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A FTIR spectroscopy study of isopropanol reactivity on alkali-metal-doped $\text{MoO}_3/\text{TiO}_2$ catalysts

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Abstract

The transformation of isopropanol on $\text{MoO}_3/\text{TiO}_2$ catalysts doped with alkali-metal cations has been studied by the pulse technique. The FTIR studies have provided evidence of the dissociative adsorption of isopropanol and the formation of isopropoxide species which decompose at higher temperatures to acetone. Catalytic measurements have shown that the addition of alkali-metal cations leads to a drastic decrease in the yield of propene, owing to the elimination of Brønsted centres originally existing on the catalyst surface, whereas the rate of dehydrogenation to acetone is affected only slightly. The extent of the changes observed depends on the nature of the doping alkali-metal cation.

Keywords: Alkali doping; FTIR spectroscopy; Isopropanol oxidation; $\text{MoO}_3/\text{TiO}_2$

1. Introduction

The transformation of isopropanol on oxides provides information about the nature and properties of surface centres. The alcohol may decompose through two parallel routes: dehydration to propene (and, at high partial pressure, to diisopropyl ether) and dehydrogenation to acetone. Several mechanisms have been proposed in the literature to explain these reactions [1–6]. It has also been postulated that dehydration proceeds on

acidic centres (Brønsted and Lewis sites), and hence the amount of propene may be a measure of the acidity of oxides, whereas redox, basic centres are involved in the dehydrogenation path [7–9]. The FTIR technique has been applied in several cases to determine the mechanism of isopropanol adsorption and transformation on oxide catalysts [10–12]; alkoxide species have been the main intermediate surface complexes detected [13].

In the present study, the FTIR technique has been applied to follow the interaction of isopropanol with $\text{MoO}_3/\text{TiO}_2$ catalysts doped with alkali-metal cations. The FTIR study has been

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supplemented with measurements of isopropanol decomposition performed by the pulse technique.

The $\text{MoO}_3/\text{TiO}_2$ system is currently used in several oxidation reactions, such as the oxidation of methanol [14–16], 1-butene and *o*-xylene [17], propene [18] and ethene [19] and the oxidative dehydrogenation of propane [20]. It has been shown that the addition of alkali cations to $\text{MoO}_3/\text{TiO}_2$ catalysts increases the tendency to form partial oxidation products while decreasing the trend towards formation of undesired carbon oxides [19,20].

In view of the correlation between the performance of oxide catalysts in selective oxidation reactions and their acid/base properties [8], it seems of interest to characterize the properties of surface centres, and their modification upon alkali-metal doping, by the adsorption of a probe molecule, such as isopropanol.

2. Experimental

All samples were prepared by impregnation of the support (TiO_2 from Degussa, $S_{\text{BET}} \approx 50 \text{ m}^2 \text{ g}^{-1}$) with aqueous solutions of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (from Panreac, p.a.) The amount of molybdenum (5.8% Mo) corresponds to that needed to yield a geometrical monolayer of molybdena [21] on the support (assuming the initial value for the specific surface area of titania), i.e., the amount required to cover completely the exposed surface of the support. The alkali cation (Alk, 1 wt%) had been previously incorporated by impregnation of the TiO_2 with an aqueous solution of the corresponding nitrate (from Fluka), using a Heidolph VV-60 rotary vacuum evaporator in order to minimize formation of carbonate species by reaction with atmospheric CO_2 . Calcination of these solids was carried out in flowing oxygen (from Sociedad Española de Oxígeno, Spain) for 3 h at 773 K (a temperature high enough to decompose heptamolybdate to molybdena). Chemical analyses for Mo and Alk were carried out by atomic absorption in an ELL-240 apparatus. Samples are denoted as MIX1, where X is Li, Na, K or Rb. Details about the phase composition of the cata-

lysts and the preparation have been given elsewhere [22–24] and the results are summarized in Table 1. Surface acidity, as determined by pyridine adsorption [23], shows the presence of surface Lewis and Brønsted acid sites in sample M1. However, for the alkali-containing samples, surface Brønsted acidity decreases as the polarizing ability of the alkali-metal cation increases, and is wholly cancelled for the Li-containing sample.

