Indian Journal of Chemistry
Vol. 33A, October 1994, pp. 937-940

Catalytic activity of lanthanum oxide for the reduction of cyclohexanone

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Received 4 January 1994; revised 18 April 1994; accepted 6 June 1994

Lanthanum oxide, La_2O_3 has been found to be an effective catalyst for the liquid phase reduction of cyclohexanone. The catalytic activities of La_2O_3 activated at 300, 500 and 800°C and its mixed oxides with alumina for the reduction of cyclohexanone with 2-propanol have been determined and the data parallel that of the electron donating properties of the catalysts. The electron donating properties of the catalysts have been determined from the adsorption of electron acceptors of different electron affinities on the surface of these oxides.

Investigations on the strength and distribution of electron donor sites on rare earth oxides revealed that two types of electron donor sites are possible on these oxides[1-6], one having electrons trapped in intrinsic defects and the other having hydroxide ions. The limit of electron transfer from the oxide surface lies between 1.77 and 2.40 eV. The electron donating capacity depends on the basicity of the medium[1]. Studies on mixed oxides of rare earth and aluminum revealed that the electron donating capacity increases with increase in the percentage of rare earth oxide, goes to a maximum and then decreases with further increase in concentration of rare earth oxide without changing the limit of electron transfer. In an attempt to correlate the electron donating properties of rare earth oxide with its catalytic activities we have studied the reduction of cyclohexanone with 2-propanol using La_2O_3 activated at 300, 500 and 800°C and its mixed oxides with alumina as catalysts.

Aluminum isopropoxide has been found to be one of the best reagents for the reduction of aldehydes and ketones with 2-propanol in liquid phase. Though other catalysts such as complexes of transition metals[7-9], zeolite[10] and oxides of silica and alumina[11,12] have also been reported, they need to be carried out in vapour phase in flow reactor systems. In this note we report the catalytic activity of La_2O_3 for the liuid phase reduction of cyclohexanone with 2-propanol.

Experimental

Lanthanum oxide (purity 99.9%) was obtained from Indian Rare Earths Ltd. Since the oxide was already heat-treated at higher temperature, it was regenerated by the hydroxide method[13] from its nitrate solution. The oxides activated by heating in air for 2h at 300, 500 and 800°C were used.

The mixed oxides of lanthanum and aluminum were prepared by co-precipitation from nitrate solution. The following mixed oxides, 10, 20, 45, 60 and 75% (by wt of La_2O_3), were prepared and were activated at a temperature of 500°C. Alumina was also prepared by the hydroxide method from its nitrate salt. The specific surface area of the oxides were determined by the BET method using Carlo Erba Strumentazione series 1800 and the values are given in Table 1. The apparatus and procedure used for adsorption study have been described previously[5]. The ESR spectra of the adsorbed samples were measured at room temperature using Varian X/Q band ESR spectrometer. The radical concentrations were estimated by comparing the area under the adsorption curves for the sample and for standard solutions of 2,2-diphenyl-1-picrylhydrazyl in benzene. The reflectance spectra of the dried adsorbed samples were recorded on a Hitachi 200-20 UV-visible spectrophotometer with a 200-0531 reflectance attachment. For catalytic activity study commercial reagents were used after purification.

Measurement of activity

To the catalyst (1 g) placed in a 25-cm^3 round-bottomed flask equipped with a reflux condenser was added cyclohexanone (0.5 g), 2-propanol (10 cm^3) and xylene (0.05 g) as an internal standard, the contents were heated under reflux and the reaction was followed by product analysis by means of a Hewlett Peckard 5730A gas chromatograph. No by-products were detected.

Results and discussion

The reaction showed a first order dependence on the concentration of ketone. The activity is reported as the first order rate coefficient for the formation of cyclohexanol per gram of the catalyst. The mechanism in Scheme 1 is suggested for

Table 1—Surface area, catalytic activity and limiting radical concentrations on the catalyst at various activation temperatures and compositions

