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Structure and catalytic properties of silica-supported Mo–Pr oxide catalysts for propene selective oxidation

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A study relating catalytic properties and structural characteristics of Mo–Pr oxide catalysts supported on silica, with Mo/(Mo + Pr) atomic ratios between 0 and 1, has been carried out. Catalytic activity for propene oxidation and selectivities to partial oxidation products were maximal in the atomic ratio range 0.8 to 1.0. The infra-red study of pyridine adsorption showed a maximum of surface acidity for the most active and selective catalysts. X-ray diffraction showed the amorphous character of phases present in the supported catalysts, despite the high active phase loading (20 wt%). FT-IR and Raman spectra showed the presence of surface polymolybdates of both octahedral and tetrahedral types of symmetry, as well as finely-divided 'free MoO_3'. The high activity and selectivity are associated with the presence of highly-dispersed polymolybdates with acidic characteristics, while praseodymium oxide is thought to have a role in oxygen activation on basic centres.

1. Introduction

The selective catalytic oxidation of olefins has been extensively studied due to its importance in the petrochemical industry. Molybdenum trioxide is an essential component of the most active and selective catalysts for propene oxidation to acrolein, and various reviews on this subject have been published in recent years [1–3]. Lattice oxygen ions are generally considered to be responsible for catalytic activity and selectivity [4]. Due to this, the structural characteristics of catalytic materials play an especially important role in selective olefin oxidation.

On the other hand, rare earth oxides catalyse a number of reactions [5], including oxidation reactions [6]. Among these oxides, praseodymium oxide has received special interest due to the high mobility of its lattice oxygens [7–9]. Kim and Weller [10] have recently reported the existence of an important promoting effect of praseodymium on molybdena-alumina for the oxidative dehydrogenation of ethylbenzene.

In a previous work [11], the influence on catalytic properties for propene oxidation of incorporating praseodymium oxide onto MoO_3 was studied. Maxima of catalytic activity and selectivity to partial oxidation products were observed in the Mo/(Mo + Pr) atomic ratio range 0.80 to 0.88. In the present work, Mo–Pr oxide catalysts supported on silica were prepared, and their catalytic properties for propene oxidation were studied. This work is mainly concerned with establishing the relationships between the structure and catalytic behaviour of these mixed oxides. Thus, the structure of the supported catalysts is characterized by means of spectroscopic techniques. In the case of techniques, such as Infrared or Raman spectroscopies, which have not been used previously for characterizing the unsupported catalysts, spectra of both unsupported and silica-supported catalysts are discussed together in order to compare the structural and catalytic features of both types of solids.

2. Experimental procedure

2.1. Catalyst preparation

Unsupported catalysts were prepared by evaporating until dry solutions of ammonium heptamolybdate and/or praseodymium nitrate, then calcinating in a forced flow of air at 823 K for 16 h. Catalyst compositions and surface areas are reported elsewhere [11]. A sample of Pr_2O_3, used for comparative purposes, was prepared by reducing Pr_6O_{11} in a 99.998% pure hydrogen stream ($50\,cm^3\,min^{-1}$) at 873 K for 4 h.

For supported catalysts, we used a silica (BASF D-11-11), pretreated in air at 1073 K for 4 h, with a surface area of $135\,m^2\,g^{-1}$, a pore volume of $0.39\,cm^3\,g^{-1}$ and a particle size between 0.42 and 0.59 mm. Reagents were $(NH)_4)_6Mo_7O_{24} \cdot 6H_2O$ (Merck), and $Pr(NO_3)_3 \cdot 5H_2O$ (Fluka). Molybdenum or praseodymium-containing catalysts were prepared by the incipient wetness method, the concentration of solutions

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being selected in order to have a final MoO_3 or Pr_6O_{11} content of 20 wt %. The remaining liquid was eliminated in a rotary evaporator at 323 K with a residual pressure of ~27 kPa. Solids were subsequently dried at 383 K for 16 h, and then calcined in a forced flow of purified air at 723 K for 4 h (Mo/Si) or 823 K for 16 h (Pr/Si).

In the case of mixed Mo–Pr/Si oxide catalysts, a double impregnation method was used, the first impregnation being carried out with an aqueous solution of ammonium heptamolybdate, and the second one with an aqueous solution of praseodymium nitrate. Concentrations of solutions were selected in order to obtain Mo/(Mo + Pr) atomic ratios ranging between 0 and 1 (Table I), and a total active phase (MoO_3 + Pr_6O_{11}) content of 20 wt %. Drying and calcination were the same as in the case of Pr/Si catalyst preparation.

