

Catalytic activity of some of the perovskite-type mixed oxides (ABO_3) consisting of rare earth and 3d transition metals

S Sugunan* & V Meera

Department of Applied Chemistry, Cochin University of Science & Technology, Kochi 682 022

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The catalytic activity of some of the ABO_3 ($A = La, Pr$ and $Sm, B = Cr, Mn, Fe, Co$ and Ni) perovskite-type oxides for the liquid phase reduction of ketone and oxidation of alcohol in 2-propanol medium has been studied. The data have been correlated with the surface electron donor properties of these oxides. The surface electron donor properties have been determined from the adsorption of electron acceptors of varying electron affinities on the oxide surface.

Perovskite-type mixed oxides (ABO_3) have a well defined bulk structure and the composition of cations at both A and B sites can be changed¹. Therefore, these mixed oxides are suitable materials for the study of the structure-property relationship of catalysts. Although investigations on the catalytic properties of these mixed oxides have multiplied in recent years, the primary mode of surface interaction on these materials remains largely undefined. The acid-base (electron donor-acceptor) interactions of electron acceptors on transition metal oxides² and rare earth oxides^{3,4} have already been investigated as a function of their activation temperature to study and characterise their electron donor properties. The catalytic activity of some of the transition metal oxides have been correlated with their surface acid-base properties^{5,6}. In this note, we report the surface electron donating properties and catalytic activity of perovskite-type mixed oxides (ABO_3) consisting of La, Pr and Sm as rare earth and Fe, Co, Ni, Cr and Mn as transition metal cations. The model reactions chosen for the catalytic activity studies are the oxidation of cyclohexanol and the reduction of cyclohexanone in 2-propanol medium.

Experimental

The mixed oxides were prepared from mixtures of the metal nitrates of each component by coprecipitation method using *n*-butylamine⁷. The precipitate was filtered, washed until no NO_3^- ions

were detected and decomposed in air at 300°C for 3 h and calcined in air at 850°C for 5-10 h. X-ray diffraction patterns obtained with a Rigaku (model D/max III VC Japan) X-ray diffractometer using Ni filtered $Cu-K_{\alpha}$ radiation ($\lambda = 1.5418 \text{ \AA}$) showed only the perovskite structure⁸. Elemental analysis was carried out using a Perkin Elmer 23-80 Atomic Absorption Spectrophotometer. Electronic spectra of the samples were taken using a Shimadzu (UV-160A) UV-visible spectrophotometer. The radical concentrations of electron acceptors adsorbed on these oxides were determined from the ESR spectra measured at room temperature using Varian E-112 X/Q band ESR spectrometer. Radical concentrations were calculated by comparison of the first derivative curves for the sample with those of standard solutions of 1,1 diphenyl-2-picryl hydrazyl in benzene. The reflectance spectra of the adsorbed samples were measured using a Hitachi 200-20 UV-visible spectrophotometer with a 200-0531 reflectance attachment. The surface area of the samples were determined by BET method using Carlo Erba Strumentazione Sorptomatic Series 1800. Rare earth oxides were regenerated from the corresponding nitrate solutions by the same method as described above and were activated at 850°C for 2 h before each experiment.

The study of the electron donor properties were carried out by the adsorption of electron acceptors of various electron affinity values. The following electron acceptors (EA) were used, (electron affinity values in brackets) 7,7,8,8-tetracyanoquinodimethane [TCNQ (2.84 eV)], 2,3,5,6-tetrachloro-1,4-benzoquinone [chloranil (2.40 eV)], *p*-dinitrobenzene [PDNB (1.77 eV)] and *m*-dinitrobenzene [MDNB (1.26 eV)]. Adsorption of EA was carried out in acetonitrile, a very weak base. All the reagents were used after purification.

The oxides activated at 850°C for 2 h were placed in a 25 ml test tube and outgassed at 10^{-5} torr for 1 h. Into the test tube, 20 ml of a solution of an electron acceptor in organic solvent was then poured in. The solution had then subsequently been stirred for 4 h at 28°C in a thermostated bath and the oxide was collected by centrifuging the solution and dried at room temperature *in vacuo*.

The activity of the oxides for reduction and oxidation reactions were determined by the following procedure.

Table 1—Limiting amount of EA adsorbed and catalytic activity of oxides

Oxide	Limiting amount of EA adsorbed (10^{-5} mol m $^{-2}$)		Rate constant (10^{-9} s $^{-1}$ m $^{-2}$) for		Surface area (m 2 g $^{-1}$)
	TCNQ	Chloranil	Reduction	Oxidation	
LaCrO $_3$	16.89	—	—	6.55	3.03
PrCrO $_3$	8.39	—	—	0.18	3.01
SmCrO $_3$	12.07	—	—	0.40	3.83
LaMnO $_3$	10.65	—	—	0.08	10.24
PrMnO $_3$	3.76	—	—	0.08	15.81
SmMnO $_3$	1.13	—	—	0.01	13.66
LaFeO $_3$	5.09	—	2.67	0.85	14.36
PrFeO $_3$	4.61	—	0.16	0.24	18.13
SmFeO $_3$	6.06	—	0.24	0.16	14.55
LaCoO $_3$	7.02	—	1.92	0.12	10.61
PrCoO $_3$	3.79	—	2.48	0.13	7.26
SmCoO $_3$	2.65	—	3.13	1.06	6.07
LaNiO $_3$	2.36	—	0.01	0.51	15.65
PrNiO $_3$	0.95	—	0.03	1.03	5.95
SmNiO $_3$	11.18	—	0.06	0.58	11.50
Fe $_2$ O $_3$	0.85	—	0.01	0.07	7.48
Co $_3$ O $_4$	5.13	—	—	—	8.40
NiO	24.57	—	—	—	3.98
Cr $_2$ O $_3$	3.66	—	—	0.86	18.19
MnO $_2$	11.71	—	—	—	9.42
La $_2$ O $_3$	39.77	12.45	1.28	1.34	35.14
Pr $_6$ O $_{11}$	29.34	4.54	2.76	3.80	14.15
Sm $_2$ O $_3$	25.96	5.70	1.46	1.78	30.01

of these oxides are determined by the cations of the transition metals at high temperatures and by the rare earth ions at low temperatures¹⁹.

The data in Table 1 show that the transition metal oxides have sufficient electron donor sites with

various electron donor strengths. But all of them are not effective in catalysing the reaction which results in a low catalytic activity. By incorporating the rare earth oxide into it, the activity is increased by increasing the concentration of active sites.

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