

# Structure and Properties of Zirconia-Supported Molybdenum Oxide Catalysts for Oxidative Dehydrogenation of Propane

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Received June 29, 1999; revised October 6, 1999; accepted October 8, 1999

Oxidative dehydrogenation (ODH) of propane was studied on zirconia-supported molybdenum oxide catalysts. The structure of the  $ZrO_2$  support and of the dispersed  $MoO_x$  species was characterized by X-ray diffraction and by Raman and UV-visible spectroscopies. The structure of dispersed molybdena depends on the Mo surface density and on the temperature at which catalyst precursors are treated in air. Polymolybdate domains were detected by Raman at Mo surface densities below  $5 \text{ Mo/nm}^2$ . At higher surface densities,  $MoO_3$  and  $ZrMo_2O_8$  are present; their relative concentrations depend on the pretreatment temperature. Below 773 K,  $MoO_3$  is the predominant structure at high surface densities, but  $ZrMo_2O_8$  forms above 773 K. UV-visible edge energies decrease with increasing surface density for samples containing polymolybdate species, suggesting that  $MoO_x$  domains become larger as the Mo surface density increases. ODH turnover rates decrease with increasing Mo surface density on samples containing polymolybdate species and  $MoO_3$ . This trend is accompanied by an increase in the initial propene selectivity and in the vibrational frequency of  $Mo=O$  bonds. Higher  $Mo=O$  vibrational frequencies reflect stronger  $Mo=O$  bonds, which show lower ODH reactivity; therefore, the lower ODH reaction rates (per Mo atom) at higher Mo surface densities arise from the lower reactivity of  $Mo=O$  bonds, while higher initial propene selectivities arise either from the decrease of exposed  $Mo-O-Zr$  bonds or the lower reactivity of  $Mo=O$  bonds as the size of  $MoO_x$  domains increases with increasing Mo surface density. At similar Mo surface densities, samples containing predominantly  $ZrMo_2O_8/ZrO_2$  show higher turnover rates and lower initial propene selectivities than those containing  $MoO_3$  species because the vibrational frequency of the  $Mo=O$  bond for  $ZrMo_2O_8/ZrO_2$  is lower than that for  $MoO_3$ . ODH turnover rates over  $ZrMo_2O_8/ZrO_2$  also decreased with increasing Mo surface density, ultimately due to the increase of the particle size which leads to lower propane accessibility. © 2000

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## INTRODUCTION

Oxidative dehydrogenation (ODH) of light alkanes has been widely studied as a route to the corresponding alkenes.

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This process is thermodynamically favored at low temperatures and the presence of  $O_2$  inhibits the carbon deposition prevalent in nonoxidative routes. Many studies have addressed the structure of ODH catalysts (1–5). The most active and selective catalysts for propane ODH are based on supported vanadia (3). Mo oxides-based catalysts have also been examined for ODH (6–10), but less thoroughly than  $VO_x$ -based catalysts, because of their lower activity. On the other hand, catalysts such as  $Mo-Mg-O$  have shown high propene selectivity in propane ODH (7).

$ZrO_2$  is an excellent support for ODH catalysts because it can be prepared with high surface area ( $>300 \text{ m}^2/\text{g}$ ), and it is structurally stable and catalytically inactive (11, 12). Strong interactions between the surface of zirconium oxyhydroxide precursors and dispersed metal oxides such as  $VO_x$ ,  $MoO_x$ , and  $WO_x$  lead to stable dispersed oxides, even in the presence of water at high temperatures (13, 14). The structure of  $ZrO_2$ -supported  $VO_x$  species and their role in propane ODH have been discussed recently (14–16), but structure–function relations for dispersed  $MoO_x$  species remain less clear. Structural studies of dispersed  $MoO_x$  species show that a metastable monolayer consisting of polymolybdate species can be formed by treatment in air at around 773 K for surface densities lower than  $5 \text{ Mo/nm}^2$  (17–20). At higher Mo surface densities, bulk  $MoO_3$  and  $ZrMo_2O_8$  form and their relative abundance depends on the temperature of the air treatment (19).

This study examines the effects of Mo surface density and catalyst treatment temperature on the structure of  $MoO_x-ZrO_2$  catalysts and relates the structure of dispersed molybdate species to their catalytic activity and selectivity for the ODH of propane. The structures of a wide range of  $MoO_x-ZrO_2$  samples were determined by a combination of textural characterization and spectroscopic methods. The surface areas of the catalysts were determined by the BET method. X-ray diffraction (XRD), Raman spectroscopy, and UV-visible spectroscopy were used to probe the structure and electronic properties of dispersed  $MoO_x$  species. The catalytic properties of  $MoO_x-ZrO_2$  for propane ODH were determined using a flow reactor equipped with on-line

gas chromatographic analysis. Rate constants for primary and secondary reaction pathways were obtained by kinetic analysis of steady-state catalytic data and they were used to compare catalysts on the basis of intrinsic kinetic parameters.

## EXPERIMENTAL

Zirconium oxyhydroxide ( $\text{ZrO}(\text{OH})_2$ ) was prepared by precipitation from a zirconyl chloride solution (98%, Aldrich, Inc.) at a pH of 10 maintained constant by controlling the rate of addition of a solution of ammonium hydroxide (29.8%, Fischer Scientific, Inc.). After precipitation, the solids were washed with mildly basic ammonium hydroxide solution (pH of approximately 8) until the effluent showed no chloride ions by a silver nitrate test. The resulting solids were dried in air overnight at 393 K.

Zirconia-supported molybdena catalysts were prepared by incipient wetness impregnation of the precipitated zirconium oxyhydroxide with a solution of ammonium dimolybdate (ADM) (99%, Aldrich, Inc.) or ammonium heptamolybdate (AHM) (99%, Aldrich, Inc.). The pH of the impregnation solution was adjusted by adding nitric acid or ammonium hydroxide. The  $\text{Mo}^{6+}$  concentration in the impregnating solution was varied to change the Mo content in the final samples. After impregnation, samples were dried overnight in air at 393 K and treated in dry air (Airgas, zero grade) at 723, 773, or 873 K for 3 h. Unless otherwise noted, all samples were prepared by using ADM as the precursor, without pH modification by  $\text{HNO}_3$  or  $\text{NH}_4\text{OH}$ .

Surface areas were measured by  $\text{N}_2$  physisorption using a Quantasorb surface area analyzer (Quantachrome Corp.) and standard multipoint BET analysis methods. Samples were degassed for 3 h at 383 K before  $\text{N}_2$  (Airgas, 99.999%) physisorption measurements. Powder XRD patterns were obtained at room temperature using a Siemens diffractometer and  $\text{Cu } K\alpha$  radiation. A small amount of catalyst was mixed with Vaseline and spread out smoothly on a thin glass plate holder.

Raman spectra were recorded using a HoloLab series 5000 research Raman spectrometer (Kaiser Optical) equipped with a Nd:YAG laser that is frequency-doubled to 532 nm. Samples (~50 mg) were pressed into wafers at 350 MPa pressure (0.9-cm diameter; 0.1-cm thickness) and placed within a quartz cell (15). The laser was operated at a power level of 75 mW. All Raman spectra were recorded at ambient conditions.

