

## Rh/ZnO-Al<sub>2</sub>O<sub>3</sub> Catalysts for Selective Hydrogenation of Crotonaldehyde

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**Abstract:** Gas phase hydrogenation of crotonaldehyde was performed over 1 wt% Rh/ZnO-Al<sub>2</sub>O<sub>3</sub> catalysts with various Zn/Rh atomic ratios. Monometallic Rh/Al<sub>2</sub>O<sub>3</sub> was also prepared for comparison. The samples were prepared by the successive impregnation of Al<sub>2</sub>O<sub>3</sub> with chloride precursors of zinc and rhodium. The solids have been characterized by H<sub>2</sub> chemisorption, temperature-programmed reduction, scanning electron microscopy, and cyclohexane dehydrogenation. Their catalytic behaviour in the gas phase crotonaldehyde hydrogenation reaction after reduction treatment in flowing hydrogen at 723 K was investigated. The relationship between catalytic activity, selectivity for crotyl alcohol, and physicochemical properties of the catalysts was examined. Results obtained showed that the presence of Zn clearly promotes the hydrogenation of the carbonyl bond. The catalyst with Zn/Rh atomic ratio of 5 displayed good catalytic stability and the highest selectivity for crotyl alcohol (70%) along with alloy formation.

**Key words:** rhodium-based catalyst; crotonaldehyde; hydrogenation; zinc oxide; selectivity

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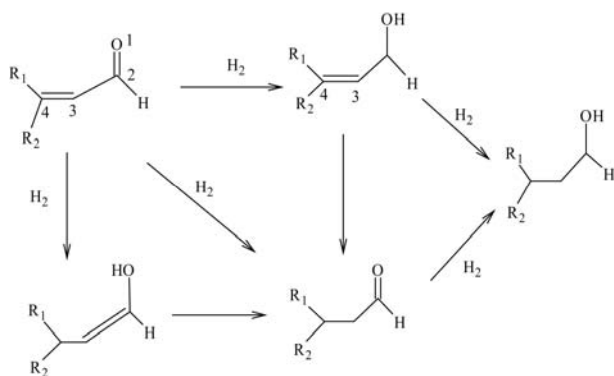
The unsaturated alcohols obtained by selective hydrogenation of the C=O group of  $\alpha,\beta$ -unsaturated aldehydes are a very important intermediate for the production of perfumes, flavours, and pharmaceuticals [1–4]. The selective hydrogenation of the carbonyl bond in the presence of an olefinic bond [5] is very difficult because the C=C group hydrogenation is thermodynamically and kinetically favored [6–8]. Thus, monometallic catalysts supported on Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> led mostly to the formation of saturated aldehyde [9]. Therefore it is necessary to promote the metal to increase selectivity of the carbonyl bond hydrogenation. This can be achieved by using bimetallic catalysts [10–15] as well as supports such as TiO<sub>2</sub> [16,17], ZnO [18], and CeO<sub>2</sub> [19–21] that can interact with the metal after a reduction treatment.

The use of zinc as a support for platinum in different reactions is currently being the subject of an intense research work. In the field of selective hydrogenations, the performance of Pt/ZnO catalysts in gas phase crotonaldehyde hydrogenation was investigated by Consoni et al. [22]. The authors [22] observed a correlation between reduction temperature and both activity and selectivity. An increase in the reduction temperature leads to a decrease in catalytic activity and an increase in crotyl alcohol selectivity along with

the formation of Pt-Zn alloy. Recently, Ammari et al. [23] reported a high crotyl alcohol selectivity of 80% during the reaction at 400 °C over Pt/ZnCl<sub>2</sub>/SiO<sub>2</sub>. This fact has been explained by a synergetic effect between Zn and chlorine. A high amount of chlorine on the catalyst surface leads to an increase of the support Lewis acidity, along with the formation of Pt-Zn alloy.

