CATALYTIC THERMAL REACTIONS OF CUMENE OVER SEPIOLITE AND PALYGORSKITE

U. Shuali*, L. Bram*, M. Steinberg** and S. Yariv**

*ISRAEL INSTITUTE FOR BIOLOGICAL RESEARCH, NESS ZIONA 70450,
**DEPARTMENT OF INORGANIC AND ANALYTICAL CHEMISTRY, THE HEBREW
UNIVERSITY, JERUSALEM 91904, ISRAEL

The catalytic activity of sepiolite and palygorskite in cracking and disproportionation reactions of cumene was studied. The formation of benzene, diisopropylbenzene and propylene characterizes Brönsted acid sites whereas that of ethylbenzene characterizes Lewis acid sites. At 150 and 250°C the reactions are determined mainly by the presence of acid sites in the channels of these clays. The yields are significantly higher in sepiolite as compared to palygorskite. The concentration of acid sites and their strength increase with the thermal loss of zeolitic and part of the bound water. At 350°C the reactions are determined by the acidity of the external surface of both minerals and yields are only slightly higher in sepiolite. At 150°C most acid sites are of the Brönsted type. With the rise in temperature the relative concentration of Lewis acid sites increases.

Clay minerals are used as catalysts in many cracking and disproportionation processes [1, 2]. The catalytic activity, which is mainly determined by the surface acidity of the mineral, results from the presence of surface groups, such as siloxane, silanol, aluminol, –Al–O and –Mg–O, located at the edges of the alumino- and magnesium-silicate frameworks, as well as from exchangeable cations and adsorbed water molecules. Most studies on the catalytic activity of clays, were dealing with swelling smectite minerals and only very little work was carried out with sepiolite and palygorskite [3–18]. These minerals are built of TOT ribbons with a width along the *b*-axis of three linked tetrahedral chains in sepiolite and two linked chains in palygorskite. The two minerals are characterized by having parallel zeolitic channels into which small molecules can penetrate [19–22]. It has been recently shown by electron microscopy that due to defects some of the chan-

nels are joined, forming a network of pores with dimensions larger than those which were previously reported from X-ray measurements [23, 24]. Consequently, larger molecules can also penetrate into these pores. It is expected that in addition to surface activity, the catalytic contribution of these two minerals will be affected by the channels and the larger pores and will be accompanied by selectivity. The present paper describes a preliminary study on the catalytic activity of sepiolite and palygorskite . The purpose of this study was to establish whether the channels contribute to the catalytic activity of these minerals.

A study of cracking and disproportionation of isopropylbenzene (cumene) under the catalytic influence of sepiolite and palygorskite is reported herewith. To the best of our knowledge no such study has been previously reported on this system. According to Jacobs [25] the cracking of alkylaromatics requires the presence of strong acid sites, equivalent to that of an aqueous 70% H_2SO_4 solution. The reaction products obtained by the catalytic effect of Lewis acid sites differ from those obtained by Brönsted sites. Corma and Wojciechowski reviewed the literature on the catalytic cracking and disproportion reactions of cumene [1] and concluded that in the presence of Brönsted acid sites, the products obtained are benzene and propylene, and to a smaller extent also diisopropylbenzene. Benzene and propylene are formed by a unimolecular cracking of cumene or the product diisopropylbenzene. Benzene and diisopropylbenzene are obtained by a bimolecular disproportionation of cumene. In the presence of Lewis acid sites the reaction products are ethyl-, n-propyl- and butylbenzenes as well as cymene. Ethyl- and butylbenzene or cymene are obtained from a bimolecular disproportionation of cumene whereas n-propylbenzene is an isomerization product of cumene.

We studied the catalytic activity of these minerals in the cracking and disproportionation reactions of cumene by determining its conversion and the yields of benzene, ethylbenzene, diisopropylbenzene and propylene. The formation of benzene, diisopropylbenzene and propylene characterized the presence of Brönsted acid sites whereas the formation of ethylbenzene characterized the presence of Lewis acid sites.