Diffuse reflectance UV-vis spectra were recorded using a Varian-Cary 4 spectrophotometer equipped with a Harrick diffuse-reflectance attachment.  $\text{MgO}$  was used as a reference. Reflectance measurements were converted to absorption spectra using the Kubelka-Munk function. UV-vis spectra were measured in the range of 1.5–6.0 eV at ambient conditions.

Selectivity and rate measurements were carried out in a packed-bed tubular quartz reactor using 0.03- to 0.3-g catalyst samples at 703 K. Quartz powder was used as a diluent with  $\text{MoO}_x\text{-ZrO}_2$  catalysts to prevent temperature gradients within the catalyst bed. The reactants were propane (Airgas, 99.9%) and oxygen (Airgas, 99.999%) at 14.03 and 1.74 kPa, respectively, and He (Airgas, 99.999%) was used as a diluent. On-line analysis of reactants and products was performed using a Hewlett-Packard 6890 gas chromatograph. Detailed analysis procedures were reported previously (14, 15).

$\text{C}_3\text{H}_8$  and  $\text{O}_2$  conversions were varied by changing the reactant flow rate between 50 and 200  $\text{cm}^3/\text{min}$ . Typical propane conversions were less than 2% and oxygen conversions were kept below 20%. Reaction rates and selectivities were extrapolated to zero residence time to determine the rates and the rate constants for primary ODH and combustion reactions. The effect of bed residence time on product yields was used to calculate rates and rate constants for secondary propene combustion reactions, as reported elsewhere (14–16).

## RESULTS

Surface areas and Mo surface densities were measured for all  $\text{MoO}_x\text{-ZrO}_2$  samples after treatment in air at various temperatures and the results are shown in Figs. 1 and 2. At each treatment temperature, surface areas increased with increasing  $\text{MoO}_3$  loading up to 20 wt%, and then decreased at higher loadings (Fig. 1). Surface areas decreased with increasing air treatment temperatures for all  $\text{MoO}_3$  loadings.

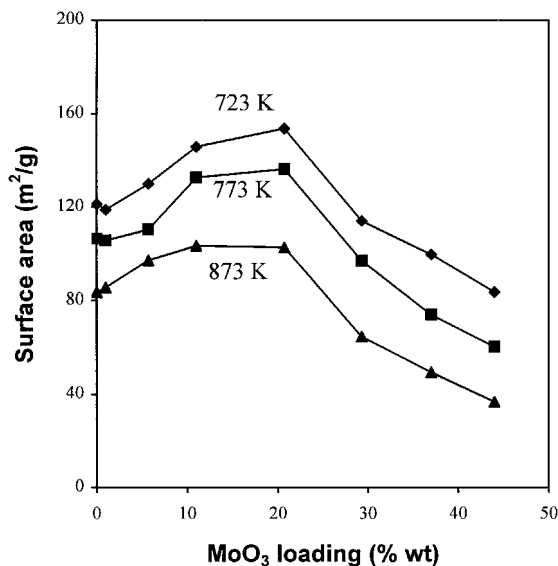


FIG. 1. BET surface areas of  $\text{MoO}_x\text{-ZrO}_2$  catalysts treated in air at various temperatures.

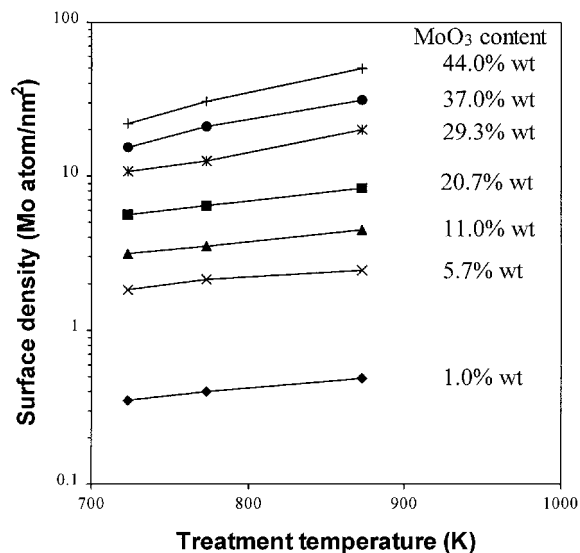


FIG. 2. Mo surface densities for  $\text{MoO}_x\text{-ZrO}_2$  catalysts with different  $\text{MoO}_3$  concentrations treated in air at different temperatures.

The Mo surface density is expressed as the number of Mo atoms per nanometer square of surface area ( $\text{Mo atoms/nm}^2$ ). It was obtained by the equation

$$\text{Mo surface density} = \frac{\text{MoO}_3 \text{ percentage} \times 6.02 \times 10^{23}}{\text{Surface area} \times 144 \times 10^{18}}$$

where the unit of the surface area is  $\text{m}^2/\text{g}$ . The effects of  $\text{MoO}_3$  loading and treatment temperature on the apparent Mo surface density are shown in Fig. 2. At each  $\text{MoO}_3$  loading, the Mo surface density increased with the calcination temperature because of the concomitant decrease in the  $\text{ZrO}_2$  surface area. Changing the initial pH of the impregnation solution from 2 to 10 had no effect on either the BET surface area or the Mo surface density for samples containing 1 wt%  $\text{MoO}_3$ .

The crystal structure of  $\text{MoO}_x\text{-ZrO}_2$  samples was probed by XRD (Figs. 3–6). Tetragonal and monoclinic phases of zirconia were detected in pure  $\text{ZrO}_2$  samples treated in air above 723 K. The intensity of the monoclinic peaks increased relative to that of peaks corresponding to tetragonal  $\text{ZrO}_2$  with increasing treatment temperatures (Fig. 3). The addition of small amounts of  $\text{MoO}_3$  to  $\text{ZrO}_2$  led to significantly higher tetragonal content at all treatment temperatures (Fig. 4). In  $\text{MoO}_x\text{-ZrO}_2$  samples with low  $\text{MoO}_3$  concentration (11 wt%  $\text{MoO}_3$ ), only tetragonal  $\text{ZrO}_2$  was observed and crystalline  $\text{MoO}_x$  phases were not detected by XRD (Fig. 5). At high  $\text{MoO}_3$  loadings (37 wt%  $\text{MoO}_3$ ), XRD patterns for  $\text{MoO}_x\text{-ZrO}_2$  depended strongly on the temperature of the air treatment (Fig. 6). Low temperature (723 K) led to the formation of crystalline  $\text{MoO}_3$ , while high temperature (873 K) led to the formation of a  $\text{ZrMo}_2\text{O}_8$

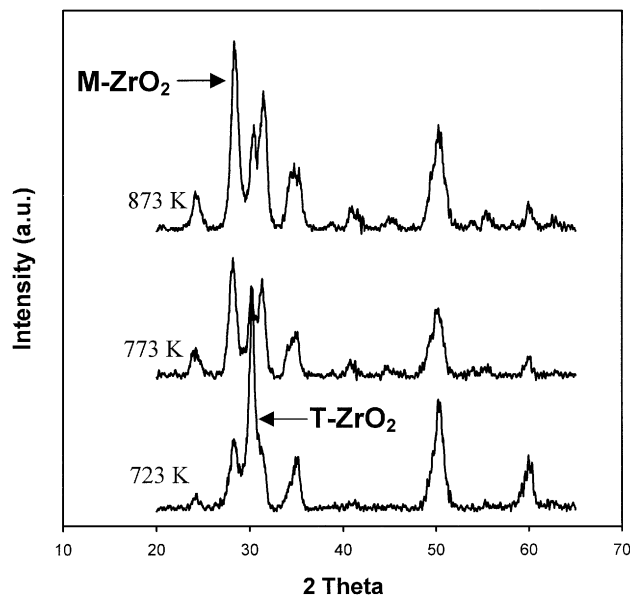


FIG. 3. XRD patterns of pure  $\text{ZrO}_2$  calcined at different temperatures.

phase. For the sample treated at 773 K, both crystalline  $\text{MoO}_3$  and  $\text{ZrMo}_2\text{O}_8$  were formed.

