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Oxidation and redispersion of a low-loaded Re/γ-Al_2O_3 catalyst

J. Okal,[a,*] L. Kępiński,[a] L. Krajczyk,[a] and W. Tylus[b]

[a] *Institute of Low Temperature and Structure Research, Polish Academy of Sciences, P.O. Box 1410, 50-950 Wrocław, Poland*
[b] *Institute of Inorganic Technology, Wrocław University of Technology, 50-353 Wrocław, Poland*

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Abstract

The interaction of sintered low-loaded Re/γ-Al_2O_3 catalysts with oxygen has been studied over a wide temperature range, 20–800 °C. The structure of the catalyst was characterized using different techniques: H_2 chemisorption, O_2 uptake, BET, TEM, and also by Raman and XPS spectroscopy. In the catalyst reduced in H_2 at 800 °C, Re is present as a nonuniform phase consisting of metallic particles with sizes of 1–4 nm and a certain amount of very small clusters (below 1 nm) undetectable by TEM. Oxidation at room temperature causes dissociative chemisorption of oxygen on rhenium with possible formation of a superficial oxide on the Re particles and complete oxidation of the clusters to Re^{4+}–Re^{7+} species. After oxidation at 150 °C only 2% of total Re remains in the reduced state which implies high affinity of highly dispersed Re to oxygen. At 200–300 °C, oxidation of Re hastens giving a mixture of Re^{4+}, Re^{6+}, and Re^{7+} ions, while at 500 °C, complete oxidation to Re_2O_7 occurs. At elevated temperatures, Re_2O_7 sublimates and instantaneously adsorbs on γ-alumina surface as monomeric ReO_4 species. At 500–800 °C, these species are strongly bound to alumina forming a kind of a surface compound with an Al–O–ReO_3 structure. This accounts for the low loss of Re observed even at 800 °C. Redispersion of rhenium was observed after a mild H_2 treatment of the oxidized rhenium catalyst.

Keywords: Re/γ-Al_2O_3 catalyst; Sintering; Oxidation of Re; Redispersion; TEM; H_2 and O_2 sorption; Raman and XPS spectroscopy

1. Introduction

Rhenium-containing catalysts have received much attention over the last three decades due to their use for hydrocarbon transformation [1–4], selective reduction of NO_x to N_2 [5], and for hydrodesulfurization and hydrodenitrogenation [6]. Whereas characterization of the supported Re catalysts was the subject of several detailed studies [7–14] little information can be found in the literature on the oxidation behavior of supported rhenium particles [9,15–20]. The oxidation treatment at elevated temperatures is a crucial step of the activation or regeneration procedures of the rhenium-containing catalysts.

The interaction between oxygen and alumina-supported rhenium is a complex process and depends strongly on the temperature and rhenium loading [9,17,19,20]. It was found that oxygen chemisorption at room temperature [21] may be used as a suitable method for determination of the rhenium dispersion in Re/γ-Al_2O_3 catalysts [9,15–18,22] or total (Pt–Re) dispersion in Pt–Re/Al_2O_3 catalysts [14,23–26]. It should be noted, however, that the stoichiometry of oxygen chemisorption on Re/γ-Al_2O_3 catalysts is still not well established: $O/Re = 0.5$ [27], 1 [18], or higher than one [9] was proposed. Generally, it is accepted that at room temperature adsorbed oxygen is completely dissociated on metallic Re but some data indicated also on nondissociative adsorption at this temperature [9,28]. Studies of the interaction between supported rhenium and oxygen at elevated temperatures are rather scarce and only a few results refer to low-loaded Re/γ-Al_2O_3 catalysts [9,15,17,19,20]. Wagstaff and Prins [15] found that for 0.7% Re/γ-Al_2O_3 catalyst an average oxidation state of rhenium at 100 °C is two, at 180 °C it is four, and at 300 °C it is seven. They suggested that the Re^{2+} state corresponds to oxygen chemisorption, while the Re^{4+} and Re^{7+} states represent true rhenium oxide on the alumina support. Yao and Shelef [9] showed that rhenium, which exists on the surface of γ-Al_2O_3 as the dispersed two-dimensional phase, may be oxidized at 500 °C only to Re^{4+}, while three-dimensional particles to Re^{7+}. Paryjczak et al. [17] reported three temperature ranges of different oxygen-rhenium interactions: superficial oxide (30–200 °C),

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[*] Corresponding author.
E-mail address: jana@int.pan.wroc.pl (J. Okal).