Experimental

Materials

Organic chemicals were purchased from Aldrich. Cumene (purity 99%) was purified first by washing with H_2SO_4, Na_2CO_3 and water, and after drying on $MgSO_4$, it was distilled and passed through a column of active alumina [26].

Sepiolite from Vallecas, Spain, and palygorskite from Quincy, Florida, were supplied by Ward's Natural Science Establishment. The clays were manually ground and sieved. A fraction with a diameter smaller than 0.3 mm was used in the present study. Specific surface areas of these samples heated at 150, 250, 350 and 900° were determined with nitrogen by the B.E.T. method using a Quanta Chrom system.

Cracking reactions and products

Cracking and disproportionation reactions were carried out in an autoclave and in a fixed bed reactor. Reaction products were identified and determined by gas chromatography using FID and TCD and columns of Porapak Q or DC-550 for gases or liquid separations, respectively. Retention times of the reaction products were compared with those of standard compounds. The columns were at 80° whereas the injection port and the detector were at 110°. Helium was used as a carrier with a flow rate of 75 cm^3/min.

Reactions in the autoclave

The autoclave was purchased from Berghoff GmbH Labortechnik (model 572). It could be used at temperatures up to 250°. Cracking and disproportionation reactions of cumene in the presence of sepiolite and palygorskite were carried out in this autoclave at 150 and 250°. Aliquots of 75 cm^3 of cumene were heated during 4 h in the presence of 10 g of ground clay. Both clays were used as received.

Preparation of the fixed bed flow reactor

The reactor was made of a pyrex tube (60 cm length, 1.5 cm i.d.) hold in a temperature-controlled furnace. The clayey-bed was made from the ground clay (fraction < 0.3 mm), extruded to ~3×1 mm pellets. It was packed between two layers of quartz wool (GC grade) supported in the middle of

this tube. Reactants were dropped directly to the head of the reactor using a doser syringe and swept by a carrier gas. Products which are liquid at room temperature were collected in a cooled trap (-5°); gaseous products were sampled directly with a sampling loop.

In order to oxidize trace impurities of organic matter and to remove interparticle, zeolitic and most bound water in the clay, the bed was first heated for three hours at 350°, under a stream of air (100 cm^3/min) followed by three hours under a stream of helium (100 cm^3/min).

Reactions in the fixed bed flow reactor

Cracking and disproportionation reactions of cumene in the presence of preheated sepiolite or palygorskite, in the fixed bed flow reactor were carried out at 350°, under a constant flow of helium (150 cm^3/min). Contact time of the inert carrier with the clay bed was 7 s. The cumene was fed in drops at the top of the reactor at a rate of 1.5 cm^3/h (1.3 g/h). Reaction products were collected during six hours but we started to collect them half an hour after the beginning of the process. In the first half hour the coke formation in this system is very intensive [27, 28] and consequently, steady state in the rate of conversion of cumene is obtained only after this period.

Parallel experiments at 350° were carried out with sepiolite and palygorskite preheated at 900°, as the bed material. Surfaces of calcined clays are inert and IR and DTA measurements showed that they do not adsorb water or organic materials.

Results

The results of cumene cracking and disproportionation reactions in the autoclave, are summarized in Table 1 and those obtained from reactions in the fixed bed flow reactor, are summarized in Table 2. Molar percentage of the conversion of cumene was assessed by comparing peak areas recorded before and after reaction. For the reaction products, molar percentage values which are given in column *A* are related to the total amount of cumene which was admitted into the reaction cell whereas values given in column *B* are related to the converted cumene.

Propylene obtained in the fixed-bed flow reactor was determined directly in the gases evolved from the reactor by collecting 10 cm^3 samples in a sampling valve and loop. There was a permanent decrease in the intensity of the propylene signal during the reaction. In sepiolite the yield was initially 10–

12 mol% of the converted cumene and droped to 4 mol%. In palygorskite the yield was initially 15 mol% and dropped to 4 mol% after 6 h.