Isopropanol (IP, from Fluka) adsorption was monitored by FTIR spectroscopy with a PC-16 Perkin-Elmer spectrometer connected to an Atao 386-SX computer, using special cells with CaF_2 windows. Nominal resolution was 2 cm^{-1} , and 100 runs were averaged to improve the signal-to-noise ratio. Samples were submitted to a conditioning treatment in situ consisting in outgassing at 670 K for 2 h (residual pressure $\approx 10^{-3} \text{ N m}^{-2}$). After equilibration with a low pressure of isopropanol, the spectrum was recorded after outgassing at temperatures ranging from ambient to 473 K. In all cases, the spectrum of the solid was subtracted using the facilities provided by the computer software.

The decomposition of isopropanol to propene and acetone was studied at 443 K by the pulse method, using dried helium as carrier gas. 0.1 g of sample and 2 ml of isopropanol were used, the total flow rate of He being 30 ml min^{-1} . The samples were heated in situ before the experiments for 2 h in flowing He at 523 K. The isopropanol pulses were injected successively until constant values of conversion and yield of products were attained. The conversion and the yield of products decreased slightly with the number of pulses up to 3–5 pulses and then remained con-

Table 1
Catalytic activity data for isopropanol decomposition (443 K)

Sample	C_3H_6^a	$\text{C}_3\text{H}_6\text{O}^a$
M1	8.10	0.31
M1Li1	0.01	0.03
M1Na1	0.10	0.47
M1K1	0.03	0.34
M1Rb1	0.37	0.57
TiO_2	0.16	0.03

^a 10^6 mol m^{-2}

stant. However, the relative amounts of propene and acetone did not change markedly with the number of pulses. The results presented later in the text pertain to the stationary state: the values of number of moles of the products produced per pulse, and referred to the specific surface area, are the average of values obtained in three successive pulses after the stationary state was attained. Analysis of the products and unreacted isopropanol was performed by GC with FID; a 2 m × 4 mm column filled with 3% Carbowax 20 M + 1.5% silicone oil DC 550 + 1% succinate on Chromosorb GAW 60/80 was used, with a column temperature of 333 K. Small amounts of di-isopropyl ether were also observed, the selectivity towards formation of this product being lower than 5%. Qualitatively, the amount of di-isopropyl ether followed the changes in propene formation, indicating that the ether was formed on acidic centres.

3. Results

3.1. Fourier-transform infrared spectroscopy

3.1.1. The original support, TiO₂

The spectrum recorded in the range 4000–3000 cm⁻¹ after the adsorption of IP at room temperature (r.t.) on this sample is shown in Fig. 1. Bands due to hydroxyl groups originally existing on the titania surface have disappeared, and two new bands were recorded at 3441 and 3280 cm⁻¹. Other bands (not shown in the figure) were recorded at 2970, 2934 and 2869 cm⁻¹ (νC–H) which, together with the bands recorded in the range 1800–1100 cm⁻¹ (Fig. 2), at 1467 cm⁻¹ (δ_{as} CH₃), 1384 and 1367 cm⁻¹ (δ_s CH₃), 1340 cm⁻¹ (γ_{out-of-plane} CH), and 1166 and 1133 cm⁻¹ (νC–C and νC–O) can be ascribed [10] to isopropoxide species, as they are coincident with bands due to titanium isopropoxide [25]. These results indicate a dissociative adsorption of IP, similar to that previously found for methanol adsorption, through condensation with hydroxyl groups of the titania surface. Formation of molecular water, which remains physisorbed on the titania surface, according to the reaction

