Journal of Catalysis **203,** 466–476 (2001)
doi:10.1006/jcat.2001.3340, available online at http://www.idealibrary.com on

Laser Raman Characterization of Oxidized Re/γ-Al_2O_3 Catalysts: Effect of Calcination Temperature

Janina Okal[1] and Jan Baran

Institute of Low Temperature and Structure Research, Polish Academy of Sciences, P.O. 1410, 50-950 Wrocław, Poland

Received April 9, 2001; revised July 6, 2001; accepted July 6, 2001

The interaction of oxygen with sintered 1.04 and 10.4 wt% Re/γ-Al_2O_3 catalysts was studied over a wide temperature range, 300–800°C. The molecular structure of the oxidated catalysts under dehydration and hydration conditions was examined using laser Raman spectroscopy. Irrespective of the temperature and time of calcination, Raman spectra revealed that rhenium in the oxidated state is present as ReO_4 monomers coordinated to the alumina support. Under dehydration conditions, ReO_4 monomers form two slightly different species. The first occurs for both loadings, while the second occurs for high loading only. Additionally, formation of the second type of surface rhenium oxide species depends on the temperature and time of calcination. The structural details of these dehydrated rhenium oxide species are not, however, clear. During oxidation of the high-loading catalyst at 300–500°C, ReO_4 monomers form a surface compound probably exibiting Al–(O–ReO_3)$_3$ structure, which is resistant to moisture but not resistant to the high-temperature treatment. The surface coverage of the rhenium declines with increasing oxidation temperature to 800°C. The remaining rhenium oxide is present as adsorbed ReO_4 monomers forming the first type of surface rhenium oxide species. © 2001 Academic Press

Key Words: **Re/γ-Al_2O_3 catalysts; rhenium oxidation; molecular structures; Raman spectroscopy.**

INTRODUCTION

Supported rhenium oxide is a system of considerable interest for at least two reasons: Re_2O_3/Al_2O_3 catalyst is very active for the olefin metathesis reaction (1) and Re_2O_7 supported on TiO_2 is a selective catalyst for the reduction of NO_x to N_2 (2). Characterization of the molecular structure of the supported rhenium oxide is difficult, since several different molecular structures may be present. Hence, in recent years, the interaction of rhenium oxide with various supports has been studied by a number of techniques: Fouier transform infrared spectroscopy (3–7), laser Raman spectroscopy (4, 6, 8–15), extended X-ray absorption fine structure (EXAFS) (17), X-ray absorption near edge structure (XANES) (12, 17), X-ray photoelectron spectroscopy (XPS) (18, 19), X-ray diffraction (20, 21), and NMR (22).

Results obtained by these techniques showed that rhenium in an oxidized state on γ-alumina exists always as a two-dimensional surface phase (3). For this reason in the calcined Re/γ-Al_2O_3 catalysts, crystalline rhenium oxide, Re_2O_7, has never been detected by either X-ray diffraction (20, 21, 23) or selected area electron diffraction (23, 24). The detailed information about the molecular structure of the rhenium oxide on the alumina support has been derived primarily from Raman spectroscopy studies (4, 6, 8–14). These studies revealed also that there is no evidence for the presence of a rhenium heptaoxide phase, and that even at high loading, the rhenium oxide is monomolecularly dispersed on the alumina surface, as ReO_4 tetrahedra (4, 6). Most of the previous studies on the Re_2O_7/Al_2O_3 catalyst were performed under ambient conditions, where moisture is present on the support surface (4, 6, 8–10, 12–14) and only few studies under dehydration conditions have been reported (4, 6, 11, 13, 14). An excellent review on the nature of the surface metal oxide species present in supported metal oxide catalysts has been given recently by Wachs (16).

It was found that under ambient conditions the surface rhenium oxide is hydrated by adsorbed moisture and exhibits the structure of the ReO_4^- ion in aqueous solution. On dehydration at elevated temperatures, the rhenium oxide species interacts with the oxide support. The dehydrated surface rhenium oxide species consists of isolated four-coordinated rhenium oxide monomers with three terminal Re=O bonds and one bridging Re–O–support bond (14). Vuurman *et al.* (6, 13) have shown by *in situ* Raman spectroscopy, IR, and TPR that two slightly different surface rhenium oxide species are present on the alumina at high surface coverage. However, in a recent study Weckhuysen *et al.* (25), employing the oxygen isotope experiments, found for Re_2O_7 supported on ZrO_2 that the surface rhenium oxide species have only a single terminal Re=O bond.

The Raman studies to date were focused on the state of rhenium oxide on the alumina surface as a function of rhenium loading at calcination temperatures of 500–580°C (4, 6, 8–14). Usually, samples for these studies were

---

[1] To whom correspondence should be addressed. Fax: +48 71 441 029. E-mail: jana@int.pan.wroc.pl.

0021-9517/01 $35.00

prepared by impregnation of a γ-alumina support with an aqueous solution of a rhenium salt such as NH_4ReO_4 or perrhenic acid ($HReO_4$), followed by drying at 100–110°C and calcination in dry air at 500–580°C. These conditions correspond to a standard procedure for obtaining catalyst active in methathesis (1). However, as shown in recent studies (22, 26, 27), the catalytic activity of Re_2O_7/Al_2O_3 catalyst may be improved by using calcination temperatures higher than that normally employed. Spronk *et al.* (26) found that the optimum calcination temperature is around 900°C, with a large jump in activity upward between 650 and 750°C. Hietala *et al.* (22) observed the same kind of jump with Re/Al_2O_3 catalyst for the ethenolysis of 1.5-cyclooctadiene (COD) when the calcination temperature was increased from 550 to 610°C. Schekler-Nahama *et al.* (27) found for Re_2O_7/Al_2O_3 that increasing the Re content and the calcination temperature (from 550 to 750°C) enhances the metathesis activity.

In the present study, the effect of loading and calcination temperature (300–800°C) on the surface rhenium oxide structures under dehydration and hydration conditions was investigated by Raman spectroscopy. Alumina-supported Re oxide catalysts were obtained by calcination in air of the reduced Re/γ-Al_2O_3 catalysts. Such a procedure, usually applied during regeneration of the spent (reduced) Re_2O_7/Al_2O_3 catalyst, leads to the redispersion of rhenium and the formation of a monolayer of supported rhenium oxide (3, 23). In a previous paper (28) we studied the interaction of oxygen with the sintered 10.4% Re/γ-Al_2O_3 catalyst over a wide temperature range, 20–800°C. Present Raman studies complement the previous characterization of this catalyst by H_2 chemisorption, O_2 uptake, HRTEM, SAED, and XRD methods. The high-loading Re/γ-Al_2O_3 catalyst investigated here was identical to that characterized in Ref. (28).

EXPERIMENTAL

1. *Preparation and Treatment*

The detailed procedure for catalyst preparation and treatment was described previously (23, 28). Here only a brief summary is given: Re/γ-Al_2O_3 catalysts with 1.04 and 10.4 wt% Re were obtained by impregnation of γ-alumina (BET area 220 m^2/g) with aqueous solutions of NH_4ReO_4. The high-purity support was prepared in another labolatory by hydrolysis of isopropoxide followed by calcination at 500°C for 16 h to obtain γ-Al_2O_3 (29). After impregnation the samples were dried in air at 100°C and then preliminarily reduced in hydrogen flow at 550°C for 10 h. Next, the catalysts underwent the following sequential heat treatment procedures.

