Catalysis Letters 18 (1993) 391–399

Al_2O_3–SnO_2 systems as a support for metallic catalysts. III. Acid–base properties of modified aluminas

Piotr Kirszensztejn [1], Wieslaw Przystajko
Faculty of Chemistry, A. Mickiewicz University, Grunwaldzka 6,
60-780 Poznan, Poland

and

Tom N. Bell
Department of Chemistry, Simon Fraser University, Burnaby, B.C.,
Canada V5A 1S6

Received 22 September 1992; accepted 8 February 1993

This study is concerned with the effect of various amounts of Sn species in modifying the surface acidic and basic properties of alumina, important in catalytic activity. The decomposition of isopropanol and conversion of cumene were chosen as a measure of the changes to the acidic/basic catalytic sites, and the adsorption of pyridine (measured by IR spectroscopy) to separate out the Brønsted and Lewis acid activity.

Keywords: Modified alumina; surface acidity; SnO_2

1. Introduction

Pure aluminas are widely used themselves as catalysts for several group reactions where they are able to activate hydrogen–hydrogen, carbon–hydrogen and carbon–carbon bonds, although with varying efficiency. Thus, the ortho-H_2–para-H_2 equilibration reaction occurs at liquid nitrogen temperature [1], C–H bond activation in isomerisation reactions is effective near room temperature [2] and C–C bond activation as in skeletal isomerisation at 600 K [3]. One of the most important uses of aluminas is as a support for noble metals, which systems find wide use in many areas of chemistry.

Notable features of alumina supports as well as their good mechanical properties are their ability to disperse the active metal phase. A considerable drawback of alumina, however, is the undesirable metal–support interactions, especially at low

---

[1] To whom correspondence should be addressed.

loadings [4]. An attempt has been made to overcome these drawbacks through alumina modification or by the use of alternative support materials.

Aluminum ions in the Al_2O_3 crystal are known to occupy octahedral and tetrahedral interstices between the surrounding densely packed oxygen ions. These ions are responsible for the local acceptor states in the band gap of the crystal energy scheme and, provided they are sterically accessible to gas-phase molecules, may act as Lewis acids.

Various transitional aluminas are classified by the ratio of octahedrally to tetrahedrally coordinated ions Al^{3+} and by the oxygen lattice packing density. The surface charge in aluminum oxides is neutralized by attached hydroxyl groups, their concentration being dependent upon the type of alumina [5,6]. The surface hydroxyl groups bind the metallic precursor from which the metal is later deposited. It is generally desirable to minimize the metal particle size so as to optimize the maximum number of exposed metal surface atoms, the active part of catalyst. A high dispersion will be found, if the metal particle is formed from a well-defined precursor complex. The type of surface precursor complex formed will depend on the types of OH groups available to the surface and on the metal complex used as a reagent. The alumina surface contains basic OH groups as well as acidic Brønsted acid sites. The former are OH groups coordinated end-on to an Al^{3+} ion. The acidic protons are bonded to bridging oxygen atoms. Their acidity depends on how and how many Al^{3+} ions the bridging oxygen atoms interconnect. For example, to prepare Pt metal particles on a metal-oxide support in a water phase, the reactant to be used can be the $PtCl_4^{2-}$ or the $Pt(NH_3)_4^{2+}$ ion. The first complex reacts with the alumina by exchange with basic OH^- groups, the second with Brønsted acid protons. At value of the pH where alumina does not dissolve and the Pt complexes are stable, the number of basic OH groups on the alumina surface is much larger than the acidic one. As a consequence the use of the $PtCl_4^{2-}$ in complex is to be preferred if a high Pt dispersion on alumina is required. The transformation of the acidic or basic centers in alumina is dependent on the presence of ions such as F^-, Cl^-, Zn^{2+}, Mg^{2+} and Na^+ [7,8], hence the activity of catalysts prepared on these different supports is dependent on the nature of the ionic species present. The chemical and mechanistic reason for such changes is not clear.

