ELECTRON DONATING, ACID-BASE AND CATALYTIC PROPERTIES OF PEROVSKITE-TYPE MIXED OXIDES OF RARE EARTHS

S. SUGUNAN and V. MEERA
Department of Applied Chemistry,
Cochin University of Science and Technology, Kochi-682022, India

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The electron donor properties of perovskite-type mixed oxides ($LaFeO_3$, $PrFeO_3$, $SmFeO_3$, $LaCoO_3$, $PrCoO_3$, $SmCoO_3$, $LaNiO_3$, $PrNiO_3$ and $SmNiO_3$) were studied based on the adsorption of electron acceptors exhibiting different electron affinity viz. 7,7,8,8-tetracyanoquinodimethane, 2,3,5,6-tetrachloro-1,4-benzoquinone, *p*-dinitrobenzene, and *m*-dinitrobenzene. The surface acidity/basicity of the oxides was determined using a set of Hammett indicators. The data were correlated with the catalytic activity of the oxides for the reduction of cyclohexanone with 2-propanol.

Perovskite-type mixed oxides (ABO_3) are typical mixed oxides and many of them are known to possess various A and B ions sites[1]. Owing to this and to the stability of the perovskite structure, the composition and oxygen vacancies as well as oxidation state of the metal atoms can be varied in a regular way. So the oxides can serve as suitable model compounds for studying the relationship between the solid state chemistry of mixed metal oxides and their catalytic effects[2,3]. The catalytic activity of some transition metal oxides have been correlated with their surface acid-base properties[4–6]. The electron donor properties of some rare earth oxides have also been reported[7–9]. However, no attempts have so far been made to study the electron donor properties of perovskite-type mixed oxides involving rare earth and 3d transition metals. In this paper we report on the electron donor properties and surface acidity/basicity of $LaFeO_3$, $PrFeO_3$, $SmFeO_3$, $LaCoO_3$, $PrCoO_3$, $SmCoO_3$, $LaNiO_3$, $PrNiO_3$ and $SmNiO_3$. The properties were correlated with the catalytic activity of the mixed oxides for the reduction of cyclohexanone with 2-propanol.

EXPERIMENTAL

The mixed oxides were prepared from mixtures of metal nitrates of the components by coprecipitation using butylamine[10]. The precipitate was filtered, washed until no NO_3^- ions were detected, 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 CuKα radiation (λ = 1.5418 Å) displayed the perovskite structure only[11]. Elemental analysis was carried out using a Perkin–Elmer 23-80 atomic absorption spectrometer. Electronic spectra of the samples were scanned on a Shimadzu (UV-160A) UV-VIS spectrophotometer. The radical concentrations of electron acceptors adsorbed on the oxides were determined based on the ESR spectra measured at room temperature using a Varian E-112 X/Q band ESR spectrophotometer. The reflectance spectra of the adsorbed samples were measured with a Hitachi 200-20 UV-VIS spectrophotometer equipped with a 200-0531 reflectance attachment. The surface area of the samples was determined by the BET method using Carlo–Erba Strumentazione Sorptomatic Series 1800. Rare earth oxides were recovered from the nitrate solutions by the same method as described above, and were activated at 850 °C for 2 h prior to adsorption.

The adsorption properties were studied with the following electron acceptors (EA), (electron affinity values in parentheses): 7,7,8,8-tetracyanoquinodimethane [TCNQ (2.84 eV)], *p*-dinitrobenzene [PDNB (1.77 eV)] and *m*-dinitrobenzene [MDNB (1.26 eV)]. The adsorption of the electron acceptors was conducted in acetonitrile, which is a very weak base. The oxides activated at 850 °C for 2 h were placed in a 25 ml test tube and outgassed at $1.3 \cdot 10^{-3}$ Pa for an hour. Subsequently, 20 ml of a solution of the electron acceptor of choice in the organic solvent was added, and the solution was stirred at 28 °C for 4 h in a thermostated bath. The oxide was then collected by centrifuging the solution and dried at room temperature in vacuo. All reagents were purified prior to use.

The acidity/basicity of the oxides was determined by using the following set of Hammett indicators, (pK_a values are given in parentheses): crystal violet (0.8), dimethyl yellow (3.3), methyl red (4.8), neutral red (6.8), bromothymol blue (7.2) and 4-nitroaniline (18.4). A visible color change was only observed with three indicators, viz. bromothymol blue, methyl red and dimethyl yellow. Acidity and basicity were determined by titration with butylamine and trichloroacetic acid, respectively.

Cyclohexanone conversion on oxide catalysts has been proposed as a test for their surface electron donor properties. A typical reduction procedure was as follows. In a 100 ml round-bottom 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 decane as the internal standard. The contents were heated under gentle reflux. The amounts of cyclohexanone were determined and its reduction was monitored by GLC on a Hewlett–Packard 5730 A instrument using a calibration plot obtained with standard samples[12].