2.2. Measurement of catalytic properties

For the determination of catalytic activity and selectivity, 1-gram catalyst samples (with a particle size in the range 0.42 to 0.59 mm) were mixed with SiC (having the same particle size) in the ratio catalyst: SiC = 1:4 (by volume). Experiments were carried out in the temperature range 573 to 703 K. The molar ratio present in the reactant mixture was $C_3H_6:O_2:He:H_2O = 20:30:30:20$. The contact time was $(W/F) = 30\,g_{cat}\,h\,mol^{-1}_{C_3H_6}$. Details of the experimental technique can be found elsewhere [12].

2.3. Catalyst characterization

Surface areas of the supported catalysts were determined by the BET method from adsorption isotherms of nitrogen at 77 K in a Micromeritics 2100-D apparatus. A value of $0.162\,nm^2$ was used for the cross-sectional area of nitrogen molecule. Surface area data are reported in Table I.

Surface acidity measurements were carried out by infra-red spectroscopy of pyridine adsorbed on catalyst surfaces. Samples were prepared in thin pellets ($\sim 0.013\,g\,cm^{-2}$) pressed at 2×10^5 kPa. Prior to carrying out the adsorption step, pellets were outgassed at 573 K and 0.13 to 1.33 Pa. They were then cooled down to room temperature and pyridine vapour was admitted at a pressure of 2.13 kPa. The contact time for adsorbate-pyridine was 30 min, followed by outgassing at room temperature for an additional 30 min. The spectral region of 1800 to $1000\,cm^{-1}$, corresponding to species associated to Brönsted and Lewis acid centres, was studied. A Perkin–Elmer 683 spectrometer was used for recording the spectra.

X-ray diffraction patterns of the catalysts were obtained with a Philips PW-1060 powder diffractometer, using nickel-filtered CuK_α radiation. FT-IR spectra of the solid catalysts were recorded in a Perkin–Elmer 1750 spectrometer. KBr pellets containing 1 wt % catalyst (total weight of pellet, 120 mg) were used. Spectra reported are the result of co-adding 50 interferograms, with a spectral resolution of $1\,cm^{-1}$.

Raman spectra were obtained in a Jewell–Ash 25–300 spectrometer. The emission line from an Ar^+ laser (Spectra Physics 165) was used for excitation. The output power of the laser was reduced to 75 to 150 mW. The sensitivity was adjusted according to the intensity of Raman scattering. Wave numbers reported in the spectra are accurate within $\sim 2\,cm^{-1}$.

3. Results and discussion

3.1. Catalytic activity and selectivity

Table I summarizes the catalytic properties for propene oxidation of Mo–Pr–O/SiO_2 catalysts with different Mo : Pr ratios. The T_s ($x_T = 5\%$) parameter is the temperature necessary to reach a total conversion of 5%. The variables s_{acrol} and s_{acet} are the selectivities to acrolein and acetaldehyde, respectively, at a conversion of 5%.

As can be seen in Table I, two maxima of catalytic activity (minimum T_s values) were obtained for catalysts with Mo/(Mo + Pr) ratios equal to 0.89 and 0.20. Optimal selectivity to acrolein was obtained for the catalyst MoPrSi–0.95, while selectivity to acetaldehyde reached a maximum value in the case of a MoPrSi–0.80 catalyst. The rest of the reaction products were carbon monoxide, carbon dioxide and small amounts of ethene. Thus, the highest values of catalytic activity and selectivity to partial oxidation products were obtained for catalyst compositions rich in molybdenum, similar to the one (Mo/(Mo + Pr) =

TABLE I Composition, surface areas and catalytic properties of Mo–Pr–O/SiO_2 catalysts