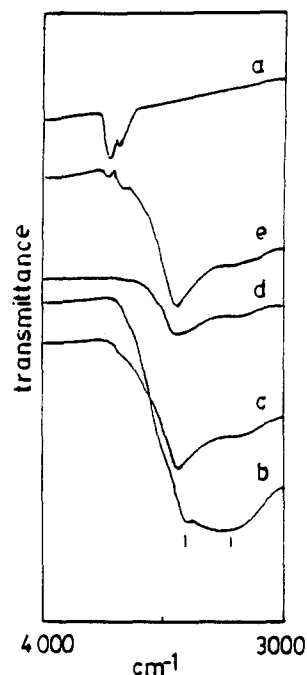
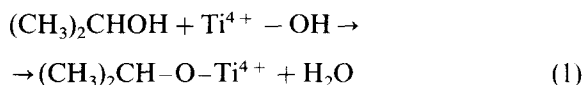


Fig. 1. (a) FTIR spectra of TiO₂ outgassed at 670 K for 2 h and after: (b) adsorption of isopropanol on TiO₂ at room temperature, and outgassing at (c) room temperature, (d) 373 K, and (e) 473 K.



is evidenced by the band at 1630 cm⁻¹ (δH₂O).

In addition, another band recorded at 1294 cm⁻¹ (δO–H), together with the band above mentioned at 3441 cm⁻¹ (νO–H), have been ascribed [10] to non-dissociated IP coordinated to Lewis acid sites (the δO–H band is recorded at 1252 cm⁻¹ in the IP monomer). The other band recorded at high wavenumbers (3280 cm⁻¹) disappeared after outgassing at room temperature, and therefore should correspond to molecular IP physisorbed through hydrogen bonding to surface basic sites [10].

As already observed upon the adsorption of IP on rutile [26], no band due to oxidized species was recorded on increasing the temperature and only a slight decrease in the intensities of the bands due to isopropoxide species was observed; the bands were completely removed after outgassing at 473 K. Simultaneously, surface hydroxyl groups were

restored (Fig. 1), thus suggesting that surface-bonded isopropoxide species undergo dehydration to propene (see catalytic activity results, Table 1).

It can thus be concluded that the adsorption of isopropanol on TiO_2 takes place through two different routes: (i) dissociative adsorption on surface acid–base sites, giving rise to monodentate alkoxide groups, and (ii) undissociative adsorption, giving rise to (a) isopropanol coordinated to surface Lewis acid sites, and (b) isopropanol hydrogen-bonded to surface basic sites. Non-dissociative adsorption takes place on (tetra-coordinated) Ti_V^{4+} sites in (110) and (111) faces of anatase, and dissociative adsorption takes place on (pentacoordinated) Ti_V^{4+} sites in (001) faces [27].

3.1.2. Undoped sample (M1)

The spectrum recorded after adsorption of IP on this sample was very similar to that obtained

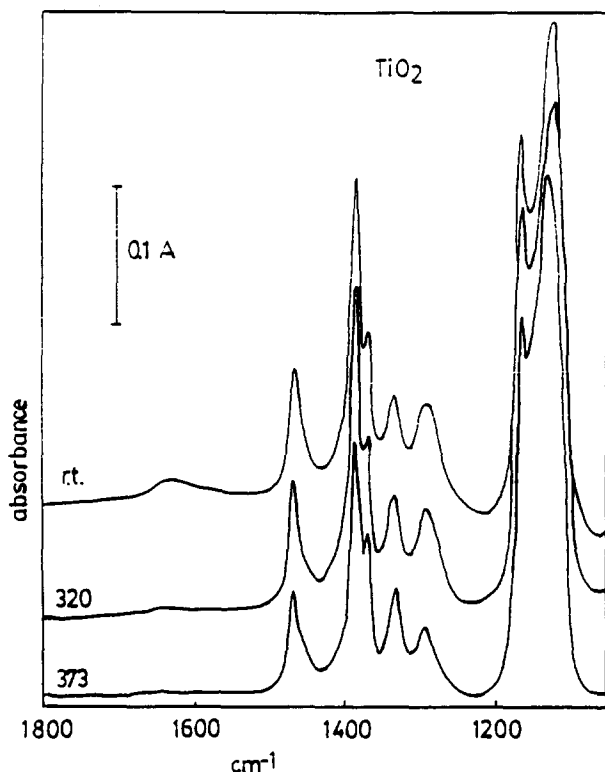


Fig. 2. FTIR spectra recorded after adsorption of isopropanol on TiO_2 at room temperature and outgassing at the temperatures given (in K; r.t. indicates room temperature).

