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SURFACE ELECTRON PROPERTIES AND CATALYTIC ACTIVITY OF Sr DOPED LANTHANA

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Abstract

The electron donating properties, surface acidity/basicity and catalytic activity of lanthana for various dopant concentrations of strontium are reported at two activation temperatures. The catalytic activity has been correlated with electron donating properties and surface acidity/basicity of the oxide.

Keywords: Sr doped lanthana, surface acidity/ basicity

INTRODUCTION

A review of earlier work in the field of surface electron donor properties and surface acidity/basicity studies revealed that no attempt has been made to study the acid/base properties and surface electron donor properties of rare earth oxides doped with other metal ions. Strontium doped lanthana is reported to be an effective catalyst for the oxidative coupling of methane [1]. The cause for its high activity and C_2 selectivity is understood from its crystal structure studies [2]. In this paper we report the acid/base properties, surface electron donor properties and the catalytic activity of Sr doped lanthana activated at 650°C and 800°C towards the liquid phase reduction of cyclohexanone in isopropanol. The

strength and distribution of electron donor sites are determined from studies on the adsorption of electron acceptors (EA) of various electron affinities in acetonitrile, a solvent of low basicity [3]. The following electron acceptors were used: (electron affinity values in eV are given in braces) 7,7,8,8-tetracyanoquinodimethane (TCNQ) {2.84}, 2,3,5,6-tetrachloro-p-benzoquinone (chloranil) {2.4}, 1,4-dinitrobenzene (PDNB) {1.77} and 1,3-dinitrobenzene (MDNB) {1.26}. The surface acidity/basicity of the oxides were determined by a titration method [4] using the following Hammett indicators (pKa of indicators 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); of these only Dimethyl yellow, Methyl red and Bromothymol blue responded to the acidity/basicity of the oxides under study. Oxides with various Sr:La molar ratios of 1:5, 1:6, and 1:7 were studied.

EXPERIMENTAL

The required amount of lanthanum nitrate (obtained from Indian Rare Earths, Ltd., Udyogamandal, Kerala) and strontium nitrate (supplied by Qualigens Fine Chemicals, India) were weighed into a china dish, moistened with a little water and evaporated to dryness. It was heat-treated from room temperature to 650°C, the final temperature was maintained for 2 h. It was then sieved to get 100-200 mesh size. Pure lanthanum oxide was also prepared in the same fashion. All the oxides were heat-treated at a particular temperature, namely 650°C or 800°C for two hours prior to each experiment. All the reagents were purified by standard methods before use. The adsorption studies were carried out by a procedure reported earlier [5]. The amount of electron acceptor adsorbed was determined by noting the concentration of the electron acceptor before and after adsorption by means of a UV-visible spectrophotometry at λ_{max} of the EA in acetonitrile, viz., at 393.5, 288, 262 and 237 nm for TCNQ, Chloranil, PDNB and MDNB, respectively.

Surface areas of the oxides were determined by the BET method using Carlo Erba Strumentazione Sorptomatic Series 1800. The ESR spectra of the adsorbed samples were measured at room temperature using a Varian E-112 X/Q band ESR spectrophotometer. The surface acidity/basicity of the oxides were determined by a procedure reported earlier [4].

The catalytic activity of the oxides was determined by the following method. 0.5 g of the oxide (100-200 mesh size) after activation, was placed in a 50 mL round-bottomed flask equipped with a reflux condenser. 5 mmol cyclohexanone and 20 mL isopropanol were then added. The contents were heated under

gentle reflux for 17 h. The progress of the reaction was followed by noting the concentration of cyclohexanone at its λ_{max} of 283 nm. The catalytic activity is expressed as the first order rate constant per m^2 of the oxide surface.

RESULTS AND DISCUSSION

The adsorption of EA on the oxides was of Langmuir type. From the Langmuir plots the limiting amounts of EA adsorbed were determined. In the case of PDNB and MDNB, adsorption was so negligible that the amount could not be detected by the spectrophotometric method. When EA was adsorbed, the surface of the oxides showed characteristic coloration owing to interaction between the EA adsorbed and the oxide surface [6]. The ESR spectrum of these colored samples gave unresolved spectral lines with g values of 2.003 and 2.011 for TCNQ and chloranil, respectively. The electronic spectrum of the adsorbed samples gave bands near 400, 600 and 700 nm corresponding to physically adsorbed state of neutral TCNQ [7], dimeric TCNQ radical [8], and to Chloranil anion radical [9], respectively. The data are given in Table 1 along with the catalytic activity. The acid/base strengths of the oxides were measured on a common H_o scale [4]. The acid/base strengths distribution curves intersect at a point on the abscissa where acidity = basicity = 0 [10]. The point of intersection is defined as $H_{o,max}$. Table 2 contains the data on acidity/basicity distribution. $H_{o,max}$ value can be regarded as a practical parameter to represent acid/base properties on solids. A solid with a large positive $H_{o,max}$ value has strong basic sites and weak acid sites and a solid with a large negative $H_{o,max}$ value has strong acid and weak basic sites.

