Acidic and Basic Properties of Titania-Alumina Mixed Oxides; Active Sites for Propan-2-ol Dehydration

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 $TiO_2-AI_2O_3$ mixed oxides have been prepared by cohydrolysis of Ti⁴⁺ and AI³⁺ isopropoxides. Textural and acid-base properties were investigated using nitrogen physisorption, adsorption of probe molecules followed by FTIR spectroscopy, and test-reactions. Catalysts were found to exhibit high surface areas and pore volumes. Results obtained from adsorbed CO₂ probe molecules and COS hydrolysis activity agreed well and showed that the hydroxy basicity of mixed oxides was lower than that of the two oxide components. Pyridine and 2,6dimethylpyridine were used to titrate Lewis and Brønsted acidic sites, respectively. A linear increase of the number of strong Lewis acid sites with alumina content was observed, whereas the number of Brønsted acid sites reached a maximum for 30% TiO_2-70 % AI_2O_3 compared with that expected from the composition and the activity of pure oxides. Comparison between probe-molecule adsorption and test reaction, points out that both types of site are involved in propan-2-ol dehydration. A transformation of Lewis acid sites into Brønsted sites is proposed when propan-2-ol is chemisorbed on Lewis acid sites.

Mixed oxides are increasingly used in catalysis because they can present properties different from those of the component single-metal oxides. A typical case is that of silica-alumina.¹ In a recent paper, we examined the acidic and basic properties of ZrO₂-Al₂O₃ and ZrO₂-TiO₂ mixed oxides using adsorption of specific probe molecules followed by FTIR, and activity towards two test-reactions: propan-2-ol dehydration and carbon oxysulfide hydrolysis.² This work concerns TiO₂-Al₂O₃ mixed oxides. Our aim was not only to determine their acidic and basic properties but also to correlate probe adsorption and catalytic activities in order to specify the nature of the active sites. For this we chose test reactions with well characterized basicity and acidity. The mechanism of COS hydrolysis is now well established.³ In particular, the active sites are basic hydroxy groups, also involved in CO₂ adsorption in the form of hydrogen carbonate species, explaining the good correlation between catalyst activity and the $\delta(OH)$ band intensity of HOCO₂⁻ species.⁴ Conversely, propan-2-ol dehydration is largely used as an acidity test, but the nature of its active sites is more complex. Indeed, catalytic activity of ZrO₂-TiO₂ mixed oxides was found to follow Brønsted acid sites detected by 2,6-dimethylpyridine (lutidine), whereas for ZrO_2 -Al₂O₃ activity seemed to be determined by the strong Al^{3+} Lewis acidity, evidenced by pyridine.² Owing to the presence of strong Lewis acidity on pure Al_2O_3 and some Brønsted acidity on pure TiO₂, Al_2O_3 -TiO₂ mixed oxides are expected to present both types of active site and are therefore interesting model catalysts.

It has recently been reported that use in hydrotreatment reactions of $TiO_2-Al_2O_3$ as supports for molybdenum sulfided catalysts, increases the specific rate for hydrodesulfurization of thiophene.⁵ Moreover, McVicker and Ziemiak showed that these mixed oxides showed, like TiO_2 , strong metal-support interactions (SMSI) with metals such as Pt or Ir.⁶ Several authors⁷⁻⁹ have characterized the properties of $TiO_2-Al_2O_3$ mixed oxides synthesized using different methods. Rodenas *et al.*⁷ found a maximum acidity for 90% Al_2O_3 when co-precipitating titanium and aluminium sulfates with ammonia. They did not detect as many acid sites when using urea as precipitating agent. Mostafa *et al.*,⁸ who hydrolysed TiCl₄ and AlCl₃ with NH₄OH, reported that both total number and strength of acid sites increased in the mixed oxides as detected by amine titration using Hammett indicators. Nakabayashi⁹ studying $TiO_2-Al_2O_3$ mixed oxides prepared from hydrolysis of isopropoxides only observed an increase of the acidity strength, whereas the number of acidic sites was unaffected. Therefore, it appears that the properties of the $TiO_2-Al_2O_3$ mixed oxides strongly depend on the preparation method used. Cohydrolysis of isopropylates has been chosen since it allows one to obtain chemically pure and homogeneous mixed oxides.^{10,11}