The Raman spectra of several  $\text{MoO}_x\text{-ZrO}_2$  samples are shown in Figs. 7–9. All samples with Mo surface densities lower than  $5 \text{ Mo/nm}^2$  showed similar Raman spectra (Fig. 7). A band at about  $829 \text{ cm}^{-1}$ , corresponding to Mo–O–Mo vibrations (19, 21), and a band at  $920\text{--}980 \text{ cm}^{-1}$ , assigned to Mo=O vibrations (19, 21–23) in two-dimensional polymolybdates, were detected in these samples. As

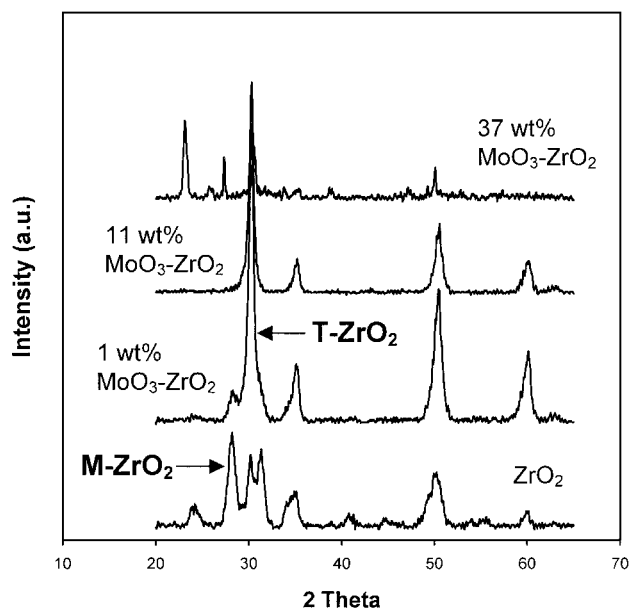


FIG. 4. XRD patterns of  $\text{MoO}_3\text{-ZrO}_2$  catalysts with different  $\text{MoO}_3$  concentrations treated in air at 773 K.

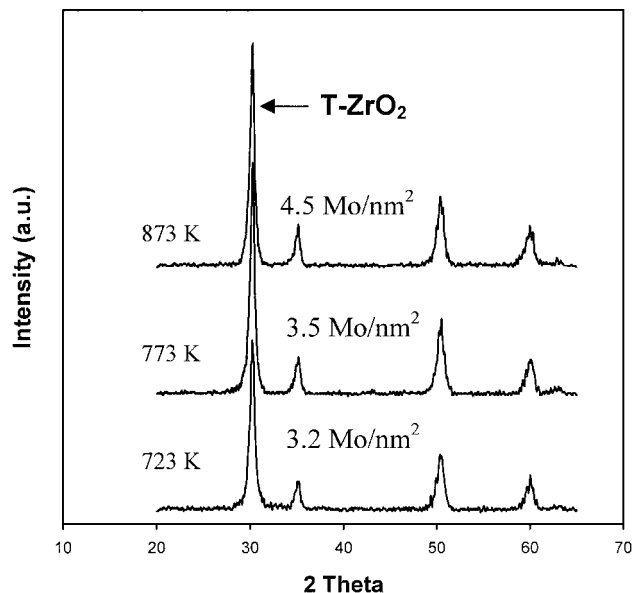


FIG. 5. XRD patterns of 11 wt% MoO<sub>3</sub>-ZrO<sub>2</sub> catalysts treated in air at different temperatures.

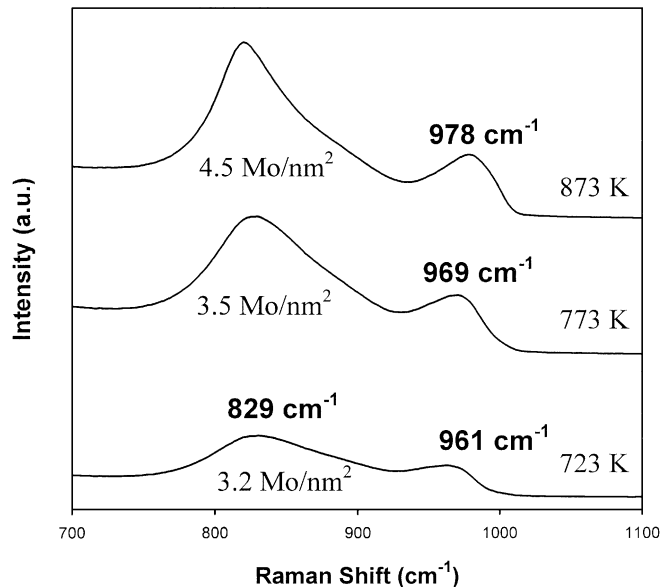


FIG. 7. Raman spectra of 11 wt% MoO<sub>3</sub>-ZrO<sub>2</sub> catalysts treated in air at different temperatures.

reported in earlier studies (19, 22, 23), the Mo=O band shifts from 920 to 980 cm<sup>-1</sup> with increasing Mo surface density. At high Mo surface densities (>10 Mo/nm<sup>2</sup>), the Raman spectrum (Fig. 8) depends strongly on the treatment temperature. Bands at 748, 945, and 1000 cm<sup>-1</sup>, assigned to ZrMo<sub>2</sub>O<sub>8</sub> (19, 21), were detected in all samples treated at 873 K, but a treatment at 723 K led only to the appearance of bands at 819 and 995 cm<sup>-1</sup>, corresponding to bulk MoO<sub>3</sub> (19, 21). The Raman spectra for samples with intermediate

Mo surface densities (5–10 Mo/nm<sup>2</sup>) (Fig. 9) were also influenced by the treatment temperature. After treatment at 873 K, bands were detected at 748, 945, and 1000 cm<sup>-1</sup> corresponding to ZrMo<sub>2</sub>O<sub>8</sub>; a band at 819 cm<sup>-1</sup>, assigned to bulk MoO<sub>3</sub>, was also observed. Another band for bulk MoO<sub>3</sub> (at 995 cm<sup>-1</sup>) was not clearly seen because it overlapped with the band at 1000 cm<sup>-1</sup> for ZrMo<sub>2</sub>O<sub>8</sub>. MoO<sub>x</sub>-ZrO<sub>2</sub> samples treated at 723 or 773 K showed a broad band at about 910 cm<sup>-1</sup>, with a shoulder at about 942 cm<sup>-1</sup>. Samples