Many of the explanations for the superior properties of the bimetallic (Sn + active metal) catalysts are based on a structural argument. On the other hand, the superior activity and selectivity may be the result of high dispersion of the active metal and the stabilization of the dispersed phase by the second component, for example tin. In this context the incorporation of various amounts of tin as the second component in aluminas has been the subject of a number of studies [9–15] and of concern is the form (metallic or ionic) of tin which is present in the support, and the stabilization of the different forms of tin when associated with metallic catalysts. At present, the changes which may occur in the alumina matrix due to the addition of tin have not been well studied. By applying the method involving coprecipitation of both aluminium and tin which we have developed [16,17], it is possible to study this problem from the point of view of the modified support.

Of particular interest is our current work on the hydrogenation of halocarbons which are of environmental concern [18,19]. These compounds, we believe, form hydrogen bonds with surface hydroxyl groups which groups are subject to modification by Sn in Al_2O_3.

2. Experimental

2.1. MATERIALS

The method of preparation of the Al_2O_3–SnO_2 systems is described in detail in previous papers [16,17,20,21]. The binary composition Al_2O_3–SnO_2 with molar ratios between 1 : 0 and 1 : 1, was synthesized by coprecipitation methods. A solution of tin(IV) acetate in carbon tetrachloride, and a solution of aluminum isopropoxide in isopropanol were used as starting materials. Homogeneous mixtures of the reagents were subject to hydrolysis at 363 K with the pH maintained between 7.0 and 7.5. Under these conditions a precipitate formed and this was aged for one week in the solution mix. The aged precipitate was filtered, washed (with isopropanol and distilled water), and dried at 373 K for 48 h, after which the product was annealed in air at 773 K for 8 h. The symbols and the composition of the samples used in the investigations are given in table 1.

2.2. FT-IR SPECTROSCOPY

Infra-red measurements were carried out in the range 4000–1100 cm^{-1} on a Bruker IFS88 FTIR spectrometer flushed with dry air. The spectra (resolution 1

Table 1
Sample, chemical composition and concentration of chemisorbed pyridine

Sample	Molar ratio Al_2O_3 : SnO_2	Pyridine ($\mu mol/m^2$)
Al	1 : 0	0.78
Sn-0.01	1 : 0.01	0.76
Sn-0.02	1 : 0.02	0.65
Sn-0.05	1 : 0.05	0.60
Sn-0.075	1 : 0.075	0.61
Sn-0.1	1 : 0.1	0.61
Sn-0.2	1 : 0.2	0.54
Sn-0.5	1 : 0.5	0.51
Sn-1.0	1 : 1	0.61

cm^{-1}; 250 scans) were recorded in the transmittance mode. The sample of alumina or Sn doped alumina was compressed into a self-supporting pellet (25 mm diameter) and placed in a greaseless IR cell equipped with NaCl windows connected to a high-vacuum system, and outgassed for 4 h at 673 K under vacuum (10^{-3} Pa). These treatment conditions produce surfaces containing a variety of "free" and hydrogen-bonded hydroxyl groups [22]. In addition a variety of strongly hydrogen-bonded forms of water are present, however, these are low in concentration as evidenced by the relatively weak intensity of the H–O–H bending vibrations in the $\sim$ 1600 cm^{-1} region. These relative intensities are shown in fig. 3 where the dashed line represents the background spectrum for sample Sn-1.0. After cooling the cell under vacuum, the IR spectrum of the outgassed sample (the reference) was recorded at room temperature. The adsorption of the probe molecule, pyridine, was then carried out on a particular reference sample as follows. Pyridine vapour (Aldrich >99.9%) was allowed to be adsorbed at room temperature for 5 min. This procedure allows for the complete saturation [23] of the alumina surface as a large excess of the probe molecule is admitted into the IR cell. The adsorption step was followed by outgassing for 1 h at 423 K (with controlled heating –10 K/min). The characteristic spectrum of pyridine adsorbed on the catalyst was found to vary as a function of the nature of the particular adsorption sites.

The samples were subject to elemental analysis in order to determine the amount of pyridine adsorbed on their surfaces. This analysis was carried out on a Perkin-Elmer 2400 CHN Elemental Analyzer.

Reactions carried out on the modified aluminas are described below.

