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Surface Structures of Molybdenum Oxide highly dispersed on ZrO_2 and Oxidation of Propan-2-ol

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Decomposition of propan-2-ol over zirconia with various Mo loadings and the surface structure of these catalysts have been studied by FTIR spectroscopy and by using a closed-circulation system. MOZ3.0 catalyst (MoO_3 3.0 wt %) shows high selectivity to acetone, while catalysts with high MoO_3 loading (>7.5 wt % of MoO_3) show high selectivity to propene. The FTIR spectra of MOZ3.0 are influenced drastically by the adsorption of propan-2-ol and water. Catalysts under the reaction conditions employed exhibit spectra very different from those of calcined samples. The quantitative FTIR characterization of catalysts has shown that there are two types of Mo=O species present in MOZ7.5, while MOZ3.0 is composed mainly of a single Mo=O species. The reactivity of surface Mo=O species varies with MoO_3 loading.

Previously, we have reported the promoter effect observed with MoO_3 and V_2O_5 on TiO_2 and ZrO_2[1-5] in the oxidation of alcohol and alkenes. In each case, an amorphous phase is formed on these supports at low loadings. Such an amorphous phase formed at low Mo or V content has been characterized by polymolybdate or polyvanadate species on titania and zirconia, bringing about enhancement of activity for oxidation reactions. With Mo-Al and Mo-Ti oxides,[6-10] it has been reported that the catalytic activities are related to these surface structures. However, as regards Mo-Zr oxides, only a few papers have reported oxidation reactions. Previously, we have reported that the acid-base properties of Mo-Zr[5] and V-Zr[11] oxides change with the Mo or V content.

In this work, the correlation between the surface structures of Mo oxides and the catalytic activities for propan-2-ol oxidation have been investigated using FTIR spectroscopy. The quantitative FTIR characterization of catalysts has been studied.

Experimental

The preparation and pretreatments of the materials used in this work have been described previously.[5,12] Mo-Zr oxide catalysts contain 3, 7.5 and 11.0 wt % MoO_3 (MOZ3.0, MOZ7.5 and MOZ11.0, respectively). The supports and unsupported MoO_3 were also studied. The BET surface areas are listed in Table 1.

The apparatus consisted of a closed-circulation system of *ca.* 290 cm^3 in volume. The catalytic oxidation or decomposition of propan-2-ol were carried out under the circulation of a mixture of propan-2-ol, oxygen and helium.

Table 1 Physical properties of Mo-Zr catalysts

catalyst	MoO_3 (wt %)	surface area /m^2 g^{-1}	fraction of amorphous MoO_3 (%)	surface concentration of amorphous oxide/μmol m^{-2} [a]
ZrO_2	—	77	—	—
MOZ3.0	3.0	49	100	4.2
MOZ7.5	7.5	46	89	10.0
MOZ11.0	11.0	39	76	15.0

[a] From ref. 5.

Results and Discussion

Decomposition and Oxidation of Propan-2-ol on Mo-Zr Oxides

The decomposition and oxidation of propan-2-ol have been examined in the temperature range 373-473 K. Fig. 1 shows the activities for the decomposition of propan-2-ol in the presence or absence of gaseous oxygen. The activities increased

