Catalysis Letters 11 (1991) 245–248

Cyclohexanol conversion as a test of the acid-base properties of metal oxide catalysts

C.P. Bezouhanova * and M.A. Al-Zihari

University of Sofia, Faculty of Chemistry, 1, A. Ivanov Ave, Sofia 1126, Bulgaria

Received 3 July 1991; accepted 8 October 1991

Cyclohexanol conversion on oxide catalysts is proposed as a test for the acid-base properties of oxide catalysts. The quantity of cyclohexene formed reflects the existence of Broensted acid sites. The dehydrogenation to cyclohexanone might be related to basic sites if at least one proton is released from the organic molecule. In some cases dehydrogenation to phenol occurred.

Keywords: Acid-base properties; oxide catalysts; cyclohexanol; cyclohexanone; cyclohexene

1. Introduction

The acidic and basic properties of oxide catalysts are very important for the development of scientific criteria in catalyst application. The methods for the determination of surface acidity were critically reviewed in [1]. Besides the non-aqueous titration and IR spectroscopy the authors consider also some model reactions as xylene isomerization and cracking combined with poisoning experiments. The recommended unsurpassed IR spectroscopy sometimes meets insurmountable obstacles due to opacity and absorbance of the sample. In addition, different substances must be used for the detection of acid and base sites. Model reactions are recommended [2] as the best method for characterizing industrial acid catalysts.

The microcalorimetric measurements of the heats of adsorption of ammonia and carbon dioxide have been used to elucidate the acidic and basic properties of a number of oxides [3]. The obtained results showed that the greater degree of covalency of the oxide expressed by higher value of the charge/radius ratio, the more likely acidity is to be found. An oxide with a low value of the charge/radius ratio is more ionic in nature and will present more basic sites.

As a measure of the base strength of metal oxide catalysts, Davis [4] suggested the alcohol conversion selectivity. The amount of 1-alkene produced by water elimination was proposed to depend on the base strength. It was found that ZnO was a stronger base than CaO and MgO, and the oxides of Zr, In, Th, Y and Eu were stronger bases than ZnO.

The amphoteric character of alcohols permits their interaction with acids and bases. Olefin formation results from the reaction of alcohols with Broensted acid sites. In the literature the ability of oxide catalysts to dehydrogenate some alcohols is also described [5–8]. Using cyclohexanol we have demonstrated the existence of acid and base sites in ZSM-5 zeolites [9]. The results are in agreement with that of Dessau [10] on diketones cyclization over ZSM-5.

Our studies on cyclohexanol conversion in the presence of different oxide catalysts showed that some of them are able to activate dehydration and dehydrogenation reactions simultaneously. We interpreted the dehydrogenation activity as related to existence of basic sites originating from the oxygens in the oxide lattice.

2. Experimental

2.1. CATALYSTS

The oxides used were reagent grade commercial products (V_2O_5, MgO, ZnO, Fe_2O_3, La_2O_3, CuO) or obtained from the appropriate salts. Mn_3O_4, NiO, and Co_3O_4 were obtained from the basic carbonate salts by heating at 803 K during 3 hours and identified by IR spectra [11]. Cr_2O_3 was obtained by decomposition of the hydroxide $Cr(OH)_3$ at 673 K.

2.2. CATALYST TESTING

The catalytic experiments were performed in a flow system on 2 g fixed bed catalyst. The catalysts were activated under air flow at 723 K and flushed with argon before the experiments. Vapours of reagent grade cyclohexanol were introduced using a calibrated syringe and evaporizer. The condensed reaction products were analyzed by GC using a 2 m column of silanized chromosorb W 60–80 mesh with 15% DC 550 at 403 K.

All the experiments were performed at 673 K and WHSV 2 hour^{-1}. Some of the oxides (for instance Mn_3O_4) were inactive towards cyclohexanol below 673 K. The results are summarized in table 1.

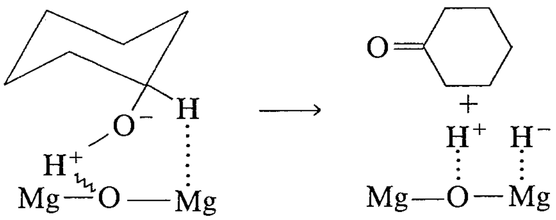
3. Results and discussion

The microcalorimetric investigations [3] permitted the oxides to be classified in 3 groups: acidic oxides A; basic oxides B; acido-basic oxides A-B.