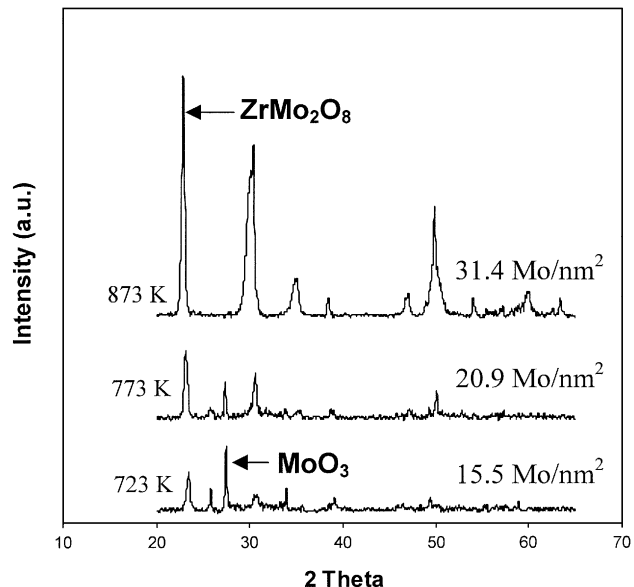


FIG. 6. XRD patterns of 37 wt% MoO<sub>3</sub>-ZrO<sub>2</sub> catalysts treated in air at different temperatures.

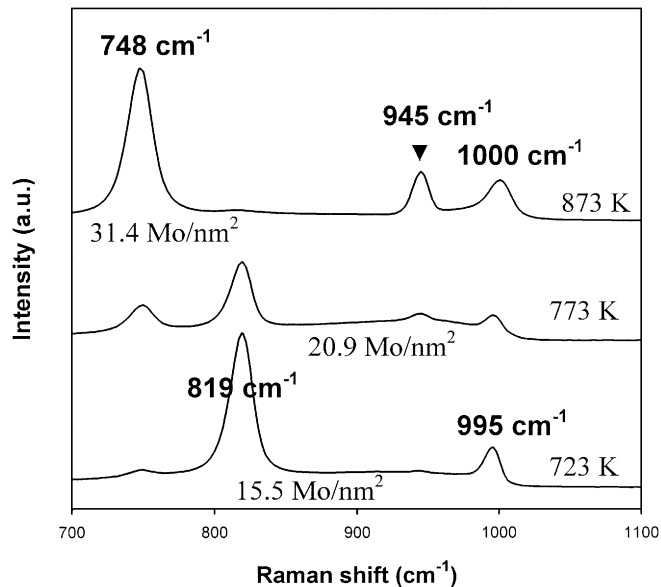


FIG. 8. Raman spectra of 37 wt% MoO<sub>3</sub>-ZrO<sub>2</sub> catalysts treated in air at different temperatures.

of 5.8 wt% MoO<sub>x</sub>/ZrO<sub>2</sub> prepared using ADM or AHM as precursors did not show detectable differences in their Raman spectra.

UV-visible absorption spectra reflect the electronic structure of valence bands in solids, but the broad nature of most charge transfer features prevalent in the spectra of metal oxides makes it difficult to define the position of these bands from the energy at maximum absorption. Absorption edge energies provide a more convenient description of the electronic properties of solids. The absorption edge in all UV-visible spectra was determined using Tauc's law for indirect and amorphous semiconductors using previously reported procedures (24). In this method, the absorption edge is defined as the intercept with the abscissa of the straight line describing the near-edge region for spectra plotted as  $[F(R_{\infty})hv]^{1/2}$ , where  $F(R_{\infty})$  is the Kubelka-Munk function (25) and  $hv$  is the energy of the incident photon. The position of the absorption edge for low-energy charge transfer transitions is shown to correlate with the domain size of oxides and other semiconductor and insulator materials (26–34). The absorption edge energy decreases with increasing domain size. This relationship was recently used to characterize the size of MoO<sub>x</sub> (33), WO<sub>x</sub> (26), and VO<sub>x</sub> (14, 15) domains in catalytic solids.

Diffuse reflectance UV-visible spectra of MoO<sub>x</sub>-ZrO<sub>2</sub> samples were measured and the absorption edge energies were calculated as described in the previous paragraph. The data are shown in Fig. 10 as a function of Mo surface density. Samples with very low Mo surface density ( $\sim 0.4$  Mo/nm<sup>2</sup>) show edge energies ( $\sim 3.46$  eV) much lower than that of ammonium dimolybdate (3.80 eV). The absorption edge energy decreased initially with increasing Mo surface den-

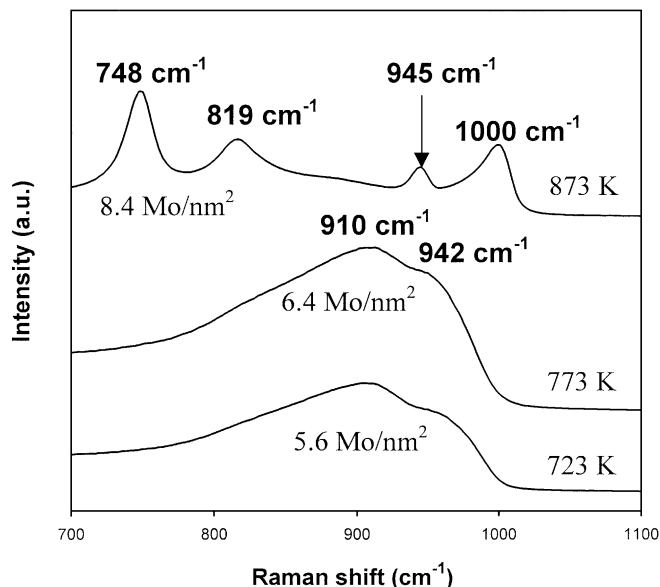


FIG. 9. Raman spectra of 20.7 wt% MoO<sub>3</sub>-ZrO<sub>2</sub> catalysts treated in air at different temperatures.

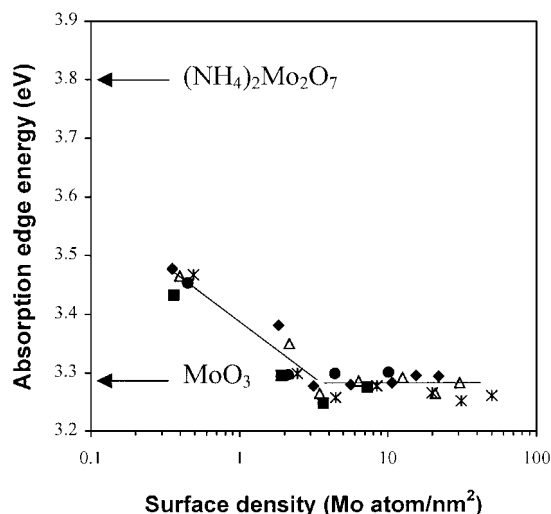


FIG. 10. Dependence of the UV-vis absorption edge energies on the Mo surface densities of MoO<sub>x</sub>-ZrO<sub>2</sub> catalysts prepared using ADM as the precursor (pretreated in air at 723 K (◆), 773 K (△), and 873 K (\*)), and using AHM as the precursor (pretreated in air at 773 K (■) and 873 K (●)).

sity, but then remained constant for Mo surface densities above 4 Mo/nm<sup>2</sup>. The absorption edge energies (3.30 eV) for the latter samples were similar to those measured for bulk MoO<sub>3</sub> crystallites (3.29 eV).