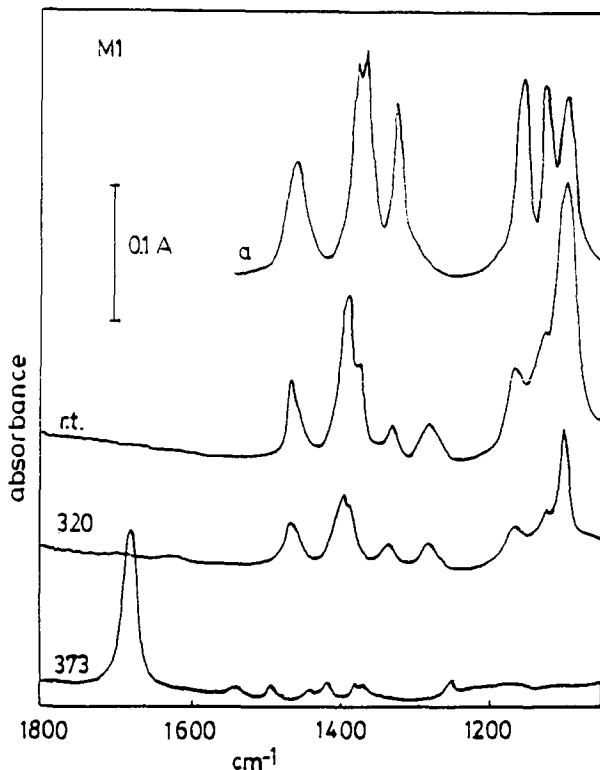


Fig. 3. FTIR spectra recorded after adsorption of isopropanol on sample M1 at room temperature and outgassing at the temperatures given (in K).

after adsorption on pure titania. Bands due to $\nu\text{C-H}$ modes were recorded at 2978, 2936, 2917 and 2884 cm^{-1} , and at lower wavenumbers (Fig. 3) bands were recorded at 1464 and 1458 (shoulder) cm^{-1} ($\delta_{\text{as}} \text{CH}_3$), 1388 and 1375 (shoulder) cm^{-1} ($\delta_{\text{s}} \text{CH}_3$), 1329 cm^{-1} ($\gamma_{\text{out-of-plane}} \text{C-H}$), 1164, 1129 and 1100 cm^{-1} ($\nu\text{C-C}$, $\nu\text{C-O}$ and ρCH_3), indicating the formation of isopropoxide species produced by dissociative adsorption of isopropanol. Similar bands were also observed after adsorption of isopropyl ether (Fig. 3(a)). A band at 1620 cm^{-1} that disappeared after desorption at room temperature is due to δ_{HOH} of molecular water, formed through condensation [reaction (1)] with surface hydroxyl groups. Non-dissociative adsorption on surface Lewis acid sites also takes place, as indicated by the $\delta\text{O-H}$ band recorded at 1282 cm^{-1} .

When the sample was outgassed at 373 K, no band due to coordinated isopropanol or to iso-

propoxide species was recorded. However, bands in different positions developed. The most intense band at 1676 cm^{-1} , together with weak bands at 1413 , 1378 and 1250 cm^{-1} , which were previously observed upon adsorption of acetone on this sample [24], could be ascribed to acetone chemisorbed on surface Lewis acid sites (coordinatively unsaturated cations). Weaker bands at 1540 and 1449 cm^{-1} have been also recorded after adsorption of acetic acid on this sample [19,28], and should be ascribed to the modes $\nu_{\text{as}}(\text{COO}^-)$ and $\nu_{\text{s}}(\text{COO}^-)$, respectively, of surface acetate species. When the sample was outgassed at 473 K all these bands disappeared.

So, isopropanol is adsorbed on sample M1 in a way similar to that on unloaded titania, through parallel dissociative and non-dissociative pathways. A fraction of the surface isopropoxide species is oxidized to acetone at 373 K , and the remaining isopropoxide species are dehydrated to form propene, which is desorbed from the catalyst surface. Only a minor fraction of isopropanol is oxidized to acetate species, which are finally desorbed as acetic acid and/or CO_2 .