Zn, used as promoter, improves unsaturated alcohol formation over Pt catalysts in the crotonaldehyde hydrogenation reaction [24,25]. A recent study [26] showed that addition of zinc to a silica-supported Co catalyst produced an increase in unsaturated alcohol selectivity. This promotion was favored by increasing reduction temperature. A similar favorable effect of Zn has been recently obtained over Cu/ZnO/SiO<sub>2</sub> catalysts [27]. The selectivity enhancement for hydrogenation of the C=O bond was explained by considering that the high temperature hydrogen treatment forms mobile ZnO<sub>x</sub> reduced species that strongly interact with Cu<sup>0</sup> crystallites. The resulting Cu<sup>0</sup>-ZnO<sub>x</sub> species preferentially catalyze the crotyl alcohol formation from crotonaldehyde.

The hydrogenation of unsaturated aldehydes can proceed via different reaction pathways as shown in Scheme 1. The 1,2-addition of hydrogen gives the unsaturated alcohol, the



**Scheme 1.** Reaction pathways in the hydrogenation of unsaturated aldehydes [28].

3,4-addition gives the saturated aldehyde, and the 1,4-addition gives the enol which isomerizes into a saturated aldehyde. Subsequent hydrogenation of either the C=C or C=O bond leads to the saturated alcohol. The target reaction for selective hydrogenation is the 1,2-addition of hydrogen.

In the current work, we studied the crotonaldehyde hydrogenation on a series of 1 wt% Rh/ZnO-Al<sub>2</sub>O<sub>3</sub> and 1 wt% Rh/Al<sub>2</sub>O<sub>3</sub> catalysts. We examined the effect of Zn/Rh atomic ratio on the distribution of hydrogenation products and also on the character of metal-support interactions and rhodium particle size distribution. Catalysts are characterised by H<sub>2</sub> chemisorption, temperature-programmed reduction (H<sub>2</sub>-TPR), scanning electron microscopy (SEM), and cyclohexane dehydrogenation. Physicochemical properties of the catalysts are correlated with the catalytic behaviour in crotonaldehyde hydrogenation.

## 1 Experimental

### 1.1 Materials preparation

The  $\gamma$ -alumina (Degussa, surface area = 210 m<sup>2</sup>/g) was calcined in flowing air for 4 h at 773 K. Prior to use, it was ground and then sieved to retain particles with sizes between 0.1–0.25 mm. The supports, ZnO-Al<sub>2</sub>O<sub>3</sub> mixed oxides with various compositions, were prepared by impregnation of the calcined alumina by an aqueous solution of zinc chloride ZnCl<sub>2</sub> (Aldrich, 98%). The supernatant solution was evaporated to dryness on a sand bath maintained at 333 K. The catalyst batch was subsequently dried overnight at 393 K and calcined in an air flow at 773 K for 4 h before storage. The resulting Al<sub>2</sub>O<sub>3</sub> and ZnO-Al<sub>2</sub>O<sub>3</sub> were further impregnated with RhCl<sub>3</sub>·xH<sub>2</sub>O (40% Rh, Fluka), dried overnight at 393 K, and calcined at 773 K for 4 h to obtain Rh/Al<sub>2</sub>O<sub>3</sub> and Rh/ZnO-Al<sub>2</sub>O<sub>3</sub> with Zn/Rh atomic ratios of 1, 2, 3, and 5, while the metal content was 1 wt% in rhodium.

### 1.2 Characterization

Before hydrogen chemisorption experiments, the catalyst sample (0.2 g) was reduced in H<sub>2</sub>/Ar by heating to 773 K at 5 K/min and held for 2 h followed by flushing with an Ar flow for 2 h at the same temperature. Then the reactor was cooled down and when the system had reached steady-state at 298 K, pulses of pure hydrogen (loop volume 0.325 cm<sup>3</sup>) were injected every 2 min at this temperature. The gas was analyzed by GC (carrier gas: Ar) on a 5A molecular sieve column using a thermal conductivity detector.

