Indian Journal of Chemistry
Vol. 38A, September 1999, pp.947-950

Acidity / basicity and electron donor properties and catalytic activity of sulphated titania

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Received 20 October 1998; revised 11 May 1999

The surface acidity/ basicity of TiO_2 (rutile) and its sulphate modified form have been determined by titration method using Hammett indicators after activation at different temperatures. The electron donating properties of these oxides are also studied from the adsorption of electron acceptors of different electron affinity values. The data have been correlated with the catalytic activity of these oxides towards esterification of acetic acid using *n*-butanol, reduction of cyclohexanone in isopropanol and oxidation of cyclohexanol in benzophenone. Catalytic activity for esterification and oxidation reaction parallels the acidity while that for reduction reaction parallels the basicity of these oxides.

The use of sulphated metal oxides is of increasing interest because of the superacidic properties induced by the presence of SO^{2-} (refs 1, 2). They have been exploited in a variety of reactions of industrial importance[3]. Though a number of studies have been reported about sulphated metal oxides the origin of superacidic properties still remains controversial. The presence of strong Bronsted acidity on sulphate containing samples is already reported. Comparison of the acidity of metal oxides like ZrO_2, TiO_2 (both rutile and anatase) and Al_2O_3 with the corresponding sulphate modified forms are already reported[4]. It was found that sulphation enhances the strength of the weakest Lewis acid sites.

The aim of the present work is to understand the sources of increased acidity after sulphate modification. That is to find out whether the increase in acidity due to sulphation is at the expense of basic sites already present on the surface or it can be due to the generation of new acid sites. Titania (rutile), a very weak base is chosen for this purpose. The electron donor properties of the oxides is a measure of surface basicity. Hence the change in electron donating properties and surface acidity and basicity are measured. Esterification of acetic acid using *n*-butanol, reduction of cyclohexanol in 2-propanol and oxidation of cyclohexanol with benzophenone are test reactions to find out catalytic activity.

Experimental

Titanium dioxide (rutile form) from sd Fine Chemicals Ltd. was used as such. Sulphation was carried out by impregnation method using 0.2M ammonium sulphate solution [5]. The samples activated at different temperatures (300, 500 and 700 °C) were used. The surface area was determined by BET method using Carlo Erba Strumentazione Sorptomatic Series 1800. The acidity and basicity were determined by standard procedure[6] using the following indicators (*p*Ka values are given in brackets): 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). The oxides under study responded only to dimethyl yellow, methyl red and bromothymol blue. Benzene used for activity measurements was purified by a standard procedure[7]. It was shaken with sulphuric acid and was subsequently washed with water and 2 % sodium carbonate solution. It was further washed with water and dried over anhydrous $CaCl_2$. It was filtered and distilled. Distillate was kept over sodium wire for one day. It was again distilled and the fraction distilling at 80 °C was collected. The titration was carried out in an automatic burette under moisture-free condition.

The strength distribution of electron donor sites on the oxide surface was determined by the adsorption of the following electron acceptors (EA) in acetonitrile as solvent (the electron affinity values are given 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). The method for adsorption studies is described elsewhere[8]. The amount of EA adsorbed was determined by UV- visible spectrophotometry and the adsorbed state of EA was studied by EPR spectra (using Varian E- 112 X/Q band) and reflectance spectra using Shimadzu UV- 160A UV visible spectrophotometer using reflectance attachment. IR spec-

Table 1 - Acidity/ basicity of titania

Catalyst	Act. Temp. °C	Surf. area (m^2g^{-1})	Basicity		Acidity		
			10^{-6} mol m^{-2}				
			H_0>3.3	H_0< 3.3	H_0< 4.8	H_0< 7.2	$H_{0,max}$
TiO_2	300	15.1	0.18	—	0.27	2.53	3.90
TiO_2	500	15.6	0.22	—	0.17	2.17	3.60
TiO_2	700	19.3	0.14	—	0.14	1.41	4.25
S-TiO_2	300	11.5	—	0.12	0.47	4.00	—
S-TiO_2	500	11.9	—	0.16	0.50	4.05	—
S-TiO_2	700	14.8	0.09	—	0.28	2.02	4.00

tra of the oxides were taken using Shimadzu IR- 470 spectrometer. Catalytic activities for reduction, oxidation and esterification reactions were determined in liquid phase by standard reported procedures[9-11].