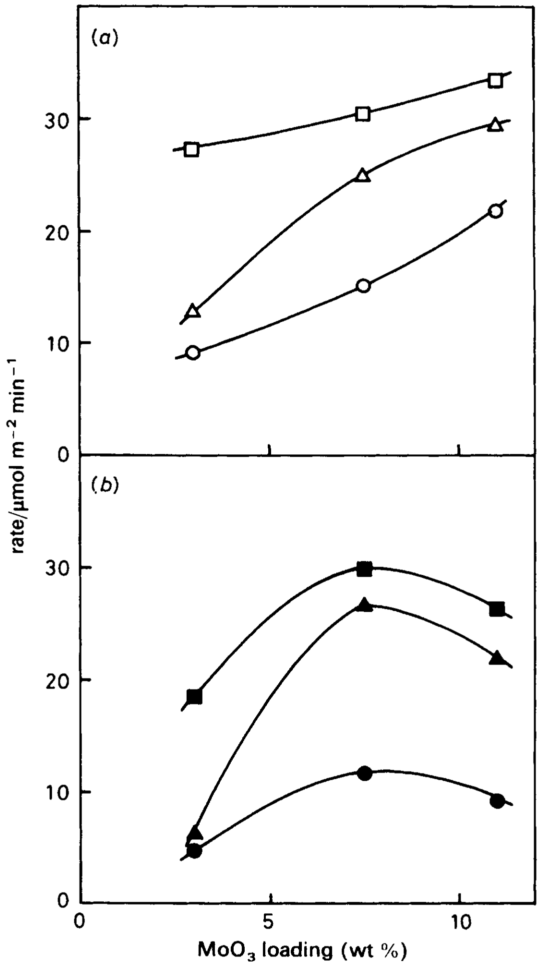

Fig. 1 The rates of decomposition of propan-2-ol on Mo-Zr catalysts. In the presence (*a*) and absence (*b*) of gaseous oxygen at 373 K (○, ●), 423 K (△, ▲) and 473 K (□, ■)

with increasing MoO_3 as well as reaction temperature, and showed maximum values at 7.5 wt % in the absence of oxygen. The rates in the latter case were slightly smaller than those in the former.

The products are mainly acetone or propene formed by dehydrogenation or by dehydration, respectively. Fig. 2 shows the selectivities to acetone and propene at various temperatures. It can be seen that these did not change significantly irrespective of the presence or absence of gaseous oxygen. The selectivities to acetone were highest with MOZ3.0 at around 30% at 423 K, while the selectivities to propene were highest for the catalysts with high MoO_3 loadings and increased with increasing temperature. Propene was not formed on MOZ7.5 and MOZ11.0 at 323 K, in agreement with previous reports.[13–15] In addition, no propene was formed on the ZrO_2 support, and the propene selectivity on the crystalline MoO_3 was *ca.* 50%. The amount of CO_2 formed on MOZ3.0, which is obtained as a result of total oxidation, was larger than that on MOZ7.5 or MOZ11.0.

The amount of amorphous Mo species has been calculated from XRD data (Table 1).[5] The conversions per amorphous species are shown in Fig. 3. The results show that the low Mo loading catalyst has a higher activity than the high Mo loading catalysts. These results, together with the difference in selectivities, suggest that the active sites on both catalysts are different. Both MoO_3 and ZrO_2 showed little or no activity for decomposition of propan-2-ol in the temperature range studied, suggesting that the Mo oxides are the active sites for this reaction. Thus, we focused on the catalysts MOZ3.0 and MOZ7.5.

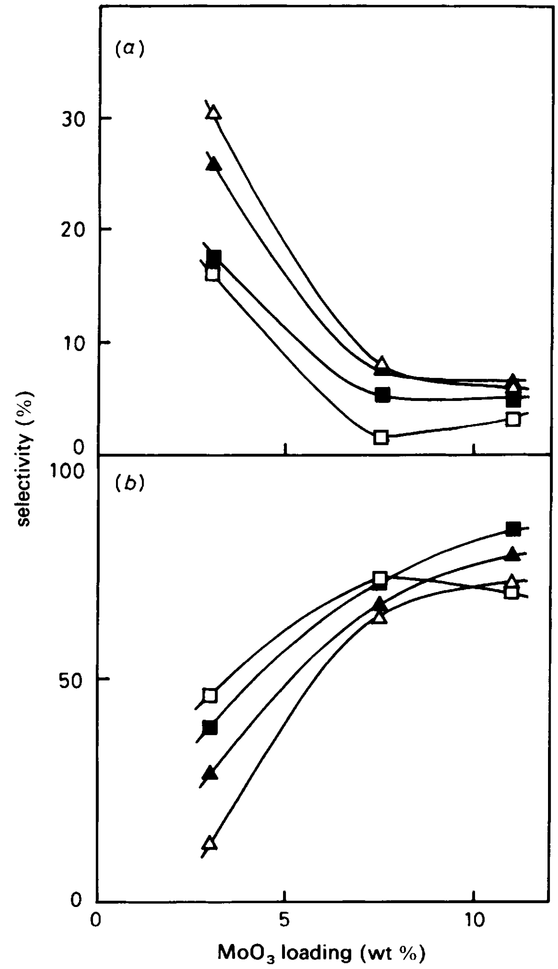

Fig. 2 Product selectivities to acetone and propene for decomposition of propan-2-ol. (*a*) Acetone, (*b*) propene, (△) 423 K, (□) 473 K. Open and closed symbols denote the presence and absence of gaseous oxygen, respectively