2.3. REACTIONS

2.3.1. Conversion of isopropanol

The dehydration of isopropanol (Merck >99.9%) on the Sn doped alumina samples was carried out in a conventional microreactor made from a quartz tube (5 mm i.d.) at atmospheric pressure. In this process the "pulse-reactant" mode was employed. In each case a catalyst sample (10 mg, particle size 100–200 μm) was placed in the reactor and heated under helium at 573 K for 3 h. Isopropanol and the dehydration products were analyzed by a Chrom-4a gas chromatograph fitted with a thermal conductivity detector on a 1 m column filled with Emulfor O (15% w/w) on Chromosorb WAW at 323 K.

2.3.2. Cracking of cumene

The cracking (at 650 K) of cumene (Aldrich >>99.9) was carried out in the apparatus similar to that used for the dehydration of isopropanol. The analysis of the products of cumene cracking was carried out on the same gas-chromatographic column as was used in the dehydration of isopropanol but at a temperature of 393 K.

3. Results and discussion

Beside the bands arising from H-bonded hydroxyl groups, transition aluminas typically exhibit up to five discrete bands in the region from 3690 to 3800 cm^{-1} arising from the stretching vibrations of different types of isolated hydroxyl groups, two of which are basic, one neutral and two acidic in character [24]. These types of OH are assigned as follows: around 3775 cm^{-1} (basic OH groups), around 3730 cm^{-1} (neutral OH groups) and around 3690 cm^{-1} (acidic OH groups) [25] which have different calculated charges varying from −0.5 to +0.5 [24]. Fig. 1 shows the IR spectra of some SnO_2/γ-Al_2O_3 catalysts containing differing amounts of SnO_2.

The adsorption intensity changes of the bands can be taken as a measure of changes in concentration of particular OH groups, and in fig. 2 an attempt has been made to show such changes with the extent of Sn doping. The addition of Sn, however, changes the optical transmittance property and hence it is only possible to make comparisons using a normalized procedure. Thus the data in fig. 2 is presented normalized to the acidic OH intensity set at 1.0. On this relative scale it is seen that the basic OH groups are relatively little affected and remain around 50% of the acidic OH, however the neutral OH groups increase significantly (0.4–1.0) as the Sn concentration ratio increases to 1 : 1. The normalization procedure pre-

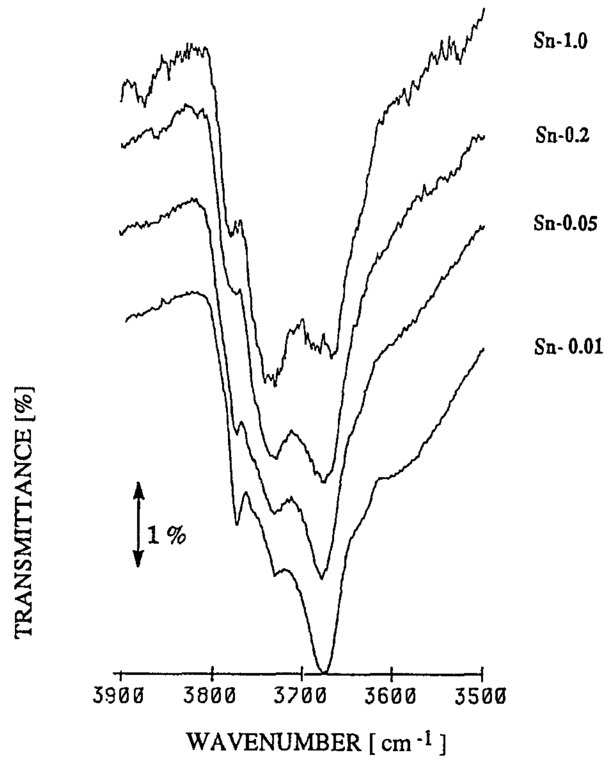

Fig. 1. IR spectra OH stretch region SnO_2/γ-Al_2O_3 samples.