Sintering. The catalysts were again reduced in H_2 with a heating rate of 6°C/min from room temperature to 550°C, held at this temperature for 20 h, and then reduced at 800°C for 5 h (28).

Oxidation. The sintered samples were oxidized with static air at 300–800°C by heating from room temperature to the desired one at 5°C/min and holding at this temperature for 1, 4 or 20 h. Next, the samples were cooled to about 300°C. The hot samples were transferred to the glass capillaries within less then 30 s and immediately sealed to enable the collection of the Raman spectra under dehydration conditions. Hydration of alumina-supported rhenia catalysts was achieved by exposing the dehydrated samples to ambient air for 20 h or for a few days.

2. *Experimental Techniques*

The Raman spectra were obtained with a Jobin-Yvon Ramanor-U 1000 spectrometer equipped with the CCD detector cooled to −130°C. The 514.5-nm line (power of 250 mW) of the Ar^+ ion laser was used as an exciting light. The focused spot size was about 100 μm. All the spectra were collected at room temperature, with an acquisition time of 30 s per scan and resolution of ca. 2 cm^{-1} (28).

The BET surface area of the catalysts was measured by nitrogen adsorption at liquid nitrogen temperature, assuming 0.162 nm^2 as the area of the adsorbate molecule. Samples were dehydrated under vacuum, at 300°C for 3 h, before surface area measurements.

3. *Chemical Analysis*

The actual rhenium content of the catalysts before and after calcination was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) with a Philips Scientific PV 7000 spectrometer. We also determined amounts of sodium and potassium impurities in the samples because their presence may change the structure of the rhenium oxide catalysts (30). The Na and K contents were found to be 0.07 and 0.02 wt%, respectively. The content of other impurities (Si, Mg, Cu, Fe) was below 10^{-3}%. XPS analysis of the 10.4% Re/γ-Al_2O_3 catalyst calcined at 500°C for 4 h and at 800°C for 20 h did not show presence of the Na ions (or K ions). Probably, the surface concentration of this ions was too low to be experimentally observed.

RESULTS

1. Characterization of the Catalysts

The main characteristics of the Re/γ-Al_2O_3 catalysts are summarized in Table 1. It appears that reduction at 800°C induced some decrease in the surface area which is somewhat less for low-loading catalyst than that shown for high-loading catalyst. Oxidation at temperatures up to 600°C did not change the Re concentrations in the catalysts, but at 800°C some rhenium left the surface of the catalysts as gaseous Re_2O_7; the loss of Re was 34 and 10% for 10.4

TABLE 1

BET Surface Area, Re Content (wt%), Dispersion (H/Re), Metal Particle Size, and Rhenium Surface Density for Re/γ-Al_2O_3 Catalysts after Various Treatments

Catalyst	Reduction T (°C)/time	Oxidation T (°C)/time	BET (m^2/g)	Re content (wt%)	(H/Re)[a]	1 (chem)[b] (nm)	Surface density (atoms Re/nm^2)
10.4% Re/γ-Al_2O_3	550/20 h	—	230	10.6	0.39	3.4	—
	800/5 h	—	153	10.6	0.25	5.4	—
		400/4 h	154	10.7	—	—	2.2
		600/4 h	153	10.0	—	—	2.1
		800/4 h	151	7.0	—	—	1.5
		800/20 h	150	6.9	—	—	1.5
1.04% Re/γ-Al_2O	550/20 h	—	211	1.0	0.77	1.7	—
	800/5 h	—	171	—	0.62	2.1	—
		400/4 h	172	1.1	—	—	0.21
		600/4 h	—	—	—	—	—
		800/4 h	—	—	—	—	—
		800/20 h	163	0.89	—	—	0.16

[a] Number of hydrogen atoms chemisorbed to the total numbers of Re atoms (H/Re).

[b] Metal particle size determined from H_2 chemisorption (28, 31).

and 1.04% Re/γ-Al_2O_3 catalysts, respectively. Oxidation of rhenium was performed on the sintered catalysts, having metallic Re particles with an average size of 5.4 nm for high-loading catalyst and 2.1 nm for low-loading catalyst (28, 31). The Re surface densities calculated from the measured BET surface area and the actual metal loading are listed in the last column of Table 1. The surface density is defined as the number of rhenium atoms per square nanometer of catalyst.

2. Raman Studies

2.1. Molecular Structure of the Re/γ-Al_2O_3 Catalysts Calcined at 600°C

Raman spectroscopic studies reported to date have concentrated primarily on the state of rhenium oxide on the alumina surface at a calcination temperature of 500°C (4, 6, 8–10, 12, 13) or 580°C (11). We begin therefore with the presentation of the results of our Raman studies for Re/γ-Al_2O_3 catalysts calcined at 600°C, which were in part presented in our recent paper (28).

The Raman spectra of the low- and high-loading Re/γ-Al_2O_3 catalysts and alumina support calcined in air at 600°C for 4 h under dehydration and hydration conditons are shown in Figs. 1 and 2, respectively. Irrespective of the degree of the hydroxylation, the support exhibits only weak, broad Raman signals at approximately 800 and 500 cm^{-1}, which are associated with a defective spinel γ-alumina structure (32). As can be seen, the molecular structure of the catalysts depends on rhenia loading and on the degree of hydroxylation of the samples. Under dehydration conditions, the Raman spectrum of the 1.04% Re/γ-Al_2O_3 catalyst (Fig. 1b) is poorly resolved and only a small peak at 1000 cm^{-1} is observed. The spectrum of the 10.4% Re/γ-Al_2O_3 catalyst (Fig. 1c) exhibits Raman bands at 1015, 1006, 980, and 343 cm^{-1}, which can be ascribed to two slightly different tetrahedrally coordinated surface rhenium oxide species (13, 28). One species shows bands at 1006 and 343 cm^{-1}, and the second, at 1015, 980, and 343 cm^{-1}. The Raman bands in the 900–1015 cm^{-1} region are assigned to the terminal Re=O stretching vibrations and those between 330 and 343 cm^{-1} to the O–Re–O bending mode of the surface oxide species (6, 16, 28). A shift in the Raman band of the terminal Re=0 bond of the first type of surface rhenium oxide species from 1000 to 1006 cm^{-1} with increasing Re loading from 1 to 10 wt% is observed (Fig. 1). The shift is attributed to decreasing hydration with increasing surface coverage (4). Under dehydration conditions, the structures of both surface species are similar; they possess three terminal Re=O bonds and one bridging Re–O–support bond (4, 6, 13, 28).

The Raman spectra from the samples exposed to atmospheric moisture for 20 h are shown in Figs. 2b and 2c. For the catalyst with low Re content it caused a shift in the main Raman band from 1000 to 973 cm^{-1} and appearance of a weak band at 330 cm^{-1}. For the high-loading catalyst the main Raman bands shifted from 1015, 1006, and 343 cm^{-1} to 995, 975, and 338 cm^{-1}, respectively. The presence of two bands at 995 and 975 cm^{-1} indicates that two different surface rhenium oxide species exist. When this sample was exposed to atmospheric moisture for a few days three bands were observed at 974, ∼920, and 337 cm^{-1} (Fig. 2d). The positions of the bands correspond to those of ReO_4^- species in an aqueous solution (4, 11). Hence, for both catalysts, under full hydration conditions the surface rhenium oxide species are not anchored to the oxide support (by Re–O–Al bonds), but are suspended in the thin aqueous layer, as perfect tetrahedral monomers (16, 33).