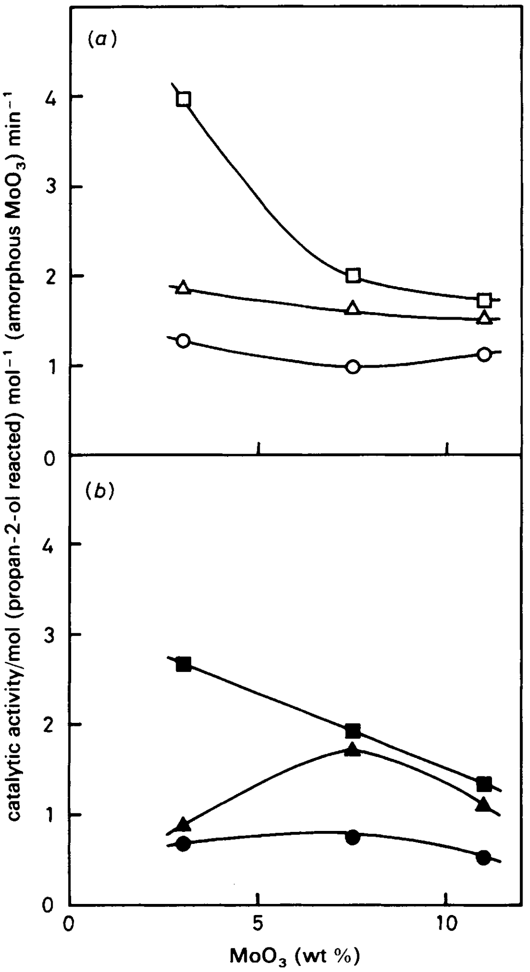

Fig. 3 Catalytic activities per amorphous Mo oxide. In the presence (*a*) and absence (*b*) of gaseous oxygen, at 373 K (○, ●), 423 K (△, ▲) and 473 K (□, ■)

FTIR Spectra of Propan-2-ol on Mo–Zr Catalysts

A small amount of propan-2-ol was introduced onto the MOZ3.0 sample. The resulting spectra are shown in Fig. 4. The spectra below 1800 cm^{-1} show the difference between the original and the catalyst itself. The spectrum exhibits a broad band around 3300 cm^{-1} due to the hydrogen-bonded OH groups, the C—H stretching band near 3000 cm^{-1} and bands in the bending region. Bands at 1467 and 1383 cm^{-1} are due to the bending modes of the CH_3 group of adsorbed propan-2-ol. Bands at 1163, 1133 and 1105 cm^{-1} are assigned to ν(C—O) of surface isopropoxide, which has been reported with various metal oxides.[4,16–19] The results suggest that various types of isopropoxide species are formed on the MOZ3.0.

The temperature of the catalyst was raised in stages in the absence of gaseous oxygen. On increasing the temperature of the disc the alkoxyl bands reduced in intensity. Simultaneously, new bands appeared at 1680 and 1250 cm^{-1} and increased in intensity at 423 K [Fig. 4(*d*)]. In addition, at 423 K a weak band appeared at 1550 cm^{-1}. At 473 K the bands at 1680 and 1250 cm^{-1} increased in intensity, being atttributable to the ν(C=O) of acetone coordinated on Lewis-acidic sites, as reported previously.[4,19] In addition, a band at 1560 cm^{-1} was observed at 473 K, being attributable to an enole-type species formed from acetone.

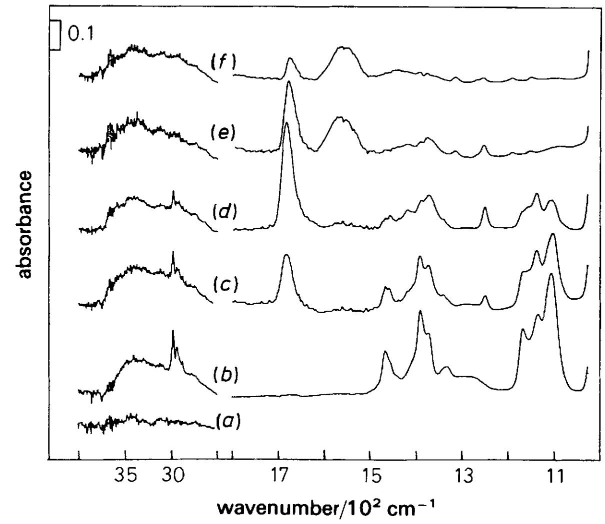

Fig. 4 FTIR spectra of propan-2-ol adsorbed on MOZ3.0: (*a*) background. Spectra (*b*)–(*f*): after introduction of propan-2-ol followed by 30 min evacuation at 293 K (*b*), followed by 30 min at 373 K (*c*), 423 K (*d*), 473 K, (*e*) and then 30 min at 523 K (*f*). The spectra below 1800 cm^{-1} in Fig. 4–6 are shown after subtraction of background