Experimental

Catalyst Preparation

Mixed oxides were prepared by cohydrolysis of titanium(IV) isopropylate (Aldrich; liquid, 98% purity) and aluminium(III) isopropylate (Fluka; solid, purity > 98%) dissolved in propan-2-ol (0.5 mmol of Al isopropylate per ml of propan-2ol). Titanium isopropylate and propan-2-ol were dried on zeolite. The total volume of the two liquids was 300 ml. Mixed solutions were vigorously stirred together for 1 h at room temperature and care was taken to avoid contact with air moisture which might cause uncontrolled hydrolysis. Cohydrolysis was carried out dropwise, pouring isopropylate solution into an excess of distilled water (0.3 mmol of isopropylate per ml of propan-2-ol) at room temperature. After a 1 h ageing period, the precipitate was filtered and washed five times with hot distilled water. The products were dried for 18 h at 383 K, moistened with 1 ml of distilled water per gram of dried hydroxide, and dried again for 24 h at 383 K. Calcination under air took place in a muffle furnace in two steps. Hydroxides were decomposed for 2 h at 573 K and then heated for 2 h at 773 K (ramp 0.66 K min⁻¹). The same procedure was followed for single-metal oxide preparation. Compositions determined after oxide dissolution by inductive coupling plasma, are summarized in Table 1.

Texture and Structure Characterization

Nitrogen physisorption isotherms were recorded at 77 K on a Micromeritics ASAP 2000 sysem. Before measurements, samples were pretreated *in situ* at 523 K for 2 h under vacuum. Specific surface areas were determined using the BET equation.¹² Total pore volumes were obtained by the

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oxide	Al ₂ O ₃ (mol%)	S _{вЕТ} /m ² g ⁻¹	pore volume /cm ³ g ⁻¹	average pore diameter /nm
TiO,	0	102	0.20	7.8
30% TiO ₂ -70% Al ₂ O ₃	70.4	267	0.48	13.0
55% TiO45% Al_O	44.3	317	0.48	4.0
70% TiO,-30% A1,O	30.4	265	0.38	3.0
Al ₂ O ₃	100	262	0.39	4.8

Table 1 Characteristics of studied oxides

amount of physisorbed N₂ for $P/P_0 = 0.95$. Pore size distributions were obtained by means of the BJH method¹³ using the Harkins-Jura equation as *t*-isotherm.¹⁴

The structures were characterised by X-ray diffraction operating at 40 kV with a filament current of 20 mA using a Ni filter for Cu-K α radiation.

Infrared Spectroscopy

The samples were pressed into self-supporting discs (20 mg, 16 mm in diameter) and activated in situ in the IR cell. They were pretreated with O₂ for 1 h at 673 K and then evacuated for 15 min at the same temperature. After freezing purification (77 K), probe molecules of CO₂ (10 Torr at equilibrium), 2,6-dimethylpyridine (1 Torr at equilibrium followed by evacuation at 423 K) or pyridine (1 Torr at equilibrium followed by evacuation at 423 K) were introduced. Spectra were recorded on a 710 FTIR Nicolet spectrometer with a 4 cm⁻¹ resolution. Every reported spectrum was normalised to 1 m² of catalyst surface area. Spectral decomposition was performed in order to distinguish pyridine adsorption on Al³⁺ centres from that on Ti⁴⁺ and 2.6dimethylpyridine adsorption on TiO₂ Brønsted acid sites from its total adsorption. Decomposition was carried out by subtracting the spectrum of one of the pure oxide components from the mixed-oxide spectrum. The intensity of the pure oxide spectrum was adjusted in order to cancel its contribution to the mixed-oxide spectrum. For pyridine adsorption, the area of the alumina contribution was integrated after adjustment. For 2,6-dimethylpyridine adsorption, the area of the bands at 1640 and 1626 cm⁻¹ observed on mixed oxides after subtraction of the contribution of pure titania from that of the mixed oxide spectrum was integrated.