Raman and XRD data showed that zirconia-supported molybdena samples can be grouped into two classes, based on the structure of the MoO<sub>x</sub> species: (1) ZrMo<sub>2</sub>O<sub>8</sub>/ZrO<sub>2</sub> samples, which consist mainly of ZrMo<sub>2</sub>O<sub>8</sub> supported on ZrO<sub>2</sub> and include all samples treated in air at 873 K with Mo surface densities higher than 5 Mo/nm<sup>2</sup>, and (2) MoO<sub>x</sub>/ZrO<sub>2</sub> samples, which consist of MoO<sub>x</sub> species supported on ZrO<sub>2</sub> and include all samples treated in air at 723 and 773 K during synthesis as well as samples treated at 873 K but with Mo surface densities below 5 Mo/nm<sup>2</sup>.

The catalytic properties of all MoO<sub>x</sub>-ZrO<sub>2</sub> samples are reported in Figs. 11–13. Figure 11 shows the effect of bed residence time on C<sub>3</sub>H<sub>8</sub> conversion and on C<sub>3</sub>H<sub>6</sub>, CO, and CO<sub>2</sub> selectivities for 11 wt% MoO<sub>3</sub>/ZrO<sub>2</sub> treated in air at 773 K ( $n_s = 3.5$  Mo/nm<sup>2</sup>). The C<sub>3</sub>H<sub>6</sub> selectivity decreased and the CO and CO<sub>2</sub> selectivities increased with increasing bed residence time, suggesting that C<sub>3</sub>H<sub>6</sub> underwent secondary combustion reactions to form CO<sub>x</sub>.

Initial propane conversion rates (normalized by the number of Mo atoms) are reported in Fig. 12 as a function of Mo surface density. They are referred to as turnover rates, even though not all MoO<sub>x</sub> species are likely to be exposed at the surface of all samples. On MoO<sub>x</sub>/ZrO<sub>2</sub> samples, turnover rates for propane conversion decreased monotonically with increasing Mo surface density. These turnover rates depended only on Mo surface density but not on the temperature of the air treatment or on the precursor used to prepare the catalysts. On ZrMo<sub>2</sub>O<sub>8</sub>/ZrO<sub>2</sub>, the turnover

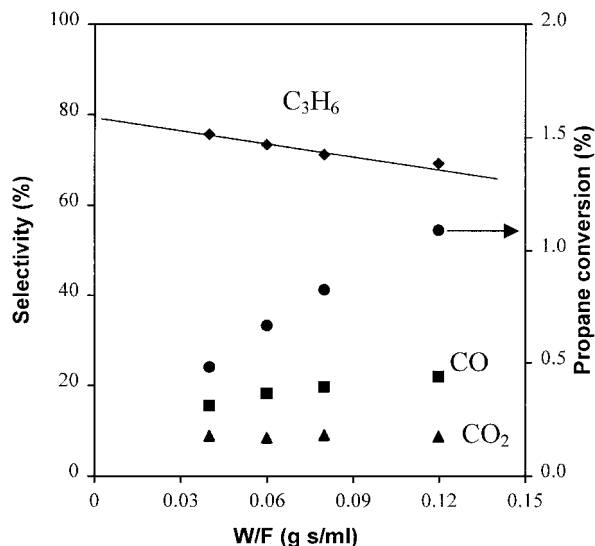


FIG. 11. Propane conversion and products selectivities for propane ODH on 11 wt% MoO<sub>3</sub>-ZrO<sub>2</sub> catalysts calcined at 773 K.

rates also decreased with increasing Mo surface density. At the same Mo surface density, however, the reaction rates on ZrMo<sub>2</sub>O<sub>8</sub>/ZrO<sub>2</sub> samples were higher than those on MoO<sub>x</sub>/ZrO<sub>2</sub> samples.

On MoO<sub>x</sub>/ZrO<sub>2</sub> samples with Mo surface densities below 10 Mo/nm<sup>2</sup>, the initial C<sub>3</sub>H<sub>6</sub> selectivity (extrapolated to zero residence time) increased with increasing Mo surface density (Fig. 13). Above 10 Mo/nm<sup>2</sup>, the initial C<sub>3</sub>H<sub>6</sub> selectivity was about 93%, and it did not depend on Mo sur-

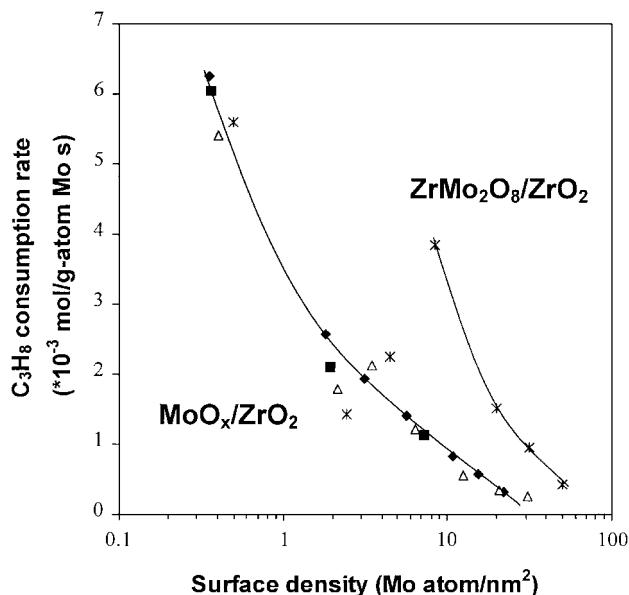


FIG. 12. Dependence of the propane consumption rates on the Mo surface densities of MoO<sub>x</sub>-ZrO<sub>2</sub> catalysts prepared using ADM as the precursor (pretreated in air at 723 K (◆), 773 K (△), and 873 K (\*)), and using AHM as the precursor (pretreated in air at 773 K (■)).