Fig. 5 shows the spectra of propan-2-ol adsorbed on MOZ7.5. Bands appeared at almost the same positions as those on MOZ3.0 at room temperature [Fig. 5(*b*)]. The C—O band of alkoxide appeared at 1163, 1133 and 1105 cm^{-1}. The intensities of the bands at 1163 and 1133 cm^{-1} are weaker than those for MOZ3.0. The theoretical coverage of Mo oxide on MOZ3.0 is 32.4%, while that on MOZ7.5 is 87.1%. Thus, it is possible that the isopropoxide species are formed on the ZrO_2 portion of catalyst together with Mo oxides. Thus, the 1105 cm^{-1} band is tentatively assigned to the isopropoxide species on Mo oxide, the bands at 1163 and 1133 cm^{-1} being assigned to the species on ZrO_2. The spectral behaviour with increasing temperature of the MOZ7.5 disc is almost the same as that for MOZ3.0. However, the band due to the enole-type species was not observed clearly.

Similar experiments were carried out in the presence of oxygen. Fig 6 shows the spectra of adsorbed propan-2-ol following oxidation at various temperatures. At 473 K new bands, which were not observed in Fig. 4, appeared at 1550, 1450, 1390 and 1345 cm^{-1}, and are assigned to the surface acetate and formate species, as have been found on various metal oxides in this frequency region.[16,17] This suggest that under the circulation of gaseous oxygen more rapid oxidation of adsorbed acetone to form surface carboxylate species occurred. In the case of MOZ7.5 [Fig. 6(*c*) and (*d*)], the spectral behaviour with oxidation of propan-2-ol is almost the same as that for MOZ3.0. The band positions and the assignments are summarized in Table 2.

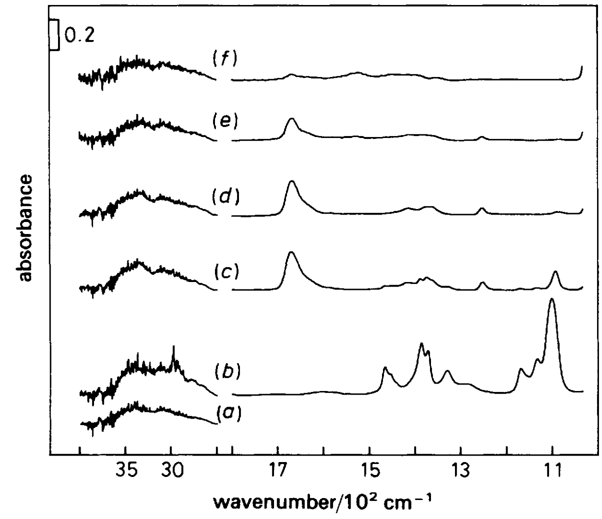

Fig. 5 FTIR spectra of propan-2-ol adsorbed on MOZ7.5: (*a*) Background. Spectra (*b*)–(*f*): after introduction of propan-2-ol followed by 30 min evacuation at 293 K (*b*), followed by 30 min at 373 K (*c*), 423 K (*d*), 473 K (*e*) and then 30 min at 523 K (*f*)