Catalyst	Mo/(Mo + Pr) atomic ratio	S_{BET} ($m^2\,g^{-1}$)	T (K) ($x_T = 5\%$)	Temperature coefficient ($kcal\,mol^{-1}$)	s_{acrol} (%) ($x_T = 5\%$)	s_{acet} (%) ($x_T = 5\%$)
MoPrSi–0.00	0.00	85	649	32	0	6
MoPrSi–0.05	0.05	86	661	27	1	5
MoPrSi–0.09	0.09	87	660	28	2	6
MoPrSi–0.15	0.15	83	637	32	2	10
MoPrSi–0.20	0.20	77	621	21	4	11
MoPrSi–0.27	0.27	82	631	21	10	13
MoPrSi–0.43	0.43	69	629	21	8	17
MoPrSi–0.57	0.57	71	629	21	8	15
MoPrSi–0.73	0.73	74	619	15	10	24
MoPrSi–0.80	0.80	71	611	15	12	29
MoPrSi–0.89	0.89	91	597	13	15	24
MoPrSi–0.91	0.91	87	608	14	16	24
MoPrSi–0.95	0.95	77	631	15	20	24
MoPrSi–1.00	1.00	106	666	25	8	24

0.89) which showed the highest activity and selectivity to acrolein in the case of unsupported catalysts [11].

It is also interesting to examine the variation of the temperature coefficient (obtained from an Arrhenius fit of kinetic results for the catalytic reaction) for catalysts with different compositions. The lowest values of the temperature coefficient are found (Table I) for Mo/(Mo + Pr), atomic ratios in the range 0.73 to 0.95, the minimum value being obtained for the MoPrSi–0.89 catalyst.

3.2. Surface acidity

Spectrum (a) of Fig. 1 corresponds to the MoPrSi–0.89 catalyst without adsorbed pyridine. This was taken as a base spectrum for studying the surface acidic properties as a function of catalyst composition. For the rest of the catalysts outgassed prior to adsorbing pyridine, very similar spectra were obtained in this wave number range.

After pyridine adsorption, bands at 1545 and 1490 cm^{-1} (associated to Brönsted acid centres) and at 1455 cm^{-1} (due to vibrations of pyridine molecules adsorbed on Lewis centres [13]) were found. While spectrum (b) (MoPrSi–0.00 catalyst) only shows a wide band at 1490 cm^{-1}, the other bands progressively develop in spectra (c) to (f) of Fig. 1. Spectrum (f) (MoPrSi–0.89 catalyst) shows the most intense bands, namely two sharp bands at 1490 and 1455 cm^{-1} and a wider band centred at 1545 cm^{-1}.

According to band intensities, we can establish the following surface acidity order for the different catalysts: MoPrSi–0.89 > MoPrSi–0.27 > MoPrSi–1.00 > MoPrSi–0.57 > MoPrSi–0.00. First we observe for some compositions, an increase of catalyst acidity when a basic component such as praseodymium oxide is added to molybdena. This kind of behaviour has been observed previously, for example when bismuth oxide is added [14]. On the other hand, surface acidity reaches a maximum value for the most active and selective catalysts for oxidation of propene to acrolein. The reason for this should lie in the fact that the activation of propene (electron donor) and oxygen (electron acceptor) are governed, respectively, by the acidic and basic properties of the catalyst [15]. Thus the most acidic catalysts will be the most selective ones to acrolein; otherwise, oxygen activation on basic centres should predominate leading to total oxidation products. This agrees, in turn, with the high stability of acrolein adsorbed on highly acidic Mo–Bi–P–O catalysts reported by Ai and Suzuki [16].

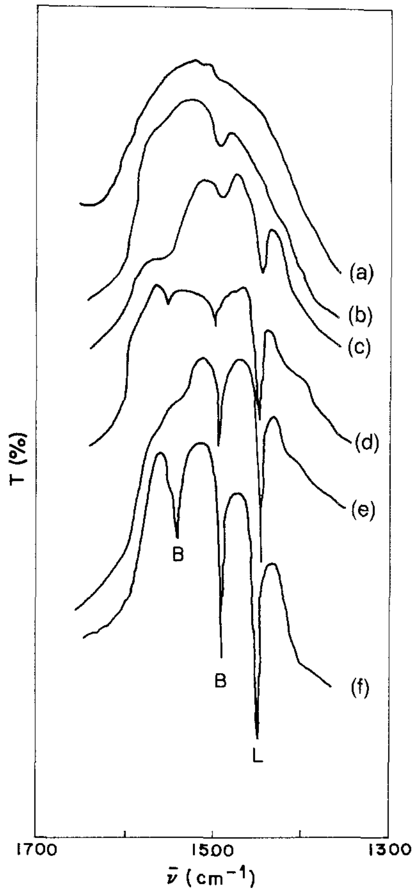

Figure 1 Infra-red spectra of pyridine adsorption on catalysts. (a), MoPrSi–0.89 catalyst prior to pyridine adsorption. (b) to (f), spectra after pyridine adsorption on catalysts with Mo/(Mo + Pr) atomic ratios of (b) 0.00, (c) 0.57, (d) 1.00, (e) 0.27 and (f) 0.89.

