationality in their design practice. However, the point more pertinent to our inquiry is on Ziegler-Natta catalysts:

> another example is the heterogeneous Ziegler-Natta $TiCl_3/MgCl_2$ catalyst for stereoselective polymerization of propene and its copolymerization with other alkenes. Once *the mechanism of its mode of action was rationally established*, it became possible to tune the catalyst structure and morphology, and the reaction conditions for predominant production of stereoregular polymers with desired physical and mechanical properties [Thomas & Zamaraev 1994, p. 310; my italics].

Not only does the history of Ziegler-Natta catalysts demonstrate that the last statement is not true, but also the *whole community* of researchers working on Ziegler-Natta catalysts remained uncertain on many features of the reaction mechanisms even after the Thomas vs. Schlögl quarrel (Sect. 2.6). Whether a research field is perceived as closed or open, is very important for an understanding of the knowledge procedures followed by scientists. Thus, the fertile doubts of the chemical community will be treated later (Sect. 2.6), while we are now more interested in Schlögl's reply, which was printed in *Angewandte Chemie* just behind the article by Thomas and Zamaraev.

Schlögl admits that "Thomas and Zamaraev give an expert description of recent ingenious developments in heterogeneous catalysis", however he adds that a "proof that these developments are based upon an understanding of the structure-reactivity relationship is lacking" (Schlögl 1994, p. 311). In Schlögl's reply, precisely on cases discussed by Thomas and Zamaraev, we find a constant reference to "working rules". "The important field of selective oxidation catalysis", in particular, "is characterized by the existence of qualitative concepts […] which summarize the practical experience of researchers over about 25 years"; even if they can not "be used in a quantitative way like a theory", "such working concepts are of great practical value in guiding the chemical intuition required in developing catalytic processes". Schlögl's epistemological conclusion is that

> the detailed knowledge about surface reactions under surface-science conditions serves as a source of background information for the development of practical catalyst systems. In this way catalysis has gained *a scientific basis in the form of intuitively founded, qualitative working rules* [Schlögl 1994, p. 312; my italics].

Schlögl claims a scientific status for industrial catalysis, connected to, but independent of the "rational approach of surface physics to the problem of interface reactivity" (*loc. cit.*).

It is clear from the preceding analysis that Schlögl looks at rules and processes, while Thomas prefers laws and things. However, the discussion has also a meaning that is not only epistemological. It was also a running debate on method, whose sociological meaning is clear: behind any *Metodenstreit,* there is always a *struggle for supremacy* within a discipline or among disciplines.[30] This is a

general and perhaps unexpected rule of the epistemological discourse, as it may easily be demonstrated through socio-linguistic analysis (Cerruti 1992). However, what is at stake in the Schlögl vs. Thomas case, as well as in other debates on catalysis (as discipline), is not only the hierarchy between academic disciplines or specialties, but also another and more meaningful one: the hierarchy – affirmed and proclaimed – between pure (or basic) research and applied (or industrial) research. Here the question is not about the prestige of academic communities, but it points directly to a central problem of epistemology, *whether the value of knowledge depends on its source*.

An industrial catalyst is a material which must demonstrate (to a high degree) that all the properties discussed above (Sect. 2.2) are not virtual, but correspond to a complex, actual behavior inside the reactor. The success of a catalyst is the result of a tremendous knowledge effort. If that success makes a material ontologically an industrial catalyst, then we have to attribute the same epistemic value to any single bit of knowledge or of practical action which contributes *in a necessary way* to the final success. The appeal to a scale of rationality is not simply an ideological move towards an easy gained academic supremacy, but it is a traditional way of affirming a cultural and social hegemony.