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bulk oxidation (200–400 °C), and above 400 °C when ReO_3 was formed. Chądzyński and Kubicka [19] found that sorption of oxygen at 20–400 °C by the 1% Re/γ-Al_2O_3 catalyst is a slow, activated process that occurs both at the surface and in the bulk of rhenium particles. On the other hand, Raty and Pakkanen [20] showed recently by temperature-programmed oxidation (TPO) that no oxygen consumption occurred on 1% Re/γ-Al_2O_3 catalyst at 20–500 °C and ascribed it to the strong interaction between reduced rhenium particles and the alumina surface. At higher rhenium contents the interaction weakens and oxidation becomes possible. At or above 300 °C rhenium heptaoxide is the main product of oxidation of Re supported on alumina [15,29], rhenium powder [30], or thin Re films [31]. Spectroscopic methods such as IR [7,32], laser Raman [32–35], XANES [33], and XPS [36] revealed that rhenium in the fully oxidized state on γ-alumina support exists always as a two-dimensional surface phase of monomoleculary dispersed ReO_4 tetrahedra.

X-ray photoelectron spectroscopy (XPS) is a powerful tool in the determination of the surface composition of the catalysts. Rhenium is particularly amenable to this method of analysis, since a chemical shift of about 7 eV occurs between rhenium metal and Re_2O_7 oxide [31]. For Re-supported catalysts, XPS was used to examine the oxidation state of Re after reduction [36–38] or after oxidation at high temperature [39,40]. Rhenium–oxygen interactions at various temperatures have also been studied using XPS, but for simpler systems, encompassing Re (0001) surfaces [41], thin Re films [31,42,43], and rhenium foils and ribbons [28,44]. In these studies the oxygen 1s peak at 530 eV, characteristic for atomic oxygen associated with the rhenium, was observed [41–43]. Unfortunately, it is of limited utility for characterizing Re/γ-Al_2O_3 catalysts due to overlapping with the strong O (1s) signal from the support [39]. Alnot and Ehrhardt [44] examined oxidation of the Re ribbons at 427 °C and 1 Torr of oxygen and found ReO_2, ReO_3, and Re_2O_7 on the surface. Tysoe et al. [31] showed that during oxidation of thin Re films deposited on Pt foil at 1 atm of oxygen, a mixture of rhenium oxides was formed above 200 °C and loss of rhenium due formation of the volatile Re_2O_7 occurred after oxidation above 300 °C.

In a previous paper [45] we presented a study of oxidation and redispersion of Re in the sintered 10.4% Re/γ-Al_2O_3 catalyst over a wide temperature range, 20–800 °C. It was found that mild reduction of the oxidized catalyst caused redispersion of rhenium resulting in a 3-fold decrease of the mean particle size of Re and uniform distribution of metallic particles on the support. The aim of this study was to examine, using a similar approach, another system—an oxygen-treated low-loaded Re/γ-Al_2O_3 catalyst (1.04 wt% Re). Such a system more resembles industrially used reforming catalysts (0.3% Re–0.3% Pt/γ-Al_2O_3). Hydrogen chemisorption, oxygen uptake, BET, TEM, and SAED methods were applied to investigate morphology changes created upon heat treatment in hydrogen and oxygen. The effect of oxidation temperature (20–800 °C) on the molecular structure of the rhenium oxide phase was investigated by Raman and X-ray photoelectron spectroscopy.

2. Experimental

2.1. Preparation and treatment of the catalyst

A 1.04 wt% Re/γ-Al_2O_3 catalyst was prepared by wet impregnation of the γ-alumina support ($S_{BET} = 220\ m^2/g$) with an aqueous solution of NH_4ReO_4. After impregnation, the sample was dried at 100 °C for 24 h and then reduced in H_2 flow at 550 °C for 10 h [35]. Next, various heat treatments procedures, similar to those used previously for the high-loading Re/γ-Al_2O_3 catalyst [45], were utilized.

2.1.1. Sintering

The sample of the catalyst was again reduced in H_2 flow (60 ml/min) at 550 °C with a heating rate of 6 °C/min, for 20 h, and next sintered at 800 °C for 5 h. After cooling to room temperature, the catalyst was closed in a glass vessel, evacuated to 10^{-2} Torr (1 Torr = 133 N/m^2), and stored until characterization.