3.3. X-ray diffraction

X-ray diffractograms of silica-supported Mo–Pr oxide catalysts (not shown) only exhibited peaks of orthorhombic MoO_3 in the case of the MoPrSi–1.00 catalyst, which does not contain any praseodymium. In the rest of the catalysts no peaks at all were observed, except a very broad band due to silica support. This indicates that badly crystallized phases and/or very small crystals are present in mixed Mo–Pr-supported catalysts. Jeziorowski *et al.* [17] have indicated that molybdena supported on silica is detectable by X-ray diffraction in catalysts with a MoO_3 content higher than 8.2 wt %. In the present study, MoO_3 is not detectable despite its high concentration; this suggests that praseodymium may act as a very effective dispersing agent.

3.4. Infrared spectroscopy

3.4.1. Unsupported catalysts

FT–IR spectra of praseodymium-rich catalysts showed a number of bands which could be ascribed to carbonate species. This is probably associated to the basic character of lanthanoid oxides, which adsorb carbon dioxide from the atmosphere. In spectra (a) to (c) of Fig. 2, strong bands appearing at 1483 and 1387 cm^{-1} are ascribable to the splitting of the doubly-degenerate band at 1440 cm^{-1} of free CO_3^{2-} ions, and correspond to the antisymmetric and symmetric stretching vibration modes, respectively, of a monodentate carbonate species, in analogy with the behaviour of CO_2 adsorbed on perovskite-type oxides [18]. Bands at 1192, 1103, 1064 and 854 cm^{-1} are also attributable to monodentate carbonate species.

Thus, apart from carbonate bands in spectrum (a), only a band at 596 cm^{-1} remains ascribable to the Pr–O bonding in the solid. The position of this band agrees with that found by Petru and Muck [19], which is in turn very near (within 1.2%) the frequency determined by the same authors using the harmonic oscillator model. Nonetheless, bands reported by other authors [20–22] for Pr_6O_{11} and other C-type rare-earth oxides fall in other spectral regions. There-

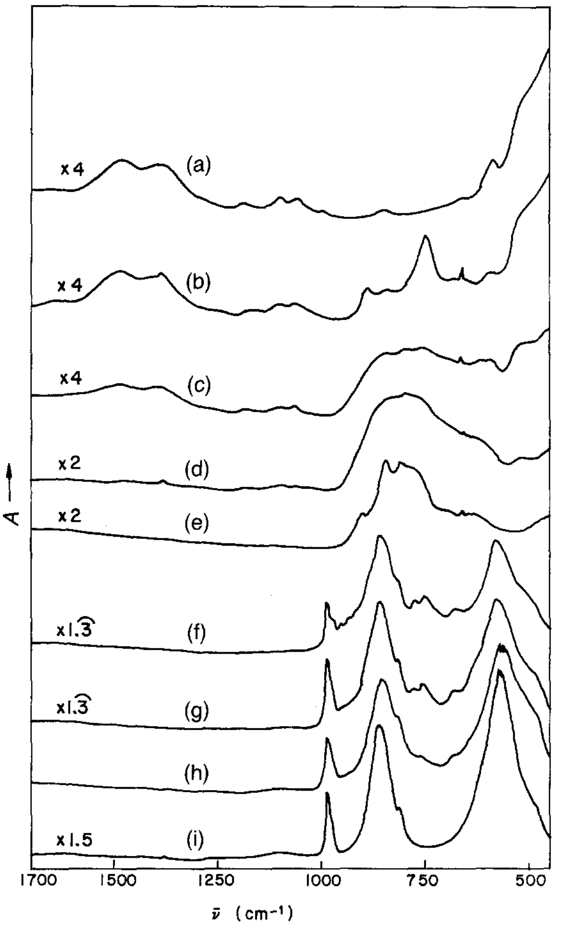

Figure 2 FT–IR spectra of unsupported Mo–Pr oxide catalysts with Mo/(Mo + Pr) atomic ratios of (a) 0.00, (b) 0.09, (c) 0.27, (d) 0.43, (f) 0.80, (g) 0.89, (h) 0.95 and (i) 1.00. Spectrum (e) corresponds to the catalyst with a ratio of 0.43 (d) heated to 1273 K.

fore infrared spectra of lanthanoid oxides commonly exhibit very broad bands which cannot be unequivocally ascribed to any specific bond vibration.