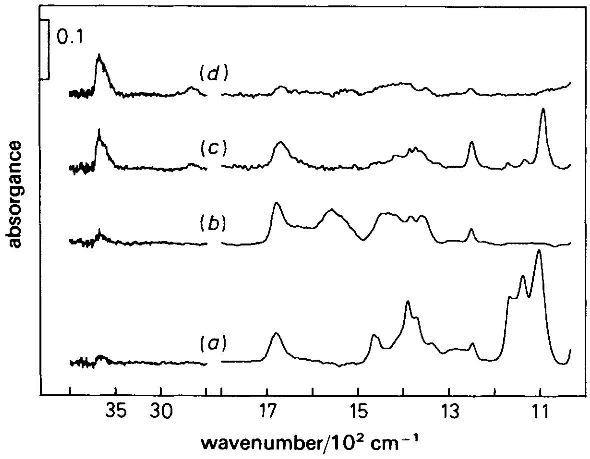

Fig. 6 FTIR spectra of propan-2-ol adsorbed on Mo–Zr oxides. MOZ3.0: (*a*) after introduction of propan-2-ol followed by 30 min at 373 K in oxygen, (*b*) followed by 30 min at 473 K in oxygen. MOZ7.5: (*c*) after introduction of propan-2-ol followed by 30 min at 373 K in oxygen, (*d*) followed by 30 min at 473 K in oxygen

Structure Characterization of Catalysts by the Mo=O band

The structure of molybdate species dispersed on zirconia has been studied by XRD and laser Raman spectroscopy. The XRD results show that *ca.* 90% of the molybdenum oxide on

Table 2 Wavenumber ($\tilde{\nu}$/cm^{-1}) and assignment of the bands of surface isopropoxide and oxygen-containing species on Mo–Zr catalysts

$\tilde{\nu}$/cm^{-1}		
room temperature	373–473 K	vibrational mode
3300		hydrogen-bonded OH
2980		$\nu(CH_3)$
2940		$\nu(CH_3)$
2880		$\nu(CH_3)$
	1680	$\nu(C{=}O)$ of acetone
	1560	$\nu(C{=}O)$ of enole species
	1550	$\nu_{as}(COO)$ of acetate and formate
1465		$\delta(CH_3)$
	1450	$\nu_s(COO)$ of acetate
	1390	
1389		$\delta(CH_3)$
1370		$\delta(CH_3)$
	1345	$\nu_s(COO)$ of formate
1335		
1285		
	1250	
1163		$\nu(C{-}O)$ of surface alkoxide
1133		$\nu(C{-}O)$ of surface alkoxide
1105		$\nu(C{-}O)$ of surface alkoxide

The subscript s refers to a symmetric stretching mode and as to an antisymmetric stretching mode

MOZ7.5 is present as an amorphous phase (Table 1), indicating that most of the molybdate species are highly dispersed on zirconia.[5] Raman studies also show that only surface molybdate species are present in the catalysts.[5]

Generally, the IR band of Mo=O in crystalline MoO_3 appears at 1000 cm^{-1}. On the other hand, the IR band at 960–980 cm^{-1} is attributable to polymolybdate. In the present study, the spectra in the Mo=O region on the adsorption of alcohol and on reaction have been investigated by *in situ* IR spectroscopy. The zirconia support showed no absorption band in the region 1100–900 cm^{-1}. Thus, the spectra on adsorption or oxidation could be observed in detail. The spectra below 1100 cm^{-1} corresponding to those in Fig. 4 and 5 are shown in Fig. 7. The spectra show the difference between the samples and zirconia alone. The Mo=O band appeared at 1000 cm^{-1} after oxidation of MOZ7.5 at 723 K [Fig. 7B(*a*)]. The introduction of propan-2-ol on the catalyst caused the 10 cm^{-1} shift to lower wavenumber and the slight reduction in intensity. At 473 K the Mo=O band was shifted to almost its original position. Thus, the reversibility in the IR band structure of highly dispersed, supported-metal catalysts has been confirmed, as reported by Raman studies.[10] The spectra of the MOZ3.0 sample are also shown in Fig. 7A. The Mo=O band appeared at 998 cm^{-1} after oxidation at 723 K [Fig. 7B(*a*)]. The introduction of propan-2-ol on the catalyst led to the reduction of the band and complex band shape. Under reaction conditions, such as at 473 K, the band still shifted to lower wavenumber. Although the IR results indicate similar surface adsorbed species, the IR bands of the Mo=O region reflect the different Mo=O/adsorbate interactions, as discussed below.

