• Research Notes

Electron Donating Property and Catalytic Activity of Perovskite-type Mixed Oxides (ABO_3) Consisting of Rare Earth and 3d Transition Metals

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The catalytic activity of Perovskite-type mixed oxides ($LaCoO_3$, $PrCoO_3$ and $SmCoO_3$) for the reduction of cyclohexanone to cyclohexanol with 2-propanol (Meerwein-Ponndorf-Verley reduction) has been studied. The data have been correlated with the surface electron donor properties of these mixed oxides.

1. Introduction

Perovskite-type mixed oxides (ABO_3) are typical mixed oxides and many are known with various A and B site ions[1]. Because of this nature and the stability of the perovskite structure, the composition and oxygen vacancies as well as oxidation state of metal ions can be varied in a regular way. These oxides are therefore suitable model compounds for the study of the relationship between solid state chemistry and the catalytic action of mixed metal oxides[2,3]. The catalytic activity of some of the transition metal oxides have been correlated with their surface acid-base properties[4–6]. The electron donor properties of some of the rare earth oxides are also reported[7–9]. However, no effort has so far been made to study the electron donor properties of perovskite-type mixed oxides consisting of rare earth and 3d transition metals. In this paper we report the electron donor properties of $LaCoO_3$, $PrCoO_3$ and $SmCoO_3$. These properties have been correlated with the catalytic activity of these mixed oxides for the reduction of cyclohexanone with 2-propanol.

2. Experimental

$LaCoO_3$, $PrCoO_3$, and $SmCoO_3$ were prepared from mixtures of the metal nitrates of each component by coprecipitation method using n-butylammine[10]. The precipitate was filtered, washed until no NO_3^- ions were detected and decomposed in air at 300°C for 3 h and then calcined in air at 850°C for 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 (λ=0.1542 nm) showed only the perovskite structure[11]. Elemental analysis was carried out using a Perkin Elmer 23-80 atomic absorption spectrometer. Electronic spectra of the samples were taken using a UV-Visible (UV-160 A) spectrophotometer. The reflectance spectra of the adsorbed samples were measured using a Hitachi 200-20 UV-Visible spectrophotometer with a 200-0531 reflectance attachment. The ESR spectra were measured at room temperature using Varian E-112 X/Q band ESR spectrophotometer. 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 adsorption. 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[12]), near 600 nm (attributed to the dimeric TCNQ radical which absorbs at 643 nm[13] and a broad band extending up to 700 nm corresponding to chloranil anion radical[14]. This assignment does not hold completely with these oxides because they also have characteristic bands in the same region. The ESR spectra of the samples analysed after TCNQ adsorption gave unresolved spectra with a g value of 2.003, identified as being those of TCNQ anion radicals[15], and those samples after chloranil adsorption gave an unresolved ESR spectra having a g value of 2.011[16].

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

Catalyst	Limiting amount of EA adsorbed, 10^{-5} mol m^{-2}				% conversion	surface area, m^2g^{-1}
	TCNQ		Chloranil			
	acetonitrile	dioxan	acetonitrile	dioxan		
$LaCoO_3$	7.02	4.20	-	-	77	10.61
$PrCoO_3$	3.79	3.25	-	-	68	7.26
$SmCoO_3$	2.55	0.40	-	-	70	6.07
La_2O_3	15.20	3.38	12.45	1.22	86	35.14
Pr_6O_{11}	14.07	7.71	4.54	3.04	84	14.15
Sm_2O_3	13.99	3.68	5.70	3.17	86	30.01
Co_3O_4	5.13	0.19	-	-	0	8.40

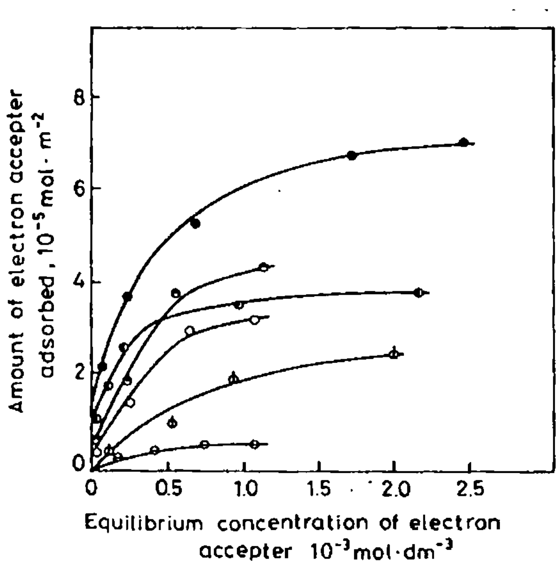

Fig.1 Langmuir adsorption isotherms of $LaCoO_3$, $PrCoO_3$ and $SmCoO_3$. ●-TCNQ in acetonitrile for $LaCoO_3$, ◐- TCNQ in acetonitrile for $PrCoO_3$, ⦶- TCNQ in acetonitrile for $SmCoO_3$, ◓-TCNQ in dioxan for $LaCoO_3$, O-TCNQ in dioxan for $PrCoO_3$, ⊖-TCNQ in dioxan for $SmCoO_3$

Cyclohexanone conversion on oxide catalysts is proposed as a test for the surface electron donor properties of the oxide catalysts. A typical procedure of the reduction is as follows.