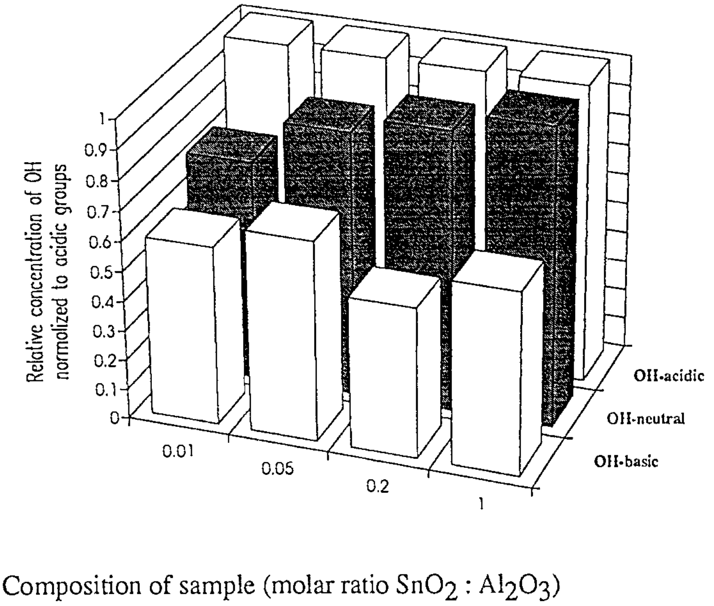

Fig. 2. Relative intensities of bands assigned to acidic, neutral and basic OH groups.

cludes any statement concerning changes in the total number of OH groups of all types.

To answer the question whether any of these OH groups or Lewis acid centers are structurally accessible to probe molecules, IR measurements with adsorbed pyridine were carried out. The spectra of alumina and alumina containing tin admixture exposed to pyridine contained four strong IR bands at 1613–1625, 1575, 1494 and 1451 cm^{-1} (fig. 3). These are assigned to the ring vibrations of ligated pyridine respectively [26,27] and confirm the existence of Lewis acid adsorption sites on the surface. The 1613–1625 cm^{-1} band is the most important in elucidating the quantity and strength of the Lewis sites. For samples poor in tin oxide, this band is clearly resolved into a number of components one of which is attributable to weak Lewis acid sites (1615 cm^{-1}), and one to strong Lewis acid sites (1625 cm^{-1}). With an increase in the tin composition, the band responsible for strong Lewis acid sites disappears.

Bands (around 1540 and 1640 cm^{-1}) characteristic of the pyridinium ion were not observed. This indicates the absence of surface Brønsted acid sites on the modified aluminas of sufficient strength to protonate pyridine. The weakly basic pyridine, is selective for strong acid sites and does not interact extensively with weak sites [28], thus, as indicated by Corma et al. [29] weak Brønsted acid sites could exist on modified aluminas, such as ours, without being detected by measurements involving pyridine.

This implication of the absence of strong Brønsted acid centers was confirmed

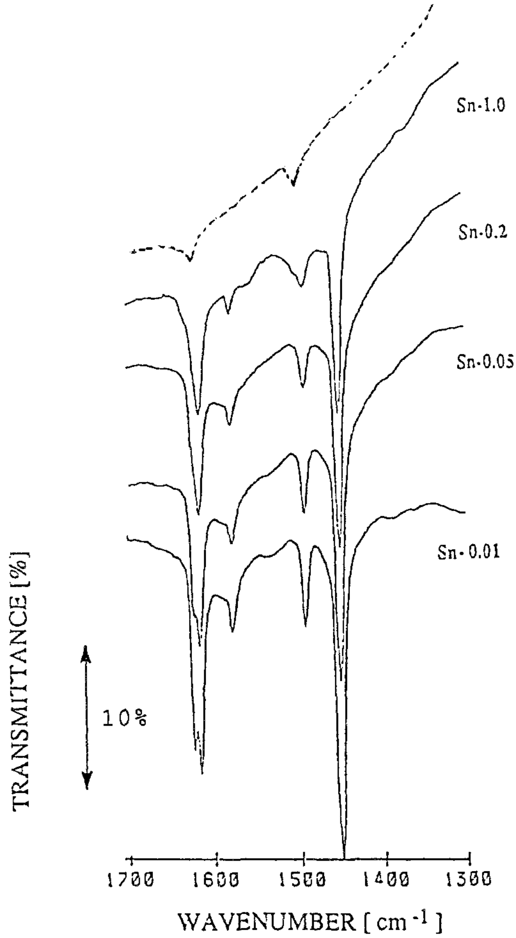

Fig. 3. IR spectra of adsorbed pyridine on SnO_2/γ-Al_2O_3 samples.

by the results from cumene cracking. The formation of α-methylstyrene would provide an indication of the dehydrogenation (and therefore hydrogenation) capacity of the catalyst, and benzene formation would indicate the presence of strong Brønsted acid sites on the surface. Our results yielded only 1% conversion to α-methylstyrene on pure γ-Al_2O_3 and no formation of benzene. The doped samples were completely inactive with respect to either reaction. We therefore conclude that strong Brønsted acid sites are absent in both γ-Al_2O_3 and the Sn doped samples.