3.1.3. Sample M1Li1

The spectrum recorded after adsorption of IP on this lithium-containing sample, Fig. 4, showed bands at 2970 cm^{-1} (strong), 2934 and 2883 cm^{-1} ($\nu\text{C-H}$), 1465 , 1404 (shoulder), 1385 and 1345 cm^{-1} ($\delta_{\text{as}}\text{CH}_3$, $\delta_{\text{s}}\text{CH}_3$ and $\gamma_{\text{out-of-plane}}\text{C-H}$) and 1164 , 1132 and 1100 cm^{-1} ($\nu\text{C-C}$, $\nu\text{C-O}$ and ρCH_3). All they correspond to isopropoxide species formed upon dissociative adsorption of isopropanol. The band at 1282 cm^{-1} was not recorded after adsorption of di-isopropyl ether, and is due to molecularly adsorbed isopropanol coordinated to surface Lewis acid sites.

Upon outgassing at increasing temperatures, the intensities of all bands decreased, Fig. 4, and the bands were completely removed when the sample was outgassed at 473 K . As previously observed for TiO_2 , no oxidation was observed at higher temperatures.

3.1.4. Samples M1Na1, M1K1 and M1Rb1

The behaviour shown by these samples was very similar. Adsorption at room temperature

gave rise to spectra, Fig. 5, with bands due to isopropoxide (dissociative adsorption) and chemisorbed isopropanol (undissociative adsorption).

On outgassing at increasing temperatures, two weak bands developed at 1713 and 1680 cm^{-1} . Similar bands were recorded after adsorption of acetone on these samples, and have been ascribed to the $\nu\text{C=O}$ mode of acetone chemisorbed through the oxygen atom to more or less strong surface acid Lewis sites, corresponding to Mo^{6+} or Alk^+ sites ($\nu\text{C=O}$ of gaseous acetone is recorded at 1734 cm^{-1}). The band at higher wavenumber, due to adsorption on the weaker acid Lewis sites (Alk^+), was removed after outgassing at 423 K , but the band at 1680 cm^{-1} remained; the position of this latter band coincides with that recorded after adsorption on the alkali-free sample up to 473 K . As previously described for other samples, no oxidation to carboxylate species has been observed.

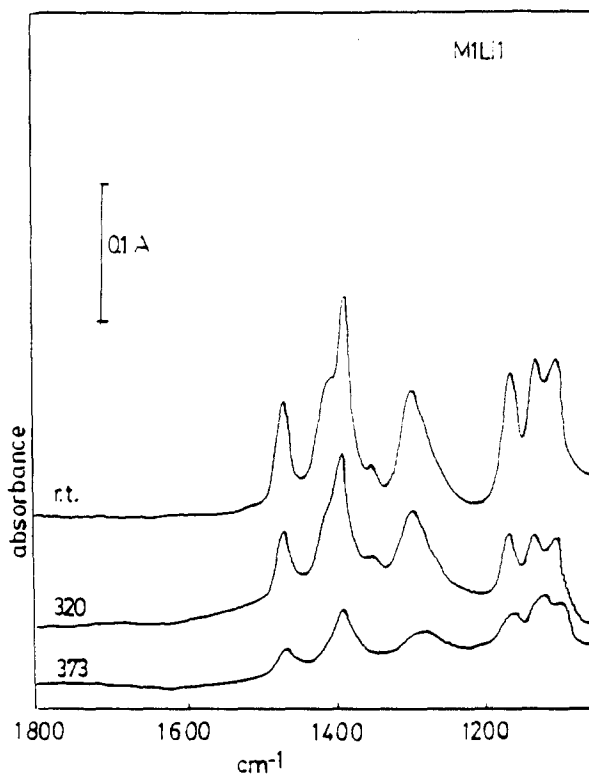


Fig. 4. FTIR spectra recorded after adsorption of isopropanol on sample M1Li1 at room temperature and outgassing at the temperatures given (in K).