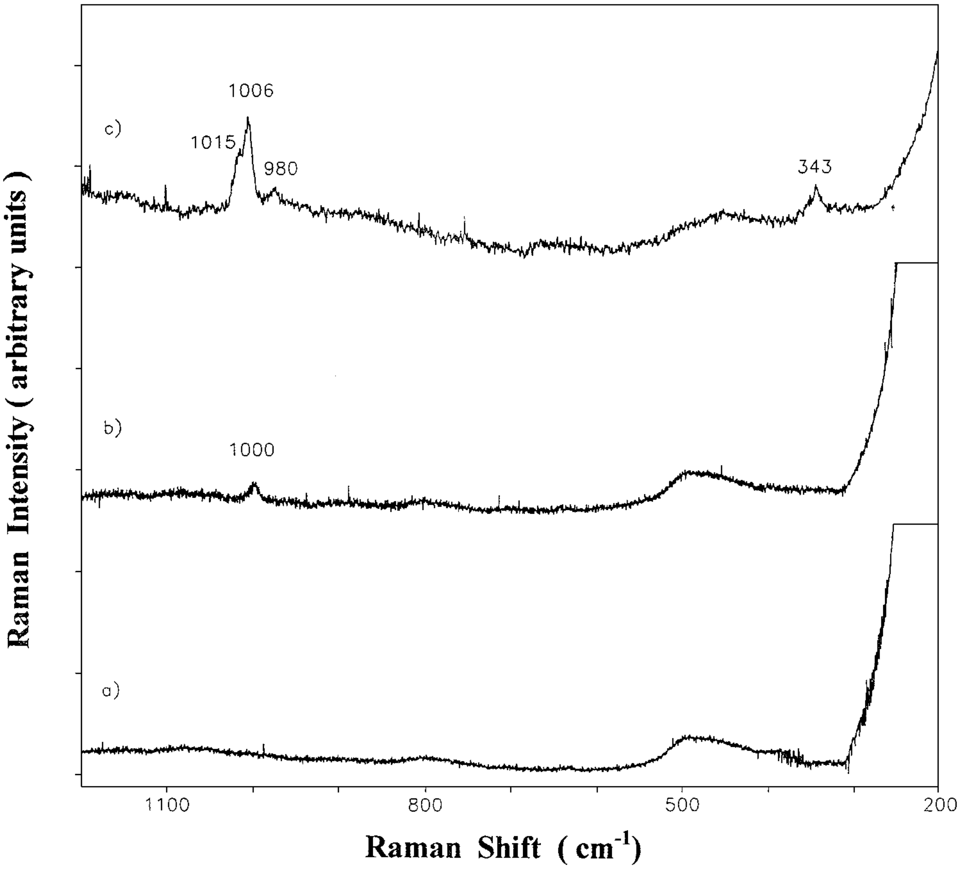

FIG. 1. Raman spectra of (a) γ-alumina, (b) 1.04% Re/γ-Al_2O_3, and (c) 10.4% Re/γ-Al_2O_3 catalyst, calcined at 600°C for 4 h; dehydration conditions.

2.2. Molecular Structure of the Re/γ-Al_2O_3 Catalyst Calcined at 300–800°C

Dehydration conditions. The Raman spectra of the 1.04% Re/γ-Al_2O_3 catalyst calcined 1 h at 300–800°C were identical to the spectrum of bare γ-Al_2O_3, showing no evidence of any rhenium oxide species. The same holds for the sample calcined at 300–500°C for 4 h. Raman spectra of the sample calcined at 600–800°C for 4 h were similar (see Fig. 1b), with one weak band at 1000 or 1004 cm^{-1} after calcination at 600 or at 800°C, respectively. The band is assigned to the terminal Re=O symmetric stretching vibration of the first type of surface rhenium oxide species. As can be seen the position of this band depends slightly on the temperature of calcination, i.e., on the degree of dehydration. The corresponding antisymmetric stretching and bending modes were not observed in the Raman spectra. An increase in calcination time to 20 h did not cause significant changes in the Raman spectra except that the Raman signal of surface rhenium oxide species was detected also for the sample calcined at 500°C (one band at 1000 cm^{-1}).

The Raman spectra of the 10.4% Re/γ-Al_2O_3 catalyst calcined at 300–800°C for 1 h and recorded under dehydration conditions are shown in Fig. 3. Irrespective of the calcination temperature the spectra show the main band at 1003 cm^{-1} (ν_s(Re=O)) and above 400°C also a weak band at 345 cm^{-1} (δ(O–Re–O)) (not shown), which can be assigned to the first type of surface rhenium oxide species. Up to 500°C the band at 1003 cm^{-1} is weak and broad, while at 700–800°C it becomes more intense and sharp. Moreover, additional weak bands are observed, indicating that two kinds of ReO_4 surface rhenium oxide species are present, like after calcination at 600°C for 4 h (Fig. 1c). At 800°C, the first species shows bands at 1003, ~896, and 345 cm^{-1}, and the second, at 1017, 978, and 345 cm^{-1}. The intensity ratio of the 1003 and 1017 cm^{-1} bands suggests, however, that the amount of the second type of surface rhenium oxide species is rather small.

An increase in the calcination time of the high-loading catalyst to 4 h caused the formation of the second type of surface rhenium oxide species already at 300°C (Fig. 4). The position of the symmetric Re=O stretch band for the both types of surface rhenium oxide species increases slightly with the temperature of calcination of the sample. However, the intensities and shapes of the Raman bands due to the surface rhenium oxide species for samples calcined