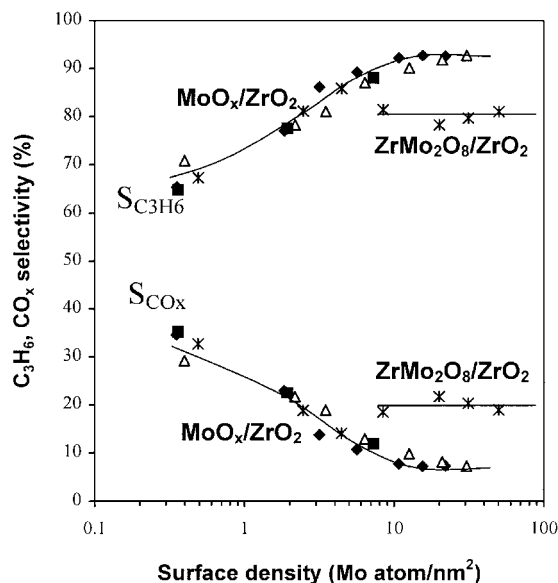


FIG. 13. Dependence of the propene and CO<sub>x</sub> selectivities on the Mo surface densities of MoO<sub>x</sub>-ZrO<sub>2</sub> catalysts prepared using ADM as the precursor (pretreated in air at 723 K (◆), 773 K (△), and 873 K (\*)), and using AHM as the precursor (pretreated in air at 773 K (■)).

face density. By contrast, the initial propene selectivity for ZrMo<sub>2</sub>O<sub>8</sub>/ZrO<sub>2</sub> remained constant (~80%) at all Mo surface densities.

## DISCUSSION

The initial dispersion of MoO<sub>x</sub> on the surface of zirconia influences both the surface area and the structure of the support. These effects are evident from the BET surface areas and the XRD data shown in Figs. 1–6. At MoO<sub>3</sub> loadings below 20 wt%, MoO<sub>x</sub> species inhibit sintering of ZrO<sub>2</sub> and its transformation from the tetragonal to the monoclinic phase. These results are similar to those reported previously for VO<sub>x</sub>/ZrO<sub>2</sub> (14) and WO<sub>x</sub>/ZrO<sub>2</sub> (35).

The structure of dispersed molybdena species depends on the Mo surface density and, in some cases, also on the temperature of treatment in air. For samples with surface densities below 5 Mo/nm<sup>2</sup>, Raman spectroscopy showed that MoO<sub>x</sub> species are present exclusively as two-dimensional polymolybdate species. The absence of XRD peaks of Mo-containing species in these samples confirms the absence of large MoO<sub>3</sub> or ZrMo<sub>2</sub>O<sub>8</sub> crystallites. The observed monotonic increase in the vibrational frequency of the Mo=O bond and the decrease in the UV-vis absorption edge energy are consistent with the growth of polymolybdate domains as the Mo surface density increases (23, 33). These conclusions are in agreement with those reported earlier by others (17–19).

For Mo surface densities above 10 Mo/nm<sup>2</sup>, the structure of the dispersed MoO<sub>x</sub> species depends strongly on the

treatment temperature. When samples were treated in air at 723 or 773 K, XRD and Raman spectroscopy detected bulk  $\text{MoO}_3$  crystallites. The UV-visible absorption edge energies in such samples (3.30 eV) were almost identical to those in bulk  $\text{MoO}_3$  (3.29 eV). Higher treatment temperatures (873 K) led to the disappearance of  $\text{MoO}_3$  and to the detection of  $\text{ZrMo}_2\text{O}_8$  in the XRD pattern and in the Raman spectrum.  $\text{ZrMo}_2\text{O}_8$  was not formed in samples with Mo surface densities below  $5 \text{ Mo/nm}^2$ , even when treated at 873 K. This suggests that the formation of  $\text{ZrMo}_2\text{O}_8$  requires  $\text{MoO}_3$  crystallites as a precursor, in agreement with earlier observation of Miyata *et al.* (36).

For Mo surface densities between 5 and  $10 \text{ Mo/nm}^2$ , the catalyst structure depended on the treatment temperature as well as on the Mo surface density. Raman spectroscopy showed no evidence for either  $\text{MoO}_3$  or  $\text{ZrMo}_2\text{O}_8$  when oxidation occurred below 773 K; only polymolybdate species independent of the temperature of the air treatment were observed. Since the anticipated Mo surface density for monolayer coverage of  $\text{ZrO}_2$  corresponds to  $5 \text{ Mo/nm}^2$  (17–19), three-dimensional polymolybdate structures should be formed at higher Mo surface densities. While the UV-visible absorption edge energy for  $\text{MoO}_x/\text{ZrO}_2$  samples with Mo surface densities above  $5 \text{ Mo/nm}^2$  oxidized at below 773 K is identical to that for  $\text{MoO}_3$ , the absence of  $\text{MoO}_3$  features in the Raman spectra of such samples suggests that the oxidation temperatures below 773 K are not high enough to transform the three-dimensional polymolybdate structures into  $\text{MoO}_3$  crystallites. Crystallites of  $\text{MoO}_3$  and  $\text{ZrMo}_2\text{O}_8$  were both detected by Raman spectroscopy and XRD when the treatment temperature was raised to 873 K, suggesting that both  $\text{MoO}_3$  and  $\text{ZrMo}_2\text{O}_8$  were formed at high temperatures.

The data in Figs. 12 and 13 show that propane conversion rates and product selectivities changed markedly when dispersed  $\text{MoO}_x$  species react with  $\text{ZrO}_2$  to form  $\text{ZrMo}_2\text{O}_8$ . Figure 12 shows that turnover rates for propane conversion decreased monotonically with increasing Mo surface density, but that for a given value of the apparent Mo surface density, turnover rates were higher on samples containing  $\text{ZrMo}_2\text{O}_8$  than on those containing predominantly  $\text{MoO}_3$  and polymolybdates. The decrease in turnover rates with increasing Mo surface density for samples with Mo surface densities lower than  $5 \text{ Mo/nm}^2$  is accompanied by an increase in the vibrational frequency of  $\text{Mo}=\text{O}$  Raman bands (shown in Fig. 14), which reflects an increase in the strength of the  $\text{Mo}=\text{O}$  bond and a decrease in the ODH reactivity. Since monolayer polymolybdate coverage on  $\text{ZrO}_2$  occurs at a Mo surface density of about  $5 \text{ Mo/nm}^2$  (17–19), the decrease in the apparent turnover rate with increasing surface density is unlikely to arise from a decrease in the availability of  $\text{Mo}-\text{O}$  species at the catalyst surface when the Mo surface density is lower than  $5 \text{ Mo/nm}^2$ . What is suggested instead is that the catalyst activity decreases as the two-dimensional

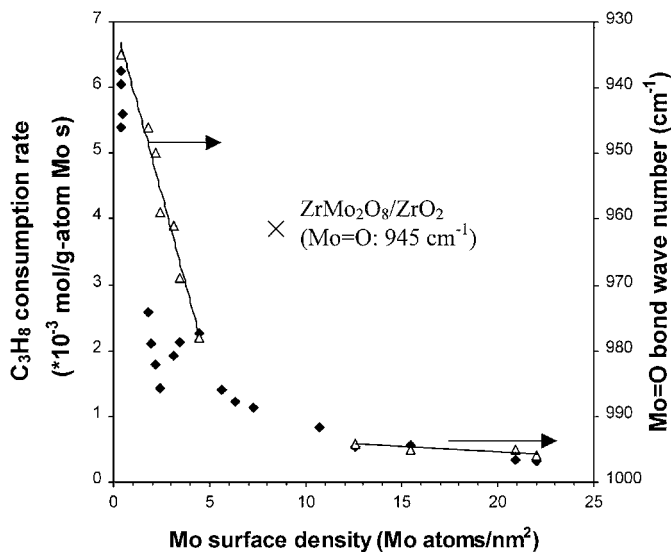


FIG. 14. Dependence of the propane conversion rate ( $\blacklozenge$ ) and  $\text{Mo}=\text{O}$  stretching frequency ( $\triangle$ ) on the Mo surface densities for  $\text{MoO}_x/\text{ZrO}_2$  samples. The ( $\times$ ) symbol represents the propane conversion rate on a  $\text{ZrMo}_2\text{O}_8/\text{ZrO}_2$  catalyst with a Mo surface density of  $8.4 \text{ Mo/nm}^2$ .