2.1.2. Oxidation

The sintered catalyst was oxidized with static air at temperature in the range of 20–800 °C. The samples were heated from room temperature to the desired one at the rate of 5 °C/min and held at this temperature for 1 or 4 h or in some cases 20 h.

2.1.3. Redispersion

The sample of the sintered or unsintered catalyst was oxidized in air at 400 °C or at 600 °C for 1 h and then reduced in H_2 at 550 °C for 20 h.

2.2. Chemical analysis

Rhenium loading in the catalyst was calculated from the amount of NH_4ReO_4 used for the impregnation. Additionally, the Re content in the samples after reduction and after oxidation was measured by the ICP-AES method. It was determined with an accuracy of better than ±0.1 wt% Re. The contents of sodium and potassium present as impurities in the catalyst were found to be 0.06 and 0.02 wt%, respectively. Determination of the Na and K amounts is important because these elements may change the structure of the rhenium oxide catalyst [46]. Other impurities (Fe, Cu, Mg, Si) were below 10^{-3}%. No Na or K was detected by XPS analysis of the catalyst oxidized at different temperatures. Probably, the surface concentration of these ions was too low to be experimentally observed.

2.3. *Experimental techniques*

2.3.1. *Adsorption methods*

BET surface area, H_2 chemisorption, and O_2 uptake measurements were conducted in the conventional volumetric glass system employed earlier (base pressure 10^{-6} Torr) [27,45]. The BET surface area of the catalyst was measured by nitrogen adsorption at liquid nitrogen temperature on samples dehydrated under vacuum at 300 °C for 3 h.

Before H_2 chemisorption, the sample (ca. 1.5 g) was heated at 520 °C in H_2 at 300 Torr for 4 h and next at the same temperature under vacuum for 2 h. This cycle was repeated three times. Next, hydrogen was introduced on the sample at 520 °C and the catalyst was cooled in hydrogen at 150 Torr to room temperature. The time of cooling was about 3 h. Finally, the total sorption of hydrogen was determined at room temperature. The total amount of bound hydrogen was used to calculate the dispersion of rhenium, assuming 1:1 stoichiometry of H:Re [27,45].

The oxygen uptake was measured at temperature range of 20–500 °C with an oxygen pressure of 100–200 Torr. The sintered catalyst sample (ca. 1.0 g) was reduced in H_2 at 520 °C for 4 h, outgassed at the same temperature for 2 h, and cooled under vacuum to room temperature. Then, the oxygen was introduced and the amount of adsorbed oxygen was determined. Typically, an equilibration time of 20 min was employed. Next, the temperature was raised to the desired oxidation temperature, at the rate 5 °C/min, kept in isothermal conditions for 1 h, and then the sample was cooled under oxygen to room temperature, where the uptake was measured.

2.3.2. *Structure studies*

Morphology and microstructure of the catalyst was studied by transmission electron microscopy (TEM) and selected area electron diffraction (SAED) with a Philips CM 20 microscope equipped with the Super Twin objective lens ($C_s = 1.2$ mm), which at 200 kV provides 0.25-nm resolution. Specimens for TEM were prepared simply by grinding a freshly prepared catalyst powder in a mortar and placing some fine powder on a cooper microscope grid covered with perforated carbon.

XPS was done using SPECS PHOIBOS-100 hemispherical analyzer operating at constant analyzer energy mode. Due to very low Re concentration in the samples narrow scans were taken with rather high 40 eV pass energy. The measurements were performed at room temperature using 100 W (wide scans) or 250 W (narrow scans) X-ray Mg anode. The base pressure in the UHV chamber was below 1×10^{-9} mbar. Sample charging was compensated using an electron flood at 0.5 mA current and 0.1 ± 0.01 eV energy. The detection angle was normal to the sample surface. The samples as a fine powder were pressed into a molybdenum sample holder that, using reproducible pressure conditions, gave tablets with a smooth and uniform surface. Thus, the XPS analyses were performed on the samples exposed to ambient conditions for few minutes. The C ls peak of the contamination carbon, at 284.6 eV, was taken as reference in calculating BEs and accounting effects. The spectra were collected and processed by using SpecsLab software. A nonlinear least-squares fitting algorithm was performed using peaks with a mix of Gaussian and Lorenzian shape and a Shirley baseline. As reference, samples of Re powder (Johnson & Matthey) and Re_2O_7 (Aldrich, purity 99.9%) were used. Before measurement the Re powder was reduced in H_2 at 400 °C, then passivated in air for a few minutes, and finally cleaned by Ar^+ sputtering inside the spectrometer. The Re_2O_7 was used as supplied. The accuracy of the measured binding energies was ±0.1 eV.