In a 100 mL round bottomed flask equipped with a reflux condenser are placed 1.5 g of the catalyst (100–200 mesh), 5 mmol of cyclohexanone, 10 mL of 2-propanol and o-xylene as internal standard. The contents were heated under gentle reflux. The amounts of cyclohexanone and its reduction products were determined with a GLC (Hewlett Packard, 5730 A) using a calibration obtained with standard samples[17].

The following electron accepters (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 two solvents: acetonitrile, a very weak base and 1,4-dioxane, a moderately weak base. The details of adsorption studies have been described elsewhere[7]. All the reagents were used after purification.

In the case of mixed oxides, the adsorption of chloranil, PDNB and MDNB was so negligible that the amount was hardly estimated in both the solvents. The component rare earth oxides gave adsorption of TCNQ and chloranil, but not for PDNB and MDNB. The limiting amounts of EA adsorbed on the oxides and the catalytic activity (expressed as the % conversion of cyclohexanone to cyclohexanol) are given in Table 1.

3. Results and Discussion

Figure 1 shows the adsorption isotherms (Langmuir type) of EA for the mixed oxides. From these plots the limiting amount of EA adsorbed is determined. The limit of electron transfer in terms of the electron affinity (eV) of the accepters is between 2.40 and 2.84 in the case of mixed oxides and between 1.77 and 2.40 for La_2O_3, Pr_6O_{11} and Sm_2O_3. Figure 2 shows the adsorption isotherms for the pure oxides.

In general, two types of sites are responsible for the electron donor properties of metal oxides [7–9]. One of these is electrons trapped in intrinsic defect sites and the other is surface hydroxide ions. Since these oxides are activated at a temperature of 850°C, the contribution from surface hydroxyl groups can not be expected. The sole effect must be from trapped electrons at intrinsic defect sites which are created at activation temperature above 500°C[18,19].

A distinct separation of the functions of the

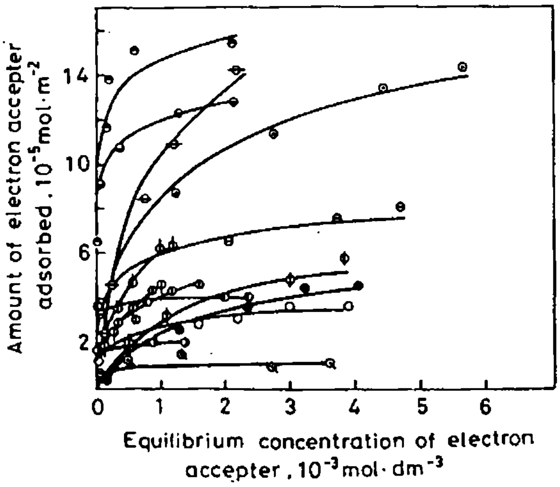

Fig.2 Langmuir adsorption isotherms of La_2O_3, Pr_6O_{11}, Sm_2O_3 and Co_3O_4. ◐-chloranil in dioxan for La_2O_3, ○-chloranil in dioxan for Pr_6O_{11}, ⏀-chloranil in dioxan for Sm_2O_3, ⊖-TCNQ in dioxan for Pr_6O_{11}, ◓-TCNQ in acetonitrile for La_2O_3, ⊙-TCNQ in acetonitrile for Pr_6O_{11}, ⊖-TCNQ in acetonitrile for Sm_2O_3, ○-TCNQ in acetonitrile for Co_3O_4, ◉-chloranil in acetonitrile for La_2O_3, ●-chloranil in acetonitrile for Pr_6O_{11}, ⏀-chloranil in acetonitrile for Sm_2O_3, ◐-TCNQ in dioxan for La_2O_3, ⏀-TCNQ in dioxan for Sm_2O_3, Q-TCNQ in dioxan for Co_3O_4

cations of the transition and rare earth metals is observed for some of the perovskites. The activity of these oxides is determined by the cations of the transition metals at high temperature and by the rare earth ions at low temperatures[20].

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 oxides would be an estimate of the number of stronger donor sites.

The data in Table 1 show that mixed oxides are weak electron donors than the rare earth oxides. The results on the catalytic activity of the mixed oxides are in agreement with this observation.

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