H<sub>2</sub>-TPR experiments were carried out on a pulse chromatograph described elsewhere [29,30]. The catalyst (0.2 g) was pre-treated under Argon at room temperature for 30 min. The TPR profile was recorded by heating the catalyst from room temperature to 773 K at a rate of 5 K/min.

SEM was carried out on a Philips XL30 FEG ESEM.

### 1.3 Catalytic tests

Cyclohexane dehydrogenation was carried out under atmospheric pressure in a continuous flow reactor at 543 K. Injection of cyclohexane was made using a calibrated motor-driven syringe. The partial pressures were 97 and 3 kPa for hydrogen and cyclohexane, respectively. All measurements were performed with a total flow rate of 100 cm<sup>3</sup>/min. Analysis of the reaction products was performed by gas chromatography (Varian 3400X) with a flame ionization detector on a HP-PLOT Al<sub>2</sub>O<sub>3</sub> “KCl” column. The only detected product was benzene.

Vapour phase hydrogenation of crotonaldehyde (2-butenal) was carried out in a glass reactor at 393 K and atmospheric pressure. The catalyst (0.2 g) was pretreated at 723 K in a 30 cm<sup>3</sup>/min flow of hydrogen for 2 h followed by cooling in a H<sub>2</sub> flow to the desired reaction temperature (393 K). A known quantity of crotonaldehyde (1 cm<sup>3</sup>/min, 99% purity, Fluka) was drawn up from the bottle using a tight syringe and then carried over the catalyst by the hydrogen flow (H<sub>2</sub>/crotonaldehyde ratio = 15). The H<sub>2</sub> gas was first purified by passing through a trap. The reaction products were drawn off the flow line at different times during the catalytic run and analyzed by gas chromatography with a 1.5 m long carbowax 1500 column using a flame ionization detector. The selectivity for different products was calculated as the molar ratio of the selected product to the total formed products.

## 2 Results and discussion

### 2.1 H<sub>2</sub> chemisorption results

Selected supported rhodium catalysts on ZnO-Al<sub>2</sub>O<sub>3</sub> with

various Zn/Rh atomic ratios are characterized by H<sub>2</sub> chemisorption after reduction at 773 K. The obtained results are listed in Table 1. The high hydrogen uptake of the mono-metallic RA catalyst reflects the high rhodium dispersion (77%). This value is analogous to that obtained by Benseradj et al. [31], and it is higher than the one obtained by Sato et al. (60%) [32]. However, chemisorption values decrease with addition of Zn, reflecting a loss in the number of surface sites, suggesting either the development of a SMSI (strong metal-support interaction) or sintering of the metal particles. This lower ability for H<sub>2</sub> chemisorption must be attributed to an increase in the support coverage by ZnO species and to a poorer dispersion.

The increase in the atomic ratio of Zn/Rh from zero to 5 increased the metal particle size from 1.42 to 2.61 nm and decreased the metal dispersion from 77% to 42%. This is explained by the larger particle formation. These results are analogous to those found by Silvester-Alberto et al. [33].

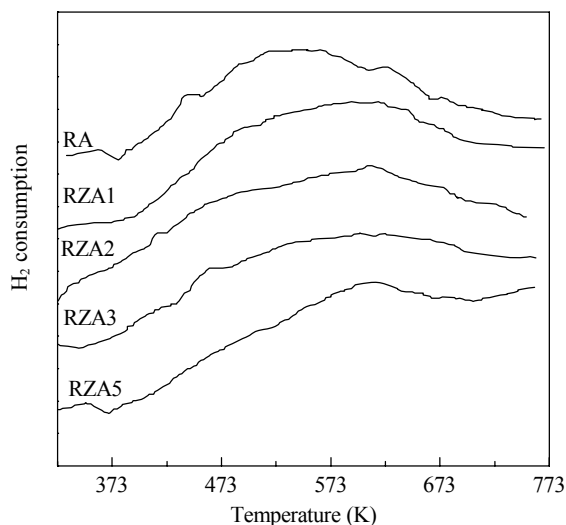
**Table 1** Characterization of Rh/Al<sub>2</sub>O<sub>3</sub> (RA) and Rh/ZnO-Al<sub>2</sub>O<sub>3</sub> (RZA) samples