During the reaction the clay beds became black probably due to coke formation [27, 28].

When calcined sepiolite and palygorskite were used as beds, there was cracking or disproportionation of cumene at 350°.

Surface areas of sepiolite at room temperature and at 150, 250, 350 and 900°are 145, 215, 275, 220 and 110 $\cdot$ 10^3 m^2/kg, respectively, and of palygorskite: 95, 140, 140, 130 and 60 $\cdot$ 10^3 m^2/kg, respectively.

Table 1 Products distribution and yields in the catalytic cracking and disproportionation of cumene (Reaction in the autoclave)

Clay	Temp., °C	Conversion of cumene, %	Conversion to products, mol %							
			Benzene		Propene		Ethyl-benzene		Diisopropyl-benzene	
			A	B	A	B	A	B	A	B
Sepiolite	150	~ 3	~0.8	~28	~0.7	~22	~0.15	~ 5	~0.25	~ 8
	250	~28	~7.8	~27	~6.2	~22	~4.5	~16	~7.6	~27
Palygor-skite	150	~ 1	~0.3	~34	~0.3	~30	~0.05	~ 5	~0.15	~15
	250	~14	~5.1	~37	~4.6	~33	~2.25	~16	~3.2	~23

Subtitle A refers to yield of products (mol %) relative to challenged cumene.

Subtitle B refers to yield of products (mol %) relative to converted cumene.

Table 2 Products distribution and yields in the catalytic cracking and disproportionation of cumene at 350°C (Reaction in the fixed-bed flow reactor)

Clay	Conversion of cumene, %	Conversion to products, % mol					
		Benzene		Ethylbenzene		Diisopropyl-benzene	
		A	B	A	B	A	B
Sepiolite	~7	~0.4	~ 6	~1.05	~15	~1.05	~15
Palygor-skite	~5	~0.5	~10	~0.75	~15	~0.75	~15

Subtitle A refers to yield of products (mol %) relative to challenged cumene.

Subtitle B refers to yield of products (mol %) relative to converted cumene.

Discussion

In the present study the thermal reactions of cumene over sepiolite and palygorskite were investigated by two techniques. In one technique cumene was isothermally heated in an autoclave at 150 or 250°, in the presence of the clay. At 150° the zeolitic water is evolved, accompanied by a very small decrease in the spacing of the prominent 001 X-ray reflection from 1.03 to 0.99 nm [29], indicating that small organic molecules can penetrate the channels. At 250° some of the bound water (water molecules coordinated to octahedral Mg or Al exposed inside the channels, at the edges of the TOT ribbons) is also evolved. At this temperature, the loss of coordinated water is reversible. Consequently, by this technique we obtained information on the catalytic contribution of the channels of these two clays.

In the second technique cumene flew through a fixed-bed flow reactor at 350°. The fixed bed consisted of palygorskite or sepiolite preheated at 350 or 900°. At 350° more than 65% of the bound water is irreversibly lost, the clay structure folds with a new c spacing at 0.92 nm [29], indicating that the zeolitic channels do not exist any more. At 900°, after the clay has been completely dehydroxylated, it recrystallizes to form clinoenstatite [30]. It is thus expected that after heating the clay either at 350 or 900° cumene molecules will not be able to penetrate into the channels. Consequently, by this technique we obtained information on the catalytic contribution of the external surfaces of these two clays.

Effects of Brönsted and Lewis acid sites in the channels on thermal reactions of cumene

The B.E.T. method, using nitrogen, characterizes mainly the external surfaces of both minerals. The rise in temperature is associated first with an increase but later with a decrease in the specific surface area. When zeolitic and interparticle water is evolved, there is an increase in the specific surface area because the interparticle space becomes more accessible for nitrogen. Also small amounts of nitrogen penetrate into the channels. The thermal decrease in the external surface area of both clays results from their folding, dehydroxylation and recrystallization. When the temperature changes from 150 to 250°, there is no correlation between changes in the reaction-products yields and changes in the surface areas of sepiolite or palygorskite. It is therefore concluded that at these temperatures the reactions of cumene are not determined by the external surface of sepiolite or palygorskite. We

are now going to show that they are determined by the internal surfaces of the channels.