Catalytic Tests

Catalytic tests were carried out in differential micro-reactors under helium flux. Catalysts were ground and sieved. The fractions between 0.4 and 1 mm were used. Activation and reaction conditions are summarised in Table 2.

Results

Texture and Structure Characterization

 N_2 adsorption and desorption isotherms on Al_2O_3 , TiO₂ and TiO₂-Al₂O₃ mixed oxides are of type IV (IUPAC classification¹⁵), showing H2 type hysteresis. It is concluded that the solids are mesoporous, presumably consisting of particle aggregates with non-regular pore shapes. Specific surface areas, pore volumes and average pore diameters are reported in Table 1. Compared to single oxides, TiO₂-Al₂O₃ mixed oxides present an increase of surface area as well as pore volume (a maximum is obtained for the 55% TiO₂-45% Al₂O₃).

The X-ray diffraction spectrum of TiO_2 presents rather broad peaks assigned to anatase. No diffraction peaks were observed either for mixed oxides or for pure alumina, indicating that none of them were crystalline.

Infrared Spectroscopy

CO₂ Adsorption

CO₂ adsorption followed either by microcalorimetry¹⁶ or by infrared spectroscopy¹⁷ has been widely used to characterize catalyst basicity. According to the nature of the adsorption site, OH^- or coordinatively unsaturated O^{2-} ions, CO_2 gives rise to hydrogencarbonate species, characterized on TiO₂ (ref. 18) by bands at 1590, 1435 and 1220 cm⁻¹, or on Al_2O_3 (ref. 19) by bands at 1640, 1440 and 1230 cm^{-1} , or to carbonate species (1530 and 1320 cm⁻¹ on TiO₂). In Fig. 1, the spectra of species formed by CO₂ adsorbed on the different oxides are presented for the range 1800-1100 cm⁻¹. No new species are detected on mixed oxides. For pure alumina and pure anatase the intensities of the $\delta(OH)$ band near 1225 cm⁻¹ characteristic of hydrogencarbonate species are quite similar. Conversely, the band intensity is quite low on spectra of mixed oxides showing that TiO₂ introduction in Al₂O₃ tends to decrease its basicity. The number of OH groups sufficiently basic to interact with CO_2 is minimal for 30% Al_2O_3 .

Pyridine Adsorption

Pyridine is a probe molecule capable of coordinating on Lewis acid centres or of accepting Brønsted acid protons.

	propan-2-ol dehydratio (acidity test)	COS hydrolysis (basicity test)		
reaction activation weight(w)/g molar stream composition total flow/ml min ⁻¹ reaction temperature/K	CH_3 →	$-CH_2 + H_2O$	$COS + H_2O \rightarrow CO_2 + 2 h at 523 K under He0.0252.3% H_2O + 96.7% He100373$	H_2S e + 1% COS
conversion per m ²	$\frac{ \text{propene} }{ \text{propene} \neq \text{unconverted propan-2-ol} } \frac{100}{S_{*p} w} \frac{ \text{CO}_2 }{ \text{CO}_2 + \text{unconverted CC} }$		$\frac{100}{ S_pw }$	



Fig. 1 IR spectra of CO₂ adsorbed on TiO₂-Al₂O₃: (a) TiO₂; (b) 70% TiO₂-30% Al₂O₃; (c) 55% TiO₂-45% Al₂O₃; (d) 30% TiO₂-70% Al₂O₃; (e) Al₂O₃

Coordination gives rise to bands near $1620-1600 \text{ cm}^{-1} (v_{8a})$ and $1450 \text{ cm}^{-1} (v_{19b})$ while protonation gives rise to characteristic bands at 1640 and 1545 cm^{-1 2,20,21} Generally, the v_{8a} wavenumber allows one to determine the Lewis acid site strength, whereas the v_{19b} band intensity characterizes their number.