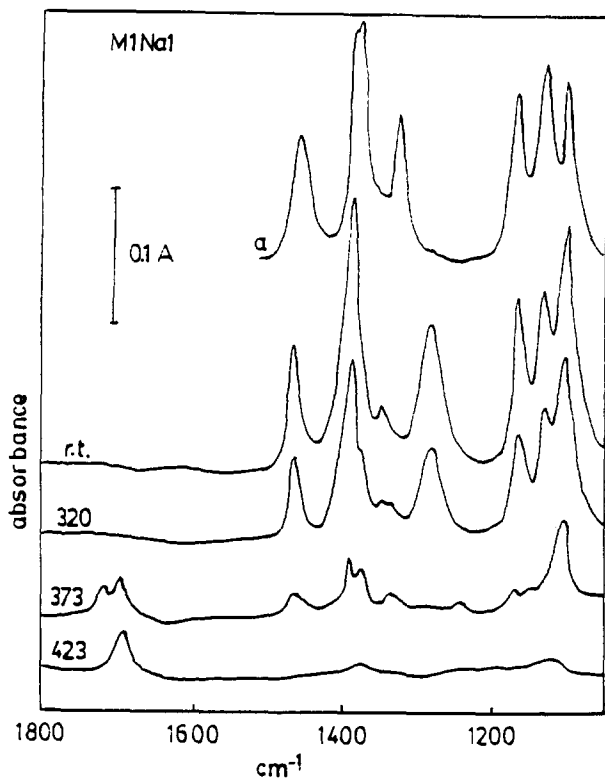


Fig. 5. FTIR spectra recorded after adsorption of isopropanol on sample M1Na1 at room temperature and outgassing at the temperatures given (in K).

3.2. Isopropanol decomposition tests

The results of catalytic decomposition of isopropanol on the studied catalysts are presented in Table 1.

Pure titania yields mainly propene, practically no acetone being observed in this case. On sample M1 the dehydration rate increases considerably and acetone is formed. Doping of the M1 catalyst with alkali-metal cations leads to a drastic decrease in the amount of propene, whereas dehydrogenation to acetone is much less affected. The nature of the doping alkali metal also affects the reaction rates; addition of Li brings about a decrease of both dehydration and dehydrogenation.

The rate of acetone formation on alkali-metal-doped catalysts is slightly higher than that on the undoped M1 catalyst and, with the exception of the Li-doped catalysts, it follows roughly the order of the electronegativity of the alkali-metal

cations. A higher dehydration rate is observed for the Mo-doped catalyst.

