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NOTE

A FTIR Study of Surface Nucleophilicity of TiO_2 and MoO_3/TiO_2 Doped with Alkaline Cations

Oxidation of olefins to yield unsaturated aldehydes and acids is one of the most important industrial processes, and supported oxides of transition metal cations have proved to be very useful for these purposes. Among the systems active in these reactions, supported molybdena has been widely studied (1–3). In these catalysts, the nature and surface distribution of the molybdenum-containing species depend, among other factors, on the preparation method, molybdenum loading, calcination temperature, nature of the support, presence of doping agents, etc., as they all control the physicochemical and catalytic properties of these solids (4–6). As oxidation of olefins lead to formation of ketones and aldehydes, in the present paper we report a study by FTIR spectroscopy on the chemisorption of acrolein and acetone in TiO_2 and MoO_3/TiO_2 only or doped with potassium or lithium, in order to analyze how the surface nucleophilic properties of titania are modified by the presence of molybdenum and alkali cations.

Preparation of the catalysts has been described elsewhere (5, 7). Briefly, the support (TiO_2 Degussa P-25, ca. 50 m^2/g) was impregnated with an aqueous solution of ammonium heptamolybdate (from Carlo Erba) and then dried. The amount of molybdenum is equivalent to 5.8% (w/w), that corresponds to one geometrical monolayer of molybdena (8). The dopant (1 or 3% w/w of K/TiO_2 or 1% w/w Li/TiO_2) was incorporated before Mo incorporation, from aqueous solutions of KNO_3 or $LiNO_3$ (from Fluka) in a rotary vacuum dessicator (Heidolph VV-60). Once dried, the samples were calcined in oxygen at 773 K for 3 h. Samples are called M1, M1K1, M1Li1, and M1K3, the figures standing for the number of monolayers of MoO_3 and the weight percentage of K or Li, respectively. The samples have been characterized (5, 7) by X-ray diffraction, V–UV and FTIR spectroscopies, adsorption of nitrogen at 77 K, and FTIR monitoring of pyridine adsorption. It has been concluded that MoO_3 and dispersed molybdates exist in sample M1, while the simultaneous presence of potassium or lithium and molybdenum leads to formation of K–Mo–O or Li–Mo–O compounds. $K_2Mo_4O_{13}$ and Li_4MoO_5 have been identified by X-ray diffraction; the presence of other species cannot be undoubtedly ruled out. Addition of alkaline cations leads to a steady decrease in the concentration of surface acid sites, especially those of Brønsted type, that are completely cancelled for alkaline loadings of 3%, while weaker Lewis sites (coordinatively unsaturated alkaline cations) are also detected (9). Adsorption of acrolein and acetone was followed by FTIR spectroscopy in special cells with CaF_2 windows, after outgassing the samples *in situ* at 673 K for 2 h.

The more significant FTIR spectra recorded upon adsorption and reaction of acetone on the bare support and on the other samples are included in Fig. 1. Adsorption at room temperature takes place without reaction on all samples M1, M1K1, M1Li1, and M1K3. All bands recorded in this region (1800–1200 cm^{-1}) can be ascribed to vibration modes of adsorbed, unreacted, molecular acetone. The band corresponding to the $\nu(C{=}O)$ mode is recorded at 1712 ± 1 cm^{-1} for samples M1K1 and M1K3, and at 1718 cm^{-1} for sample M1Li1, while for sample M1 it is resolved into two components at 1690–1713 cm^{-1}. These values are ca. 20–44 cm^{-1} lower than those corresponding to gaseous acetone, 1734 cm^{-1} (10), this shift being due to the electron release from the oxygen atom of the carbonyl group in acetone to fairly weak surface Lewis sites. The splitting of the $\nu(C{=}O)$ band in the undoped sample indicates the presence of acetone species coordinated to Lewis acid surface sites with different acid strength, probably differently coordinatively unsaturated Ti^{4+} cations at the titania surface. Such a shift is less evident for those samples containing alkali species (mainly in the case of the lithium-containing samples), due to the lower acidity of the surface Lewis sites, as shown by adsorption of pyridine (7, 9), and associated to coordinatively unsaturated alkaline cations. This interaction can be also concluded from the shift of the $\nu_{as}(C{-}C{-}C)$ mode from 1215 cm^{-1} for gaseous acetone (10) to 1240–1228 cm^{-1} in our samples. Other bands at 1423 and 1370 cm^{-1} are due to bending modes of the methyl groups.

