Catalysis Letters 31 (1995) 405–410

Transformation of an alcohol in the presence of a ketone as a model reaction to characterize the acidity and the basicity of oxide catalysts

M. Berkani, J.L. Lemberton[1], M. Marczewski[2] and G. Perot

Laboratoire de Catalyse en Chimie Organique, UA CNRS 350, UFR Sciences,
40 avenue du Recteur Pineau, 86022 Poitiers Cedex, France

Received 22 October 1994; accepted 25 January 1995

The reaction of cyclopentanol in the presence of cyclohexanone at 350°C over amorphous solids or zeolites led to alkenes and hydrogen transfer products. It was shown that these products were formed respectively on the acid sites and on the basic sites of the catalysts. Consequently, this reaction made it possible to estimate at the same time the acid and basic properties of the catalysts.

Keywords: alcohol–ketone hydrogen transfer; alcohol dehydration; acid–base catalysts; magnesium oxide; Cs-exchanged NaX zeolites; alumina; K-impregnated alumina; acid–base properties

1. Introduction

The aim of the present work was to investigate the possibility of using the mixture of an alcohol and a ketone to estimate at the same time the basicity and the acidity of solid catalysts. It was considered that the hydrogen transfer activity of the catalysts was related to their basicity, while their activity for dehydration was related to their acidity.

Indeed, solid basic catalysts, such as magnesium oxide [1,2], are highly selective for the hydrogen transfer from alcohols to carbonyl compounds (aldehydes or ketones), through a mechanism similar to that of the Meerwein–Ponndorf–Verley reaction. On the other hand, it is well known that alcohols dehydrate into olefins on Brønsted acid sites [3]. However, olefins can also be produced without protonation of the alcohols if alkoxide intermediates are formed on the surface [4,5]. These intermediates can either dehydrogenate into carbonyl compounds, or dehydrate

---

[1] To whom correspondence should be addressed.

[2] Present address: Institute of Organic Technology, Warsaw Technical University (Politechnicka), Koszykowa 75, 00-662 Warsaw, Poland.

into olefins [6,7]. However, according to some authors [8,9], it seems that acid sites would be responsible for the dehydration of alcohols, and dehydrogenation would be catalyzed by basic sites.

In this work we report the transformation of a cyclopentanol–cyclohexanone mixture on several catalysts, each having expectedly different acid–base properties: magnesium oxide, a well-known basic oxide [10]; Cs-exchanged NaX zeolites, the basicity of which increases with the Cs content [11]; alumina, which is amphoteric [10,12], and K-impregnated alumina, supposedly more basic than alumina [13]. The cyclopentanol–cyclohexanone system was chosen first because it was convenient to feed into the reactor, and because the reaction products were easy to analyse. Other molecules, such as isopropanol [14], could be also excellent hydrogen donors. However, isopropanol dehydration would yield propene, which is a very efficient coking agent [15]. The validity of the model reaction was checked using CO_2 adsorption for the basicity [14,16], and pure alcohol dehydration for the acidity.

2. Experimental

The reaction was carried out at 350°C under atmospheric pressure in a glass flow reactor. The cyclopentanol/cyclohexanone mixture was injected using a syringe pump. The cyclopentanol/cyclohexanone molar ratio was 4, the partial pressure of the mixture 0.2 bar (carrier gas: nitrogen, 0.8 bar). The reaction of cyclopentanol alone was performed under the same conditions as above, with a 0.2 bar cyclopentanol partial pressure. The reaction products were condensed at the outlet of the reactor in an ice bath, then analyzed by GC using a 25 m WCOT-Silica Cyclodextrin capillary column (Chrompack). The gas chromatograph was calibrated periodically using mixtures of pure commercial samples.

CO_2 poisoning experiments were carried out during the reaction by replacing part of the nitrogen carrier gas by CO_2 at a partial pressure of 0.2 bar, with a nitrogen partial pressure of 0.6 bar.