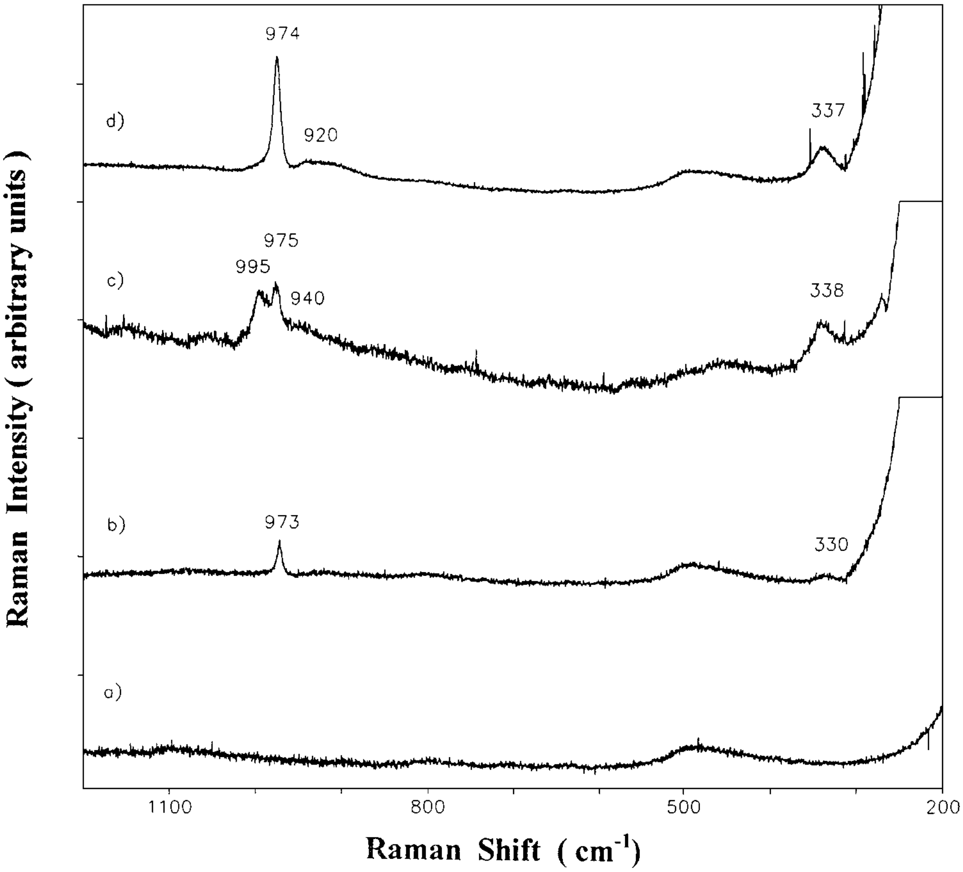

FIG. 2. Raman spectra of (a) γ-alumina, (b) 1.04% Re/γ-Al_2O_3, and (c) 10.4% Re/γ-Al_2O_3 catalyst, calcined at 600°C for 4 h and exposed to ambient conditions for 20 h. (d) Sample c exposed to air for a few days.

at 300–800°C for 1 or 4 h are very similar (Figs. 3 and 4). According to Chan *et al.* (34), the Raman bands of the supported surface oxide species for various transition metal oxide systems sharpen and shift in frequency at elevated temperatures due to the desorption of water from the surface. The removal of the water molecules is believed to decrease the degree of disorder on the surface of the support and affects the Re=O stretch.

Prolonged calcination of the high-loading catalyst did not cause large changes in Raman spectra until 800°C. The spectrum of the sample calcined at 800°C for 20 h exhibits a single intense band at 1002 cm^{-1} and weak bands at 974, ~896, and 337 cm^{-1} (spectrum is not shown). Bands at 1002, ~896, and 337 cm^{-1} are ascribed to the first type of surface rhenium oxide species. The origin of the band at 974 cm^{-1} is not entirely clear, but under dehydration conditions this band is usually assigned to the antisymmetric stretching mode of the second type of surface rhenium species (6). Since no band ascribed to the symmetric stretching mode of second type of surface rhenium oxide species is observed, we suppose that after prolonged calcination at 800°C only the first type of surface rhenium oxide species is present on the alumina surface. This surface-coordinated species, firmly bonded to alumina, has a distorted ReO_4 structure, e.g., possesses three terminal Re=O bonds and one Re–O–support bond (6). The second type of surface rhenium oxide species with a weaker Re–O–support bond is evaporated from the surface of alumina or transformed partially to the first surface rhenium oxide species.

Hydration conditions. For all studied dehydrated low-loaded samples, which exhibit Raman signals, exposure to atmospheric moisture for 20 h caused a shift in the Raman band from 1000–1004 to 973 cm^{-1} and appearance of a weak band at 330 cm^{-1} (see Fig. 2b). This indicates that at low coverage, the surface rhenium oxide species is fully hydrated by adsorbed moisture. The sample calcined at 800°C for 20 h was even more easily hydrolyzed, since 3 h conctact with atmospheric moisture was sufficient to produce a spectrum characteristic of supported rhenium oxide under ambient conditions.

The Raman spectra of the 10.4% Re/γ-Al_2O_3 catalyst calcined at 300–800°C for 4 h and exposed to atmospheric moisture for 20 h are presented in Fig. 5. The spectra of the samples calcined at 300–500°C exhibit only a small change on hydration (cf. Figs. 4 and 5). The spectra show a

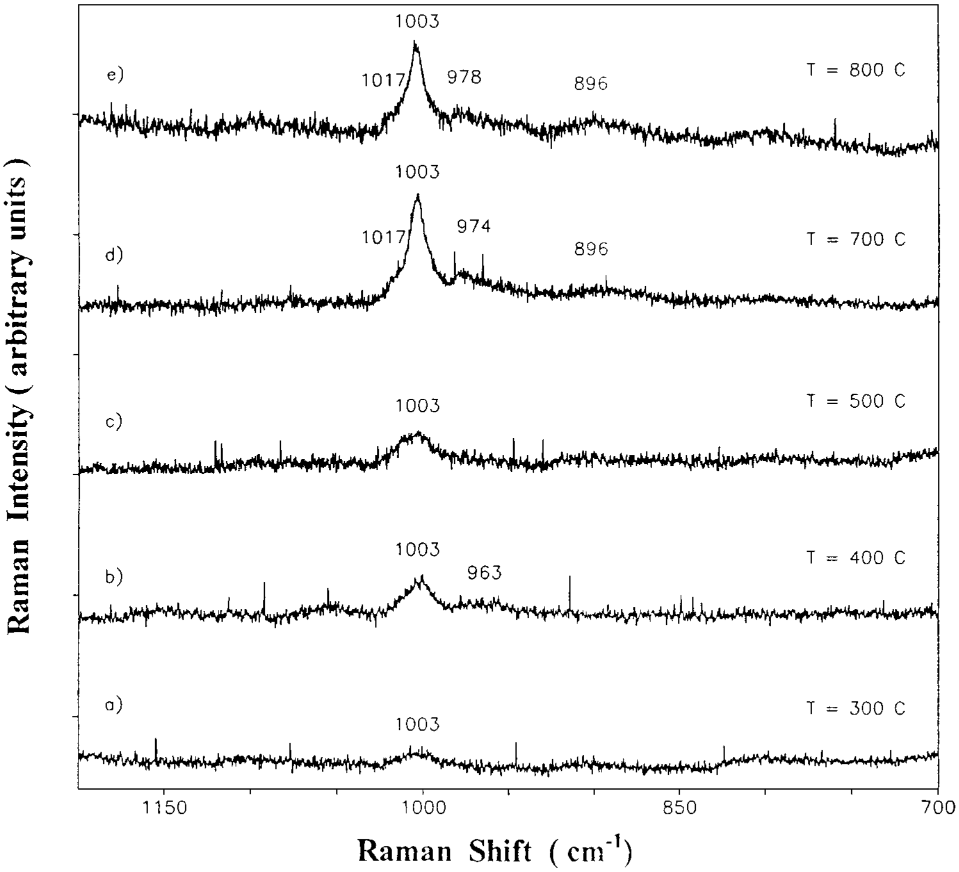

FIG. 3. Raman spectra recorded for the 10.4% Re/γ-Al_2O_3 catalyst calcined for 1 h at (a) 300°C, (b) 400°C, (c) 500°C, (d) 700°C, and (e) 800°C; dehydration conditions.

broad band in the Re=O stretching region at about 999 cm^{-1}, with some broadening on the high-frequency side, and a weak band at ~340 cm^{-1} in the bending mode (not shown). Hence, it appears that atmospheric moisture has a rather small effect on the structure of the surface rhenium oxide species created during calcination at 300–500°C. The spectra from the samples calcined at 600, 700, and 800°C changed significantly after exposure to atmospheric moisture. The bands corresponding to the Re=O stretching modes of distorted tetrahedral ReO_4 species gradually shifted to lower frequencies, which indicates hydrolysis of the Re–O–Al bonds (4, 6, 16, 28). However, the rate of hydrolysis of this bond depends on the initial temperature of calcination of the sample. Spectra d and e in Fig. 5 confirm, moreover, that the two main bands at 995 and 975 cm^{-1} (after calcination at 600°C) and at 988 and 975 cm^{-1} (after calcination at 700°C) are still present, so that two different surface rhenium oxide species exist. The sample calcined at 800°C for 4 h is easily hydrolyzed and a spectrum with bands at 973, ~920, and 336 cm^{-1}, similar to the Raman spectrum of the ReO_4 species in an aqueous solution (4, 11), was obtained.