2.5.3 A language game on 'political' and 'rational'

At this point, I cannot refrain from a simple language game, the substitutions of 'rational' for 'political', and of 'catalytic' for 'natural' in a suitable text. I played the game while reading the above quoted essay on the landscape sensitivity. In the original text Allison and Thomas are discussing the presence of global environmental issues on the political agenda, such as rises in sea level, shifts in world climatic belts, *etc*. These topics are, at the same time, of deep concern for a large sector of the world community, and of keen interest for several scientific disciplines. However, the authors' opinion is somewhat disconsolate:

> the difference between *political* perception on one hand and scientific unknowns on the other is considerable, with the complexity of *natural* systems frequently precluding the establishment of *politically* desirable, simple straightforward solutions [Allison & Thomas 1993, p. 2; my italics].

Now we can read the text after the substitutions, and referring it to our discussion on the problems of a rational design of catalysts:

> the difference between *rational* perception on one hand and scientific unknowns on the other is considerable, with the complexity of *catalytic* systems frequently precluding the establishment of *rationally* desirable, simple straightforward solutions.

The discussion of the historical and philosophical connections between *ratio* and *pólis* is completely outside the scope of the present essay,[31] but it seems to me that the preceding, elementary language game (as the more serious girls' and boys' games) mimics the social reality, where the political discourse makes continuous appeal to 'reason'.

2.6 Epistemic uncertainty and disciplinary openness: a glance on the disciplinary makeup

In June 1994, a symposium was held in Milan in honor of Giulio Natta. Fifty papers were presented, forming an imposing body of knowledge on the "Synthetic, Structural and Industrial Aspects of Stereospecific Polymerization", as it was stated by the symposium theme. I have used the volume of *Macromolecular Symposia* as *corpus* for a close investigation on the epistemic status of Ziegler-Natta catalyst mechanism(s).

In his opening lecture, Paolo Corradini, one of the 'midwives' of the birth of stereospecific polymerization, speaks of "*possible* mechanism"[32] and states that "[m]olecular mechanics studies, relative to models for the Ziegler-Natta catalysts stereospecific polymerization, *lend support to the hypothesis* that the differences in the rates of insertion of units having different configurations are mainly ought to non-bonded interactions at the catalytic site" (Corradini 1995, p. 8). In the succeeding papers of the volume, we find many statements on the 'certainty' of the reaction mechanism:

> *opinions are divided* on the relation between the substitution [of electron donors] and stereoregularity of the active centers [Kashiva & Kojoh 1995, p. 28].

A precise description of the active site for heterogeneous stereospecific catalysts for propene polymerization *has not been achieved*, taking into account the effect of all the components of the catalytic system. […] There is now *a consensus to admit* that the [internal Lewis base] does not belong to the active site. […] Of course *many question remain open* [Guyot *et al.* 1995, pp. 39, 44, 52].

Molecular modelling studies have enabled us to formulate *models of active sites* […] These models *could explain, at least in part*, the exceptional increase of isotactic polymer productivity observed [Albizzati *et al.* 1995, pp. 73-89].

many explanations have been proposed. According to *the most generally accepted interpretations* the role of the internal donor should be […] [Sacchi *et al.* 1995, pp. 91-92] [33].

One can hope that the accumulation of additional data on the polymerization kinetics will allow *a reasonably substantive guesson the nature* of the active centers in heterogeneous Ti-based Ziegler-Natta catalysts [Kissin 1995, p. 123].

The fact that […] *supports the idea of the existence* of a chemical bond. […] *It seems that* bimetallic reactions of the active centers play an important role [Kaminsky 1995, pp. 215-216].

It is thus demonstrated that *the scope of 'rational catalyst design'* in the field of metallocene catalysts *is still limited*. […] In some cases *these explanation rationales turn out worthless* when applied to different structural types of metallocene frameworks [Spaleck *et al.* 1995, pp. 237, 243].

I close this synopsis of uncertainty with a very recent, general assessment of the question:

because of the complexities of Ziegler-Natta polymerization, *no comprehensive or unified kinetic scheme has emerged* that adequately takes into account surface adsorption, catalyst-cocatalyst interaction, decay of catalyst activity, catalyst morphology, particle size, and so on [Stevens 1999, p. 241].