Nature of Surface Molybdenum Oxides

Most Raman or IR spectroscopic characterizations of catalysts in their oxidised state have not addressed the effect of adsorbed H_2O on the spectral characteristics of the catalysts. Recently, Stencel *et al.*[10] showed that the adsorption of H_2O onto calcined Mo–Al oxide catalysts caused a substantial decrease in the frequency of a band attributed to a Mo=O stretching vibration and they reported the reversibility in the Raman band structure of highly dispersed, supported-metal oxides during O_2 calcination–H_2O exposure cycles. As described above, the Mo=O bands show complex behaviour on adsorption and reaction and seem to be composed of two or more bands. Therefore, band-separation techniques[20,21] have been applied to the Mo=O band region. The behaviour of the Mo=O band on adsorption or on reaction has been investigated in detail.

Fig. 8A shows the original and separated peaks of the Mo=O region in MOZ7.5 after oxidation and evacuation at 723 K. The band was separated into two peaks at 1006 and 993 cm^{-1} together with a weak band at 981 cm^{-1}, suggesting that at least two different species of molybdenum oxide are present on MOZ7.5. The Mo=O band after adsorption of propan-2-ol at room temperature was separated into three peaks as shown in Fig. 8B. The band at 1006 cm^{-1} was reduced in intensity and simultaneously the 978 cm^{-1} band increased in intensity. The total intensity of Mo=O region was also reduced. The peak at 1100 cm^{-1} is due to the alkoxyl species. Reaction of propan-2-ol at 473 K lead to the complex band shape and peak saturation of the Mo=O band as shown in Fig. 8C. A new band appeared at 1023 cm^{-1}. The band intensities, together with peak positions, are summarized in Table 3.

The above results show that the Mo=O band is composed mainly of three peaks in the ranges 1008–1003, 995–993 and 981–978 cm^{-1}. The 995–993 cm^{-1} peak remains unchanged in both position and integrated intensity irrespective of adsorption or reaction at high temperatures. In addition, the position of this peak is in agreement with that found for bulk MoO_3 (or crystalline MoO_3).

The 1008–1003 cm^1 peak is affected by adsorption and reaction. The reduction or increase in intensity of this peak seems to be accompanied by the appearance (or increase in intensity) or reduction of the 980 cm^{-1} peak, respectively,

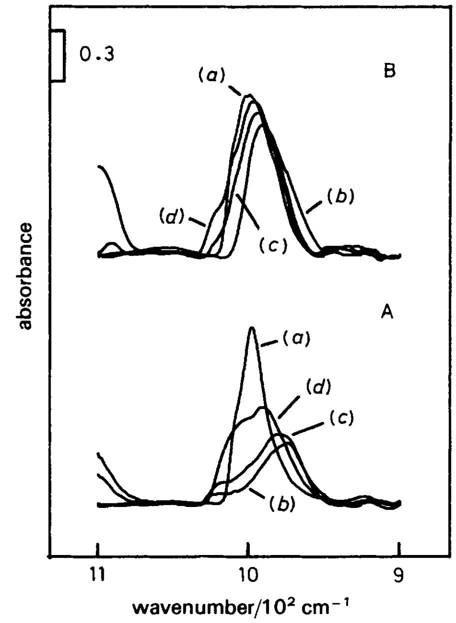

Fig. 7 FTIR spectra of the Mo=O stretching region of propan-2-ol adsorbed on Mo–Zr oxides. (A) MOZ3.0, (B) MOZ7.5, (*a*) background, (*b*) after adsorption of propan-2-ol at 293 K, (*c*) as for (*b*) followed by 30 min at 373 K, (*d*) as for (*c*) followed by 30 min at 473 K