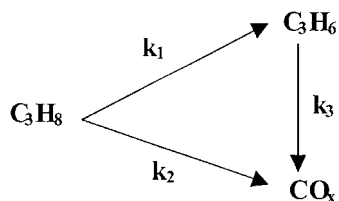
polymolybdate domains grow in size with increasing surface density. Since the rate-determining step in ODH involves activation of the C–H bond in  $\text{C}_3\text{H}_8$  using lattice oxygen atoms (16), it is reasonable to expect the ODH rate to depend on the strength of the  $\text{Mo}=\text{O}$  bond. For Mo surface densities above  $5 \text{ Mo/nm}^2$ , the observed decrease in the turnover rate is ascribed to the lower propane accessibility due to the formation of three-dimensional polymolybdate structures or small crystallite  $\text{MoO}_3$ .

$\text{MoO}_x$  species present in  $\text{ZrMo}_2\text{O}_8/\text{ZrO}_2$  give higher apparent turnover rates than three-dimensional polymolybdate species in  $\text{MoO}_x/\text{ZrO}_2$  of similar Mo surface densities (Fig. 12). The higher turnover rates on  $\text{ZrMo}_2\text{O}_8$  reflect the fact that the  $\text{Mo}=\text{O}$  bonds in this material are weaker than those in three-dimensional polymolybdate species. Structural analysis of  $\text{ZrMo}_2\text{O}_8$  shows that the  $\text{Mo}^{6+}$  cations are located in tetrahedral sites (37). Of the four oxygens surrounding each  $\text{Mo}^{6+}$  cation, one is bonded only to Mo while the other three are shared by a  $\text{Zr}^{4+}$  cation and a  $\text{Mo}^{6+}$  cation. The  $\text{Mo}-\text{O}$  bond length for the oxygen atom associated only with  $\text{Mo}^{6+}$  is 1.690 Å, and the other three  $\text{Mo}-\text{O}$  bonds have an average length of 1.764 Å. Based on a correlation reported between the  $\text{Mo}-\text{O}$  bond length and vibrational frequency (38), the shorter  $\text{Mo}-\text{O}$  bond in  $\text{ZrMo}_2\text{O}_8$  is assigned to  $\text{Mo}=\text{O}$  vibrations. The frequency at  $945 \text{ cm}^{-1}$  is considerably lower than that for  $\text{Mo}=\text{O}$  bonds in either  $\text{MoO}_3$  ( $995 \text{ cm}^{-1}$ ) or in a polymolybdate monolayer ( $985 \text{ cm}^{-1}$ ) (see Fig. 14). Following this logic, the apparent turnover rate of  $\text{ZrMo}_2\text{O}_8$  might be expected to be equivalent to that of polymolybdate species exhibiting a similar  $\text{Mo}=\text{O}$  bond vibrational frequency (Mo surface

density is  $\sim 2 \text{ Mo/nm}^2$ ). Figure 14 shows that the rate predicted by this means is about  $\sim 20\%$  higher than that measured for  $\text{ZrMo}_2\text{O}_8$ , which may be ascribed to the decrease in  $\text{Mo}=\text{O}$  availability as a consequence of the three-dimensional character of  $\text{ZrMo}_2\text{O}_8$ . The decrease in the apparent turnover rate (normalized to the total Mo content) with increasing Mo surface density also reflects the expected decrease in the dispersion of the supported  $\text{ZrMo}_2\text{O}_8$  crystallites as the Mo content increased or the total surface area decreased.

The data in Fig. 13 show that the selectivities to  $\text{C}_3\text{H}_6$  and  $\text{CO}_x$  also depend on whether  $\text{ZrMo}_2\text{O}_8$  or dispersed  $\text{MoO}_x$  species are present. On samples containing predominantly polymolybdate or  $\text{MoO}_3$  species, initial  $\text{C}_3\text{H}_6$  selectivities increased with increasing surface density and reached a constant value (93%) above  $10 \text{ Mo/nm}^2$ . On  $\text{ZrMo}_2\text{O}_8$  samples, the propene selectivity is lower than this value ( $\sim 80\%$ ), but independent of Mo surface density ( $10\text{--}50 \text{ Mo/nm}^2$ ). The gradual increase in  $\text{C}_3\text{H}_6$  selectivity with increasing Mo surface density suggests that high selectivity may require complete coverage of the  $\text{ZrO}_2$  surface by a mixture of molybdate oligomers; i.e., the exposure of the  $\text{Zr-O-Mo}$  bond is unfavorable for selective oxidation. Similar conclusions have also been obtained with  $\text{VO}_x/\text{ZrO}_2$  (14). The gradual increase in  $\text{C}_3\text{H}_6$  selectivity with increasing Mo surface density may also be related to the increase in the strength of  $\text{Mo}=\text{O}$  bonds in  $\text{MoO}_x$  species with increasing domain size—stronger  $\text{Mo}=\text{O}$  bonds being associated with higher selectivity, albeit lower activity. Consistent with these proposals,  $\text{ZrMo}_2\text{O}_8$  catalysts show  $\text{C}_3\text{H}_6$  selectivities lower than that of  $\text{MoO}_3$ . The absence of surface density effects on the initial  $\text{C}_3\text{H}_6$  selectivity of  $\text{ZrMo}_2\text{O}_8$ -containing samples confirms the proposal that  $\text{ZrMo}_2\text{O}_8$  domains increase in size with increasing Mo surface density without significant changes in their local structure or surface properties.

The observed effects of residence time on product selectivity (Fig. 11) are consistent with  $\text{C}_3\text{H}_8\text{-O}_2$  reactions occurring via parallel and sequential steps, as shown below.