The samples calcined at 600 and 700°C required a few days of contact with atmospheric moisture to produce the Raman spectra characteristic of fully hydrated surface rhenium oxide species (see Fig. 2d). The rhenium oxide species in the samples calcined at 300, 400, and 500°C were much more resistant to hydrolysis of the Re–O–Al bonds. Even after 30 days exposure to atmospheric moisture, broadbands at about 1000 and 340 cm^{-1} (sample calcined at 400°C) and at 1002, ~900, and 332 cm^{-1} (sample calcined at 500°C) were observed (spectra are not shown).

DISCUSSION

The Re_2O_7/γ-Al_2O_3 catalysts studied in the present work were prepared by reaction of oxygen with reduced (sintered) Re/γ-Al_2O_3 catalysts. Recently, we have shown by measurement of oxygen uptake that 1 h oxidation of the reduced 10.4% Re/γ-Al_2O_3 catalyst at 300–500°C is sufficient to complete oxidation of metallic Re to rhenium heptaoxide, Re_2O_7 (28). In contrast, Chądzyñski and Kubicka (35) found that the catalyst with low Re content (~1 wt%) is more resistant to oxidation. After 1 h oxidation at 300 and

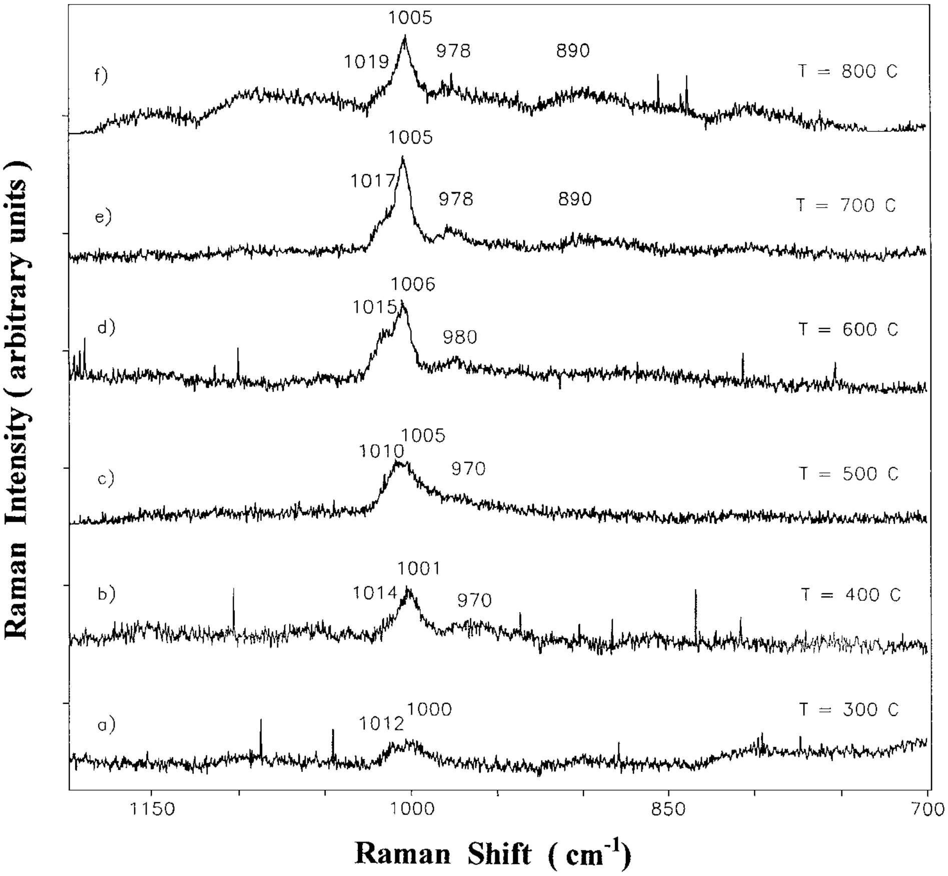

FIG. 4. Raman spectra recorded for the 10.4% Re/γ-Al_2O_3 catalyst calcined for 4 h at (a) 300°C, (b) 400°C, (c) 500°C, (d) 600°C, (e) 700°C, and (f) 800°C; dehydration conditions.

400°C the O/Re ratio was 2.55 and 2.62, respectively, which is about 20% lower than 3.5 corresponding to the complete oxidation of Re to Re_2O_7. The present Raman results indicate that oxidation of 10.4% Re/γ-Al_2O_3 catalyst already at 300°C for 1 h is enough to obtain a monomolecularly dispersed oxide phase. For 1.04% Re/γ-Al_2O_3 catalyst the Raman signal of surface rhenium oxide species could be detected only after calcination at 500°C for 20 h or at 600°C and above for 4 h. These results also confirm that a catalyst of low rhenium content is more resistant to oxidation than a catalyst of high Re content.

The Re surface density in the samples studied in this work (maximum value: 2.2 Re atoms/nm^2 (see Table 1)) does not exceed that of the monolayer coverage of 2.3 Re atoms/nm^2, determined by Vuurman *et al.* (6) for Re_2O_7/Al_2O_3 catalyst. Raman spectra presented in this study show no strong Re–O–Re vibrations (at ~800, ~450, and the 200–150 cm^{-1} region), suggesting that the surface rhenium oxide species are isolated (12). A comparison of the present data with the Raman studies reported previously for Re_2O_7/Al_2O_3 catalysts (4, 6, 8–14, 30) under hydration and dehydration conditions and with those of some rhenium oxide compounds in different coordinations (6, 30) clearly indicates that only isolated tetrahedrally coordinated surface rhenium oxide species, ReO_4, exist on the alumina surface independent of the temperature of calcination. *In situ* IR studies (3, 5, 7) showed that hydroxyl groups on the alumina surface are removed by the supported rhenium oxide phase. Sibeijn *et al.* (5) and Turek *et al.* (7) found that during deposition the ReO_4^- ions react predominantly with the basic alumina hydroxyls and, at higher loadings of rhenia, also with the neutral and acidic alumina OH groups. In the present investigation OH groups from alumina support were also eliminated by heat treatment up to 800°C.