Catalyst	Zn/Rh molar ratio	Q <sub>H<sub>2</sub></sub> /(μmol/g)	D <sub>H<sub>2</sub></sub> /%	d/nm
RA	0	75	77	1.42
RZA1	1	62	64	1.72
RZA2	2	55	54	2.00
RZA3	3	49	49	2.23
RZA5	5	42	42	2.61

Q<sub>H<sub>2</sub></sub>: amount of chemisorbed hydrogen. D<sub>H<sub>2</sub></sub>: metal dispersion. *d*: metal particle size. The metal dispersion and metal particle size were measured by hydrogen chemisorption at ambient temperature [34].

## 2.2 H<sub>2</sub>-TPR results

Figure 1 displays the H<sub>2</sub>-TPR profiles of supported rhodium catalysts after calcination at 773 K. The TPR profiles



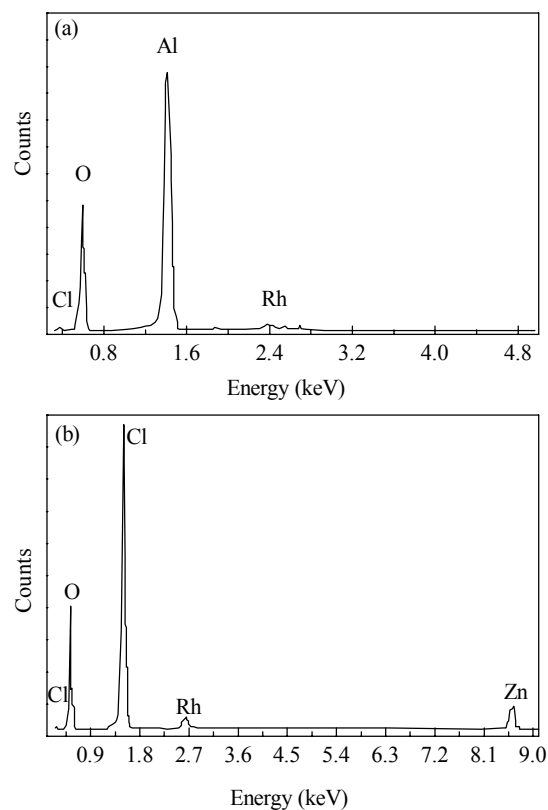
**Fig. 1.** H<sub>2</sub>-TPR profiles of RA and RZA samples.

reveal that the reducibility is dependent on the presence of Zn. For the RA catalyst, a large peak of hydrogen consumption appears at the low reduction temperature of 523 K. This reduction temperature maximum is in agreement with that reported by Benseradj et al. [35] while it is higher than that found by Ojeda et al. [36]. This peak is ascribed to the reduction of Rh<sub>2</sub>O<sub>3</sub> to metallic rhodium. The modification of support alumina by zinc increases the reduction temperature maximum. In the reduction temperature range of 473–673 K, the RZA samples display one reduction peak that can be correlated with the same peak observed on RA catalyst.

The TPR profile of the RZA5 sample displays a second hydrogen consumption peak that appears above 673 K. The second peak can be attributed either to reduction of ZnO or to metal support interactions.

## 2.3 SEM results

The elementary analysis of the synthesized RA and RZA5 samples are shown in Fig. 2 and Table 2. The results show the presence of Al, O, Cl, and Rh for the RA catalyst and Al, O, Cl, Zn, and Rh for the RZA5 catalyst. The percentage of Rh in RA and RZA5 (0.77–0.78 wt%) is close to that used in the catalysts preparation (1 wt%). The atomic Zn/Rh obtained (4.27) is close to the value used in the RZA5 preparation.