Spectra of adsorbed pyridine species on TiO₂, Al₂O₃ and TiO₂-Al₂O₃ mixed oxides are presented in Fig. 2. No bands characteristic of pyridine protonation are detected. Pyridine adsorption on pure anatase reveals the presence of weak Lewis acid sites as characterized by the v_{Ba} band at 1610 cm⁻¹.² On pure alumina, two v_{Ba} bands at 1622 and 1617 cm⁻¹ are observed, indicating a relatively strong Lewis acidity. Morterra *et al.*²⁰ assigned these bands to adsorption on a pair of cus Al³⁺ in tetrahedral and octahedral positions, respectively. Their relative intensity implies a quasiamorphous sample.²¹

On mixed oxides, the presence of the coordinatively unsaturated Al^{3+} and Ti^{4+} sites are characterized by the corresponding v_{8a} band. The total number of Lewis acid sites can be measured from the intensity of the v_{19b} band near 1450 cm⁻¹. As shown in Fig. 3, this does not vary signifi-



Fig. 3 Variation with the catalyst's alumina content, of the area of bands characteristic of: (Δ) the total number of Lewis acid sites (pyridine, 1450 cm⁻¹); (\bigcirc) the strongest Lewis acid sites (pyridine, 1622 + 1617 cm⁻¹); (+) the Brønsted acid sites (lutidine, 1640 + 1626 cm⁻¹)

cantly with alumina content, the substantial decrease as soon as alumina is introduced in TiO₂ excepted. From the spectral decomposition of bands in the 1625–1605 cm⁻¹ region on mixed oxides, it appears that the intensity of the 1622–1617 cm⁻¹ bands follows a linear variation with the Al₂O₃ percentage (Fig. 3).

Lutidine Adsorption

2,6-Dimethylpyridine (lutidine) is a probe molecule specific to Brønsted acidity.²²⁻²⁴ For example, in our previous study,² lutidine was used to titrate Brønsted acid sites of TiO₂-ZrO₂ mixed oxides when pyridine failed to reveal their presence. This ability to detect Brønsted acid sites relies on its higher basicity (p K_{a} is 6.7 for lutidine and 5.2 for pyridine) whereas the steric hindrance induced by methyl groups partially pre-vents the nitrogen atom coordination.²⁴ Spectra of lutidine species adsorbed on the different oxides are presented in Fig. 4. On pure TiO₂ and on every mixed oxide, lutidine protonation occurs, as shown by the appearance of bands at 1640 and 1626 cm^{-1} . It is possible to evaluate the intensity of these bands by subtracting that observed at 1615 cm⁻¹ characteristic of lutidine coordination on Al₂O₃ or TiO₂. Fig. 3 shows the variation of the intensity of these bands with composition. The number of Brønsted acid sites decreases from TiO_2 to Al_2O_3 but not as fast as expected, since twice their expected amount is detected on 30% TiO₂-70% Al₂O₃.



Fig. 2 IR spectra of pyridine desorbed at 423 K on $TiO_2-Al_2O_3$: (a) TiO_2 ; (b) 70% TiO_2-30 % Al_2O_3 ; (c) 55% TiO_2-45 % Al_2O_3 ; (d) 30% TiO_2-70 % Al_2O_3 ; (e) Al_2O_3



Fig. 4 IR spectra of lutidine desorbed at 423 K on $TiO_2-Al_2O_3$: (a) TiO_2 ; (b) 70% $TiO_2-30\%$ Al_2O_3 ; (c) 55% $TiO_2-45\%$ Al_2O_3 ; (d) 30% $TiO_2-70\%$ Al_2O_3 ; (e) Al_2O_3



Fig. 5 Variation of the COS hydrolysis conversion at 373 K with alumina content of the catalyst

Some extra Brønsted acid sites are then generated or induced in the mixed oxides.

Catalytic Activities

COS Hydrolysis

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As presented in our previous papers,^{3,4} COS hydrolysis can be used as a test reaction specific to OH basicity. As shown in Fig. 5, the conversion drastically decreases as soon as alumina is introducted in TiO_2 ; then it increases linearly with the amount of alumina. As far as hydroxy groups are concerned, mixing causes a loss of basicity.