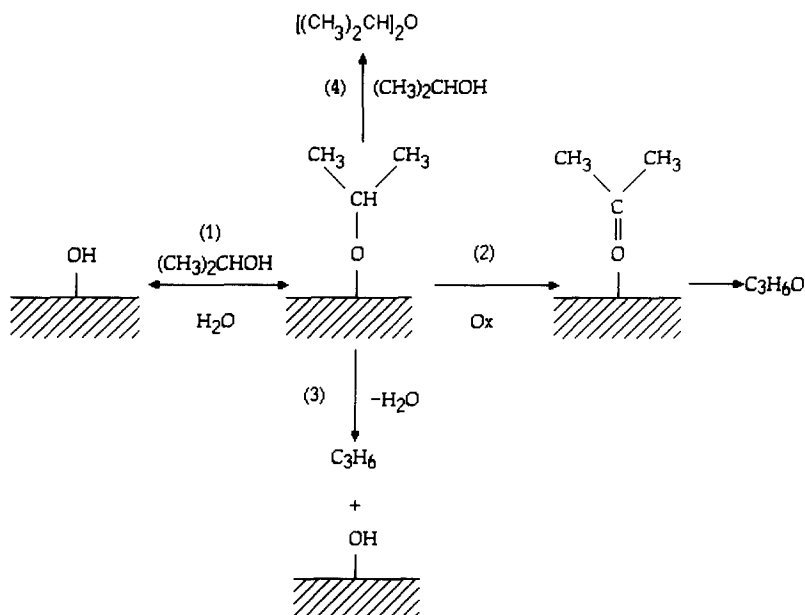
4. Discussion

The results obtained show that the deposition of molybdenum oxide on titania leads to the development of dehydrogenation properties, acetone being observed both by FTIR spectroscopy and in isopropanol decomposition measurements. Also, large amounts of propene are observed in pulse experiments. Addition of alkali-metal cations reduces drastically the rate of propene formation, whereas acetone formation is only slightly affected. This result is in agreement with previous data on isopropanol decomposition on K-doped $\text{MoO}_3/\text{TiO}_2$ catalysts [20]. The type of alkali cation also affects the rate of acetone formation. Addition of Li seems to block the dehydrogenating centres, as shown by the trace levels of acetone bands in the FTIR spectra. This may be due to the presence of lithium molybdates and Li–Ti–O species detected by XRD [22].

The other alkali cations increase the rate of acetone formation, as shown in the pulse study, but the intensities of acetone bands in the FTIR spectra are similar or even weaker on doped catalysts than that on the undoped M1 sample. The amount of acetone formed on the doped samples (relative to the M1 catalyst) was larger than that observed in the adsorbed state in the FTIR study, and may be due to an easier desorption of acetone from the surface in the case of alkali-doped catalysts.

The mechanism depicted in Scheme 1 can be proposed to explain the different chemical transformations observed.

As in the case of methanol, isopropanol is initially adsorbed dissociatively, giving rise to isopropoxide species (1); strengthening of the δ_{HOH} band at $1620\text{--}1640\text{ cm}^{-1}$, the intensity of which decreases sharply as the samples are outgassed at room temperature, indicates that such a process takes place through condensation with surface hydroxyl groups. The isopropoxide groups may undergo abstraction of a hydrogen atom, thus becoming oxidized to acetone (2), or be dehy-



Scheme 1. Possible mechanism for observed transformations of isopropanol on the samples studied.

drated to propene (3), or even condense with another isopropanol molecule, yielding di-isopropyl ether (4).

Another mechanism proposed as an alternative to (3) for the dehydration reaction to propene involved formation of a carbonium ion [29] by proton donation from the surface to an isopropanol molecule. It cannot be unequivocally concluded which mechanism operates for propene formation in the case of $\text{MoO}_3/\text{TiO}_2$ catalysts. Production of large amounts of propene on the M1 catalyst (where Brønsted sites ($\text{Mo}-\text{OH}$) have been observed [23]), suggests that the protonation mechanism is involved. The decrease in propene formation on alkali-metal-doped catalysts would be then easily explained, as the Brønsted centres are not observed for these catalysts. On pure titania, for which only Lewis acidity has been reported [12,30,31], the small amounts of propene obtained would be formed by the elimination routes or from the alkoxide species through the mechanism proposed by Hussein et al. [12].

Substitution of the Brønsted sites by alkali-metal cations will modify also the basicity [24] of the neighbouring $\text{Mo}-\text{O}$ centres, enhancing the transformation of the isopropoxide species to acetone.

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References

- [1] K. Kochloeff, M. Kraus and V. Bazant, Proc. Fourth Int. Congr. Catal., Moscow, 1968, Vol. 2, Akadémiai Kiado, Budapest, 1971, p. 490.
- [2] H. Knozinger, H. Bulh and K. Kochloeff, *J. Catal.*, 24 (1972) 57.
- [3] J. Sedlacek and M. Kraus, *React. Kinet. Catal. Lett.*, 2 (1975) 57.
- [4] L. Nondek and J. Sedlacek, *J. Catal.*, 40 (1975) 34.
- [5] J. Cunningham, B.K. Hodnett, M. Ilyas, J. Tobin and E.L. Leahy, *Faraday Discuss. Chem. Soc.*, 72 (1981) 283.
- [6] M. Castiglioni, R. Giordano and E. Sappa, *J. Mol. Catal.*, 37 (1986) 287.
- [7] M. Ai and S. Suzuki, *Bull. Chem. Soc. Jpn.*, 46 (1973) 321, 1208; *Bull. Jpn. Pet. Inst.*, 16 (1974) 118; *Bull. Chem. Soc. Jpn.*, 47 (1974) 3074.
- [8] B. Grzybowska-Swierkosz, *Mater. Chem. Phys.*, 17 (1987) 121.
- [9] A. Ouqour, G. Coudurier and J.C. Vedrine, *J. Chem. Soc. Faraday Trans.*, 89 (1993) 3151.