In the context of the present inquiry, the epistemic terms used by the above quoted researchers have two meanings. On the whole, they constitute a *negative epistemic evaluation* of the grade of certainty on the molecular mechanism of the Ziegler-Natta catalysts. Against this epistemic setting, the statement of Thomas and Zamaraev that "the mechanism of [their] mode of action was rationally established" before 1994 stands out as pure wishful thinking. However, the same uncertainty expressed by so many leaders of the community has a clear *positive sociological appraisal*: the field is open and very far from being worked out.

The dialectics between epistemic uncertainty and disciplinary openness is not simple and painless, in particular because of the huge economic interests which press the scientific community working on Ziegler-Natta catalysts and, more generally, on industrial catalysis. In a lecture given at the 10th International Congress on Catalysis, J.A. Rabo said that – in his opinion – "the most important future objective in catalysis science" is the "*characterization of catalytic sites at the atomic and molecular level*" (Rabo 1993, p. 23; italics in the original text). In the final part of his discourse, entitled "The Discipline of Catalysis", he stressed that "the makeup of the discipline in catalysis is continuously evolving". In particular he referred to "surface science, material science, inorganic synthesis, theory" in the past, and to "biocatalysis and new areas of inorganic synthesis for catalytic materials" for the future (*ibid.*, p. 28).

The important theme of the *disciplinary makeup* introduced by Rabo was resumed at the 11th International Congress, in two general lectures by Alfons Baiker (ETH, Zürich) and Ian Maxwell (Koninklijke / Shell-Laboratorium, Amsterdam). For sake of compactness, I have listed the components of their 'recipes' in Table 6. Both of the lectures were highly interesting (from our point of view, too). At the end of my essay, I mention only two enlightening passages of Maxwell's opening lecture. He spoke of a "perceived gap between academic basic research and industrial applied research", and of consequent political moves in the United Kingdom and in the Netherlands, in order to foster also in the academic world a "multi-disciplinary approaches to problem solving". (Maxwell 1996, pp. 7-8). After having listed the eight disciplines of Table 6, Maxwell stated that "innovation in this field is therefore very often achieved by lateral thinking across these different disciplines" (*ibid.*, p. 1). I am sure that this *lateral thinking* is not for the less intelligent.

Maxwell 1996   **Baiker 1996**

heterogeneous and homogeneous catalysis	catalysis
materials science	surface analytical instrumentation
process technology	surface science
reactor engineering	organometallic chemistry
separation technology	theoretical chemistry
surface science	solid state chemistry
computational chemistry	material science
analytical chemistry	reaction engineering

Table 6: The makeup of a discipline

2.7 Conclusions

In the preceding sections, we have treated several aspects of catalysts and catalysis concerning both the material and the social side of the field. Starting from the first side, it resulted that *catalysts are complex materials*, and that the chemical community draws this conclusion at about the beginning of the 1990s (Sect. 2.2). The fact that catalysts are materials, and not chemical substances, has many consequences, first for our understanding of catalysis as chemical activity at the microscopic level. In fact, an actual *meso-world* is born from the complex interactions of the many material components of a particular industrial catalyst with one another and with the operational context. *This meso-world is particularly fragile*, and its behavior depending on small context changes was likened to the behavior of a terrestrial landscape (Sect. 2.3). The actual results of this *kinetic landscaping* have been illustrated in three cases of α-olefins reactions (Sect. 2.4). At this point, the philosophical inquiry shifted to the other side of the question, from catalysis as chemical process to catalysis as chemical discipline. In this new context, it has been demonstrated that the use of typical epistemic words such as 'empirical' and 'rational' has several *political overtones*. However, the differences between basic and industrial research are not ideological, but depend on the different constrains imposed on the two scientific activities (Sect. 2.5). Eventually, it has been pointed out that the *epistemic uncertainty* about Ziegler-Natta catalysis is an element of a more general openness of catalysis as a research field. Some leaders of the community have interpreted this openness as an opportunity to reorganize academic research towards a more *holistic approach* (Sect. 2.6).