Catalyst	Activation temp. (°C)	Surface area ($m^2 \cdot g^{-1}$)	Catalytic activity ($10^{-5}s^{-1}$)	Electron acceptor	Solvent	Radical Conc. (10^{18} spins·m^2)
				TNCQ	Acetonitrile	1.675
				"	Dioxan	0.170
La_2O_3	300	39.8	0.148	chloranil	Acetonitrile	—
				"	Dioxan	—
				TCNQ	Acetonitrile	5.565
				"	Dioxan	0.287
La_2O_3	500	38.28	0.352	chloranil	Acetonitrile	0.014
				"	Dioxan	0.004
				TCNQ	Acetonitrile	7.859
				"	Dioxan	1.749
La_2O_3	800	29.75	2.723	chloranil	Acetonitrile	0.389
				"	Dioxan	0.038
				TCNQ	Acetonitrile	3.543
				"	Dioxan	2.340
Al_2O_3	500	193.91	0.075	chloranil	Acetonitrile	0.069
				"	Dioxan	0.037
10%				TCNQ	Acetonitrile	4.380
La_2O_3/				"	Dioxan	3.862
Al_2O_3	500	169.12	0.094	chloranil	Acetonitrile	0.088
				"	Dioxan	0.080
20				TCNQ	Acetonitrile	5.213
La_2O_3/				"	Dioxan	3.441
Al_2O_3	500	157.47	0.233	chloranil	Acetonitrile	0.086
				"	Dioxan	0.072
45%				TCNQ	Acetonitrile	5.015
La_2O_3/				"	Dioxan	1.144
Al_2O_3	500	149.70	0.587	chloranil	Acetonitrile	0.109
				"	Dioxan	0.034
60%				TCNQ	Acetonitrile	3.043
La_2O_3/				"	Dioxan	1.116
Al_2O_3	500	144.65	1.373	chloranil	Acetonitrile	0.082
				"	Dioxan	0.028
75%				TCNQ	Acetonitrile	2.444
La_2O_3/				"	Dioxan	0.629
Al_2O_3	500	81	0.381	chloranil	Acetonitrile	0.082
				"	Dioxan	0.005

the reduction of ketone with 2-propanol catalysed by La_2O_3. Above 500°C the activity increases appreciably with increasing activation temperature. It is parallel to the electron donating capacity (Table 1 and Fig. 1). It might be expected that the trapped electron centres are solely responsible for the electron transfer on the surface La_2O_3 activated at higher temperautre and the concentrations of such trapped electron centres increases with increase in temperature above 500°C.

The electron donating properties of these oxides were studied from the adsorption of the following electron acceptors (electron affinity values are given in brackets), 7,7,8,8-tetracynoquinodimethane [TCNQ (2.84 eV)], 2,3,5,6-tetrachloro 1,4-benzoquinone [chloranil (2.40 eV)] and *p*-dinitrobenzene [PDNB (1.77 eV)] in acetonitrile, a very weak base, and in 1-4 dioxan, a moderately weak base[5]. In the case of PDNB the adsorption was so negligible that the amount was hardly estimated. The adsorption isotherms of TCNQ and chloranil from these two solvents were classified as Langmuir types. The plot of radical concentration against the equilibrium concentration of electron acceptors adsorbed was also of Langmuir type. From these plots the limiting radical concentration is calculated (Table 1). Figure 1 shows the increase in limiting amount of TCNQ and chloranil adsorbed acetonitrile and in 1,4-dioxan with the increase in activation temperature of La_2O_3.

When electron acceptors were adsorbed from solvents on the surface of the oxides, the surface showed coloration characteristic for the kind of acceptors like bluish green for TCNQ and light

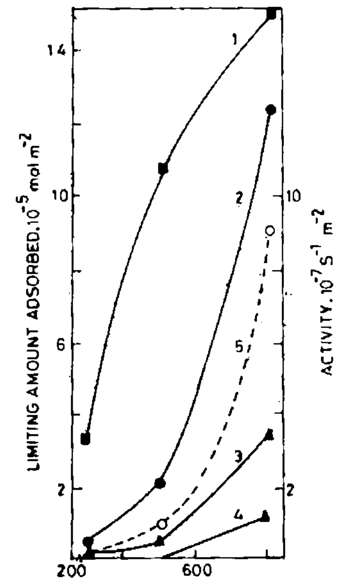
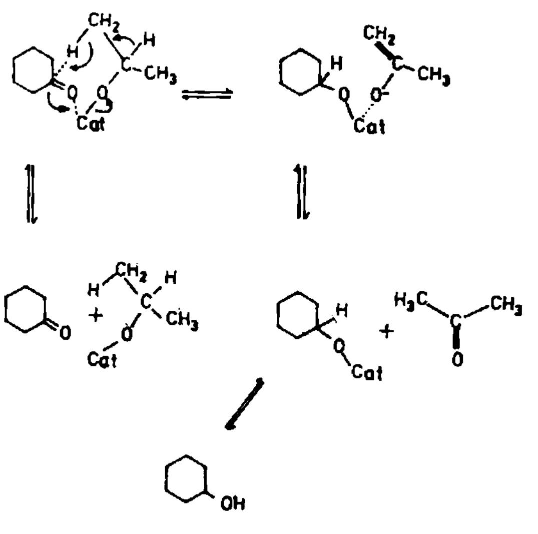