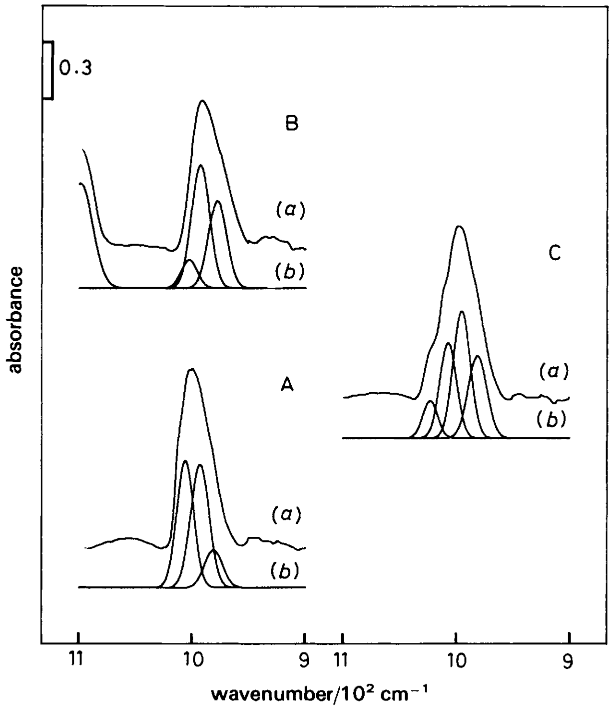

Fig. 8 Band-shape analysis of IR spectra of the Mo=O stretching region of propan-2-ol adsorbed on MOZ7.5. (A) After heat treatment at 723 K, (B) after adsorption of propan-2-ol at 293 K, (C) followed by heating at 473 K, (*a*) original curve, (*b*) separated peaks

Table 3 Peak parameters of the Mo=O bands

condition	MOZ7.5 wavenumber/cm^{-1}	MOZ7.5 integrated intensity[a]	MOZ3.0 wavenumber/cm^{-1}	MOZ3.0 integrated intensity[a]
after heat treatment	1006	12590	1008	3870
	993	13350	998	18340
	981	4000	982	4730
propan-2-ol adsorption	1003	2680	1016	1670
	993	13150	993	3580
	978	9400	975	9110
oxidation of alcohol at 473 K	1007.	9450	1012	7130
	995	12880	995	9050
	981	9090	980	11230

[a] In arbitrary units.

although the integrated intensities of these bands are not related quantitatively. The results suggest that the species producing the 1005 cm^{-1} peak is converted to that corresponding to the 980 cm^{-1} peak. The 980 cm^{-1} peak appeared only after adsorption of alcohol, and reduced in intensity at reaction temperatures such as 473 K. This may be attributed to the Mo=O species interacting with some chemisorbed species.

The above results can be explained as follows: The 995 cm^{-1} peak is attributed to the Mo=O species of the second or third layer of molybdenum oxide in the MOZ7.5 catalyst. Thus, it would be expected that the Mo=O bond does not interact with adsorbed species. As described above, crystalline MoO_3 may also contribute to this band. However, as described previously,[5] the composition of the crystalline phase in MOZ7.5 is only 10% (24% in MOZ11). Thus, the amorphous molybdate species contribute mainly to the 995 cm^{-1} peak.

From a similar consideration as for the 995 cm^{-1} peak, the 1005 and 980 cm^{-1} peaks are attributed to the Mo=O species in the top layer (surface species) of molybdenum oxide in the catalyst. Some OH groups may be formed on the catalyst surface by the reaction of alcohol with surface Mo=O in the top layer. This may cause the reduction of the Mo=O band at 1005 cm^{-1}, because the introduction of a small amount of water enhances the Brønsted sites.[5] However, we could observe little or no difference in the OH band region.

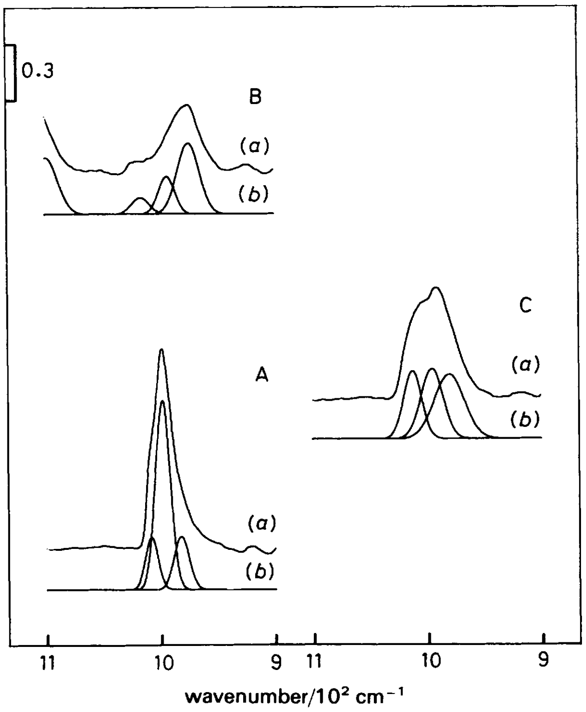

Fig. 9 Band-shape analysis of IR spectra of Mo=O stretching region of propan-2-ol adsorbed on MOZ3.0. (A) After heat treatment at 723 K; (B) after adsorption of propan-2-ol at 293 K, (C) followed by heating at 473 K, (*a*) original curve, (*b*) separated peaks

