# Catalytic activity of some of the perovskite-type mixed oxides (ABO<sub>3</sub>) consisting of rare earth and 3d transition metals

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The catalytic activity of some of the ABO<sub>3</sub> (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<sub>3</sub>) have a well defined bulk structure and the composition of cations at both  $\Lambda$  and B sites can be changed<sup>1</sup>. 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 oxides<sup>2</sup> and rare earth oxides<sup>3,4</sup> 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<sup>5,6</sup>. In this note, we report the surface electron donating properties and catalytic activity of perovskite-type mixed oxides (ABO<sub>3</sub>) 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-butylamine<sup>7</sup>. 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 ( $\lambda = 1.5418 \, \text{A}^{\circ}$ ) 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.

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### Reduction

In a 100 ml round bottomed flask equipped with a reflux condenser were placed 1.5 g of the catalyst (100-200 mesh), 5 mmol of cyclohexanone, 10 ml of 2-propanol and *n*-decane as intrernal standard. The contents were heated under gentle reflux.

### Oxidation

In a 100 ml round bottomed flask equipped with a reflux condenser were placed 1.5 g of the catalyst (100-200 mesh), 10 cm<sup>3</sup> of a toluene solution of cyclohexanol (0.25 mmol), benzophenone (14.6 mmol) and *n*-decane as internal standard. The contents were heated under gentle reflux. The amount of the reactants and the corresponding products were determined with a GLC (8510 Chemito) using a calibration obtained with standard samples<sup>9</sup>.

# Results and discussion

In general, two types of sites are responsible for the electron donor properties of metal oxides. One of these is electrons trapped in intrinsic defect sites and the other is surface hydroxyl groups<sup>10</sup>. The surface hydroxyl concentration of a few of the perovskites were determined by exchange with D<sub>2</sub> as a function of the dehydroxylation temperature. The results suggest that the surface chemistry of these materials resemble that of certain other oxide systems such as alumina and titania<sup>11</sup>. Since these oxides are activated at a temperature of 850°C, the contribution from surface hydroxyl group cannot be expected. The sole effect must be from trapped electrons at intrinsic defect sites which are created at activation tempeature above 500°C (refs 12,13).

In the case of mixed oxides and transition metal oxides, the adsorption of chloranil, PDNB and MDNB was so negligible that the amount was hardly estimated in the solvent. The component rare earth oxides gave adsorption of TCNQ and chloranil, but not for PDNB and MDNB. The amount of EA adsorbed on these oxides were determined from the concentration difference of the EA before and after adsorption. Figure 1 shows the adsorption isotherms (Langmuir type) of EA for the mixed oxides. From these plots the limiting amount of EA adsorbed are determined.

A strong EA (TCNQ) can accept electrons from both strong and weak donor sites whereas a weak EA like MDNB can accept electrons from strong donor sites only. The difference in limiting amounts of TCNQ and chloranil adsorbed on the metal oxide would be an estimate of the number of stronger donor sites.

The limit of electron transfer in terms of the

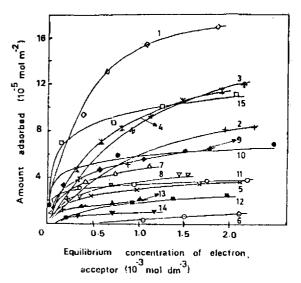


Fig. 1—Amount of electron acceptor (TCNQ) adsorbed vs equilibrium concentration of the electron acceptor for the mixed oxides in acetonitrile. (1, LaCrO<sub>3</sub>; 2, PrCrO<sub>3</sub>; 3, SmCrO<sub>3</sub>; 4, LaMnO<sub>3</sub>; 5, PrMnO<sub>3</sub>; 6, SmMnO<sub>3</sub>; 7, LaFeO<sub>3</sub>; 8, PrFeO<sub>3</sub>; 9, SmFeO<sub>3</sub>; 10, LaCoO<sub>3</sub>; 11, PrCoO<sub>3</sub>; 12, SmCoO<sub>3</sub>; 13, LaNiO<sub>3</sub>; 14, PrNiO<sub>3</sub>; and 15, SmNiO<sub>3</sub>)

electron affinity (eV) of the acceptors is between 2.40 and 2.84 in the case of mixed oxides and transition metal oxides and between 1.77 and 2.40 for La<sub>2</sub>O<sub>3</sub>, Pr<sub>6</sub>O<sub>11</sub> and Sm<sub>2</sub>O<sub>3</sub>. The limiting amount of EA adsorbed on the oxides and the catalytic activity (expressed as the first order rate constant per m<sup>2</sup> of the catalyst surface) are given in Table 1.

To study the nature of the interaction during adsorption, reflectance spectra of the samples were measured. The spectrum gave bands appearing at 400 nm (corresponding to physically adsorbed state of neutral TCNQ which has an absorption band at 395 nm<sup>14</sup>) near 600 nm (attributed to the dimeric TCNQ radical which absorbs at 643 nm15) and a broad band extending up to 700 nm (corresponding to chloranil anion radical16). This assignment does not hold completely with these oxides because they also have characteristic bands in the same region. The samples analysed after TCNQ adsorption gave unresolved ESR spectra with a g value of 2.003, identified as being those of TCNQ anion radicals<sup>17</sup> and those samples after chloranil adsorption gave an unresolved ESR spectra having a g value of 2.011 (ref. 18). The isotherms obtained by plotting the radical concentration of the EA against the equilibrium concentration are of Langmuir type and are of the same shape as shown in Fig.1. Limiting radical concentrations are also calculated from these plots.

A distinct separation of the functions of the cations of the transition metals and rare earth metals is observed for some of the perovskites<sup>19</sup>. The activity

Table 1—Limiting amount of EA adsorbed and catalytic activity of oxides					
Oxide	Limiting amount of EA adsorbed (10 <sup>-5</sup> mol m <sup>-2</sup> )		Rate constant (10 °6s ° m° 2) for		Surface area (m <sup>2</sup> g <sup>-1</sup> )
	TCNQ	Chloranil	Reduction	Oxidation	
LaCrO <sub>3</sub>	16.89	_		6.55	3.03
$PrCrO_3$	8.39	_		0.18	3.01
$SmCrO_3$	12.07	_	_	0.40	3.83
LaMnO <sub>3</sub>	10.65			0.08	10.24
PrMnO <sub>3</sub>	3.76	_		0.08	15.81
SmMnO <sub>3</sub>	1.13			0.01	13.66
LaFeO <sub>3</sub>	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 <sub>3</sub>	7.02		1.92	0.12	10.61
PrCoO <sub>3</sub>	3.79		2.48	0.13	7,26
SmCoO <sub>3</sub>	2.65	_	3.13	1.06	6.07
LaNiO <sub>3</sub>	2.36		0.01	0.51	15.65
PrNiO <sub>3</sub>	0.95		0.03	1.03	5.95
SmNiO <sub>3</sub>	11.18		0.06	0.58	11.50
Fe <sub>2</sub> O <sub>3</sub>	0.85		0.01	0.07	7.48
$Co_3O_4$	5.13				8.40
NiO	24.57	=	_	_	3.98
$Cr_2O_3$	3.66		_	0.86	18.19
$MnO_2$	11.71				9.42
$La_2O_3$	39.77	12.45	1.28	1.34	35.14
$Pr_6O_{11}$	29.34	4.54	2.76	3.80	14,15
$Sm_2O_3$	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 temperatures<sup>19</sup>.

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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