Fig. 1—Limiting amount of electron acceptors adsorbed and catalytic activity as a function of activation temperaute. (1, TCNQ in acetonitrile; 2, Chloranil in acetonitrile; 3, TCNQ in dioxan; 4, Chloranil in dioxan and 5, rate constant)



Scheme 1

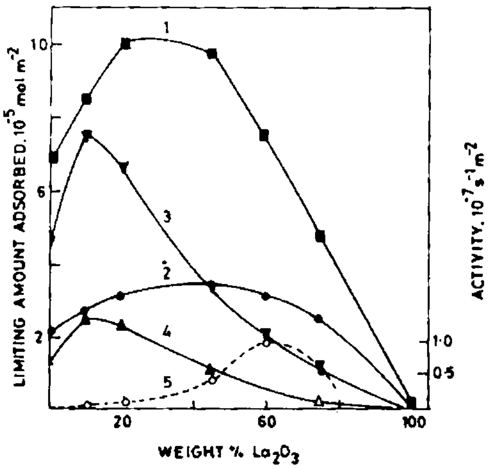


Fig. 2—Limiting amount of electron acceptors adsorbed and catalytic activity as a function of composition of La_2O_3-Al_2O_3. (1, TCNQ in acetonitrile; 2, Chloranil in acetonitrile; 3, TCNQ in dioxan; 4, Chloranil in dioxan and 5, rate constant)

pink for chloranil. These colorations were due to the interaction between the acceptor adsorbed and the oxide surface.

The ESR spectrum of the sample colored with adsorption of TCNQ and chloranil gave unresolved spectral line with a g value of 2.003 and 2.011 respectively with a width of approximately 30 G indicating the presence of anion radicals on the surface. The electronic spectrum of the adsorbed sample gave bands near 400, 600 and 700 nm corresponding to physically adsorbed state of neutral TCNQ, dimeric TCNQ radical and to chloranil anion radical[14,15]. In the case of oxides studied this assignment does not hold completely because these oxides have characteristic bands in the same region.

Figure 2 shows the increase in activity of the catalyst as a function of the composition of the mixed oxide. The change in activity as a function of activation temperature and composition can be understood in terms of the electron donating capacity of the oxide surface. The limiting amount of the electron accepter adsorbed increases with in percentage of La_2O_3 in the mixed oxide as a consequence of the increase in concentration of $Al-O-La$ bonds. Further addition of La_2O_3 decreases the limiting amount of the increase in concentration of La_2O_3 in the oxide lattice because La_2O_3 has lower electron donating capacity then Al_2O_3. A strong electron acceptor like TCNQ is capable of forming radical anions even from weak donor sites whereas a weak electron acceptor like PDNB is capable of forming radical anions only at strong donor sites. Hence the radical concentration of TCNQ anions is an estimate is an estimate of the total concentration from both weak and strong donor sites. Figure 1 shows that the catalytic activity data parallel that for the limiting amount of chloranil adsorbed in acetonitrile. The change in shape of the plot from acetonitrile to dioxan can be understood in terms of the basicity difference between the two solvents. The radical anion concentration data show that only those sites having electron donor strength capable of forming chloranil anion radicals (donor strength >2.40 eV in terms of the electron affinity of the acceptor) are involved in the reduction. The relative contribution towards the reduction reaction from the two possible electron sources on the catalyst surface may vary. This may be one of the reasons why the activity data do not parallel exactly the electron donating capacity data in the case of mixed oxides that are activated at a temperature of 500°C.

Acknowledgement

The authors wish to acknowledge their sincere gratitude to the CSIR, New Delhi for the award of a Junior research fellowship to KBS.

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