As a conclusion, it seems to me that this long inquiry supports the following picture of industrial catalysis as academic discipline. The professional standpoint is relevant to the understanding, description, and control of the chemical process (catalysis), while the actual performance of an industrial catalyst tests the efficacy of the professional understanding. Along with a constant and common reference to this economic level of reality (the industrial production), scientists select their epistemic arguments both for a better understanding of the microscopic level of reality (the chemical process), and a higher, personal status at the social level of reality (the chemical community).

Notes

[1]   Without any formal procedure, I will adopt a functional theory of language as social semiotics (Halliday 1978). This theoretical attitude supports an analysis which tries to "relate the patterns of language produced by linguistic analysis to the social context of the text's use [, and] to locate the registers, genres, ideologies, and discourses within institutional structures and in relation to power" (Threadgold 1997, p. 134); in my philosophical enquiry I will adopt a similar (implicit) theoretical attitude.

[2]   Reference to a word as a dictionary lemma is indicated by single quotation marks.

[3] For a more meaningful portrait of Karl Ziegler, see Ziegler 1968 , Wilke 1975, McMillan 1979, Elsch 1983.

[4] On Giulio Natta see McMillan 1979, Carrà *et al.* 1982, Cerruti 1989.

[5] A very readable history was written by Frank M. McMillan (1979); other sources are in Seymour & Cheng 1986; some essays by industrial researchers are somewhat unfair, and in this sense particularly interesting. I will say nothing on the question of priority, important from the economic point of view, but tedious in history and dull in epistemology; moreover, on this question I completely agree with the conclusions of Piero Pino (Pino & Moretti 1987).

[6] Until then polyethylene had been produced by a very high-pressure process discovered in the 1930s at ICI (Ballard 1986). The ICI polyethylene resulted from a chain radical reaction, and it had molecules with branched chain. Ziegler's polymer had a higher density than ICI polymer, so the two materials were named 'high density polyethylene' (HDPE) and 'low density polyethylene' (LDPE), respectively.

[7] Table 2 refers to catalytic materials functioning in industrial plants, whose high cost and low flexibility limits the quick renewal of processes.

[8] *Vide infra*, Sect. 2.6.

[9] The term 'recipe' sounds ironic. The study of the actual microscopic function of 'internal' and 'external donors' is now a very active research field.

[10] *Vide infra*, Sect. 2.2, and Note .

[11] A single-site catalyst is something as a Holy Grail in the catalysis world.

[12] I will treat at length the opposition empirical/rational in Sect. 2.5.2.

[13] "Detailed guidelines have been developed for the selection of supports with optimal composition, particle size, pore size distribution, and surface OH group density, and for their treatment with various alkyl aluminum and aluminoxane activators" (Brintzinger *et al.* 1995, p. 1163).

[14] The microreactor metaphor is in use at least since 1988; see reference in (Karol 1995, p. 574).

[15] '*Musterung*' is used also in the military register, for inspection of *troops 'von Truppen'*, or for the medical examination for military service '*von Rekruten*'.

[16] This is a very interesting definition, and I will return later on to its usefulness.

[17] The star is used here for 'catalyticity' in order to pay attention to a possible non-grammaticality of the term. However, in the rest of the present essay I will use 'catalyticity' without any star.

[18] See, for example, a recent 'explanation' of this exploit in Kelly 1998.

[19] Just before the quoted list Cavani and Trifirò (1994, p. 11) wrote, "The catalyst remains, in general, unaltered at the end of the catalytic process".

[20] This is an important ontological point, which regards the level of reality pertaining to the catalyst performance. We have seen above that the morphology of the Ziegler-Natta catalyst particles rules the morphology of the resulting polymer particles. Thus, a molecular process is controlled by geometrical factors and reproduces the same factors at a larger scale; see for example the figure in (Whiteley *et al.* 1992, p. 501).

[21] This term is particularly curious because "[t]hese 'dormant' species might still be quite reactive, however, with regard to other important transformations, such as chain termination or catalyst deactivation reactions" (Brintzinger *et al.* 1995, p. 1165, note 34).