We found that under dehydration conditions the molecular structure of the rhenium oxide supported on γ-alumina depends on the rhenium loading and, for high-loaded catalyst, also on the temperature and time of calcination. The first kind of surface species corresponding to ν_s(Re=O) of 1000–1006 cm^{-1} was observed for both catalysts. The position of band ν_s(Re=O) depended slightly on the calcination temperature and on Re loading. The second type of surface species, corresponding to ν_s(Re=O) of 1012–1019 cm^{-1}, was formed only at the surface of the catalyst with high loading of Re, in accord with literature Raman data obtained for dehydrated R_2O_7/Al_2O_3 catalyst (4, 6,

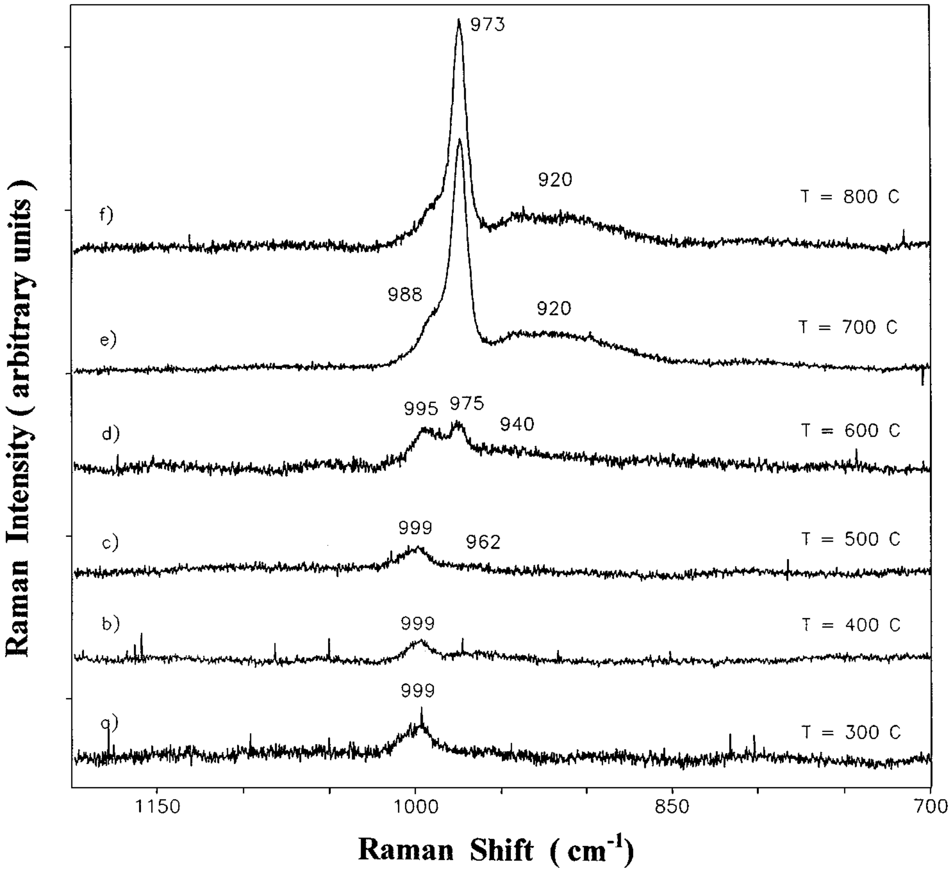

FIG. 5. Raman spectra recorded for the 10.4% Re/γ-Al_2O_3 catalyst calcined for 4 h at (a) 300°C, (b) 400°C, (c) 500°C, (d) 600°C, (e) 700°C, and (f) 800°C and exposed to ambient conditions for 20 h.

13). Wang and Hall found two bands at 1014 and 1006 cm^{-1} in an *in situ* IR spectrum of Re_2O_7/Al_2O_3 and also concluded the presence of two surface species (4). Our data show that calcination of the sample above 600°C for 1 h or prolongation of the calcination time to 4 or 20 h at mild temperatures is required for a second type of surface rhenium oxide species to be formed. According to the literature (4, 6, 13, 28) the two monomeric surface rhenium oxide species possess three terminal Re=O bonds and one bridging Re–O–Al bond. Recent developments in ^{18}O exchange experiments over Re_2O_7/ZrO_2 catalyst, however, showed the presence of a single terminal Re=O bond (30). This result indicates also that more than one type of surface rhenium oxide species is present on the oxide support.

It has been proposed by Turek *et al.* (7) that the slight difference between the two surface rhenium oxide species may be due to the distortions brought about by the presence of a proton at the Re–O–support bond of one of the rhenium oxide species. This causes the shift of the Raman band of the terminal Re=O bonds from 1000–1006 to 1012–1019 cm^{-1}. Such a shift can also be interpreted as a weakening of the bridging Re–O–Al bond strength (6, 13). In the previous study of the 10.4% Re/γ-Al_2O_3 catalyst (28) we showed also that the surface rhenium oxide species with weaker interactions with γ-Al_2O_3 may be extracted from the catalyst surface more easily by washing with cold water. After extraction, only one surface rhenium oxide species was observed with a single sharp band at 1003 cm^{-1} and a weak band at 342 cm^{-1} (28). The amount of Re extracted from the catalyst increased slighty with the temperature of calcination (400–800°C), indicating that the amount of rhenium oxide species with weaker interactions with the support also increased.

The present Raman data suggest that calcination of high-loading catalyst at 800°C for 20 h causes complete removal of the second type of surface rhenium oxide species. It is, however, connected to the loss of rhenium and decreasing its surface density to 1.5 Re atoms/nm^2. The spectrum of this sample, besides bands ascribed to the first type of the surface rhenium species (1002, ~896, and 337 cm^{-1}), contains also the band at 974 cm^{-1} which we cannot assign. As shown in recent study by Mitra *et al.* (30) addition of Na to high-loading Re_2O_7/Al_2O_3 catalysts causes a shift in dehydrated Raman bands to 975 (strong), 918, 947 (weak), and 335 (strong) cm^{-1}. Hence, it is probable that the

Raman bands at 974 and 337 cm^{-1} observed after prolonged calcination at high temperatures, i.e., when diffusion of Na (or K) impurities to the surface alumina is possible, may be consistent with the formation of $NaReO_4$ compound as suggested in Ref. (30). XPS surface analysis of the high-loading catalyst calcined at 800°C, 20 h and at 500°C, 4 h did not show, however, the presence of the Na ions (or K ions). Probably, the surface concentration of this ions was too low to be experimentally observed. We suppose also that a certain amount of the second type of surface species may be transformed, by a temperature-induced surface diffusion, to the first type of surface rhenium oxide species. Such diffusion of ReO_4 groups over the surface of the alumina may be facilitated by an extensive dehydroxylation of the alumina support during prolonged calcination at high temperature (26, 36–38). Spronk *et al.* (26) explained the increase in activity of the 6% Re_2O_7/γ-Al_2O_3 catalyst calcined at 900°C by redistribution of ReO_4 units over the alumina surface, for which spectroscopic evidence (FTIR) was presented. Since the rhenium oxide is mobile at higher calcination temperatures a nearly random distribution of ReO_4 groups over all types of sites on the alumina surface occurs, thus increasing the activity (26). The authors showed that rhenium does not react with alumina at temperatures up to 1000°C, and is present as stabilized surface-coordinated ReO_4 groups. A similar conclusion may be drawn from a Raman study by Hardcastle *et al.* (12), who stated that even after calcination at 950°C the rhenium oxide on alumina is still present as adsorbed surface ReO_4 species (study under ambient conditions). This is in contrast to the systems WO_3/Al_2O_3 (39–41) and MoO_3/Al_2O_3 (42, 43) in which $Al_2(WO_4)_3$ and $Al_2(MoO_4)_3$ compounds were formed after calcination at high temperatures. Only for Re_2O_7 supported on MgO has formation of $Mg(ReO_4)_2$ been observed after treatment in oxygen at 640–750°C (44) or 500°C (14).