For low Mo/(Mo + Pr) ratios, broad bands (896, 806 and 754 cm^{-1}) were obtained which did not permit any specific assignment to be made (spectra (b) to (d) of Fig. 2). The resolution was slightly improved in the spectrum of the MoPr–0.43 catalyst heated at 1273 K in order to favour the formation of molybdate species. This resulted in bands at 906, 862, 806, 725 (shoulder) and 650 cm^{-1}, spectrum (e), which are near to the MoO$_3$ and polymolybdate bands reported below.

Much more important differences are evident in catalysts with increasing molybdenum contents, starting with an atomic ratio Mo/(Mo + Pr) equal to 0.80. The main bands show the characteric features of MoO$_3$. Spectrum (i), which corresponds to a catalyst which does not contain any praseodymium, is identical to those reported in previous works [23, 24] for MoO$_3$. Spectra (f) to (h) show some additional features. First, for increasing praseodymium contents, a progressive inversion of the relative intensities of bands at 870 and 570 cm^{-1} takes place. The same phenomenon can be observed in spectra reported by Vergnon *et al.* [24] for samples of very divided (particle size, 30 to 200 nm; surface area, 100 m^2 g^{-1}) nonporous MoO$_3$ obtained by the flame-reactor method, with respect to the spectrum of a conventional low-surface-area MoO$_3$. This fact seems to be associated with the state of division of the solid, which would cause a distortion of MoO$_3$ octahedra, with elongation in the *xz* plane and shortening along the *y* axis. The resulting polymorphic variety would be responsible for a number of small bands (those at 962, 783 and 762 cm^{-1}, for the catalyst with an atomic ratio Mo/(Mo + Pr) equal to 0.80), which fall within the ranges usually ascribed to polymolybdate species [25, 26].

On the other hand, the intensity of the Mo = O band at 996 cm^{-1} does not vary appreciably with decreasing molybdenum loading, although some decrease would be expected in the intensity of this band with a decrease of crystallinity of MoO$_3$, according to Okamoto *et al.*'s results [27]. Therefore the constancy of intensity of the Mo = O band is consistent with the fact that selectivity for partial oxidation showed a maximum for these catalysts, since according to Trifirò and Pasquon [28] this selectivity is associated with terminal Mo = O bonds.

3.4.2. *Silica-supported catalysts*

In the case of catalysts with high praseodymium contents (spectra (b) and (c) of Fig. 3), no spectral