[22]   Here I am referring to a pragmatic (from *prâgma*: fact, action) field in order to characterize an exploration which continuously looks at events outside the intermediate world of language; only in this last realm a 'pure' semantic analysis is possible.

[23]   The important case of autocatalytic systems falls within my discourse, with simple 'grammatical' modifications.

[24]   Personally I have an analogous aesthetic (sometimes ecstatic) and emotional attitude towards the best results (and descriptions) of several scientific disciplines, including classical and quantum mechanics. I invite the readers of this footnote to look quietly at the figure on p. 286 of the splendid book of Levine and Bernstein (1987). The figure shows on a time scale of 10^{-14} s the wave-packet evolution for the collinear $H + H_2$ ($\blacksquare = 1$) collision.

[25]   The term 'dormant' is used in the specialized register on Ziegler-Natta catalysts for the ionic species inactive concerning the chain growth; 'dormant' brings several unusual semantic traits into the microscopic description. The traits are of teleological, anthropomorphic, estimative sort; see also the preceding Note .

[26]   Vincent Brian Wigglesworth dedicated his research life to the study of insect physiology, and discovered the juvenile hormone and its function in the control of growth and form in insects. During the war he was Director of the Agricultural Research Council Unit of Insect Physiology.

[27]   *E.g.*, for *extrusion*: "Water content if often exceptionally critical: a change as small as 1% (in the usual range 30-50%) could be sufficient to make extrusion impracticable" (Pernicone 1994, p. 397).

[28]   *E.g.*, for *precipitation* the supersaturation dependence on concentration, temperature and pH (Perego & Villa 1994, p. 27), and for *tableting* the "very crude relationship […] between ductility, melting point, elastic modulus and Mohr's scale of hardness" (*ibid.*, p. 38).

[29]   The position of the catalytic reaction is also graphically central in fig. 1 of Schlögl 1993.

[30]   In the 1890s, the methodological struggle that was dubbed Methodenstreit was fought by Karl Lamprecht against the political history of G. von Below and of the majority of German historians.

[31]   My suspects on a too liberal use of 'reason' grew many years ago, when I read a splendid essay on the history of the word '*razza*' by the great linguist Leo Spitzer (Spitzer 1948, pp. 147-169); in fact Spitzer had demonstrated the connection between the Italian '*razza*' and the Latin '*ratio*'. From Italy '*razza*' was exported and adapted in other European countries, so that the English 'race', the French '*race*', and the German '*Rasse*' derived from the Italian word.

[32]   All the italics in this subsection are mine.

[33]   The same title of this paper is interesting.

References

Allison, R.J., Thomas, D.S.G.: 1993, "The Sensitivity of Landscapes", in: Thomas, D.S.G.; Allison, R.J. (eds.), *Landscape Sensitivity*, Wiley, Chichester, pp. 1-5.

Albizzati, E.; Giannini, U.; Morini, G.; Galimberti, M.; Barino, L.; Scordamaglia, R.: 1995, "Recent Advances in Propylene Polymerization with $MgCl_2$ Supported Catalysts", *Macromolecular Symposia*, **89**, 73-89.

Baiker, A.: 1996, "Towards Molecular Design of Solid Catalyst", in: Hightower *et al.* 1996, pp. 51-62.

Ballard, D.G.H.: 1986, "The Discovery of Polyethylene and its Effect on the Evolution of Polymer Science", in: Seymour & Cheng 1986, pp. 9-53.

Benson, S.W.: 1976, *Thermochemical Kinetics. Methods for the Estimation of Thermochemical Data and Rate Parameters*, Wiley, New York.

Brintzinger, H.H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R.M.: 1995, "Stereospecific Olefin Polymerization with Chiral Metallocene Catalysts", *Angewandte Chemie International Edition*, **34**, 1143-1170.

Burwell, R.L.: 1996, "A Retrospective View of Advances in Heterogeneous Catalysis: 1956-1996, Science", in: Hightower *et. al.* 1996, pp. 63-68.