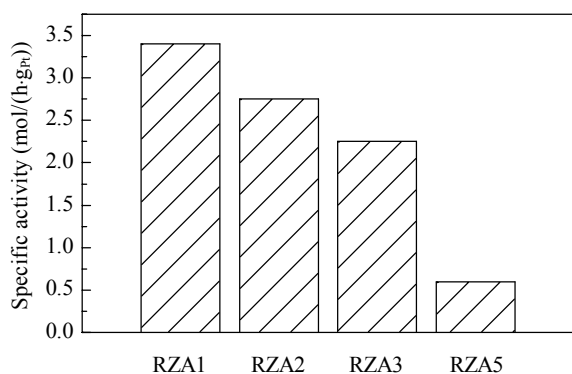
**Fig. 2.** Elementary analysis of RA (a) and RZA5 (b) catalysts.

**Table 2** Elementary analysis of Ra and RZA5

Element	Mass content (%)		Atomic content (%)	
	RA	RZA5	RA	RZA
Cl	7.86	5.14	12.66	7.78
O	46.29	44.37	54.72	54.78
Al	45.06	44.49	32.29	31.95
Rh	0.78	0.77	0.33	1.14
Zn	—	4.87	—	4.87

## 2.4 Cyclohexane dehydrogenation

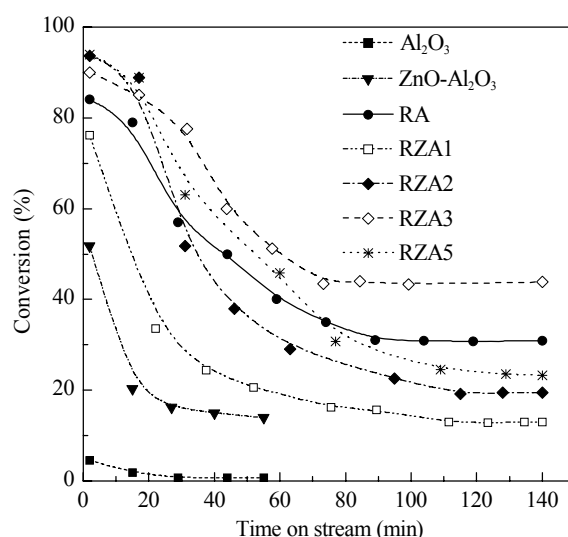
The catalysts are tested at 543 K under atmospheric pressure in a structure insensitive reaction [37–39], the cyclohexane dehydrogenation. This reaction allows the evaluation of the interaction between Zn and the metallic active phase after reduction. The evolution of the catalytic properties of all rhodium based catalysts is shown in Fig. 3. It can be seen from it that the specific activity decreases as the Zn/Rh atomic ratio increases. This result indicates that Rh dispersion decreases with increasing Zn amount, which is consistent with the formation of large Rh particles as evidenced by H<sub>2</sub> chemisorption experiments. The decrease in specific activity is likely due to interactions between Rh and Zn leading to Rh-Zn alloy formation and this increased with Zn/Rh ratio. The same phenomenon is reported by Lafaye et al. [40] for RhGe/TiO<sub>2</sub> catalysts.



**Fig. 3.** Specific activity of RZA catalysts for cyclohexane dehydrogenation at 543 K. Reaction conditions:  $p(\text{cyclohexane}) = 3 \text{ kPa}$ ,  $p(\text{H}_2) = 97 \text{ kPa}$ , total flow rate  $100 \text{ cm}^3/\text{min}$ , atmospheric pressure, 543 K.

## 2.5 Crotonaldehyde hydrogenation

The deactivation curves obtained over Al<sub>2</sub>O<sub>3</sub>, ZnO-Al<sub>2</sub>O<sub>3</sub>, RA, and RZA catalysts during crotonaldehyde hydrogenation are compared in Fig. 4 as a function of time on stream. Before reaction, all samples are in situ reduced at 723 K for 2 h. The modification of the alumina support by zinc improves the initial activity, which is nearly inactive. Indeed, initial conversion determined at the first two minutes increases from 4.5 for Al<sub>2</sub>O<sub>3</sub> to 54% for ZnO-Al<sub>2</sub>O<sub>3</sub>. Initially,



**Fig. 4.** Evolution of total conversion of crotonaldehyde as a function of time on stream at 393 K over Al<sub>2</sub>O<sub>3</sub>, ZnO-Al<sub>2</sub>O<sub>3</sub>, RA, and RZA catalysts. Reaction conditions: H<sub>2</sub>/crotonaldehyde ratio = 15, crotonaldehyde  $1 \text{ cm}^3/\text{min}$ , atmospheric pressure, 393 K.