The Raman spectra were obtained with a Jobin–Yvon Ramanor-U 1000 spectrometer equipped with the CCD detector cooled to −130 °C and with the 514.5-nm line of an Ar^+ ion laser as the excitation source [35,45]. The laser power at each sample was about 250 mW. The instrument resolution was determined to be better than 2 cm^{-1}. The samples after oxidation at appropriate temperatures were cooled to about 300 °C, next transferred to the glass capillaries within less than 30 s, and immediately sealed. This procedure allowed the collection of the Raman spectra under dehydration conditions. Hydration of the catalyst samples was achieved by exposing the dehydrated samples to ambient air for 20 or 3 h. All spectra were measured at room temperature with a 30-s time exposure per scan.

3. Results

3.1. *Overall characteristics of the catalyst*

General characteristics of the catalyst are given in Table 1. BET surface area of the catalyst after reduction at 550 °C was only slightly less than of alumina support (220 m^2/g). Reduction at 800 °C caused about 20% decrease in the surface area, while the following oxidation up to 800 °C did not change the BET surface area of the catalyst. Analysis data show that the Re content in the catalyst up to oxidation at 600 °C is equal to the amount of Re used for

Table 1
BET surface area, Re content (wt%), and rhenium surface density for 1.04% Re/γ-Al_2O_3 catalysts after various heat treatments

Reduction T (°C)/time	Oxidation T (°C)/time	BET (m^2/g)	Re content[a] (wt%)	Surface density[b] (atoms Re/nm^2)
550/20 h	–	211	1.0	–
800/5 h	–	171	n.d.[c]	–
800/5 h	400/4 h	172	1.1	0.21
800/5 h	600/4 h	170	0.98	0.19
800/5 h	800/4 h	166	0.92	0.18
800/5 h	800/20 h	163	0.89	0.16

[a] Accuracy better than ±0.1 wt% Re.

[b] Defined as the number of Re atoms per square nanometer of the catalyst.

[c] Not determined.