Exposure of dehydrated Re/γ-Al_2O_3 catalysts to atmospheric moisture caused hydration of the surface rhenium oxide species. The low-loaded catalyst, irrespective of the calcination temperature, was easily hydrated ($\nu_s(Re{=}O)$ in the range 973–971 cm^{-1}). For the high-loading catalyst the extent of hydration depends on the calcination temperature and time of exposure to moisture. For calcination temperatures to 500°C rhenium oxide on alumina hardly undergoes hydrolysis of the Re–O–Al bond, even after prolonged exposure to air ($\nu_s(Re{=}O)$ in range of $\sim$1000 cm^{-1}). Hydrolysis of this bond in samples calcined at higher temperatures was easier, although two different surface rhenium species were still observed (in samples calcined at 600 and 700°C) after 20 h of contact with atmospheric moisture. Prolonged exposure to air produces fully hydrated surface rhenium oxide species, similar to that in the low-loaded catalyst. Our Raman results indicate that the first type of surface rhenium oxide species is more prone to the hydrolysis than the second type present only at higher coverage of Re. This is probably caused by the different local environments of the two tetrahedral species and, to some extent, by the difference in the bridging Re–O–support bond strength of both surface species.

Comparison of the Raman spectra of the high-loading catalyst calcined at 300–500°C under dehydration and hydration conditions suggests the possibility of a surface compound formation since the Raman bands at $\sim$1000 and 340 cm^{-1} are not affected by hydration. Chan *et al.* (34) and Wachs (45, 46) showed that Raman spectroscopy easily discriminates between surface metal oxide species and surface oxide–oxide compounds since only the Raman bands of the former are affected by the presence of adsorbed water molecules.The Raman band samples calcined at 300–500°C are not consistent with the formation of $NaReO_4$ compound, although at 800°C it was not excluded. The bulk $NaReO_4$ exhibits Raman bands at 963, 928, 890, and 331 cm^{-1} (47). We suppose that a very low level of support impurities (Na/Re atomic ratio $\leq$0.085; K/Re atomic ratio $\leq$0.02) and moderate temperatures of calcination are not sufficient to effect a change in the our Raman spectra. Thus, we suggest rather the formation of an surface compound between rhenium oxide and alumina support. Since nearly all metal cations form stable perrhenates (48), the formation of an aluminum perrhenate, $Al(ReO_4)_3$, in the calcined Re/γ-Al_2O_3 catalyst, is a very real possibility. To date the possible formation of this compound in Re_2O_7/Al_2O_3 catalyst has received little consideration (16). Salvati *et al.* (49) obtained the Raman spectrum of bulk $Al(ReO_4)_3$ and found that the spectrum was similar to the spectra of other polycrystalline perrhenates. The spectrum is characterized by a group of bands at 1031–971 cm^{-1} ($\nu_s(Re{=}O)$, the most intense band at 1031 cm^{-1}); at 959–850 cm^{-1} ($\nu_{as}(Re{=}O)$, weak bands) and at 382–293 cm^{-1} ($\delta_{s,as}$(O–Re–O), the most intense band at 369 cm^{-1}). It shuld be noted that none of our Raman spectra show bands at 1031 and at 369 cm^{-1}, and thus we have no direct proof for the existence of this compound in a bulk-like form.

In recent study of 10.4% Re/γ-Al_2O_3 catalyst calcined at 300–500°C we observed by high-resolution electron microscopy very small particles ($\sim$0.6–1.0 nm) uniformly distributed on γ-alumina (28). We interpreted these features as aggregate ReO_4 species grouped around special sites on γ-Al_2O_3 to form surface Al $(ReO_4)_3$ species. As another possible interpretation of the HRTEM results we considered particles with sizes below 1 nm as Re clusters formed inside the electron microscope by reduction of Re oxide. The direct identification of this phase, however, could not be done by HRTEM or SAED since the particles were to small to exhibit lattice fringes or visible diffraction features (28). Results of the extraction experiments indicated that the formation of surface aluminum perrhenate could be expected only during calcination of the high-loading catalyst at 400–600°C (28). Bulk aluminum perrhenate forms by direct solid–solid reaction between Re_2O_7 and dehydrated Al_2O_3 at 450°C (50). Such conditions actually exist during calcination of our samples. Formation of this surface compound may also be expected during the oxidation step of the regeneration procedure of the Pt-Re/γ-Al_2O_3 reforming catalyst, when separation of Pt and Re occurs. Schekler-Nahama *et al.*, based on results obtained from water extraction (51) and from activity measurements and IR study (27), also suggested that surface aluminum perrhenate, $Al(ReO_4)_3$, or its decomposition product exists on the surface of the calcined Re/γ-Al_2O_3 catalyst. Summarizing we have to conclude that the structural details of supported rhenium oxide species under dehydrated conditions are still lacking and require further studies.

CONCLUSIONS

Oxidation experiments were performed on Re particles with an average size of about 5 and 2 nm obtained by sintering of the Re/γ-Al_2O_3 catalysts in hydrogen at 800°C. On oxidation at 300–800°C, various physical and chemical processes occur on the surface of the catalysts. At 300°C or even below, oxidation of metallic Re leads to formation of Re_2O_7 which instantaneously sublimes (28). Re_2O_7 molecules from the gas phase dissociate on adsorption on γ-alumina into monomeric ReO_4 species, as is evidenced by the Raman spectra presented in this work. The catalyst with low coverage of Re requires higher temperature (500°C) to produce Raman spectra characteristic of ReO_4 species. Under dehydration conditions, ReO_4 monomers supported on γ-Al_2O_3 form two slighty different species: one occurring at all Re loadings and all calcination conditions and the second at high loading only. The formation of the second type of rhenium oxide species, with a weaker Re–O–Al bond, depends on temperature and time of calcination. Both types of ReO_4 species possess three terminal Re=O bonds and one bridging Re–O–support bond. During calcination of the high-loading sample at 300–500°C, the formation of the surface compound with the Al–$(O–ReO_3)_3$ structure is also possible. This hypothesis is supported by Raman data presented here and other results reported in previous work (28). This surface compound is relatively resistant to moisture but decomposes above 600°C. At high temperatures ReO_4 monomers may migrate over alumina to sites where ReO_4 is easily hydrolyzed (under ambient conditions), and simultaneously part of the Re oxide sublimes as Re_2O_7. After prolonged calcination at 800°C, part of rhenium oxide remaining at the surface is firmly bonded to alumina, as distorted ReO_4 tetrahedra, and forms the first type of surface rhenium oxide species. Under hydration conditions this species is easily hydrolyzed by adsorbed moisture.