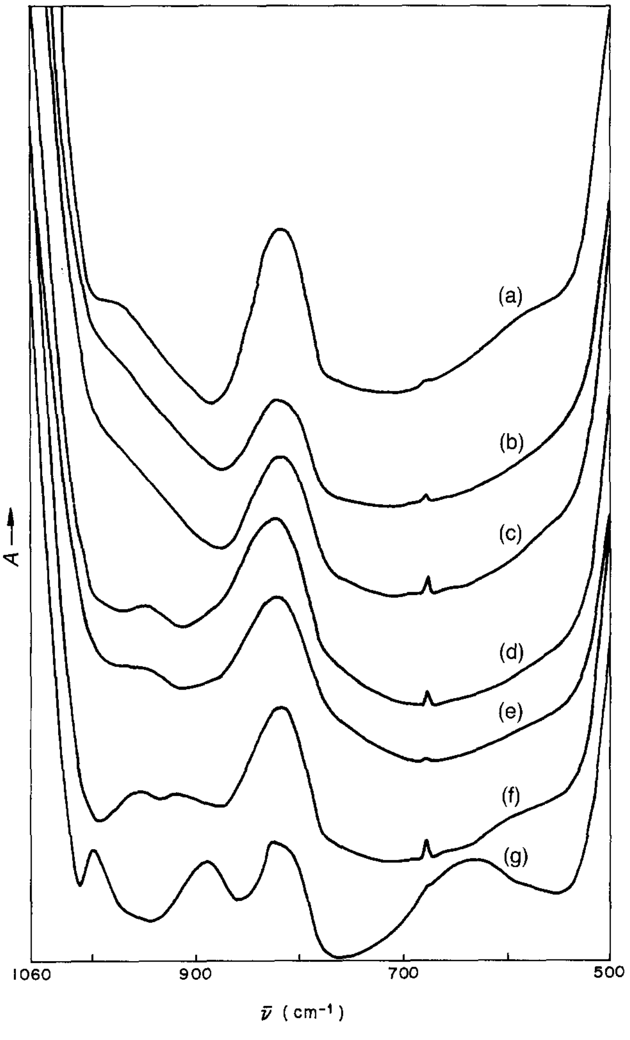

Figure 3 FT–IR spectra of silica-supported Mo–Pr oxide catalysts with Mo/(Mo + Pr) atomic ratios of (b) 0.00, (c) 0.15, (d) 0.43, (e) 0.57, (f) 0.89 and (g) 1.00. Spectrum (a) corresponds to pure silica support.

features different from those corresponding to pure silica support, spectrum (a), are observed. For higher molybdenum loadings, a band at 942 cm^{-1} appears, spectra (d) and (e), and a second band at 911 cm^{-1} develops in spectrum (f). Finally, spectrum (g), which corresponds to the catalyst containing only molybdenum, shows bands at 989, 882, 817 (shoulder) and 628 cm^{-1}. These bands appear at wave numbers close to those observed for pure MoO$_3$ (spectrum (i) of Fig. 2), and the shifts observed are likely due to the high degree of dispersion of this oxide supported on silica [25, 29].

According to previous studies, bands appearing in the range 1000 to 900 cm^{-1} in the IR spectra of the most active and selective catalysts are attributable to surface polymolybdate species. Seyedmonir *et al.* [30] found bands at 970 and 925 cm^{-1} in the FT-IR spectra of Mo–Si oxides, while Ono *et al.* [25], studying the same materials, attributed bands at 960 to 940, 925 and 905 cm^{-1} to polymolybdate species. Therefore, the presence of simpler (praseodymium) molybdate species, such as MoO$_4^{2-}$ or MoO$_4^{4-}$ is unlikely, since these only yield adsorption bands at wave numbers lower than 900 cm^{-1} [31, 32]. On the other hand, according to Czeskleba *et al.* [33, 34], praseodymium molybdates are only formed at high temperatures (1273 to 1673 K).

In a previous study [11], X-ray diffraction showed the presence of Pr$_2$O$_3$ in unsupported Mo–Pr catalysts. In order to check by FT–IR spectroscopy the presence of this phase in unsupported and/or supported catalysts, a sample of Pr$_2$O$_3$ was prepared by reducing Pr$_6$O$_{11}$ in a hydrogen stream at 873 K. In addition to a strong hydroxyl band at 3606 cm^{-1}, this solid yielded a strong band at 688 cm^{-1} which was absent from all the catalysts studied. A band at 669 cm^{-1}, appearing in the spectra of some catalysts, is merely due to atmospheric CO$_2$.

3.5. Raman spectroscopy

3.5.1. Unsupported catalysts

Spectrum (a) of Fig. 4, corresponding to a catalyst which contains only praseodymium, does not show any peaks at all and is only included as a reference. As molybdenum content increases, some bands appear, for example, spectrum (c) exhibits three wide bands centred at 850, 550 and 330 cm^{-1}, as well as a small band at 895 cm^{-1} and two sharp bands at 719 and 700 cm^{-1}. For increasing molybdenum loading a dramatic change in spectra takes place, bands in spectra (d) and (e) strongly resembling those of spectrum (f), which corresponds to pure molybdena. Spectrum (f) shows bands at 998, 820, 660, 380, 365, 340, 287, 280, 245, 220 and 199 cm^{-1}, all of them being ascribable to bulk MoO$_3$ according to a number of previous studies [35, 36].