For pure γ-Al_2O_3 and for most of the samples doped with tin, the only products of isopropyl alcohol decomposition are the dehydration products (propene and water). The general tendencies in the change of activity of the Al_2O_3–SnO_2 system activity in the alcohol dehydration reaction are shown in fig. 4. As the amount of the tin admixture increases, the activity of these samples decreases, the activity for the Sn-1.0 (molar ratio 1 : 1) sample is several times smaller than for the sample not doped with tin.

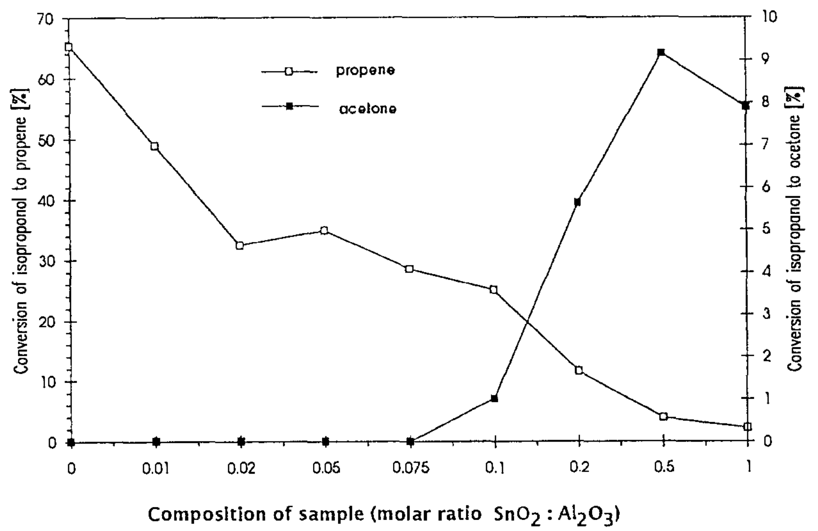

Fig. 4. Conversion of isopropyl alcohol to propene and to acetone.

The results of elemental analysis (table 1) of the amount of adsorbed pyridine indicate that the total concentration of the acid centers in samples containing tin admixture varies very little. Hence, we are inclined to conclude that the drop in activity as observed in the dehydration of isopropanol can be attributed to the acceptor strength of these sites. Such a conclusion seems to be confirmed by the measurements of the IR spectra of adsorbed pyridine where a clearly resolved band (components 1615 and 1625 cm^{-1}) is observed. These band components are attributed to weak and strong Lewis acid sites respectively, and are observed to vary in relative intensity as a function of Sn content in the Al_2O_3 sample fig. 3.

Another confirmation of our conclusion is provided by a quantum-chemical model of Lewis acidity on the surface of γ-Al_2O_3 developed by Shimanskaya and coworkers [30], which presented cluster modeling interactions between the surface Lewis acid sites and water molecules. The values they reported for adsorption-complex stabilization energies, electron density transfer from water molecule to surface site and optimal H_2O–Al distance clearly show that aluminium ions which occupy the tetrahedral interstices between the surrounding densely packed oxygen ions, act as stronger Lewis acids than the octahedrally coordinated Al ions.

Preliminary studies on the conversion of halocarbons to hydrogenated species using H_2 indicate that adsorption of the halo system to the aluminas is an important mechanistic requirement. Presumably this occurs through a Hal–H–O center. Modification of the alumina with Sn markedly affects the adsorption of the halocarbon, and hence the rate of hydrogenation. These studies include both metallic, e.g. with Pt, and non-metallic aluminas and a significant difference in observed products occurs.

4. Conclusion

The binary composition Al_2O_3–SnO_2 synthesized by coprecipitation methods shows a wide variety of acidic–basic sites of various strength which are dependent on the concentration of SnO_2. Strong Lewis acid sites are diminished by the addition of Sn and strong Brønsted acid sites do not appear. This does not, however, exclude formation of weak Brønsted acid sites.