Strontium doping decreases the catalytic activity of lanthana towards the liquid phase reduction of cyclohexanone in isopropanol. The active sites for the reaction may be surface OH^-, O^{2-} or lattice disorders such as trapped electrons formed in the system. The latter two increase in concentration at high activation temperatures. Surface O^- are formed by sintering of surface OH^-. Due to the hydration resistance developed in the doped lanthana [2], the number of surface OH^- and surface O^- will be less and this causes a decrease in its catalytic activity in cyclohexanone reduction. The increase in activation temperature was found to favor the catalytic activity.

Table 1

Catalytic activity, surface area, $H_{o,max}$ and limiting amount of EA adsorbed on lanthana doped with Sr

Mole ratio Sr:La	Surface area (m^2g^{-1})	Limiting amount adsorbed		Catalytic activity $10^{-6}s^{-1}m^{-2}$	$H_{o,max}$
		TCNQ	Chloranil		
		$(10^{-6}\,mol\,m^{-2})$			
Activation temperature 650°C					
0:1	21.39	1.49	1.48	1.82	12.0
1:7	27.50	0.88	0.83	1.61	5.2
1:6	16.91	2.57	1.65	0.0	8.9
1:5	10.49	4.38	1.83	0.0	9.3
Activation temperature 800°C					
0:1	13.77	2.64	1.95	2.80	5.3
1:7	13.66	3.04	1.62	1.98	5.9
1:6	4.71	8.83	3.82	0.64	--
1:5	7.97	3.80	1.92	2.20	5.2

Surface basicity of lanthana ($H_o \geq 3.3$ and 4.8) is decreased due to strontium doping. Basic lanthana at $H_o = 7.2$ is made acidic by strontium doping. Increase in pretreatment temperature increases the acidity of the oxide and decreases its basicity. The catalytic activity showed a dependence on both surface acidity and basicity, however, the relationship is not straightforward. The decrease in activity with basicity suggests that basic sites play an important role in the catalytic activity. Weak acid sites created by pre-treatment at 800°C are found to be favorable for the reaction. This accounts for the increase in activity with increase in activation temperature even though the basicity decreases. The lack of a linear relationship between activity and basicity implies the involvement of acid sites also in the reaction, the exact nature being unknown [11].

The limiting amount of TCNQ adsorbed is a measure of the total number of electron donor sites on the surface. The electron donor capacity of lanthana was improved by strontium doping. The increase in electron donicity with pre-treatment temperature parallels the trend in catalytic activity. Two possible electron sources exist on the oxide surface capable of electron transfer, namely electrons trapped in intrinsic defects and surface hydroxide ions [3]. It has been reported at higher activation temperatures that the donor sites consist of a co-ordinatively unsaturated O^{2-} associated with a nearby OH^- group and the concentration of these sites is related to the base strength of the surface [11].

The more basic the surface, the higher is the number of O^{2-} which can transfer electrons to the EA.

Table 2

Acid/base strength distribution of the oxides

Mole ratio Sr:La	Act. temp (°C)	Basicity (mmol g⁻¹)			Acidity (mmol g⁻¹)		
		$H_0\leq$ (3.3)	$H_0\leq$ (4.8)	$H_0\leq$ (7.2)	$H_0\geq$ (3.3)	$H_0\geq$ (4.8)	$H_0\geq$ (7.2)
0:1	650	0.0598	0.0408	0.0299	--	--	--
	800	0.0479	0.0058	--	--	--	0.0247
1:7	650	0.0718	0.0340	0.0116	--	--	--
	800	0.0479	0.0116	--	--	--	0.0495
1:6	650	0.0718	0.0116	--	--	--	0.0247
	800	0.0718	0.0233	--	--	--	0.0247
1:5	650	0.0718	0.0116	0.0116	--	--	--
	800	0.0479	0.0116	--	--	--	0.0495

REFERENCES

1. J.M. Deboy, R.F. Hicks: *J.Catal.*, 113, 517 (1988).
2. T. Levan, M. Che, J.M. Tatibouet: *Catal. Lett.*, 14, 321 (1992).
3. K. Esumi, K. Meguro: *J. Colloid Interface Sci.*, 59, 43 (1977).
4. O. Johnson: *J. Phys. Chem.*, 827 (1955).
5. S.Sugunan, G. Devika Rani, K.B. Sherly : *React.Kinet. Catal. Lett.*, 43, 375 (1991).
6. M. Che. C. Naccache, B. Imelik : *J.Catal.*, 24, 328 (1972).
7. K. Meguro, K. Esumi: *J. Adhesion Sci. Technol.*, 4, 393 (1990).
8. F.H. Boyd, W.D. Philips : *J. Chem. Phys.*, 43, 2927 (1965).
9. R. Foster, T.J. Thomson : *Trans. Faraday Soc.*, 58, 860 (1962).
10. T. Yamanaka, K. Tanabe : *J. Phys.Chem.*, 80, 1723 (1976)
11. V.R. Choudhary, V.H. Rane : *J.Catal.*, 130, 411 (1911).