After outgasing at increasing temperatures, Fig. 1, the

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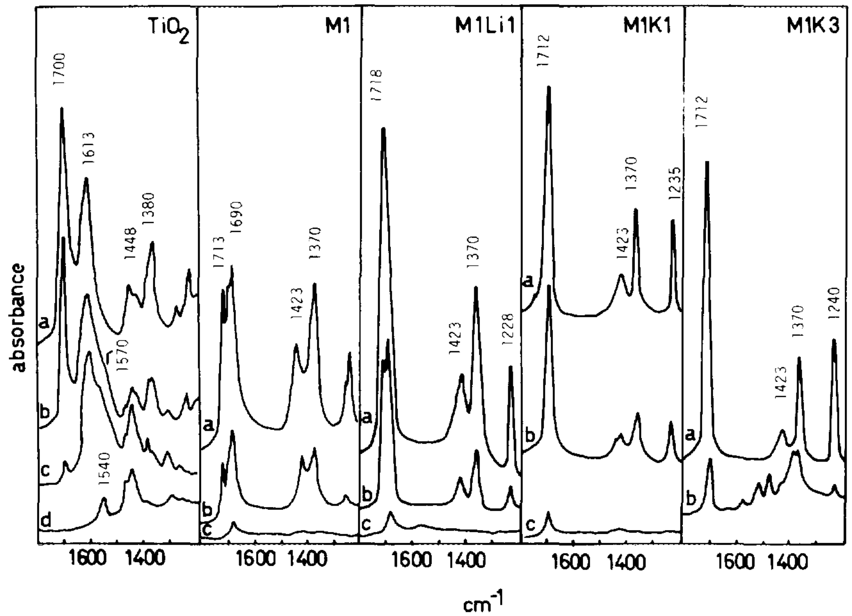

FIG. 1. FTIR spectra recorded upon adsorption of acetone after outgassing at (a) r.t., (b) 373 K, (c) 473 K, and (d) 573 K on the samples indicated.

bands due to molecularly adsorbed acetone remain, although slightly weakened, for samples M1, M1K1, and M1Li1, the bands being finally removed upon outgassing at temperatures above 473 K. The high wavenumbers band due to ν(C=O) is removed in sample M1 upon outgassing at 373 K, indicating a weak bonding of coordinated acetone to the surface. On the contrary, for sample M1K3, new bands are recorded at 1487–1574 cm^{-1} after outgassing at 373 K; these bands are similar to those previously recorded by different authors (12, 13) upon adsorption of acetic acid on ionic oxides, and have been ascribed to formation of coordinated acetate species. If the temperature is increased (473 K), these bands also disappear.

In order to check if the adsorption process takes place through hydrogen bonding (an alternative route for adsorption of acetone on oxide surfaces), the 4000–3000 cm^{-1} range of the spectrum (where bands due to ν(O–H) modes are expected) has been studied. However, no significant change is observed in this region upon adsorption of acetone. This fact, together with the fairly high outgassing temperature required to remove chemisorbed acetone, confirms its bonding to the surface only through coordination to surface Lewis sites.

For bare titania, Fig. 1, the situation is completely different from that depicted for samples M1, M1K1, and M1Li1. Even at room temperature, in addition to bands at 1700 and 1613 cm^{-1} (νC=O) and 1425 and 1364 cm^{-1} (methyl bending) due to acetone associatively adsorbed through the C=O on surface Lewis sites, weak shoulders are recorded at 1448 and 1380 cm^{-1}. Upon outgassing at increasing temperatures a new shoulder at 1570 cm^{-1} is detected that shifts toward lower wavenumbers (1540 cm^{-1}) and increases its intensity as the outgassing temperature is further increased. The intensity of the band at 1448 cm^{-1} also increases when the outgassing temperature is increased. Bands similar to those described here (1570 and 1380 cm^{-1}) have been reported by several authors upon adsorption of acetone on different oxide systems (11, 13), and have been ascribed to the antisymmetric and symmetric modes of enolate anions, $^-$O–C=C/O=C–C$^-$,