- [10] P.F. Rossi, G. Busca, V. Lorenzelli, O. Saur and J.C. Lavalley, *Langmuir*, 3 (1987) 52.
- [11] G. Ramis, G. Busca and V. Lorenzelli, *J. Chem. Soc. Faraday Trans. 1*, 83 (1987) 1591.
- [12] G.A. M. Hussein, N. Sheppard, M.I. Zaki and R.B. Fahim, *J. Chem. Soc. Faraday Trans. 1*, 83 (1989) 1723.
- [13] F. Castagno, M. Castiglioni, E. Sappa, A. Tiripicchio, M. Tiripicchio Camellini, P. Braunstein and J. Rosé, *J. Chem. Soc. Dalton Trans.*, (1989) 1477.
- [14] D. Soung Kim, Y. Kurusu, I.E. Wachs, F.D. Hardcastle and K. Segawa, *J. Catal.*, 120 (1989) 325.
- [15] Y. Matsuoka, M. Niwa and Y. Murakami, *J. Phys. Chem.*, 94 (1990) 1477.
- [16] K. Bruckman, B. Grzybowska, M. Che and J.M. Tatibouet, *Appl. Catal. Gen.*, 96 (1993) 279.
- [17] E. Filipek, B. Grzybowska, E. Serwicka, Y. Barbaux, J.P. Bonelle and J. Grimblot, in G. Centi and F. Trifiro (Eds.), *New Developments in Selective Oxidation, Studies in Surface Science and Catalysis*, Vol. 55, Elsevier, Amsterdam, 1990, p. 767.
- [18] C. Martín, I. Martín, C. Mendizábal and V. Rives, in L. Guzzi, F. Solymosi and P. Tétény (Eds.), *New Frontiers in Catalysis, Studies in Surface Science and Catalysis*, Vol. 75, Elsevier, Amsterdam, 1993, p. 1987.
- [19] C. Martín, I. Martín and V. Rives, *J. Chem. Soc. Faraday Trans.*, 89 (1993) 4131.
- [20] B. Grzybowska, P. Mekss, R. Grabowski, K. Wcislo, Y. Barbaux and L. Gengembre, in S. Vic Bellón and V. Cortés Corberán (Eds.), *New Developments in Selective Oxidation, Studies in Surface Science and Catalysis*, Elsevier, Amsterdam, 1994, p. 151.
- [21] T. Fransen, P.C. van Berge and P. Mars, in B. Delmon, P.A. Jacobs and G. Poncelet (Eds.), *Preparation of Catalysts*, Elsevier, Amsterdam, 1976, p. 405.
- [22] P. Malet, C. Martín, I. Martín and V. Rives, *J. Catal.*, 147 (1994) 465.
- [23] C. Martín, I. Martín, C. del Moral and V. Rives, *J. Catal.*, 146 (1994) 415.
- [24] C. Martín, I. Martín and V. Rives, *J. Catal.*, 145 (1994) 239.
- [25] O. Koga, T. Onishi and K. Tamaru, *J. Chem. Soc. Faraday Trans. 1*, 76 (1980) 19.
- [26] C.H. Rochester, J. Graham and R.J. Rudham, *J. Chem. Soc. Faraday Trans. 1*, 80 (1984) 2459.
- [27] I. Carrizosa and G. Munuera, *J. Catal.*, 49 (1977) 174.
- [28] C. del Moral, M.Sc. Thesis, University of Salamanca, 1991.
- [29] F.C. Whitmore, *J. Am. Chem. Soc.*, 54 (1932) 3274.
- [30] G. Busca, H. Saussey, O. Saur, J.C. Lavalley, V. Lavalley and V. Lorenzelli, *Appl. Catal.*, 14 (1985) 245.
- [31] K. Tanaka and J.M. White, *J. Phys. Chem.*, 86 (1982) 4708.