CO_2 thermodesorption experiments were carried out in a small glass reactor connected to a thermal conductivity detector. The catalyst (0.2 g) was first pretreated in situ for 8 h under helium at 500°C, then saturated with CO_2 at 50°C. The reactor temperature was then increased by 50°C stages from 100 to 500°C, i.e. the temperature at which the catalyst was pretreated. Indeed, higher desorption temperatures would have perhaps provoked the desorption of other molecules than CO_2, for example water, which would have affected the results. The surface areas of the CO_2 desorption peaks were compared with those measured previously by injecting known amounts of CO_2 directly into the thermal conductivity detector. This allowed the estimation of the number of moles of CO_2 desorbed at each stage, hence the total number of moles adsorbed on the catalyst. The number of moles remaining adsorbed at a give temperature can be obtained by subtraction.

Magnesium oxide (MgO) was prepared by precipitation of $Mg(NO_3)_2$ by NH_4OH. Alumina (A) was a commercial gamma alumina (Rhône Poulenc). Potassium was impregnated on the same alumina from a KOH solution; the catalyst obtained (AK) contained 4.1 wt% K. The NaCsX zeolites were obtained through exchange of a NaX zeolite (13X from Union Carbide) by CsCl solutions. Three catalysts designated as $NaCsX_1$, $NaCsX_2$ and $NaCsX_3$ were prepared, containing respectively 36, 23 and 14 wt% Cs. Before the reaction, all the catalysts were pretreated in situ for 12 h under nitrogen at 500°C.

3. Results and discussion

Preliminary experiments indicated that no product was obtained when the cyclopentanol/cyclohexanone mixture was allowed to react without a catalyst. Moreover, whatever the catalyst used in this work, cyclohexanone was not converted when processed alone, even when hydrogen was used instead of nitrogen as the carrier gas. Lastly (table 1C), the transformation of pure cyclopentanol yielded only cyclopentene, but no cyclopentanone was formed, at the difference of what was observed by other authors with basic zeolites [17]. This result indicates that alkoxide intermediates, which should yield both cyclopentene and cyclopentanone, were not formed here. Hence, the formation of cyclopentene can be attributed to a purely acid mechanism.

Table 1

Activities of the catalysts for the formation of the reaction products (10^{-3} mol h^{-1} g^{-1}). Transformation of: (A) the cyclopentanol/cyclohexanone mixture; (B) the cyclopentanol/cyclohexanone mixture in the presence of 0.2 bar CO_2; (C) cyclopentanol; (D) cyclopentanol in the presence of 0.2 bar CO_2

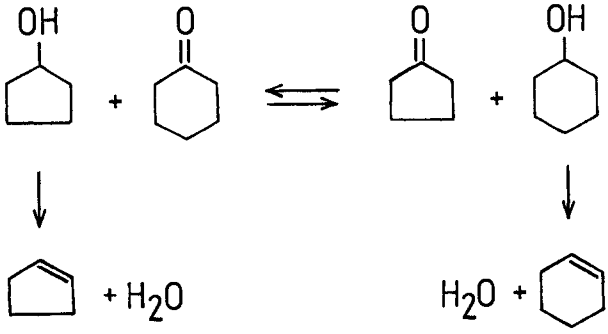
Experiment		Catalyst activity					
		MgO	A	AK	$NaCsX_1$	$NaCsX_2$	$NaCsX_3$
A	cyclohexanol	33	0	23	7	5	2
	cyclohexene	0	10	1	1	2	2
	cyclopentene	0	92	2	3	15	29
	H transfer	33	10	24	8	7	4
	dehydration	0	92	2	3	15	29
B	cyclohexanol	14	0	11	5	3	1
	cyclohexene	0	6	traces	1	1	1
	cyclopentene	0	89	2	3	14	29
C	cyclopentene	0	248	3	5	49	79
	cyclopentanone	0	0	0	0	0	0
D	cyclopentene	0	239	3	5	48	74
	cyclopentanone	0	0	0	0	0	0

The activities of all the catalysts for the transformation of the cyclopentanol/cyclohexanone mixture decreased slightly during the first hour of the reaction, before reaching stability. Table 1A reports the activities after stabilization for the formation of the different reaction products obtained from the cyclopentanol/cyclohexanone mixture.