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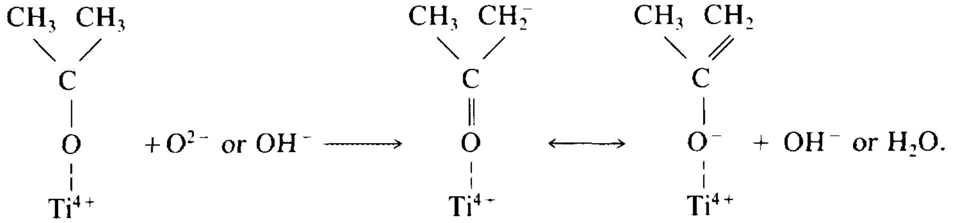

$$(CH_3)_2C{-}O{-}Ti^{4+} + O^{2-} \text{ or } OH^- \longrightarrow CH_3(CH_2^-)C{=}O{-}Ti^{4+} \longleftrightarrow CH_3(CH_2{=})C{-}O^-{-}Ti^{4+} + OH^- \text{ or } H_2O.$$

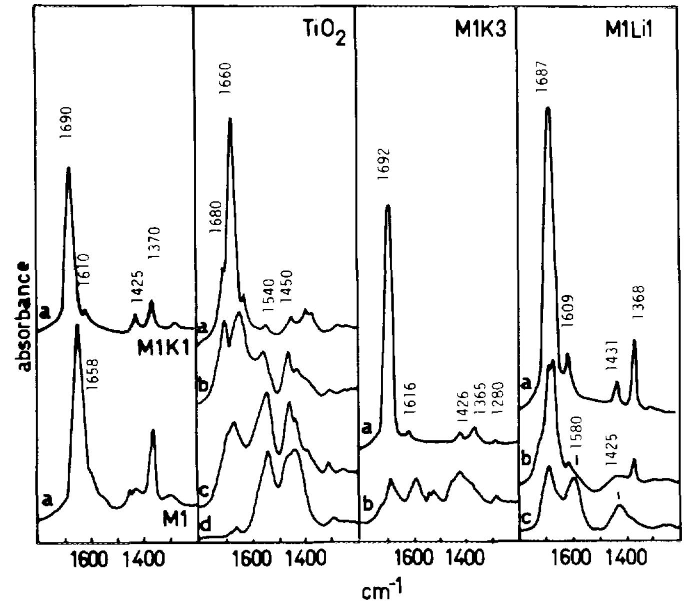

FIG. 2. FTIR spectra recorded upon adsorption of acrolein on the different samples after outgassing at (a) r.t., (b) 373 K, (c) 473 K, and (d) 573 K.

Bands recorded at 1540 and 1448 cm^{-1} can be due to carboxylate species, probably as acetates (14). Upon outgassing at 573 K, all bands due to adsorbed species are removed. So, with regards to the titania support, it can be concluded that acetone is strongly held on its surface; slightly above room temperature it dissociates to form enolates that immediately are oxidized to strongly coordinated acetates. These acetates are more stable on bare titania than on sample M1K3, as on the support they are only desorbed after outgassing at high temperatures.

Spectra recorded upon adsorption of acrolein on samples M1 and M1K1, Fig. 2, are very similar and at room temperature the bands recorded are ascribed to molecularly adsorbed acrolein, coordinated to surface Lewis acid sites. The strongest band, due to the ν(C=O) mode, is recorded at 1658 cm^{-1} for M1 and at 1690 cm^{-1} for M1K1, the shift from 1724 cm^{-1} for gaseous acrolein (15) being originated by the strong interaction with surface acid Lewis sites, in a similar way to that above reported for acetone adsorption, and is due to the weaker nature of the Lewis sites in the K-doped sample, thus accounting for a weaker interaction with the carbonyl group. A weak shoulder is also recorded at 1605–1610 cm^{-1}, due to the νC=C mode; bands at 1425, 1370, and 1287 cm^{-1} are originated by –CH deformation modes and C–C stretching modes (15, 16). Upon outgassing at increasing temperatures the spectrum is modified only very slightly, thus indicating that the surface species are very stable. The bands due to adsorbed species are completely removed after outgassing at 473 K, and bands due to carboxylate species are not recorded at all.