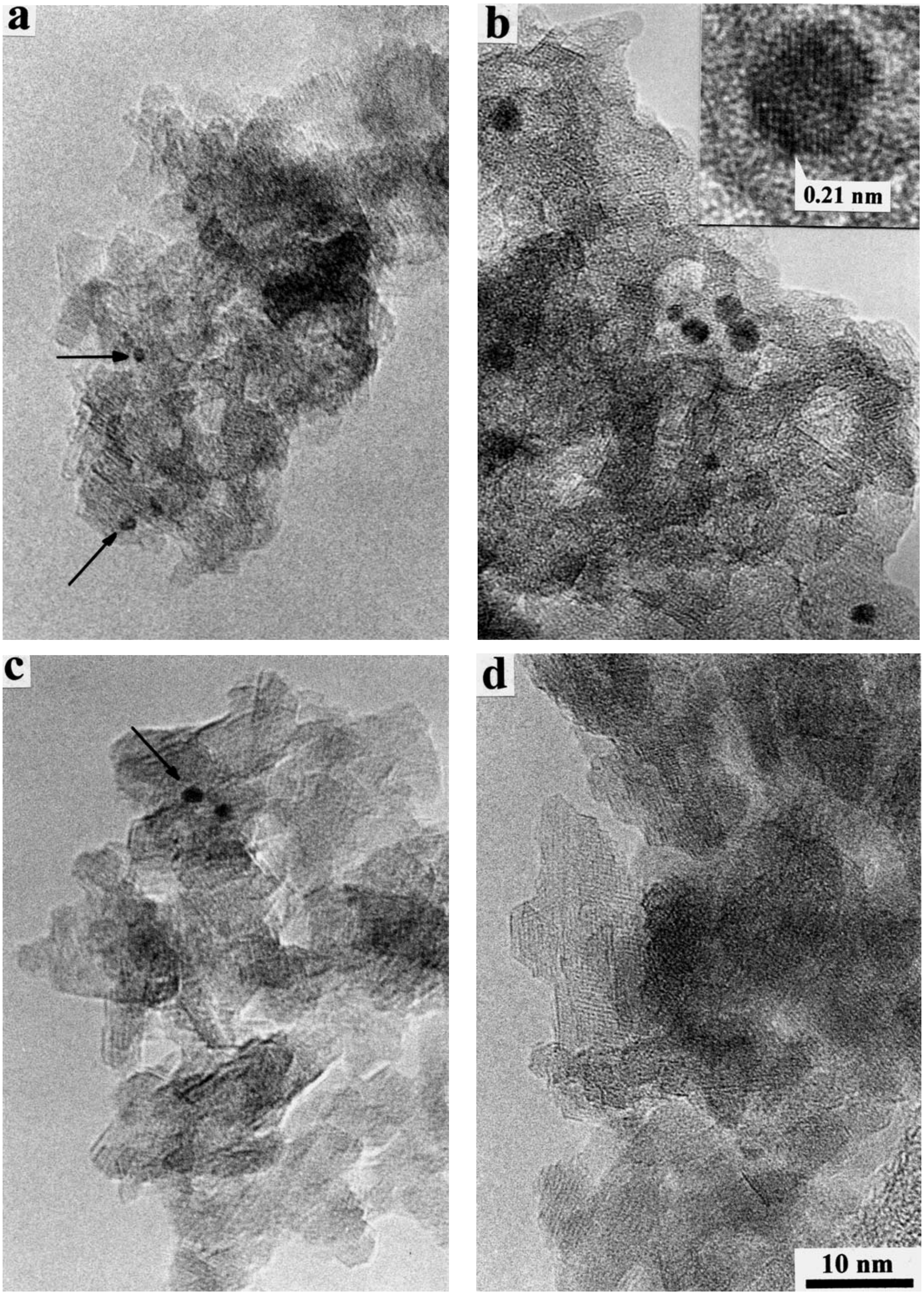

Fig. 1. TEM micrographs of the 1.04% Re/γ-Al_2O_3 catalyst reduced at 550 °C (a), 800 °C (b), oxidized at 150 °C (c), and redispersed (d). Magnified HRTEM image of Re crystallite exhibiting (101) fringes is shown as inset in b.

impregnation (within the experimental error), but at 800 °C about 10% rhenium loss was observed. The Re surface densities calculated from BET surface area and the actual metal loading are only slightly influenced by the oxidation temperature. These values are much below the monolayer coverage of 2.3 Re atoms/nm^2 determined by Vuurman et al. [32].

3.2. Structure characterization by TEM

It is quite difficult to detect rhenium in TEM images of a low-loaded Re/γ-Al_2O_3 catalyst. For the sample reduced at 550 °C for 20 h, only few particles with size of ~1.5 nm, possibly of metallic Re, could be found (Fig. 1a). In the

SEAD pattern (not shown) only broad rings of γ-Al_2O_3 are visible. Obviously, the dark particles noted above may not contain the whole amount of Re present in the sample. The remaining part must be distributed as a highly dispersed (possibly monolayer) phase. It is clearly proved by the TEM images of the sample sintered in H_2 at 800 °C, where Re particles with size 1–4 nm are easily observed (Fig. 1b). In HRTEM image (see inset to Fig. 1b), a 4-nm particle exhibiting 0.21-nm lattice fringes corresponding to Re (101) is seen. Upon oxidation of the sintered samples the detection of the Re-containing phase in TEM became difficult. In the sample oxidized at 150 °C only few particles with size ~1.5 nm could be found (Fig. 1c), while for higher oxidation temperatures, no sign of Re-containing phase was detected. The same was true for the sample subjected to a redispersion procedure, where no Re particles could be observed in HRTEM micrographs (Fig. 1d).

3.3. Chemisorption of hydrogen

The H_2 chemisorption capacities and dispersion data obtained for the 1.04% Re/γ-Al_2O_3 catalysts after various heat treatments are shown in Table 2. Reduction at 800 °C lowers the H_2 uptake as compared to reduction at 550 °C but a corresponding decrease of rhenium dispersion is rather small (27%), which agrees well with the high resistance of rhenium to sintering, characteristic for metals of high melting points (for Re: m.p. = 3180 °C). The average particle size of rhenium in the sample reduced at 800 °C, determined from chemisorption data (2.5 nm), is slightly higher than measured by TEM. Oxidation of the sintered catalyst at 600 or at 400 °C followed by reduction in H_2 at 550 °C resulted in redispersion of rhenium producing very small Re particles with an average size of 1.5 nm. The same size of the Re particles was obtained when the unsintered catalyst sample was subjected to the redispersion procedure. This result is consistent with HRTEM data showing that no Re particles could be detected (cf. Fig. 1d).