The products are cyclopentanone and cyclohexanol resulting from the hydrogen transfer reaction, and cyclopentene resulting from the dehydration of cyclopentanol. Moreover, the presence of cyclohexene, due to the dehydration of the cyclohexanol formed, can also be observed (cf. scheme 1). Consequently, the hydrogen transfer activity of the catalyst can be estimated from the formation of cyclohexanol and cyclohexene. It must be noted that this allows one to estimate the hydrogen transfer from the amount of cyclohexene formed even when cyclohexanol can no longer be observed (as is the case with alumina). On the other hand, the formation of cyclopentene, which competes with the hydrogen transfer reaction, allows one to measure the activity of the catalyst for dehydration.

Results in table 1A indicate that MgO is inactive for dehydration. Alumina (A) is clearly the most active catalyst for this reaction; its activity decreases when it is potassium-impregnated (AK). The dehydration activity of the NaCsX zeolites is all the more significant as their Cs content decreases from $NaCsX_1$ to $NaCsX_3$. Table 1C indicates that the order of activity of the catalysts for the dehydration of pure cyclopentanol is exactly the same as the one measured for the dehydration of cyclopentanol in the presence of cyclohexanone. Consequently, the amount of cyclopentene formed during the conversion of the model mixture can be considered as representative for the acid activity of the catalyst.

MgO is the most active catalyst for hydrogen transfer (table 1A), followed by AK, A and the NaCsX zeolites. For these latter, the activity for hydrogen transfer decreases when the Cs content decreases from $NaCsX_1$ to $NaCsX_3$, which is exactly the contrary of what was observed for the dehydration activity. Similarly, the activity for hydrogen transfer of alumina is lower than that of AK, while its activity for dehydration was higher.



Scheme 1. Transformation of the cyclopentanol/cyclohexanone mixture.

Table 1B gives the results obtained when adding CO_2 to the carrier gas during the reaction. If one compares these results to those in table 1A, it is clear that CO_2 poisons only the hydrogen transfer reaction: the amounts of cyclohexanol and cyclohexene formed decrease when CO_2 is added, whereas the amount of cyclopentene remains constant. This latter result is confirmed by the absence of any effect of CO_2 on the transformation of pure cyclopentanol (table 1D). Hence, it can be concluded that hydrogen transfer occurs only on the basic sites of the catalysts, and dehydration only on the acid sites.

The amounts of CO_2 remaining adsorbed on the catalysts after desorption at different temperatures are presented in fig. 1. It can be seen that MgO, A and AK retain CO_2 at least up to 450°C, whereas the NaCsX catalysts retain it only up to 350, 250 or 200°C, depending on the Cs content. This indicates that the basic sites are stronger on MgO, A and AK than on the NaCsX zeolites whose basic strength decreases when the Cs content decreases. Moreover, the amount of CO_2 remaining adsorbed at the highest desorption temperature decreases from MgO to AK then A, which indicates that the number of the strongest basic sites is greater on MgO than on AK, and much greater than on A. Consequently, the order of basicity estimated from CO_2 desorption, taking into account both the strength and the number of the basic sites, is MgO > AK > A > $NaCsX_1$ > $NaCsX_2$ > $NaCsX_3$. This order is

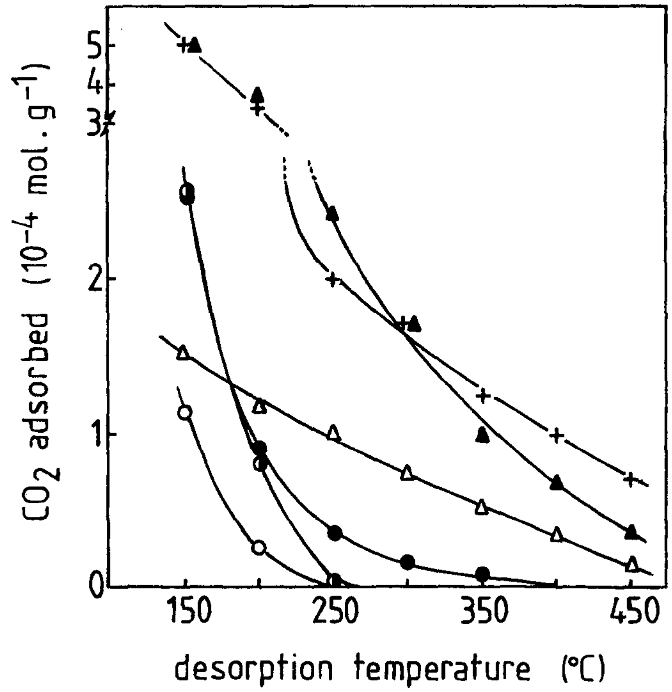


Fig. 1. Effect of the desorption temperature on the amount of CO_2 remaining adsorbed on the catalyst. (+) MgO, (▲) AK, (△) A, (●) $NaCsX_1$, (◐) $NaCsX_2$, (○) $NaCsX_3$.