Busico, V.; Cipullo, R.: 1995, "New Results in the Isotactic Polymerization of Propene promoted by Homogeneous Metallocene Catalysts", *Macromolecular Symposia*, **89**, 277-287.

Carpenter, S.R.: 1974, "Modes of Knowing and Technological Action", *Philosophy Today*, **18**, 162-166.

Carrà, S.; Parisi, F.; Pasquon, I.; Pino, P. (eds.): 1982, *Giulio Natta. Present significance of his scientific contribution*, Editrice di chimica, Milano.

Cavani, F.; Trifirò, F.: 1994, "Classification of Industrial Catalysts and Catalysis for the Petrolchemical Industry", in: Sanfilippo 1994, pp. 11-24.

Cerruti, L.: 1989, "Natta, Giulio", in: *Dictionary of Scientific Biography, Suppl.*, Vol. I, Scribner, New York, pp. 635-637.

Cerruti, L.: 1992, "Procedure conoscitive e culture disciplinari. Un' analisi storiografica", in: G. Battimelli, E. Gagliasso (eds.), *Le comunità scientifiche fra storia e sociologia della scienza*, (Quaderni della *Rivista di Storia della Scienza*, n. 2), pp. 83-122.

Corradini, P.: 1995, "The Impact of the Discovery of Stereoregular Polymers in Macromolecular Science", *Macromolecular Symposia*, **89**, 1-11.

Crespi, G.; Luciani, L.: 1981, "Olefin Polymers (Polypropylene)", in: *Kirk-Othmer Encyclopedia of Chemical Technology*, Vol. 16, Wiley, New York, pp. 453-469.

Cusumano, J.A.: 1995, "Environmentally Sustainable Growth in the 21st Century. The Role of Catalytic Science and Technology", *Journal of Chemical Education*, **72**, 959-964.

Durbin, P.T. (ed.): 1984, *A Guide to the Culture of Science, Technology and Medicine*, Free Press, New York.

Elsch, J.J.: 1983, "Karl Ziegler. Master Advocate for the Unity of Pure and Applied Research", *Journal of Chemical Education*, **60**, 1009-1014.

Farkas, A.: 1986, "Catalysis and Catalysts", in: *Ullmann's Encyclopedia of Industrial Chemistry*, Vol. A 5, VCH, Weinheim, pp. 313-367.

Galli, P.: 1995, "Forty Years of Industrial Developments in the Field of Isotactic Polyolefins", *Macromolecular Symposia*, **89**, 13-26.

Galli, P.; Luciani, L.; Cecchin, G.: 1981, "Advances in the polymerization of polyolefins with coordination catalysts", *Angewandte Makromolekulare Chemie*, **94**, 63-89.

Goodall, B.L.: 1986, "The History and Current State of the Art of Propylene Polymerization Catalysts", *Journal of Chemical Education*, **63**, 191-195.

Grasselli, R.K.: 1986, "Selective Oxidation and Ammoxidation of Olefins by Heterogeneous Catalysis", *Journal of Chemical Education*, **63**, 216-221.

Guczi, L.; Solymosi, L.; Tétényi, P. (eds.): 1993, *New Frontiers in Catalysis. Proceedings of the 10th International Congress on Catalysis, 19-24 July, 1992, Akadémiai Kiadó*, Elsevier, Budapest.

Guyot, A.; Spitz, R.; Journaud, C.; Eisenstein, O.: 1995, "A mechanistic Approach to $MgCl_2$ Supported Stereospecific Propene Polymerization: A New Model of Active Sites", *Macromolecular Symposia*, **89**, 39-54.

Halliday, M.A.K.: 1978, *Language as Social Semiotics: The Social Interpretation of Language and Meaning*, Arnold, London.

Hawkins, J.M.; Allen, R. : 1991, *The Oxford Encyclopedic English Dictionary*, Clarendon Press, Oxford.