ZnO-Al<sub>2</sub>O<sub>3</sub> deactivates rapidly before reaching stability after 30 min of reaction.

Addition of Rh to Al<sub>2</sub>O<sub>3</sub> and ZnO-Al<sub>2</sub>O<sub>3</sub> improves the initial crotonaldehyde conversion. All samples deactivate with time on stream before reaching a steady state, as already reported in the literature [41–43]. As reported by several authors [44,45], deactivation could be due to coverage of a portion of the active sites by coke formation and/or chemisorption of CO formed by decomposition of crotonaldehyde or the unsaturated alcohol. The same observation is reported by Lafaye et al. [46] for citral hydrogenation in liquid phase over Rh-Ge/Al<sub>2</sub>O<sub>3</sub> catalysts.

In order to improve the crotyl alcohol selectivity, Al<sub>2</sub>O<sub>3</sub> is modified by addition of various amounts of zinc before rhodium impregnation. The catalytic behaviour of the samples is compared in the gas phase hydrogenation of crotonaldehyde at 393 K under atmospheric pressure after reducing under hydrogen at 723 K. The crotonaldehyde conversion and selectivities obtained at steady state are listed in Table 3. On the Al<sub>2</sub>O<sub>3</sub> support crotonaldehyde is exclusively converted into butanal. This shows that the C=C bond is preferentially hydrogenated. These results are analogous to those obtained by Touroude et al. [9].

On the ZnO-Al<sub>2</sub>O<sub>3</sub> support butanol is the main product formed (98%) and the desired crotyl alcohol product is not formed.

Over rhodium supported catalysts the formation of crotyl alcohol increases with Zn amount. This indicates that the Rh metal properties are modified by Zn addition. These results are in agreement with the literature [23]. Selectivities for the unsaturated alcohol depend on the Zn/Rh atomic ratio (Ta-

**Table 3** Hydrogenation of crotonaldehyde over different samples

Sample	Conversion (%)	Selectivity (%)		
		Butanal	Butanol	Crotyl alcohol
Al <sub>2</sub> O <sub>3</sub>	3	100	0	0
ZnO-Al <sub>2</sub> O <sub>3</sub>	30	2	98	0
RA	30	2	95	3
RZA1	15	100	0	0
RZA2	20	60	21	19
RZA3	46	41	21	38
RZA5	25	30	0	70

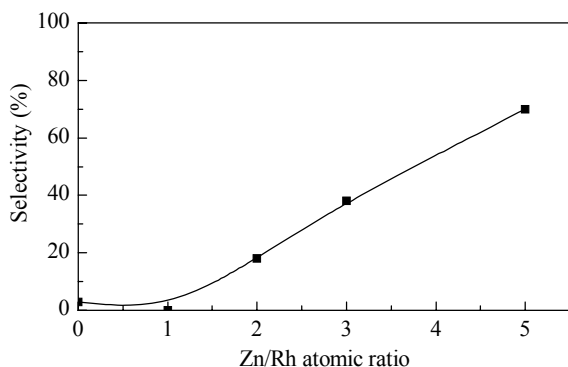
Reaction conditions: H<sub>2</sub>/crotonaldehyde ratio = 15, crotonaldehyde 1 cm<sup>3</sup>/min, atmospheric pressure, 393 K.

ble 3). The RA sample is selective in butanol (95%). Crotyl alcohol formation increases with time on stream and reaches a maximum of 20% after 80 min of reaction before to decrease until 3% after 130 min of reaction. This behaviour is similar to that obtained by Silvester-Albero et al. [40] in a recent work.