RESULTS AND DISCUSSION

With the mixed oxides, the adsorption of 2,3,5,6-tetrachloro-1,4-benzoquinone (chloranil), PNDB and MDNB was so low that the amount could hardly be estimated in the solvents. The component rare-earth oxides exhibited adsorption of TCNQ and chloranil, but not of PDNB and MDNB and the component 3d metal oxides exhibited adsorption of TCNQ solely. Figure 1 shows the adsorption isotherms (Langmuir type) of the electron acceptors for the mixed oxides, based on which the limiting amounts of the adsorbed electron acceptors were determined. The limit of electron transfer in terms of the electron affinity (eV) of the acceptors is between 2.40 and 2.84 for the mixed oxides and between 1.77 and 2.40 for La_2O_3, Pr_6O_{11} and Sm_2O_3. The limiting amounts of the electron acceptors adsorbed on the oxides and the catalytic activity (expressed as the first-order rate constant per m^2 of the catalyst surface) are given in Table I.

The reflectance spectra of the samples were measured in order to gain insight into the nature of the interaction during the adsorption. The spectra exhibited bands at 400 nm (corresponding to the physically adsorbed neutral TCNQ which displays an absorption

TABLE I
Limiting amount of adsorbed electron acceptors and catalytic activity of oxides

Oxide	EA_{lim}, 10^{-5} mol m^{-2}		Rate constant 10^{-6} s^{-1} m^{-2}	$H_{0,max}$	Surface area m^2 g^{-1}
	TCNQ	chloranil			
$LaFeO_3$	5.09	–	2.67	4.5	14.36
$PrFeO_3$	4.61	–	0.16	–	18.13
$SmFeO_3$	6.06	–	0.24	–	14.55
$LaCoO_3$	7.02	–	1.92	4.20	10.61
$PrCoO_3$	3.79	–	2.48	5.25	7.26
$SmCoO_3$	2.65	–	3.13	–	6.07
$LaNiO_3$	2.36	–	0.01	–	15.65
$PrNiO_3$	0.95	–	0.03	–	5.95
$SmNiO_3$	11.18	–	0.06	–	11.50
La_2O_3	39.77	12.45	1.28	12.5	35.14
Pr_6O_{11}	29.34	4.54	2.76	10.5	14.15
Sm_2O_3	25.96	5.70	1.46	7.8	30.01
Fe_2O_3	0.85	–	0.0	–	7.48
Co_3O_4	5.13	–	0.0	–	8.40
NiO	24.57	–	0.0	–	3.98

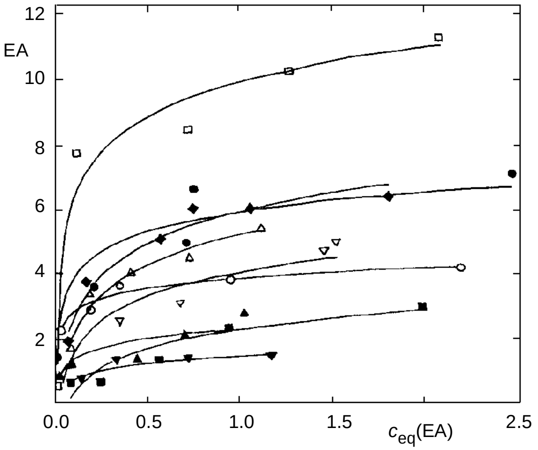

FIG. 1
Amount of electron acceptor (EA) TCNQ (in 10^{-5} mol m^{-2}) vs its equilibrium concentration (c_{eq}(EA) in 10^{-3} mol dm^{-3}). Δ $LaFeO_3$, ∇ $PrFeO_3$, ◆ $SmFeO_3$, ● $LaCoO_3$, ❍ $PrCoO_3$, ■ $SmCoO_3$, ▲ $LaNiO_3$, ▼ $PrNiO_3$, ❐ $SmNiO_3$

band[13] at 395 nm), near 600 nm (attributed[14] to the dimeric TCNQ radical which absorbs at 643 nm) and a broad band extending as far as 700 nm, corresponding to the chloranil anion radical[15]. This assignment does not hold completely with these oxides because they also possess characteristic bands in the same region. The samples analyzed after TCNQ adsorption showed unresolved ESR spectra with a *g* value of 2.003, attributed to TCNQ anion radicals[16], and the samples after chloranil adsorption gave unresolved ESR spectra with a *g* value of 2.011 (ref.[17]). For the mixed oxides, Fig. 2 shows the radical concentration of adsorbed TCNQ plotted against the equilibrium concentration of TCNQ in solvent. The isotherm obtained is Langmuir type and its shape is the same as in Fig. 1. The limiting radical concentrations were also calculated from the plots.