Hightower, J.W.; Delgass, W.N.; Iglesia, E.; Bell, A.T. (eds.): 1996, *11th International Congress on Catalysis. 40th Anniversary*, Elsevier, Amsterdam.

Kaminsky, W.: 1986, "Synthesis of Polyolefins with Homogeneous Ziegler-Natta catalysts of High Activity", in: Seymour & Cheng 1986, pp. 257-270.

Kaminsky, W.: 1995, "Stereospecific Oligo- and Polymerization with Metallocene Catalysts", *Macromolecular Symposia*, **89**, 203-219.

Karol, F.J.: 1995, "Catalysis and the UNIPOL® Process in the 1990s", *Macromolecular Symposia*, **89**, 563-575.

Kashiva, N.; Kojoh, S.: 1995, "Stereoregularity and Regioregularity of Active Centers in Propene Polymerization", *Macromolecular Symposia*, **89**, 27-37.

Kelly, A.: 1998, "Materials science – why so fashionable?", *Interdisciplinary Science Reviews*, **23**, 321-324.

Kissin, Y.V.: 1995, "Kinetics of Olefin Coplymerization with Heterogeneous Ziegler-Natta catalysts", *Macromolecular Symposia*, **89**, 113-123.

Levine, R.D.; Bernstein, R.B.: 1987, *Molecular Reaction Dynamics and Chemical Reactivity*, Oxford UP, New York.

Lewis, R.J.: 1993, *Hawley's Condensed Chemical Dictionary*, Van Nostrand, New York.

Maxwell, I.E.: 1996, "Driving Forces for Innovation in Applied Catalysis", in: Hightower *et. al.* 1996, pp. 1-9.

McMillan, F.M.: 1979, *The Chain Straighteners. Fruitful Innovation: the Discovery of Linear and Stereoregular Synthetic Polymers*, MacMillan, London.

Mills, G.A.; Cusumano, J.A.: 1979, "Catalysis", in: *Kirk-Othmer Encyclopedia of Chemical Technology*, Vol. 5, Wiley, New York, pp. 16-61.

Mitcham, C.: 1984, "Philosophy of Technology", in: Durbin 1984, pp. 283-363.

Natta, G.; Pino, P.; Corradini, P.; Danusso, F.; Mantica, E.; Mazzanti, G.; Moraglio, G.: 1955, "Crystalline High Polymers of α -olefins", *Journal of the Americal Chemical Society*, 77, 1708-1710.

Obenaus, F.; Droste, W.; Neumeister, J.: 1985, "Butenes", in: *Ullmann's Encyclopedia of Industrial Chemistry*, Vol. A 4, VCH, Weinheim, pp. 483-494.

Perego, C.; Villa, P.: 1994, "Catalyst Preparation Methods", in: Sanfilippo 1994, pp. 25-64.

Pernicone, N.: 1994, "Scale-up of Catalyst Production", in: Sanfilippo 1994, pp. 388-403.

Pino, P.; Moretti, G.: 1987, "The impact of the discovery of the polymerization of the α -olefins on the development of the stereospecific polymerization of vinyl monomers", *Polymer*, **28**, 683-692.

Polanyi, M.: 1983, *Personal Knowledge. Towards a Post-Critical Philosophy*, Routledge, London.

Rabo, J.A.: 1993, "Catalysis: Past, Present and Future", in: Guczi *et al.* 1993, pp. 1-30.

Reuben, B.G.; Burstall, M.L.: 1973, *The chemical economy. A guide to the tecnology and economics of the chemical industry*, Longman, London.

Sacchi, M.C.; Forlini, F.; Tritto, I.; Locatelli, P.: 1995, "Stereochemistry of the Initiation Step in Ziegler-Natta Catalysts Containing Dialkyl Propane Diethers. A Tool for Distiguish the Role of Internal and External Donors", *Macromolecular Symposia*, **89**, 91-100.

Sanfilippo, D. (ed.): 1994, *The catalytic process from laboratory to the industrial plant*, SCI, Melegnano.