Butanal selectivity decreases from 100% to 30% with increasing Zn/Rh ratio from 1 to 5. Crotyl alcohol selectivity increases from 0 for RZA1 to 70% for RZA5. This increase in crotyl alcohol selectivity is caused by the activity enhancement for hydrogenating the C=O bond. Zn addition would inhibit the hydrogenation of -C=C- bonds, which is reflected in a decrease of butanal formation. A similar effect of Zn promotion on the selectivity for unsaturated alcohols is observed over Co/ZnO-SiO<sub>2</sub> [27] and Cu-ZnO/SiO<sub>2</sub> catalysts [48].

The selectivity for crotyl alcohol (desired product) is plotted in Fig. 5 as function of Zn/Rh atomic ratio at 393 K after reduction at 773 K. Crotyl alcohol selectivity increases with Zn addition and reaches a value of 70% with highest Zn/Rh atomic ratio (Zn/Rh = 5). These results could be related to the formation of large Rh particles. This effect was also observed for Pt on various supports [25].

The positive effect of Zn on crotyl alcohol selectivity is reported for Cu/SiO<sub>2</sub> [49], Co/SiO<sub>2</sub> [50,51], and Pt/ZnO



**Fig. 5.** Selectivity for unsaturated alcohol as a function of Zn/Rh atomic ratio.

catalyst [52] during crotonaldehyde hydrogenation.

According to Marchi et al. [49] the interaction between mobile reduced ZnO<sub>x</sub> species with Cu<sup>0</sup> crystallites over Cu-ZnO/SiO<sub>2</sub> enhances the selectivity for crotyl alcohol. Specifically, crotonaldehyde would interact via the C=O bond with cationic Zn sites thereby favouring its selective hydrogenation to the unsaturated alcohol by atomic hydrogen activated on neighbouring Cu<sup>0</sup> sites.

For Ammari et al. [52] the modification of electronic properties of platinum by both alloy formation with Zn and ZnO Lewis acidity favours hydrogenation of the C=O bond. Alloy formation is also observed by Homs et al. [53] on PtZn/CeO<sub>2</sub> catalysts, which enhances unsaturated alcohol formation.

In this study, alloy formation between Zn and Rh is evidenced by both H<sub>2</sub> chemisorption results and the cyclohexane dehydrogenation reaction. Results in Table 1 clearly show an increase of the particles size and a decrease of the amount of chemisorbed H<sub>2</sub> with increasing Zn/Rh ratio. This lets us suggest a partial coverage of the exposed rhodium atoms by Zn, thereby decreasing the effective number of the exposed surface Rh metal atoms.

The specific activity values decrease with Zn addition during the cyclohexane dehydrogenation reaction. This indicates a high electronic effect between Rh and Zn, meaning a high concentration of RhZn alloy particles. These alloys would adsorb the crotonaldehyde by binding to the carbonyl bond, leading to a better crotyl alcohol selectivity.

The selective hydrogenation of the carbonyl group and the inhibition of the hydrogenation of -C=C- bonds of crotonaldehyde would require a particular structure of the metallic surface [54]. Assuming that ionic Zn would enhance the polarization of the oxygen atom in the carbonyl group, the positive charge on the carbon atom of the carbonyl group increases and favors its reaction with hydrogen atoms dissociated on the neighboring Rh atoms.

### 3 Conclusions

The catalytic behaviour of rhodium supported alumina and zinc-alumina catalysts after reduction at 723 K is compared in the hydrogenation of crotonaldehyde in the gas phase. The activity and the selectivity greatly depend on both the nature of the support and the atomic ratio of Zn/Rh. The RA sample is less selective toward the formation of crotyl alcohol. Supported rhodium catalysts show a much higher initial activity although they also deactivate with time on stream; on the other hand, the selective hydrogenation of the carbonyl bond to crotyl alcohol is improved by the presence of zinc achieving a maximum value of 70% after 70 min of reaction time.

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