exactly the same as the one obtained from the hydrogen transfer activity (table 1A).

4. Conclusions

The activities of the oxide catalysts for the dehydration of cyclopentanol and for the hydrogen transfer from cyclopentanol to cyclohexanone depend on their acido-basic properties. Magnesium oxide exhibits only basic properties, and is active only for hydrogen transfer. The basicity of NaCsX zeolites and their activities for hydrogen transfer increase when the Cs content increases. Similarly, the basicity of alumina and its activity for hydrogen transfer increase with impregnation of potassium. On the other hand, the acidity of the catalysts and their activities for dehydration follow the reverse trend. This indicates that, in all cases where the dehydrogenation of the alcohol into a ketone does not occur, the reaction of the cyclopentanol/cyclohexanone mixture makes it possible to estimate at the same time the acid and the basic properties of oxide catalysts.

References

[1] J. Kijenski, M. Glinski and J. Reinhercs, in: *Heterogeneous Catalysis and Fine Chemicals,* Studies in Surface Science and Catalysis, Vol. 4; eds. M. Guisnet, J. Barrault, C. Bouchoule, D. Duprez, C. Montassier and G. Perot (Elsevier, Amsterdam, 1988) p. 231.

[2] J. Kijenski, J. Ruszczynski, I. Knedler and M. Glinski, React. Kinet. Catal. Lett. 49 (1993) 287.

[3] S.J. Gentry and R. Rudham, J. Chem. Soc. Faraday Trans. I 70 (1974) 1685.

[4] H. Miyata, M. Wakamiya and Y. Kubokawa, J. Catal. 34 (1974) 117.

[5] M.I. Zaki and N. Sheppard, J. Catal. 80 (1983) 114.

[6] M. Bowker, R.W. Petts and K.C. Waugh, J. Catal. 99 (1986) 53.

[7] K.C. Waugh, M. Bowker, R.W. Petts, H.D. Vandervell and J. O'Malley, Appl. Catal. 25 (1986) 121.

[8] T. Yashima, H. Suzuki and N. Hara, J. Catal. 33 (1974) 486.

[9] P.A. Jacobs, M. Tielen and J.B. Utterhoeven, J. Catal. 50 (1977) 98.

[10] K. Tanabe, *Solid Acids and Bases* (Academic Press, New York, 1970).

[11] D. Barthomeuf and A. de Mallmann, in: *Innovation in Zeolite Materials Science,* Studies in Surface Science and Catalysis, Vol. 37, eds. P.J. Grobet, W.J. Mortier, E.F. Vanasant and G. Schulz-Ekloff (Elsevier, Amsterdam, 1988) p. 365.

[12] J.B. Peri, J. Phys. Chem. 69 (1965) 211; 69 (1965) 220.

[13] S. Malinowski, in: *Catalysis by Acids and Bases*, Studies in Surface Science and Catalysis, Vol. 20, eds. B. Imelik, C. Naccache, G. Coudurier, Y. Ben Taarit and J.C. Vedrine (Elsevier, Amsterdam, 1985) p. 57.

[14] P.E. Hattaway and M.E. Davis, J. Catal. 116 (1989) 263.

[15] P. Magnoux, P. Roger, C. Canaff, V. Fouché, N.S. Gnep and M. Guisnet, in: *Catalyst Deactivation,* Studies in Surface Science and Catalysis, Vol. 34, eds. B. Delmon and G.F. Froment (Elsevier, Amsterdam, 1987) p. 317.

[16] J.B. Peri, J. Phys. Chem. 79 (1975) 1582.

[17] C.B. Dartt and M.E. Davis, Catal. Today 19 (1994) 151.