Table 1
Conversion of cyclohexanol on oxide catalysts. Temperature 673 K, LHSV 2 hour^{-1}

Catalyst	Products (wt.%)			
	C-hexene	C-hexanol	C-hexanone	Phenol
MgO	–	64.0	30.6	1.4
ZnO	3.9	26.1	67.6	–
Fe_2O_3	8.9	65.9	22.7	1.0
Mn_3O_4	3.3	75.0	18.0	1.2
V_2O_5	99.7	–	–	–
Cr_2O_3	16.5	42.1	36.4	–
CuO	–	17.7	65.3	11.3
Co_3O_4	11.7	50.3	26.5	4.3
NiO	3.7	46.6	40.2	6.3
La_2O_3	1.2	79.9	16.6	–

Our experiments with cyclohexanol showed that V_2O_5 was a typical acid, while MgO was a typical base. This is in accordance with the results in [3]. Taking into account the suggestion that heterolytic dissociation of hydrogen can occur on MgO [12], the following hydrogen abstraction from cyclohexanol can be postulated:



The metal cation is acting as a Lewis active site.

No Broensted acid sites were found in CuO. NiO and Mn_3O_4 revealed small activity in dehydration.

In accordance with the results in [3] V_2O_5 possessed only Broensted acid sites, because the only reaction product was cyclohexene. Acid sites also occur in Cr_2O_3, Co_3O_4, Fe_2O_3, ZnO, Mn_3O_4, NiO, and La_2O_3 in decreasing order of activity.

ZnO is considered as a solid base [3,13], but some acidic properties have been also established [14]. The most active materials in dehydrogenation are ZnO and CuO. It is well known [15] that Zn- and Cu-catalysts find industrial application in dehydrogenation of cyclohexanol to cyclohexanone at 673–723 K and atmospheric pressure. In the conditions of our experiments CuO and NiO dehydrogenated the cyclohexanol to phenol as well.

While the dehydrogenation of the alcohol hydroxyl group may proceed on hydrogen accepting sites with base character-oxygen atoms from the oxide lattice, the dehydrogenation of the ring seems to be related rather to the transition metal.

In conclusion most of the metal oxides studied have acid sites and hydrogen accepting sites, i.e. they must be considered members of the A–B group (according to [3]). Not only the metal ions, but also basic oxygen atoms have a hydrogen accepting ability. The cyclohexanol conversion is a simple and fast method to determine the functionality of an oxide catalyst.

References

[1] H.A. Benesi and B.H.C. Winquist, Advan. Catal. 27 (1978) 97.

[2] M. Guisnet, Acc. Chem. Res. 23 (1990) 392.

[3] A. Auroux and A. Gervasini, J. Phys. Chem. 94 (1990) 6371.

[4] B.H. Davis, in: *Adsorption and Catalysis on Oxide Surfaces*, eds. M. Che and G.C. Bond, Stud. Surf. Sci. Catal., Vol. 21 (Elsevier, Amsterdam, 1985) p. 309.

[5] O.V. Krylov, C.Z. Roginskii and E.A. Fokina, Izv. AN SSSR, otd. chim. nauk (1957) 421.

[6] A.A. Tolstopyatova, A.A. Balandin and V.Kh. Matyushenko, Izv. AN SSSR, otd. chim. nauk (1960) 787.

[7] A.A. Balandin and I.D. Rozhdestvenskaya, Zh. Phys. Chim. 34 (1960) 1336.

[8] H. Pines and J. Manassen, Advan. Catal. 16 (1966) 49.

[9] C. Bezouhanova, C. Dimitrov, V. Nenova, Yu. Kalvachev and H. Lechert, in: *Zeolites: Facts, Figures, Figure*, eds. P.A. Jacobs and R.A. van Santen, Studies in Surface Science and Catalysis, Vol. 49 (Elsevier, Amsterdam, 1989) p. 1223.

[10] R.M. Dessau, Zeolites 10 (1990) 205.

[11] *Gmelins Handbuch der anorganische Chemie*, 8. Auflage (Springer Verlag, Berlin-Heidelberg-New York, 1974) p. 90.

[12] H. Hattori, in: *Adsorption and Catalysis on Oxide Surfaces*, eds. M. Che and G.C. Bond, Stud. Surf. Sci. Catal., Vol. 21 (Elsevier, Amsterdam, 1985) p. 319.

[13] N. Cardona-Martinez and J.A. Dumesic, J. Catal. 127 (1991) 706.

[14] H. Knoezinger, Adv. Catal. 25 (1976) 184.

[15] K. Weissermel and H.J. Arpe, *Industrial Organic Chemistry* (Verlag Chemie, Weinheim, New York, 1978) p. 223.