Pseudo-first-order rate coefficients for primary dehydrogenation ( $k_1$ ) and combustion ( $k_2$ ) pathways and for secondary combustion of propene ( $k_3$ ) can be obtained from the measured effects of reactor residence time data on product concentrations (1–3). The assumption that all steps are proportional to the respective hydrocarbon concentra-

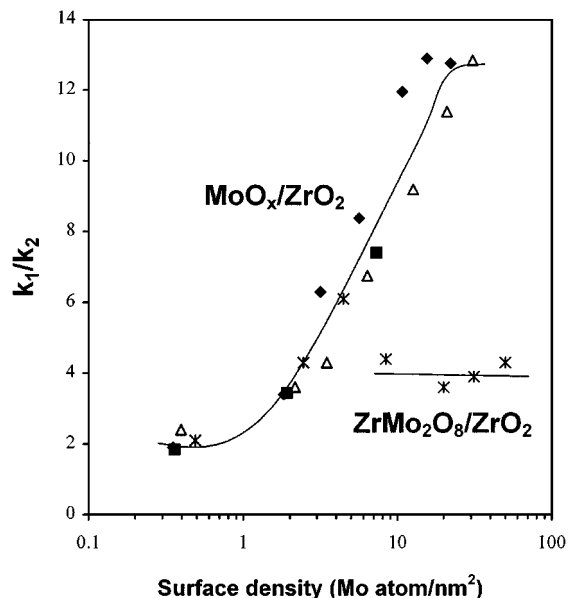


FIG. 15. Dependence of the  $k_1/k_2$  ratios on the Mo surface densities for  $\text{MoO}_x\text{-ZrO}_2$  catalysts prepared using ADM as the precursor (pretreated in air at 723 K ( $\blacklozenge$ ), 773 K ( $\triangle$ ), and 873 K ( $*$ )), and using AHM as the precursor (pretreated in air at 773 K ( $\blacksquare$ )).

tion was confirmed experimentally for  $\text{MoO}_x\text{-ZrO}_2$  catalysts.

Figures 15 and 16 show the effects of Mo surface density on  $k_1/k_2$  and  $k_3/k_1$ . The dependence of  $k_1/k_2$  on Mo surface density is very similar to that observed for the initial  $\text{C}_3\text{H}_6$  selectivity (Fig. 13), and it reflects the relative rates of ODH

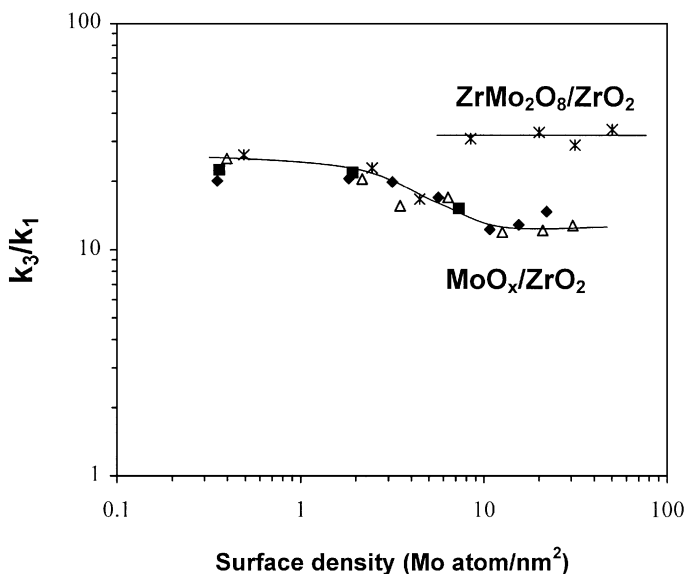


FIG. 16. Dependence of the  $k_3/k_1$  ratios on the Mo surface densities of  $\text{MoO}_x\text{-ZrO}_2$  catalysts prepared using ADM as the precursor (pretreated in air at 723 K ( $\blacklozenge$ ), 773 K ( $\triangle$ ), and 873 K ( $*$ )), and using AHM as the precursor (pretreated in air at 773 K ( $\blacksquare$ )).



and  $C_3H_8$  combustion reactions. On  $ZrMo_2O_8/ZrO_2$ ,  $k_1/k_2$  remained constant at a value of about 4 for the Mo surface densities of 10–50  $Mo/nm^2$ . On  $MoO_x/ZrO_2$ , however,  $k_1/k_2$  increased with increasing Mo surface density and reached a maximum value of about 13 for surface densities above 10  $Mo/nm^2$ . The  $k_1/k_2$  ratios measured on samples treated at 773 K were a little bit lower than those for samples treated in air at 723 K for all Mo surface densities above 5  $Mo/nm^2$ . This is attributed to the presence of small amounts of  $ZrMo_2O_8$  (detected by Raman) in addition to the predominant  $MoO_x$  species. As shown in Fig. 15, the value of  $k_1/k_2$  for  $ZrMo_2O_8/ZrO_2$  is lower than that for  $MoO_3/ZrO_2$ .

On every sample examined,  $k_3/k_1$  ratios were much greater than unity (Fig. 16), indicating that propene combustion occurs more rapidly than propane ODH. This is the main reason why propene selectivities decrease markedly as propane conversion increases. The range of  $k_3/k_1$  values (10–40) on all catalysts is similar to that measured on  $VO_x/ZrO_2$  catalysts at 603 K (14, 15). The  $k_3/k_1$  ratio on  $ZrMo_2O_8/ZrO_2$  is higher than that on  $MoO_x/ZrO_2$  at similar Mo surface densities. On  $MoO_x/ZrO_2$ ,  $k_3/k_1$  decreased slightly with increasing Mo surface density and then remained constant for Mo surface densities above 10  $Mo/nm^2$ . These results confirm the proposal that exposure of Mo–O–Zr bonds favors the combustion of propene.

## CONCLUSIONS

The structure of  $MoO_x$  species dispersed on zirconia depends strongly on the Mo surface density and on the temperature of thermal treatment, but not on the composition of the precursors or pH of the impregnation solution. Two-dimensional polymolybdate  $MoO_x$  species are favored in samples with Mo surface densities lower than that calculated for a polymolybdate monolayer (5  $Mo/nm^2$ ). At surface densities above 5  $Mo/nm^2$ , the structure of  $MoO_x$  species depends strongly on the temperature of the catalyst oxidation. Low temperatures (723 K) lead to the sintering of polymolybdate into  $MoO_3$  crystallites, whereas high-temperature treatments (above 773 K) lead to the observation of  $ZrMo_2O_8$  by reaction between  $MoO_3$  and  $ZrO_2$ . Catalysts can be divided into two types based on molybdenum-containing species structures:  $MoO_x/ZrO_2$ , which mainly consists of  $MoO_x$  and  $ZrO_2$ , and  $ZrMo_2O_8/ZrO_2$ , which is mainly composed of  $ZrMo_2O_8$  dispersed on  $ZrO_2$ .

Catalytic and spectroscopic data showed that  $MoO_x$  and  $ZrMo_2O_8$  are active in propane oxidative dehydrogenation. On both  $ZrMo_2O_8/ZrO_2$  and  $MoO_x/ZrO_2$  catalysts, turnover rates (per total Mo atoms) decrease with increasing Mo surface density because of either the lower propane accessibility or lower Mo=O bond reactivity as  $MoO_x$  domains grow. Mo=O bonds are active for C–H bond activa-

tion. Weaker Mo=O bonds lead to higher catalytic activity because they are involved in rate-determining C–H bond activation steps requiring lattice given oxygen atoms. The exposure of Mo–O–Zr bonds is undesirable since they contribute to the combustion of  $C_3H_6$  to  $CO_x$ .

## ACKNOWLEDGMENTS

This work was supported by the Director, Office of Basic Energy Sciences, Chemical Science Division of the U.S. Department of Energy under Contract DE-AC03-76SF00098.

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