References

[1] F.H. van Cauwelaert and W.K. Hall, Trans. Faraday Soc. 66 (1970) 457.
[2] J.W. Hightower and W.K. Hall, Trans. Faraday Soc. 60 (1970) 477.
[3] D.S. Maciver, W.H. Wilmot and J.M. Bridges, J. Catal. 3 (1964) 502.
[4] P.M. Boorman, K. Chong, R.A. Kydd and J.M. Levis, J. Catal. 128 (1991) 537.
[5] H. Knözinger, Adv. Catal. 25 (1976) 184.
[6] J.M. Dumas, C. Geron, A. Kribii and J. Barbier, Appl. Catal. 47 (1989) L9.
[7] P. Berteau, S. Ceckiewicz and B. Delmon, Appl. Catal. 31 (1987) 361.
[8] P. Berteau, M.A. Kellens and B. Delmon, J. Chem. Soc. Faraday Trans. 7 (1991) 1425.
[9] Y.X. Li and K.J. Klabunde, J. Catal. 126 (1990) 173.
[10] Y.X. Li, K.J. Klabunde and B.H. Davis, J. Catal. 128 (1991) 1.
[11] J. Margitfalvi, M. Hegedus, S. Gobolos, E. Kern-Talas, P. Szedlacsek, S. Szabo and F. Nagy, in: *Proc. 8th Int. Congr. on Catalysis*, Vol. 4, Berlin 1984 (Verlag Chemie, Weinheim, 1984) p. 903.
[12] E. Kern-Talas, M. Hegedus, S. Gobolos, P. Szedlacsek and J. Margitfalvi, in: *Preparation of Catalysts IV*, eds. B. Delmon, P. Grange, P.A. Jacobs and G. Poncelet (Elsevier, Amsterdam, 1987) p. 689.
[13] Cs. Vertes, E. Talas, I. Czako-Nagy, J. Ryczkowski, S. Gobolos, A. Vertes and J. Margitfalvi, Appl. Catal. 68 (1991) 149.
[14] G. Meitzner, G.H. Via, F.W. Lytle, S.C. Fung and J.H. Sinfelt, J. Phys. Chem. 92 (1988) 2925.
[15] O. Beeck, Discussions Faraday Soc. 8 (1950) 118.
[16] P. Kirszensztejn, Mat. Chem. Phys. 27 (1991) 117.
[17] P. Kirszensztejn, Mat. Chem. Phys. 27 (1991) 129.
[18] T.H. Ballinger and J.T. Yates Jr., J. Phys. Chem. 96 (1992) 1417.
[19] I. Mochida, A. Uchino, H. Fujitsu and K. Takeshita, J. Catal. 51 (1978) 72.
[20] P. Kirszenstejn and S. Zielinski, Polish Patent WP-216-275654 (1988).
[21] P. Kirszenstejn, L. Wachowski and S. Zielinski, Polish Patent WP-217-275653 (1988).
[22] T.P. Beebe Jr., J.E. Crowell and J.T. Yates Jr., J. Phys. Chem. 92 (1988) 1296.
[23] P.O. Scocart, F.D. Declerck, R.E. Sempels and P.G. Rouxhet, J. Chem. Soc. Faraday Trans. I 73 (1977) 359.
[24] H. Knözinger and P. Ratnasamy, Catal. Rev.-Sci. Eng. 17 (1978) 31.
[25] J.A.R. van Veen, G. Jonkers and W.H. Hesseling, J. Chem. Soc. Faraday Trans. I 85 (1989) 389.
[26] E.P. Parry, J. Catal. 2 (1963) 371.
[27] K. Nakamoto, in: *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th Ed. (Wiley–Interscience, New York, 1986).
[28] M.C. Kung and H.H. Kung, Catal. Rev.-Sci. Eng. 27 (1985) 425.
[29] A. Corma, V. Fornes and E. Ortega, J. Catal. 92 (1985) 284.
[30] M.B. Fleisher, L.O. Golender and M.V. Shimanskaya, J. Chem. Soc. Faraday Trans. 87 (1991) 745.