3.4. Uptake of oxygen

The uptake of oxygen by the 1.04% Re/γ-Al_2O_3 catalyst sintered in H_2 at 800 °C as a function of the oxidation temperature is shown in Fig. 2. The O/Re values given in Fig. 2 denote the ratio of the number of atomically adsorbed oxygen to the total number of Re atoms in the catalyst. In this uptake study, a fresh sample was used for each data point. The uptake of oxygen was low at room temperature and increased considerably on raising the oxidation temperature. However, even at 500 °C the uptake did not reach maximum and corresponded to an O/Re ratio of 2.98, i.e., 15% lower than the value of 3.5 expected for complete oxidation of rhenium to Re_2O_7 oxide. For unsupported metallic Re, oxidation to Re_2O_7 occurs already at 300 °C [30,31]. The volatilization of rhenium heptaoxide was not observed (see Table 1) and thus it could not be responsible for the underestimation of the O/Re ratio. Also, the samples were subjected to a severe reduction procedure, which should be sufficient to produce metallic rhenium. This was confirmed by reproducible behavior of this catalyst for hydrogen chemisorption [27]. However, data published by other authors showed difficulties in the reduction of rhenium, especially in low-loaded Re/γ-Al_2O_3 catalysts [9,11,15,18].

Table 2
H_2 chemisorption data and metal particle size for 1.04% Re/γ-Al_2O_3 catalysts after various heat treatments

Treatment	H_2 chemisorption			l (TEM)[b]
T (°C)/time/gas	μmol g^{-1} cat.	D[a]	l (chem.)[b]	
550/20 h/H_2	20.7	0.74	1.8	~1.5
+				
800/5 h/H_2	15.1	0.54	2.5	2.0
+				
600/4 h/air	25.2	0.90	1.5	Not visible
+				
550/20 h/H_2				

[a] Dispersion of Re, number of hydrogen atoms chemisorbed to the total number of Re atoms (H/Re) [27].

[b] Metal particle size (nm) determined from H_2 chemisorption and TEM, respectively.

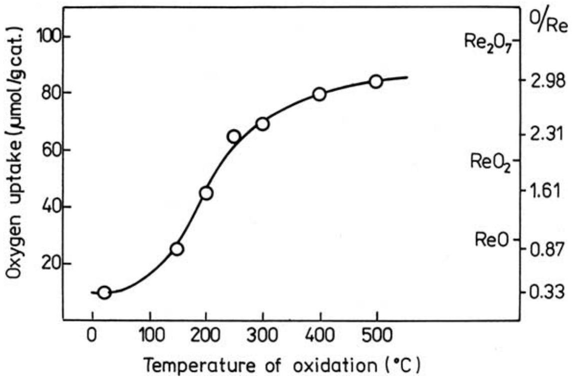

Fig. 2. Oxygen uptake measured as a function of the oxidation temperature for the 1.04% Re/γ-Al_2O_3 catalyst reduced at 800 °C. Formal Re–O stoichiometry corresponding to the measured uptakes is given for comparison.

3.5. XPS studies

The XPS technique was used to establish the oxidation states of the surface rhenium atoms in the catalyst after different treatments. Fig. 3 shows the XPS spectra of the Re powder and Re_2O_7 oxide, as references for Re^0 and Re^{7+} oxidation states, respectively, and the 1.04% Re/γ-Al_2O_3 catalyst oxidized at room temperature. The spectrum of Re powder in the Re 4f region shows two well separated spectral lines at 40.5 and 42.9 eV, assigned to the Re $4f_{7/2}$ and Re $4f_{5/2}$ spin-orbit components, respectively (Fig. 3c). Cimino et al. [30] reported for Re powder the Re $4f_{7/2}$ peak at 40.7 eV, in close agreement with our data. The XPS spectrum of pure Re_2O_7 oxide also shows two, but less separated, spectral lines at 46.9 and 49.3 eV, in good agreement with

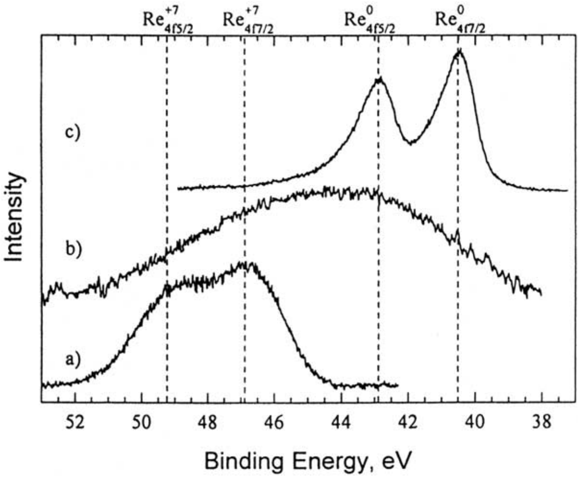

Fig. 3. XPS spectra of the Re 4f region of crystalline Re_2O_7 oxide (a), 1.04% Re/γ-Al_2O_3 catalyst sintered in H_2 and oxidized at room temperature (b), and rhenium powder (c).