Types of surface acid sites in the channels of sepiolite and palygorskite were recently characterized by infrared thermospectrometry, from the adsorption of n-butylamine, pyridine and trimethylpyridine [31]. At room temperature or at 100° most of the adsorbed amines form hydrogen bonds with zeolitic and bound water molecules where the organic amine is a proton acceptor and the water molecule is a proton donor. This indicates that at room temperature and at 100°, most of the surface acidity of these two minerals stems from weak Brönsted acid sites originating mainly from zeolitic water and to a smaller extent also from bound water. Pyridine is a weak base and the adsorbed pyridine is not protonated, indicating the absence of strong Brönsted acid sites. Butylamine is a stronger base, however, only a very small fraction of the adsorbed butylamine is protonated, resulting in the appearance of ammonium cations. This is characteristic of medium-strong Brönsted acid sites, originating from the dissociation of bound water molecules. When the amine treated sepiolite and palygorskite are heated, water is lost and amine molecules coordinate directly to octahedral Mg or Al cations exposed to the channels, indicating that the latter behave as Lewis acid sites.

Table 1 shows that cumene cracking and disproportionation over sepiolite at 150 and 250° are much higher than those over palygorskite. This is in agreement with the larger cross section of the channels in sepiolite (1060 × 370 pm) as compared to palygorskite (640 × 370 pm) and is an indication that the reactions at these temperatures are controlled mainly by the acidity in the channels. From the formation of benzene, ethylbenzene, diisopropylbenzene and propylene during the thermal treatment it is obvious that both types of acid sites exist in the channels. This is in agreement with our IR thermospectrometry study [31].

Table 1 also shows that the temperature has a significant effect on the yields of the reaction products. The amount of cumene which reacts at 250° is 10 or 14 times higher as compared to that which reacts at 150°, in the presence of sepiolite or palygorskite, respectively. At 150° there are still zeolitic water which contribute to the acidity of the channels, whereas at 250° the channels contain only bound water molecules the acidity of which is stronger than that of the zeolitic water, due to the polarizing power of Mg or Al at the edge of the octahedral sheet framework [31]. At 150° many of these sites are screened by the zeolitic water and their catalytic effect is not apparent. At 250° some of the bound water is lost, leaving several of the terminal Mg and Al coordinated by only one water molecule. Consequently, the

polarizing effect of terminal Mg and Al becomes more powerful, thus the acid strength of these coordinating water molecules is enhanced. The rise in temperature from 150 to 250° highly increases the formation of benzene by the factors 9.75 and 17 and of diisopropylbenzene by the factors 30 and 21, in the presence of sepiolite and palygorskite, respectively.

The loss of some of the bound water at 250° leads to the exposure of several Mg and Al cations at the edges of the octahedral sheet frameworks inside the channels, and thereby Lewis acid sites become available to the organic molecules. Indeed, the rise in temperature from 150 to 250° highly increases the yields of ethylbenzene by factors of 30 and 45 in the presence of sepiolite and palygorskite, respectively. The factor for palygorskite is higher than that for sepiolite because the former loses more bound water at 250° than the latter. These factors are much higher than those of the entire cracking reaction, determined by the total conversion of cumene, when the temperature rises from 150 to 250°. At the higher temperature the entire cracking of cumene is only 10 or 14 times higher in the presence of sepiolite or palygorskite, respectively, as compared to that which is converted at the low temperature. This is an indication that when temperature rises from 150 to 250°, the increase in concentration of Lewis acid sites is much higher than that of Brönsted acid sites.