The band-separation techniques have been applied to the MOZ3.0 catalyst. As shown in Fig. 9, the Mo=O band in MOZ3.0 was composed mainly of a single peak at 998 cm^{-1}, although weak peaks at 1008 and 982 cm^{-1} also appeared. This suggests that the molybdenum oxide in MOZ3.0 is uniformly dispersed on the catalyst surface. The Mo=O band in the catalyst is severely affected by adsorption and reaction. After the introduction of alcohol on the sample, the Mo=O band shows two or more peaks (Fig. 9B). Under the reaction conditions at 473 K, the Mo=O band consists of three peaks as shown in Fig. 9C. The position of the 998 cm^{-1} peak is in agreement with that of the 995 cm^{-1} peak of MOZ7.5. However, the spectra on adsorption of alcohol are quite different, suggesting that the 998 cm^{-1} peak for MOZ3.0 is due to a different type of species than the corresponding peak for MOZ7.5. It has been reported that the Mo=O band in the Raman spectra is affected by the surface OH content of the catalyst.[10] Therefore, similar experiments were carried out using water and similar spectra and band separations to those found for alcohol were obtained (not shown in figure).

Under the reaction conditions at 473 K with alcohol, MOZ3.0 exhibits peaks due to the Mo=O species interacted with surface compound, while the MOZ7.5 sample exhibits peaks due to Mo=O with only small interactions with other species. The above results indicate that the structure or chemical nature of the molybenum oxide varies with MoO_3 loading. Although the value of 7.5 wt % is estimated to be the MoO_3 content within a complete monolayer, it is possible that at this loading the molybdenum oxide aggregates during the calcination process and forms part multilayers. Recently Machej *et al.*[22] have reported that the impregnation procedures lead to poor dispersion of molybdena on the titania surface, which is due to the clustering of molybdena when the MoO_3 loadings do not exceed the theoretical monolayer coverage. Similar phenomena have been observed with V–Zr oxide catalysts.[11]

Structure, Surface Acidity and Catalytic Activity

As described above, we can conclude that polymolybdates formed on ZrO_2 support are active sites for the decomposition of propan-2-ol. As reported previously,[5] MOZ7.5 has sites with high Brønsted acidity, while MOZ3.0 has only Lewis-acid and little or no Brønsted-acid sites. FTIR studies have revealed the reaction pathway for dehydrogenation of propan-2-ol, *i.e.*, the isopropoxide species adsorbed on a Lewis-acidic site[13] is dehydrogenated acetone which is oxidized to the carboxylate *via* the enolate species.

For the dehydration reaction, different mechanisms have been reported by many workers. In those cases, surface OH groups, which act as Brønsted-acidic sites, are involved in the reaction pathway. Zaki and Sheppard[17] have reported that the dehydration activity depends both on the strength of Brønsted acidity and on the number of Lewis-acidic sites. Bond and Flamerz[23] suggest that dehydration requires only acidic OH groups, which may be present on the basal surface as a consequence of the hydration of V=O and V—O—V groups. Propene produced by the dehydration reaction seems to be more weakly interacted with the catalyst surface than is acetone. Thus, we could observe only dehydrogenation products.

Previously,[5] we have reported that the surface Mo=O species and Lewis-acidic sites on MOZ7.5 easily convert to Brønsted-acidic sites under reaction conditions. Thus, it is believed that the Brønsted-acidic sites play an important role in the dehydration reaction of propan-2-ol. As judged from the position (998 cm^{-1}) of the Mo=O bond, MOZ3.0 has a weakened Mo=O bond and the Mo=O species are affected by the presence of reactants and products during the oxidation reaction. In other words, the Mo=O species of MOZ3.0 have stronger basic properties than MOZ7.5 and MOZ11.0. Thus propan-2-ol dehydrogenation reactions take place more easily on the MOZ3.0 catalyst.

The position, at 1006 cm^{-1}, of the Mo=O stretching mode for calcined MOZ7.5 compared with that at 998 cm^{-1} for calcined MOZ3.0 suggests that previous interpretations[6,10] concerning aggregate size- or symmetry-dependent frequency shifts may still be realistic. However, the mode of interaction between reactant and the surface molybdate is still not understood; its elucidation will provide fundamental insight into the interaction of metal oxides with support oxides.

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