The most interesting feature is the appearance of new bands (especially in the 1000 to 840 cm^{-1} range) in the spectra of the most active and selective catalysts. Thus, in spectra (d) and (e) new bands arise at 985, 950, 925, 895, 875, 860, 845 and 330 cm^{-1}; their intensities increase with praseodymium loading. As in the case of FT–IR spectra, appearance of bands in the 1000 to 840 cm^{-1} region can be ascribed to the presence of polymolybdate species. Bands at wave numbers higher than 900 cm^{-1} correspond to symmetric and antisymmetric Mo–O stretching modes, while bands in the 900 to 840 cm^{-1} range correspond to the antisymmetric stretching mode of Mo–O–Mo bridges [37, 38].

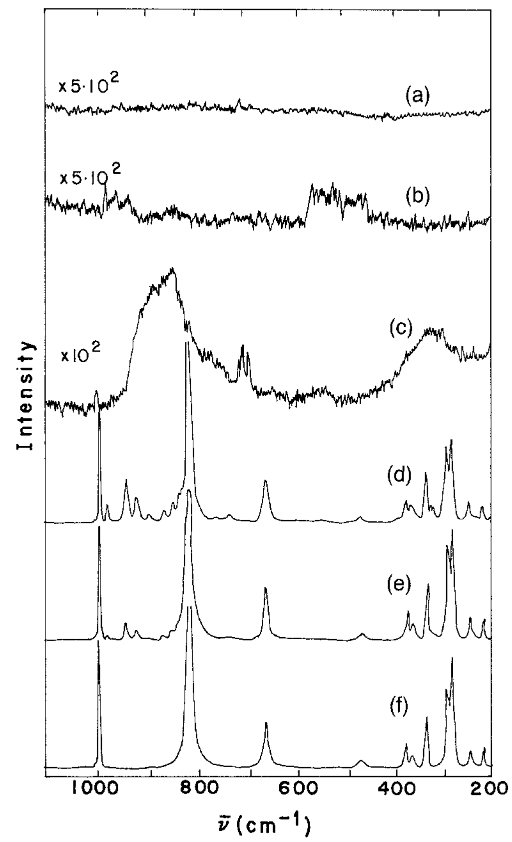

Figure 4 Raman spectra of unsupported Mo–Pr oxide catalysts with Mo/(Mo + Pr) atomic ratios of (a) 0.00, (b) 0.27, (c) 0.45, (d) 0.80, (e) 0.89 and (f) 1.00.

A further question concerns establishing the nature of these polymolybdates. It seems clear from the literature that bands at wave numbers higher than 945 cm^{-1} correspond to octahedral species, while bands at lower wave numbers correspond to tetrahedral species [36, 37]. According to this criterion, both types of species are present in the most active and selective Mo–Pr catalysts.

As in FT–IR spectra, some changes in the relative intensities of MoO$_3$ bands are observed in molybdenum-rich catalysts. This fact prompted us to calculate intensity ratios in the same way already done by other authors [17, 35, 38]. In the case of unsupported Mo–Pr catalysts, neither the I_{998}/I_{820} nor the I_{287}/I_{280} ratio showed a continuous trend, resulting in little information. However, Jeziorowski *et al.* [17] observed a decrease in I_{998}/I_{820} ratio for supported MoO$_3$ catalysts with respect to bulk molybdena, associated with the interaction of small crystallites of MoO$_3$ with the silica support.

3.5.2. Supported catalysts

Catalysts with high praseodymium loadings show wide bands which are difficult to interpret (spectra (a) to (c) of Fig. 5). For Mo/(Mo + Pr) atomic ratios