Effects of the external acid sites on the thermal cracking of cumene

At 350° both clays do not contain interparticle and zeolitic water, more than 65% of the bound water is lost, the mineral skeletons are folded and the channels are not accessible to cumene. Cracking can be catalyzed by the external surface of both clays. From the results which are summarized in Table 2 it is obvious that at this temperature the external surfaces of sepiolite and palygorskite have both Brönsted and Lewis acid sites. In the absence of water, Brönsted acid sites must be due to the presence of surface silanol, aluminol and magnesol groups. Lewis acid sites become available due to the exposure of Mg or Al at the external edges of the octahedral sheet framework.

The amounts of ethylbenzene which are obtained at 350° in the presence of sepiolite or palygorskite are equal to those of diisopropylbenzene obtained with the same clays, respectively. At 150 or 250°, on the other hand, the amounts of diisopropylbenzene are much higher. Furthermore, the relative amounts of benzene which is formed during the thermal treatment are much higher at 150 or 250° than at 350°. This observation indicates that the

concentrations of Lewis acid sites relative to Brönsted acid sites in both clays increase at 350°.

Table 2 shows that the entire reaction, as determined by the total conversion of cumene, is higher in the presence of sepiolite than of palygorskite by the factor 1.4 (catalytic activity ratio). In other words, the catalytic activity of sepiolite is only slightly higher than that of palygorskite. It can be related on the one hand to the surface areas of these minerals at 350°, and on the other to their Al/Mg content. The ratio between surface areas of sepiolite and palygorskite at 350° is 1.7, slightly higher than 1.4, the catalytic activity ratio. This difference is attributed to differences in acid strength of surface sites. It is expected that the composition of the bulk reflects surface composition. The two samples were analyzed in our laboratory and we found that Al_2O_3 contents is sepiolite and palygorskite are 1.52 and 8.02% and those of MgO are 23.08 and 8.40%, respectively. Since aluminol and Al^{3+} are stronger Brönsted and Lewis acids than magnesol and Mg^{2+}, respectively, the high Al to Mg ratio in palygorskite leads to its higher surface acidity as compared to sepiolite.

Effect of calcination on Brönsted and Lewis acidity of the external surfaces of sepiolite and palygorskite

After calcination at 900°, both clays became inert and lost their catalytic activities, indicating the loss of all acid sites. The thermal treatment leads to dehydroxylation, followed by the recrystallizations of meta-sepiolite and meta-palygorskite and the formation of clinoenstatite [30]. At this stage surface acid groups, such as silanol, aluminol and magnesol, or terminal Mg and Al at the external edges of the octahedral sheet framework, are not accessible. Only oxygens are exposed, belonging to groups such as Si-O-Si, Si-O-Al, Si-O-Mg, Al-O-Al or Mg-O-Mg, which are inert or basic in their nature and no thermal cracking or disproportionation of cumene was detected.

References

1 A. Corma and B. W. Wojciechowski, Catal. Rev. -Sci. Eng., 27 (1985) 29.
2 M. L. Occelli, S. D. Landau and T. J. Pinnavaia, J. Catal., 90 (1984) 256.
3 Y. Kitayama and A. Michishita, J. Chem. Soc., Chem. Comm., (1981) 401.
4 Y. Kitayama, T. Hoshima, T. Kimura and T. Asakawa, Proc. 8th Int. Congress Catal. Berlin V, (1984) 647.
5 Y. Kitayama and M. Kamimura, Chemistry Express, 5 (1990) 545.
6 A. J. Dandy and M. S. Nadiye-Tabiruka, Clays Clay Miner., 30 (1982) 347.