On the contrary, the behaviour shown by bare titania is rather different. As shown in Fig. 2, in addition to the bands due to acrolein adsorbed on Lewis acid sites (1688 and 1660 cm^{-1}) other bands are recorded at 1540 and 1450–1400 cm^{-1}. These bands are highly characteristic of the antisymmetric and symmetric modes of the carboxylate moiety in the acetate anion, when acting as a bidentate ligand (17). On outgassing at increasing temperatures, the intensities of these bands are enhanced, while those bands due to molecularly adsorbed acrolein vanish; the bands originated by adsorbed oxidized species are recorded even after outgassing at 673 K, thus again indicating the high stability of the oxidized species formed.

Samples M1K3 and M1Li1 show a behaviour in some sort of way intermediate between that of unloaded titania and those shown by samples M1 and M1K1. After adsorption and outgassing at room temperature, only bands due to acrolein are detected at 1692 (νC=O), 1616 (νC=C), 1426, 1365, and 1280 cm^{-1}, ascribed to δC–H and νC–C (15, 16) for sample M1K3, and 1687, 1609, 1431, 1368 and 1279 cm^{-1} for sample M1Li1. However, when the outgassing temperature is raised up to 373 K, new, weak bands are recorded at 1570–1520, 1460, and 1390 cm^{-1} for sample M1K3, and 1590, 1425, and 1387 cm^{-1} for sample M1Li1. These bands can be tentatively ascribed to carboxylate species, although, contrary to the behaviour of the support, these bands are removed after outgassing at temperatures below 473 K for M1K3 and 573 K for M1Li1; it seems that in the case of the doped samples, as surface acidity is decreased, the stability of adsorbed carboxylates is increased.

Aldehydes and ketones are probe molecules to determine the strength of nucleophilic sites on the surface of oxides, as reaction of these sites (surface oxide anions) with the electrophilic carbon atom of the carbonyl group may lead to formation of carboxylate species. In the case of the samples here studied, a different behaviour is observed, specially with regards to acrolein adsorption, as it is more sensitive than acetone to nucleophilic attack by hydroxides and oxides. For the support, acetone and acrolein are oxidized even at room temperature to yield very stable carboxylate species that remain even after outgassing at 673 K, thus indicating the presence of strong surface nucleophilic sites. On the contrary, only molecularly adsorbed acetone and acrolein is observed for samples M1 and M1K1, and it is removed even after outgasing at medium temperatures. However, when the potassium content is increased, sample M1K3, or the doping cation is lithium, M1Li1, a partial transformation to carboxylate species is also observed.

The results obtained indicate that for samples M1 and M1K1 the selective interaction of the oxomolybdenum species with the surface sites (hydroxyl groups) of the titania during impregnation to prepare the samples (18, 19) leads to cancellation of the nucleophilic sites, responsible for decomposition of carbonyl-type compounds. This behaviour would account for the role played by molybdena–titania catalysts in selective oxidation processes, as cancellation of such strong nucleophilic sites would favour desorption of the partially oxidized species, thus avoiding its further oxidation.

When K (3%) or Li (1%) is also added on the support after addition of molybdenum, formation of potassium molybdate or lithium molybdate decreases the selective interaction of the oxomolybdenum species with the support (i.e., the above described cancellation of the surface nucleophilic sites) and the surface basicity is simultaneously increased; consequently, these samples exhibit a behaviour intermediate between that of the bare support and that of the sample containing molybdenum and lower amounts of potassium. As the carboxylate species are desorbed at temperatures lower than those needed to remove them from the surface of the support, it can be concluded that the nucleophilic character of these surface sites has been weakened after incorporation of alkali and molybdenum, although such a weakening is less pronounced for high alkaline loadings or when a more basic alkaline (lithium) is used.

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