Santacesaria, E.; Forzatti, P.; Tronconi, E.: 1994, "Kinetics and Transport Phenomena", in: Sanfilippo 1994, pp. 197-209.

Satterfield, C.N.: 1980, *Heterogeneous Catalysis in Practice*, McGraw-Hill, New York.

Schlögl, R.: 1993, "Heterogeneous Catalysis – Still Magic or Already Science", *Angewandte Chemie International Edition*, **32**, 381-383.

Schlögl, R.: 1994, "Reply", *Angewandte Chemie International Edition*, **33**, 311-312.

Schlüter, A.-D.: 1999, *Synthesis of Polymers*, Wiley-VCH, Weinheim.

Schummer, J.: 1998, "The Chemical Core of Chemistry I: A Conceptual Approach", *HYLE*, **4**, 129-162.

Schwab, G.M.: 1981, "History of Concepts in Catalysis", *Catalysis in Science and Technology*, **2**, 1-11.

Seymour, R.B.; Cheng, T.: 1986, *History of Polyolefins. The World's Most Widely Used Polymers*, Reidel, Dordrecht.

Spaleck, W.; Aulbach, M.; Bachmann, B.; Küber, F.; Winter, A.: 1995, "Stereospecific Metallocene Catalysts: Scope and Limits of Rational Catalyst Design", *Macromolecular Symposia*, **89**, 237-247.

Spitz, P.H.: 1988, *Petrochemicals. The Rise of an Industry*, Wiley, New York.

Spitzer, L.: 1948, *Essays in Historical Semantics*, Vanni, New York.

Stevens, M.P.: 1999, *Polymer Chemistry. An Introduction*, Oxford UP, New York

Tait, P.J.T. : 1986, "The Development of High Activity Catalysts in α -olefins Polymerization", in: Seymour & Cheng 1986, pp. 213-242.

Tait, P.J.T.; Zohuri, G.H.; Kells, A.M.: 1995, "Comparative Kinetic and Active Centre Sudies on Magnesium Chloride Supported Catalysts in Propylene Polymerization", *Macromolecular Symposia*, **89**, 125-138.

Thomas, J.M. : 1994, "Turning Points in Catalysis", *Angewandte Chemie International Edition*, **33**, 913-937.

Thomas, J.M.; Zamaraev, K.I.: 1994, "Rationally Designed Inorganic Catalysts for Environmentally Compatible Technologies", *Angewandte Chemie International Edition*, **33**, 308-311.

Threadgold, T.: 1997, "Literary Structuralism and Semiotics", in: Lamarque, P.V.; Asher, R.E. (eds.): 1997, *Concise Encyclopedia of Philosophy of Language*, Pergamon, Exeter, pp. 129-146.

Wagner, F.S.: 1978, "Acetic Acid", in: *Kirk-Othmer Encyclopedia of Chemical Technology*, Vol. 1, Wiley, New York, pp. 124-147.

Whiteley, K.S.; Heggs, T.G.; Koch, H.; Mawer, R.L.; Immel, W.: 1992 "Polyolefins", in: *Ullmann's Encyclopedia of Industrial*

Chemistry, Vol. A 21, VCH, Weinheim, pp. 487-577.

Wilke, G.: 1975, "Karl Ziegler, in Memoriam", in: J.C.W. Chien (ed.), *Coordination Polymerization. A Memorial to Karl Ziegler*, Academic Press, New York.

Ziegler, K. : 1968, "A Forty Years Stroll through the Realms of Organometallic Chemistry", *Advances in Organometallic Chemistry*, **6**, 1-17.

Ziegler, K.; Holzkamp, E.; Breil, H.; Martin, H.: 1955a, "Polymerisation von Äthylen und anderen Olefinen", *Angewandte Chemie*, **67**, 426.

Ziegler, K.; Holzkamp, E.; Breil, H.; Martin, H.: 1955b, "Das Mülheimer Normaldruck-Polyäthylen-Verfahren", *Angewandte Chemie*, **67**, 541-547.

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