7 A. Corma and Perez-Pariente, Clay Miner., 22 (1987) 233.

8 J. M. Campelo, A. Garcia, D. Luna and J. M. Marinas, Clay Miner., 22 (1987) 233.

9 J. M. Campelo, A. Garcia, D. Luna and J. M. Marinas, React. Kinet. Catal. Lett., 41 (1990) 13.

10 A. Corma, C. Rodellas and V. Fornes, J. Catal., 88 (1984) 374.

11 E. Ruiz-Hitzky and B. Casal, J. Catal., 92 (1985) 291.

12 M. A. Aramendia, V. Borau, J. F. Gomez, C. Jimenez and J. M. Marinas, React. Kinet. Catal. Lett., 30 (1986) 329.

13 M. A. Aramendia, C. Jimenez, J. M. Marinas and M. E. Sempere, React. Kinet. Catal. Lett., 32 (1986) 525.

14 M. A. Aramendia, V. Borau, F. Castellanos, C. Jimenez and J. M. Marinas, React. Kinet. Catal. Lett., 36 (1988) 251.

15 F. V. Melo, E. Sanz, A. Corma and A. Mifsud in "Preparation of Catalysts" IV. Editors: B. Delmon, P. Grange, P. A. Jacobs and G. Poncelet, Elsevier 1987 p. 557.

16 S. Mendioroz, J. M. Palacios, J. L. G. Fierro and A. Agudo, Bull. Soc. Chim. Belg., 96 (1987) 891.

17 M. L. Occelli, Am. Chem. Soc., Div. Pet. Chem. - Prepr., 32 (1987) 658.

18 C. J. Groenenbaum and P. A. Wiringa, EP 219174 (22 Apr. 1987), CA 106:216824.

19 R. M. Barrer, N. Mackenzie and D. M. McLeod, J. Phys. Chem., 58 (1954) 560, 568.

20 A. J. Dandy, J. Phys. Chem., 72 (1968) 334.

21 A. J. Dandy, J. Chem. Soc. (A), (1971) 2383.

22 G. Manara and M. Taramasso, J. Chromatogr., 65 (1972) 349.

23 M. Rautureau and A. Mifsud, Clay Miner., 12 (1977) 309.

24 M. Rautureau, G. Clinard, A. Mifsud and S. Caillere, 104th Cong. Nat. Soc. Savantes, Bordeaux, Sciences, Sacs III, (1979) 199.

25 P. A. Jacobs "Carboniogenic Activity of Zeolites" 1977

26 D. D. Perrin, W. L. F. Armarego and D. R. Perrin, Purification of Laboratory Chemicals, Pergamon Press, Oxford 1966.

27 A. Corma and B. W. Wojchiechowski, Canad. J. Chem. Eng., 58 (1980) 620.

28 C. D. Prater and R. M. Lago, in "Advances in Catalysis", 8 (1956) 293.

29 A. Singer in "Minerals in Soil Environment", Chapter 17, 829 (1989).

30 J. L. Martin Vivaldi and P. Fenoll Ach-Ali, in "Differential Thermal Analysis" (Editor: R. C. Mackenzie), Academic Press 1970.

31 U. Shuali, L. Bram, M. Steinberg and S. Yariv, Thermochim. Acta, 148 (1989) 445.

32 U. Shuali, S. Yariv, M. Steinberg, M. Müller Vonmoos, G. Khar and A. Rub, Thermochim. Acta, 135 (1988) 291.

Zusammenfassung — Es wurde die katalytische Aktivität von Sepiolith und Palygorskit in Krack- und Disproportionierungsreaktionen von Kumol untersucht. Die Bildung von Benzol, Diisopropyl- benzol und Propylen charakterisieren Aziditätsstellen nach Bronsted, während die Bildung von Ethylbenzol Aziditätsstellen nach Lewis charakterisiert. Bei 150°C und 250°C werden die Reaktionen hauptsächlich durch die Gegenwart von Aziditätsstellen in den Tunnelgebilden dieser Tonerden bestimmt. Bezogen auf Palygorskit sind die Ausbeuten bei Sepiolith eindeutig höher. Die Konzentration der Aziditätsstellen und ihre Stärke nehmen mit der thermischen Abgabe von zeolithischem und eines Teiles des gebundenen Wassers zu. Bei 350°C werden die Reaktionen durch die Azidität der externen Oberfläche beider Mineralien bestimmt und die Ausbeuten sind in Sepiolith kaum höher. Bei 150°C sind die meisten Aziditätsstellen vom Brönsted-Typ. Mit ansteigender Temperatur nimmt auch die relative Anzahl von Lewis-Aziditätsstellen zu.