Propan-2-ol Dehydration

Dehydration of propan-2-ol is widely used as a test reaction characterizing catalyst acidity, and a number of correlations have been published between catalyst activity towards dehydration and acidity measured titrimetrically,^{25–27} by TPD of ammonia^{28,29} or pyridine,³⁰ or adsorption of bases followed by thermogravimetry,^{31,32} FTIR² or microcalorimetry.³³ Some authors indicate that dehydrogenation of propan-2-ol to acetone can also reveal basicity.^{34–41} However, the validity of this assumption has not yet been totally proven^{35–38} and is indeed seriously questioned,^{39–42} since acetone formation can occur by a redox mechanism, particularly at low temperature.

Only dehydration products (propene and traces of diisopropyl ether) are formed on $TiO_2-Al_2O_3$ mixed oxides in the conditions used. Variation of their intrinsic activity with



Fig. 6 Variation of the propan-2-ol dehydration conversion with alumina content of the catalyst for various reaction temperatures; 473 K (\triangle); 483 K (\bigcirc); 493 K (+)

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composition is presented in Fig. 6 for different reaction temperatures. Alumina is about five times more active towards propan-2-ol dehydration than is anatase. The mixed oxide activity grows when the alumina content increases and the activity of 30% TiO₂-70% Al₂O₃ is slightly higher than that of pure alumina.

Discussion

The $TiO_2-Al_2O_3$ mixed oxides prepared from isopropylate hydrolysis are amorphous after calcination at 773 K. They exhibit a high surface area similar to that of pure alumina whatever the mixed oxide composition. Therefore, $TiO_2-Al_2O_3$ mixed oxides present textural and structural properties different from those of a mechanical mixture of their parent oxides. This is an indication of the formation of a 'real' mixed oxide; even if it is not a proof, we use this notation.

As in the case of Al_2O_3 -ZrO₂ and TiO₂-ZrO₂ catalysts, TiO₂-Al₂O₃ basicity measured from CO₂ adsorption followed by IR spectroscopy is also lower than expected. This is confirmed by the weak activity in COS hydrolysis. It is worth noticing that data relative to TiO₂-Al₂O₃ catalysts confirm the previously reported correlation between COS activity and the intensity of the δ (OH) of hydrogencarbonate species formed from CO₂ adsorption, since the data points lie around the previously reported relation (Fig. 7).

As for acidity, pyridine adsorption provides evidence for Lewis acid sites, the strength of these being that observed for the two oxide components: Al_2O_3 , (1622, 1617 cm⁻¹) and TiO₂ (1610 cm⁻¹). Pyridine is not able to detect Brønsted acid sites, as already stated in the literature.^{5,8} However, 2,6lutidine adsorption reveals the presence of such sites on TiO₂ and on mixed oxides, whatever their composition. This demonstrates the usefulness of this probe, more especially as these sites were found to be responsible for TiO₂-ZrO₂ mixed oxide activity towards isopropyl alcohol dehydration.²

The variation of the catalytic activity towards propan-2-ol dehydration versus catalyst composition (Fig. 6) shows a maximum of activity for a composition close to 30% TiO₂-70% Al₂O₃. Neither a maximum of the number of total or strong Lewis acid sites nor a maximum of the number of Brønsted acid sites corresponds to such a composition (Fig. 3). Nevertheless, the activity tends to increase with alumina content, which indicates that Al³⁺ strong Lewis acid sites are responsible for some of the activity as in the case of Al₂O₃-ZrO₂ catalysts. Moreover, the catalyst which presents the maximum activity is that for which the number of Brønsted acid sites is a maximum with respect to that expected. The simplest way to account for both sites activity contribution is to add their specific activity as given by that



Fig. 7 Relation between COS hydrolysis activity and the number of hydrogencarbonate species formed from adsorbed CO₂ [intensity of the δ (OH) band at *ca.* 1225 cm⁻¹] for TiO₂-Al₂O₃ (\triangle), TiO₂-ZrO₂ (\bigcirc) and ZrO₂-Al₂O₃ (+) catalysts