ACKNOWLEDGMENTS

The authors thank Dr. L. Kêpiñski for valuable discussions and critical reading of the manuscript and Dr. W. Tylus for performing XPS measurements.

REFERENCES

1. Mol, J. C., *Catal. Today* **51**, 289 (1999).
2. Wachs, I. E., Deo, G., Andreini, A., Vuurman, M. A., and de Boer, M., *J. Catal.* **160**, 322 (1996).
3. Olsthoorn, A. A., and Boelhouwer, C., *J. Catal.* **44**, 197 (1976).
4. Wang, L., and Hall, W. K., *J. Catal.* **82**, 177 (1983).
5. Sibeijn, M., Spronk, R., van Veen, J. A. R., and Mol, J. C., *Catal. Lett.* **8**, 201 (1991).
6. Vuurman, M. A., Stufkens, D. J., Oskam, A., and Wachs, I. E., *J. Mol. Catal.* **76**, 263 (1992).
7. Turek, A. M., Wachs, I. E., and De Canio, E., *J. Phys. Chem.* **96**, 5000 (1992).
8. Kerkhof, F. P. J. M., Moulijn, J. A., and Thomas, R., *J. Catal.* **56**, 279 (1979).
9. Wachs, I. E., and Hardcaste, F. D., *in* "Proceedings, 9th International Congress on Catalysis, Calgary, 1988" (M. J. Phillips and M. Ternan, Eds.), p. 1449. Chem. Inst. of Canada, Ottawa 1988.
10. Edreva-Kardjieva, R. M., Vuurman, M. A., and Mol, J. C., *J. Mol. Catal.* **76**, 297 (1992).
11. Williams, K. P. J., and Harrison, K., *J. Chem. Soc. Faraday Trans.* **86**, 1603 (1990).
12. Hardcastle, F. D., Wachs, I. E., Horsley, J. A., and Via, G. H., *J. Mol. Catal.* **46**, 15 (1988).
13. Vuurman, M. A., and Wachs, I. E., *J. Phys. Chem.* **96**, 5008 (1992).
14. Kim, D. S., and Wachs, I. E., *J. Catal.* **141**, 419 (1993).
15. Dunn, J. P., Stenger, H. G., Jr., and Wachs, I. E., *J. Catal.* **181**, 233 (1999).
16. Wachs, I. E., *Catal. Today* **27**, 437 (1996).
17. Ellison, A., Diakun, G., and Worthington, P., *J. Mol. Catal.* **46**, 131 (1988).
18. Shpiro, E. S., Avaev, V. I., Antoshin, G. V., Ryashentseva, M. A., and Minachev, K. M., *J. Catal.* **55**, 402 (1978).
19. Kirlin, P. S., Strohmeier, B. R., and Gates, B. C., *J. Catal.* **98**, 308 (1986).
20. Maksimov, Y. V., Kushnerev, M. Y., Dumesic, J. A., Nechitailo, A. E., and Fridman, R.A., *J. Catal.* **45**, 114 (1976).
21. Arnoldy, P., Van Oers, E. M., Bruinsma, O. S. L., De Beer, V. H. J., and Moulijn, J. A., *J. Catal.* **93**, 231 (1985).
22. Hietala, J., Root, A., and Knuuttila, P., *J. Catal.* **150**, 46 (1994).
23. Okal, J., Kubicka, H., Kêpiñski, L., and Krajczyk, L., *Appl. Catal. A* **162**, 161 (1997).
24. Laiyuan, Ch., Yuegin, N., Jingling, Z., Liwu, L., Xihui, L., and Sen, Ch., *J. Catal.* **145**, 132 (1994).
25. Weckhuysen, B. M., Jeng, J. M., and Wachs, I. E., *J. Phys. Chem. B* **104**, 7382 (2000).
26. Spronk, R., van Veen, J. A. R., and Mol, J. C., *J. Catal.* **144**, 472 (1993).
27. Schekler-Nahama, F., Clause, O., Commereuc, D., and Saussey, J., *Appl. Catal. A* **167**, 237 (1998).
28. Okal, J., Kêpiñski, L., Krajczyk, L., and Drozd, M., *J. Catal.* **188**, 140 (1999).
29. Stolarek, G., and Wrzyszcz, J., *Chem. Stosow.* **20**, 297 (1976).
30. Mitra, B., Gao, X., Wachs, I. E., Hirt, A. M., and Deo G., *Phys. Chem. Chem. Phys.* **3**, 1144 (2001).
31. Kubicka, H., and Okal, J., *React. Kinet. Catal. Lett.* **48**, 195 (1992).
32. Mariotto, G., Cazzanelli, E., Carturan, G., Di Maggio, R., and Scardi, P., *J. Solid State Chem.* **86**, 263 (1990).
33. Deo, G., and Wachs, I. E., *J. Phys. Chem.* **95**, 5889 (1991).
34. Chan, S. S., Wachs, I. E., Murrell, L.L., Wang, L., and Hall, W. K., *J. Phys. Chem.* **88**, 5831 (1984).
35. Chądzyñski, G. W., and Kubicka, H., *Termochim. Acta* **158**, 369 (1990).
36. Knozinger, H., and Ratnasamy, P., *Catal. Rev. Sci. Eng.* **17**, 31 (1978).
37. Chung, J. S., Zhang, J. P., and Burwell, R. L., Jr., *J. Catal.* **116**, 506 (1989).
38. Morterra, C., and Magnacca, G., *Catal. Today* **27**, 497 (1996).

39. Thomas, R., Kerkhof, F. P. J. M., Moulin, J. A., Medema, J., and de Beer, V. H. J., *J. Catal.* **61**, 559 (1980).
40. Chan, S. S., Wachs, I. E., and Murrell, L. L., *J. Catal.* **90**, 150 (1984).
41. Chan, S. S., Wachs, I. E., Murrell, L. L., and Dispenziere, N. C., Jr., *J. Catal.* **92**, 1 (1985).
42. Giordano, N., Bart, J. C. J., Vaghi, A., Castellan, A., and Martinotti, G., *J. Catal.* **36**, 81 (1975).
43. Peeters, I., van der Gon, A. W. D., Reijme, M. A., Kooyman, P. J., de Jong, A. M., van Grondelle, J., Brongersma, H. H., and van Santen, R. A., *J. Catal.* **173**, 28 (1998).
44. Gazzoli, D., Valigi, M., Vielhaber, B., and Knozinger, H., *J. Less-Common Met.* **134**, 67 (1987).
45. Wachs, I. E., *J. Catal.* **124**, 570 (1990).
46. Chan, S. S., and Wachs, I. E., *J. Catal.* **103**, 224 (1987).
47. Beattie, I. R., and Ozin, G. A., *J. Chem. Soc. A*, 2615 (1969).
48. Rouschias, G., *Chem. Rev.* **74**, 531 (1974).
49. Salvati, Jr., L., Jones, G. L., and Hercules, D. M., *Appl. Spectrosc.* **34**, 624 (1980).
50. Baud, G., and Capestan, M., *Bull. Soc. Chim. Fr.* **11**, 3608 (1969).
51. Schekler-Nachama, F., Clause, O., Commereuc, D., and Saussey, J., *Appl. Catal. A* **167**, 247 (1998).