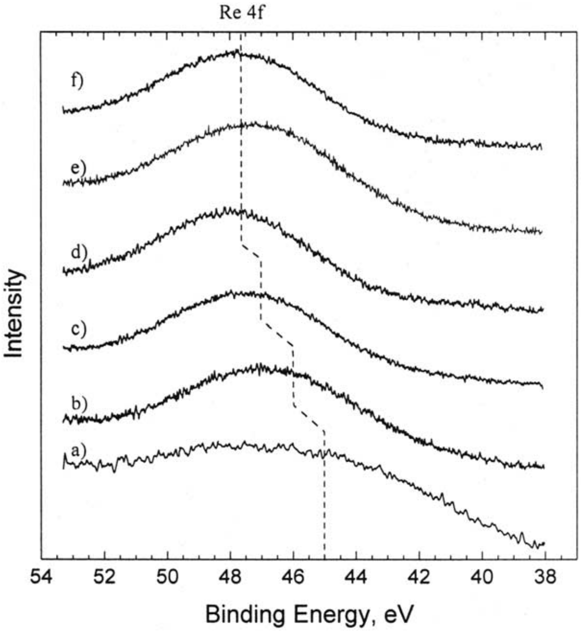

Fig. 4. XPS spectra of the Re 4f region of the 1.04% Re/γ-Al_2O_3 catalyst sintered in H_2 and then oxidized at room temperature for few minutes (a), at 150 °C for 1 h (b), at 300 °C for 1 h (c), at 500 °C for 1 h (d), at 600 °C for 1 h (e), and at 800 °C for 1 h (f).

literature data [30,31,36,37]. Some spectral line broadening observed may be due to partial surface reduction of Re_2O_7 oxide as was found by Cimino et al. [30]. The spectrum of the reduced low-loaded catalyst, after short contact with air, shows a very strong broadening of the Re 4f peak so that the splitting of Re $4f_{5/2}$ and Re $4f_{7/2}$ lines could not be observed. However, the shape and position of the peak indicate that a mixture of the oxidation states of the Re is present.

Fig. 4 shows the Re 4f spectra obtained for the catalyst oxidized at 20–800 °C. Each spectrum exhibits only one broad peak, with an average binding energy increasing with the oxidation temperature. Such spectral broadening has been previously observed for low-loaded Re/γ-Al_2O_3 catalysts [36,37,47] and was attributed to the interaction of the rhenium species with the alumina support. It is evident that the oxidation state of rhenium increases with the oxidation temperature up to 500 °C and remains constant at higher oxidation temperatures. The distribution of the Re oxidation states in the oxidized catalysts was estimated by the deconvolution of Re 4f spectra as shown in Fig. 5. In the curve-fitting routine the relative intensity, FWHM, and separation of the spin orbit doublet were fixed for each doublet. For example, for the sample oxidized at room temperature (Fig. 5a), the best fitting was obtained if we assumed four different oxidation states of rhenium. The deconvoluted peaks at 40.5, 42.8, 44.8, and 46.6 eV are assigned to Re $4f_{7/2}$ peaks and suggest the existence of Re^0, Re^{4+}, Re^{6+}, and Re^{7+} species, respectively [31,36]. The presence of small amounts of the Re in oxidation states between 0 and 4 cannot be excluded, but their identification is difficult because of low metal loading [36,37,47]. Oxidation at 150 °C caused enhanced formation of Re^{6+} and Re^{7+} species, but a trace amount of metallic Re was still present (Fig. 5b). At 300 °C most of rhenium was as Re^{7+} species (Fig. 5c) and after oxidation at 500 °C only Re^{7+} species are present on the surface of the catalyst (Fig. 5d).