The strength of an acid or base site can be expressed in terms of the Hammett acidity function H_0, which is measured by using indicators adsorbed on the solid surface[18]. If acid sites with a H_0 value which is lower than or equal to the pK_a of the indicator exist on the solid surface, the colour of the indicator changes to that of its conjugate acid. If a neutral acid indicator is adsorbed on the solid base, the colour of the indicator changes to that of its conjugate base provided that the solid has a sufficiently high basic strength. The acidity and basicity were determined on a common H_0 scale. The acidity measured with an indicator shows the number of acidic sites whose acid strength $H_0 \leq \mathrm{p}K_a^{ind}$ whereas the basicity shows the number of basic sites whose base strength $H_0 \geq \mathrm{p}K_a^{ind}$. The acid-base strength distribution curves meet at a point on the abscissa, $H_{0,max}$, where acidity = basicity = 0. The $H_{0,max}$ value can be regarded as a practical

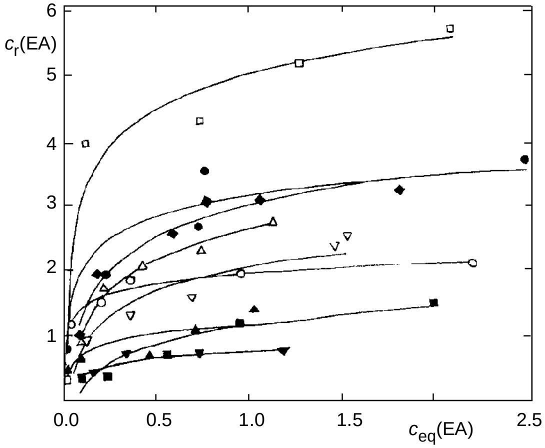

FIG. 2

Radical concentration of electron acceptor (c_r(EA), 10^{18} spins m^{-2}) as a function of equilibrium concentration of the electron acceptor (c_{eq}(EA), 10^{-3} mol dm^{-3}). Δ $LaFeO_3$, ∇ $PrFeO_3$, ◆ $SmFeO_3$, ● $LaCoO_3$, ❍ $PrCoO_3$, ■ $SmCoO_3$, ▲ $LaNiO_3$, ▼ $PrNiO_3$, ❐ $SmNiO_3$

parameter to represent the acid-base properties of solids which is sensitive to surface structure. The $H_{0,\max}$ values determined from the points of intersection of acid-base distribution curves with abscissa are given in Table I. The acid-base distribution curves for $LaCoO_3$, $PrCoO_3$ and $SmCoO_3$ are shown in Fig. 3.

Generally, two types of sites are responsible for the electron donor properties of metal oxides[7–9]: one is due to electrons trapped in intrinsic defect sites, the other is due to surface hydroxide ions. Since the oxides were activated at 850 °C, no contribution from surface hydroxyl group can be expected, so that there only remains the effect of trapped electrons at intrinsic defect sites created at activation temperatures above 500 °C (refs[19,20]).

A distinct separation of the functions of the transition and rare-earth metal cations is observed for some perovskites[21]. The activities of the oxides are governed by the transition metal cations at high temperatures and by the rare-earth ions at low temperatures[21].

A strong electron acceptor (TCNQ) can accept electrons from both strong and weak donor sites whereas a weak electron acceptor such as MDNB can accept electrons from strong donor sites only. The difference between the limiting amounts of TCNQ and chloranil adsorbed on the metal oxides can serve as an indicator of the number of stronger donor sites.

The data in Table I show that the transition metal oxides possess considerable electron donor properties, but a low activity. By including the rare-earth oxides it was found that while the electron donor properties of these metal oxides remain basically

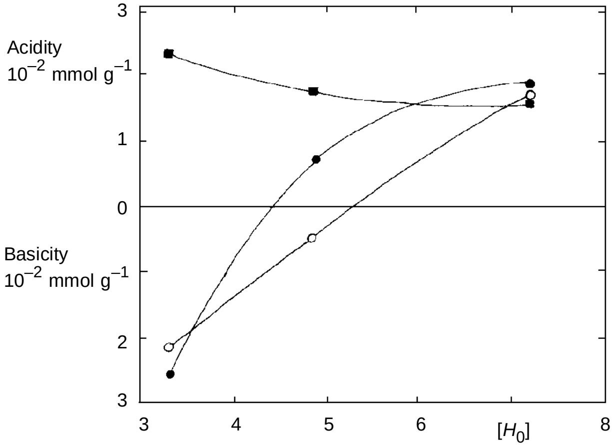

FIG. 3
Acid-base strength $[H_0]$ distribution of $LaCoO_3$ (●), $PrCoO_3$ (○) and $SmCoO_3$ (■).

unchanged, the acitivity increases considerably. The $H_{0,\max}$ values of the oxides are also consistent with this result.

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