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of the component oxides taking into account the number of each type of active site determined from the intensity of the characteristic bands:

$$C_{\text{calc}} = \frac{I_{\text{Brénsted}}}{I_{\text{Brénsted TiO}_2}} \times C_{\text{TiO}_2} + \frac{I_{\text{strong Lewis}}}{I_{\text{strong Lewis}}} \times C_{\text{Al}_2\text{O}_3} \qquad (1)$$

in which: C_x is the intrinsic conversion measured on TiO₂ (C_{TiO_2}) , on Al₂O₃ $(C_{\text{Al}_2\text{O}_3})$ or calculated for TiO₂-Al₂O₃; I_x corresponds to the intrinsic intensities of IR bands characteristic of Brønsted acidity revealed by 2,6-dimethylpyridine on mixed oxides $(I_{\text{Brønsted}})$ or on TiO₂ $(I_{\text{Brønsted TiO}_2})$ and strong Lewis acidity revealed by pyridine on mixed oxides $(I_{\text{strong Lewis}})$ or Al₂O₃ $(I_{\text{strong Lewis}})$.

Since $C_{Al_2O_3}$ is much higher than C_{TiO_2} (Fig. 6), the mixedoxides activity is mainly related to the number of strong Lewis acid sites they present. Nevertheless, the excellent agreement between calculated conversion and measured conversion (Fig. 8) confirms the participation of both sites. The maximum activity for 30% TiO₂-70% Al₂O₃ can be explained by a synergic effect developing a maximum of Brønsted acid sites. The relation is obviously applicable to $ZrO_2-Al_2O_3$ and ZrO_2-TiO_2 mixed oxides as a result of ZrO_2 inactivity this oxide presenting neither Brønsted acidity nor strong Lewis acidity.²

Eqn. (1) involves two different types of active site and so possibly two types of mechanism for a given catalyst. Alcohol dehydration via protonation of its hydroxy group is a widely accepted pathway.43 However, a concerted mechanism involving an O^{2-} basic site and a Lewis acid centre has been proposed to explain, for instance, propan-2-ol dehydration on ceria.44 In our opinion, transformation of strong Lewis acid sites into Brønsted sites by alcohol (reactant) or water (product) adsorption should also be considered. Alcohol chemisorption on metal oxides gives rise to alkoxy species via a dissociative adsorption involving a Lewis acid-base site pair, or to coordinatively adsorbed species involving only Lewis acid sites. In this latter case, it is well known that coordination increases the strength of the alcohol proton acidity, explaining the formation of 1.2 complex.⁴⁵ The greater the strength of Lewis acidity, the greater should be the acidity of the proton, explaining why only the strongest Lewis acid sites would be active. In the case of a dissociative adsorption, it has been shown that acidic alcohols can promote the conversion of an acidic test reaction such as but-1-ene isomerization on alumina.⁴⁶ It was explained by inductive effects from the alkoxy group to the neighbouring hydrogen. Similar results could also arise from water adsorption, although it has been



Fig. 8 Comparison between measured propan-2-ol dehydration conversion and that calculated from eqn. (1)

specified that water adsorption on $TiO_2-Al_2O_3$ does not convert Lewis acid sites into Brønsted ones.⁷ However, this result was obtained using pyridine as a probe molecule. In our opinion, and as shown by the present study, 2,6-lutidine is more specific to Brønsted acid sites and would be a better probe to study such site conversion.

Conclusion

This study shows that relations already obtained on $ZrO_2-Al_2O_3$ and ZrO_2-TiO_2 catalysts, between probe molecule adsorption and activity towards carbon oxysulfide hydrolysis and propan-2-ol dehydration are applicable to $TiO_2-Al_2O_3$ mixed oxides. As for basicity, the good agreement between COS hydrolysis and CO_2 adsorption points out the low hydroxy basicity of $TiO_2-Al_2O_3$ mixed oxides. For acidity as expected on such catalysts, both Brønsted acid sites and strong Lewis acid sites are present. Correlation between 2,6-dimethylpyridine and pyridine adsorption and activity in propan-2-ol dehydration reveals that both sites are involved in the reaction. This points out the usefulness of 2,6-dimethylpyridine as a probe when Brønsted acidity is supposed to play a catalytic role.

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Paper 4/07351G; Received 1st December, 1994