Results and discussion

The acidity and basicity were determined on a common H_0 scale where strength of the basic sites was expressed as H_0 of the conjugate acid. Results are given in Table 1. The acid base distribution curves intersect at a point on the abscissa where acidity = basicity = 0 and it is termed $H_{0,max}$ (ref.12). It is a practical parameter to represent acid base properties of solids which is very sensitive to surface structure. From the data it can be seen that for unmodified titania the maximum number of acid sites is at H_0 = 7.2 and maximum number of basic sites at H_0 = 3.3 implying the presence of only weak acid and base sites on the surface. The $H_{0,max}$ values show that activation temperature has not much effect on acidity/ basicity of titania. During sulphation of titania, acidity is generated at H_0 values of 3.3, 4.8 and 7.2. It is already reported that surface chemistry of titania, particularly acidity depend on the method of preparation and the amount of impurity present. Eventhough sulphation can generate superacidity in titania, since we have used only 0.2 normal ammonium sulphate for modification of rutile form it is not showing the superacidity. The IR spectra of the sulphated samples showed absorption bands at 960-980, 1060-1070, 1130-1150 and 1210 cm^{-1} which are assigned to the bidentate sulphate coordinated to the metal. The I.R. spectra of metal oxides are given in Fig.1. The strong acidity on sulphate modification is attributed to the electron withdrawing anion groups which lead to coordinatively unsaturated and electron deficient metal centers behaving as strong Lewis acid sites[13]. In the presence of water vapour Lewis acid sites are converted to Bronsted acid sites with very reactive protons[14].

Considering the surface electron donating properties of these oxides it can be seen that in the case of PDNB and MDNB the amount adsorbed was so negligible that it could be hardly determined. The adsorption of TCNQ and chloranil was of Langmuir type and from such plots the limiting amount of EA adsorbed was calculated. The data are given in Table 2. The formation of anion radicals was confirmed by EPR and reflectance spectra of adsorbed samples. The oxides after TCNQ and chloranil adsorption gave colouration (pink and light yellow respectively) showing the generation of new adsorbed species on the solid surface. From the data in Table 2 it can be seen that electron donocity of both titania and sulphated titania decreases with increase in temperature goes through a minimum at 500 °C and then increases on heating to 700 °C. The initial decrease in electron donocity may be due to the decrease in surface hydroxyl groups with increase in temperature. The increase in electron donocity by heating above 500 °C may be due to the increase in number of electrons trapped in defect sites which is another source of electron donor sites in metal oxides. On modification with sulphate ion the electron donating capacity decreases implying that some of the basic sites are converted to acidic sites. It is already re-

Table 2 - Limiting amount of EA adsorbed and catalytic activity

Act. Temp. °C	Limiting amount of EA adsorbed (10^{-5} mol m^{-2}) Chloranil	TCNQ	Ester.	Catalytic activity (10^{-6} mol m^{-2} s^{-1}) Redn.	Oxdn
Titania					
300	5.89	9.34	3.77	2.26	0.78
500	4.75	8.15	4.44	2.14	1.56
700	6.12	10.57	1.01	2.39	—
Sulphated titania					
300	2.05	2.21	5.24	0.33	3.31
500	1.66	1.72	23.90	0.02	3.80
700	5.20	10.21	1.39	0.82	1.07

ported that the mechanism of sulphation is an anion exchange between SO_4^{2-} and OH^- [ref. 15]. The electron donating capacity of sulphated titania is almost equal to that of unmodified one when the activation temperature is 700 °C because trapped electrons are solely responsible for basicity at high temperatures. Further there is no OH^- for exchange with SO_4^{2-} at high temperatures. The data on the catalytic activity for the various reactions studied are also included in Table 2. Sulphated titania catalyses the esterification reaction more effectively compared to unmodified ones which can be accounted by the greater acidity and higher acid strength. As the activation temperature increased to 700 °C the catalytic activity decreases in accordance with acid base properties. It has been reported that on activating sulphated titania at 750 °C the mass of the sample was the same as it was before sulphation implying that all SO_4^{2-} are removed[16]. The catalytic activity of both modified and unmodified titania is nearly the same which can be understood on the same lines.

Reduction of cyclohexanone in 2-propanol by titania is analogous to Meervin- Pondrof-Verley (MPV) reduction. The mechanism involves hydride ion transfer from alcohol to the carbonyl carbon of ketone[17]. From the data it can be seen that reaction proceeds effectively over pure titania due to its higher basicity compared to sulphated titania. For reduction to take place there must be hydride ion transfer from adsorbed isopropanol to adsorbed carbonyl group. Basic sites favor hydride ion transfer and activity parallels basicity of the oxides. The lower catalytic activity can be attributed to the conversion of some of the basic sites into acidic sites on sulphation which is in agreement with the observation that the limiting amount of EA adsorbed (both TCNQ and chloranil) is smaller for sulphated oxides.

Oxidation of cyclohexanol over metal oxides is analogous to Oppenauer oxidation. For a catalyst to be active in oxidation reaction it must participate in the following processes: activation of reactant molecules and activation of O_2 when a catalyst is potent in the activation of oxygen[18]. In other words it has an oxidising power that depends on two factors, namely number of oxidising sites and mobility of oxygen at a site. Titania is only weakly acidic. The higher catalytic activity of modified catalyst may be accounted by the greater acidity and higher acid strength. It has been reported that the ability of an oxide to catalyse dehydrogenation of isopropanol to acetone takes place through a concerted mechanism involving both acidic and basic sites[19]. A Lewis acid site can abstract an electron from a molecule giving rise to oxidation. The higher activity of sulphated titania for oxidation can thus be understood.

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