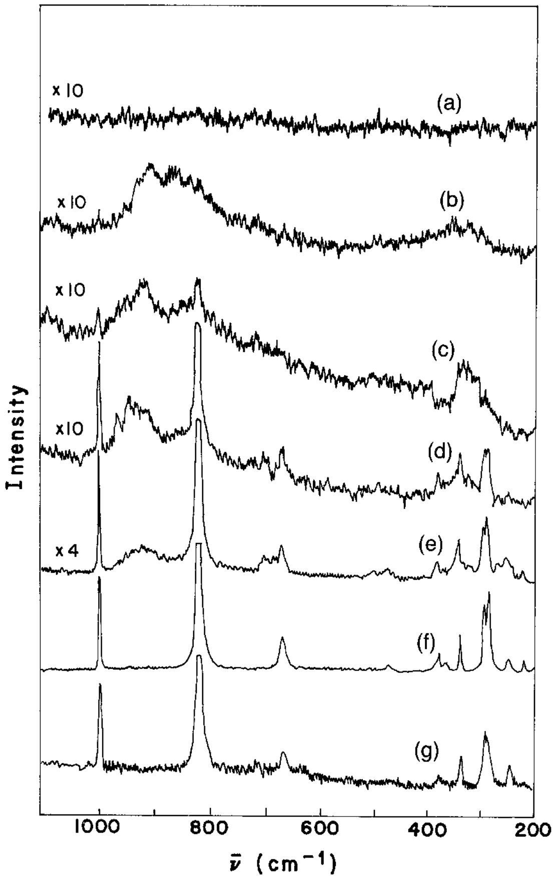

Figure 5 Raman spectra of silica-supported Mo–Pr oxide catalysts with Mo/(Mo + Pr) atomic ratios of (a) 0.00, (b) 0.15, (c) 0.27, (d) 0.43, (e) 0.57, (f) 0.89 and (g) 1.00.

larger than 0.4, peaks typical of MoO_3 and polymolybdates (as in the case of unsupported catalysts) are observed. Finally, in the spectrum of the MoPrSi–1.00 catalyst, which contains 20 wt % MoO_3 on silica, bands at wave numbers identical to those found in the unsupported catalyst (spectrum (g) of Fig. 4) are obtained.

Bands that can be ascribed to polymolybdate species are less well defined than in unsupported catalysts For example, spectra of catalysts in the Mo/(Mo + Pr) atomic ratio range 0.9 to 0.7 are virtually identical to the spectrum of pure molybdena supported on silica in the appearance of bands in the 1000 to 850 cm^{-1} range. A wide band centred at ~920 cm^{-1} appears in spectrum (e), while spectrum (d) shows a wide band along the 980 to 880 cm^{-1} range, where peaks at 970 and 950 cm^{-1} are superimposed.

Intensities of bands of 'free' MoO_3 at 998 and 820 cm^{-1} decrease with decreasing molybdenum content. Unlike the behaviour of relative band intensities of unsupported catalysts, the I_{998}/I_{820} and I_{287}/I_{280} ratios steadily decrease with molybdenum loading. Thus the presence of molybdenum trioxide in the form of small crystallites is clearly inferred. The broadening and splitting of MoO_3 bands also indicates a high degree of dispersion of this phase on the support. The incorporation of praseodymium oxide to the molybdena–silica system thus seems to have an effect similar to those of oxides of cobalt, nickel, manganese and others [17, 25, 26, 39, 40].

4. Conclusions

Mo–Pr oxide catalysts supported on silica exhibit a maximal surface acidity for those catalyst compositions (Mo/(Mo + Pr), atomic range 0.7 to 1.0) showing the highest activity and selectivity for partial oxidation. This is undoubtedly associated with the activation of the olefin on electron-acceptor centres of the catalyst, essentially molybdenum ions in various chemical environments and/or oxidation states.

X-ray diffraction failed to detect phases present in the catalysts, thus showing that they are essentially amorphous despite the high active phase concentration (20 wt %). Infra-red and Raman results evidence the presence of polymolybdate species in both unsupported and silica-supported types of catalysts. Moreover, 'free' molybdenum trioxide in the form of small, distorted crystals is detected by both techniques. Therefore it must be kept in mind that the polymolybdate species have a low specific adsorption coefficient for infra-red radiation, this being coupled to the fact that crystalline phases such as MoO_3 show much higher Raman intensities than surface species such as polymolybdates [25, 38, 41], so that MoO_3 is probably overestimated in both types of spectra.

Consequently, polymolybdates may play an important role in determining the acid–basic properties responsible for catalytic activity and selectivity. Praseodymium seems to act as a texture promoter, inducing the dispersion of molybdenum-containing phases. The high degree of dispersion of molybdenum ions in polymolybdates explains the simultaneous increase of catalytic activity and selectivity. On the other hand, praseodymium oxide is probably the phase carrying basic centres necessary for oxygen activation. The high basicity of praseodymium-rich catalysts (shown by the fact that they adsorb large amounts of CO_2) is probably associated with their low selectivity for partial oxidation, since highly basic centres cause excessive activation of oxygen, leading to an electron-rich species active for total oxidation [4]. The Pr_2O_3 phase, present in the most active and selective Mo–Pr catalysts (as previously shown by X-ray diffraction [11]), contains a low-mobility oxygen in its lattice which would favour oxidation to partial oxidation products.

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