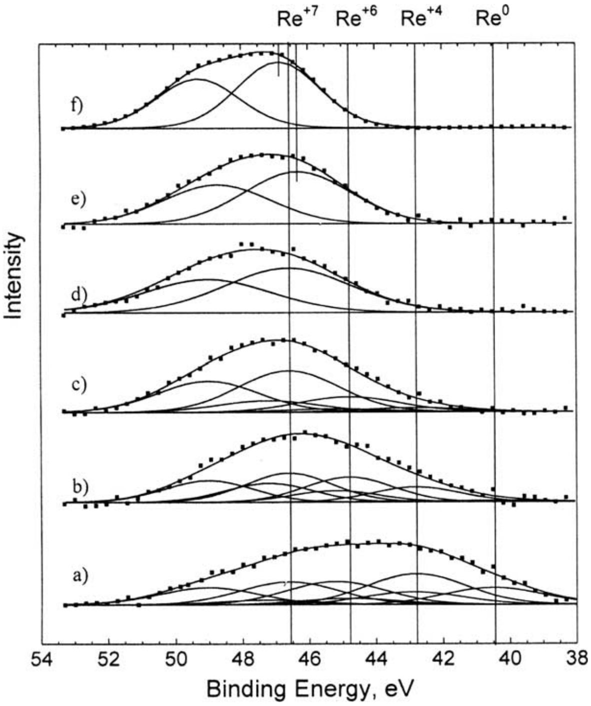

Fig. 5. Deconvolution of the measured XPS spectra: 1.04% Re/γ-Al_2O_3 catalyst oxidized at room temperature (a), 150 °C (b), 300 °C (c), 500 °C (d), 600 °C (e), and Re_2O_7 oxide (f).

Table 3 summarizes curve-fitting results for the reference compounds and the Re/γ-Al_2O_3 catalyst oxidized at all studied temperatures. It includes the binding energies of the most intense Re $4f_{7/2}$ component of each doublet, the distribution of oxidation states of Re ions, and the surface Re/Al atomic ratios. It can be noted that estimation of dis-

Table 3
X-ray photoelectron spectroscopy analysis of the reference compounds and the 1.04% Re/γ-Al_2O_3 catalyst oxidized at different temperatures[a]

Sample	Oxidation temperature	Re $4f_{7/2}$[b]				Re/Al
	(°C)	Re^0	Re^{4+}	Re^{6+}	Re^{7+}	
Re powder[c]	–	40.5 (100)				
Re_2O_7	–			Trace	46.9 (100)	
1.04% Re/γ-Al_2O_3	20	40.5 (21)	42.8 (41)	44.8 (4)	46.6 (33)	0.0024
	150	40.5 (2)	42.8 (24)	44.8 (30)	46.6 (44)	0.0049
	300		42.8 (7)	44.8 (25)	46.6 (68)	0.0050
	500				46.6 (100)	0.0048
	600				46.3 (100)	0.0048
	800				46.6 (100)	0.0050

[a] All binding energies were referenced to C 1s = 284.6 eV.

[b] Binding energies (eV) and concentrations (%) of Re $4f_{7/2}$ species. The numbers in parentheses represent the percentage participation of the Re species.

[c] After reduction at 400 °C and Ar^+ sputtering.

tribution of oxidation states of Re in our samples may be associated with relatively large uncertainty. We suppose that error analysis is about 20% [48]. The Re $4f_{7/2}$-binding energy of the sample oxidized at 600 °C is 0.3 eV lower than that of Re^{7+} ions in the sample oxidized at 500 or 800 °C (46.6 eV) (see Table 3 and Fig. 4e). It was, however, much higher than that for ReO_3, i.e., Re^{6+} species [30,31,36]. To confirm this observation we repeated the experiment with fresh sample and we obtained identical an XPS spectrum. We suppose that increase oxidation temperature causes some diffusion of Re^{7+} species over the surface of the alumina and the environment of the Re ions or a distribution of support interactions may be slightly different from that in the sample oxidized at 500 or 800 °C [36]. Cimino et al. [39] found by XPS that the Re^{7+} species may be located on an SiO_2 support in nonhomogeneous situations (broadening of the Re peak was observed).

From XPS analysis, the surface atomic concentrations of Re and Al were obtained and the Re/Al atomic ratios were calculated (last column in Table 3). In the sample oxidized at room temperature the XPS-determined Re/Al atomic ratio is the same as the bulk atomic ratio, $(Re/Al)_{bulk} = 0.0029$, calculated from the overall chemical composition of the catalyst. After oxidation at 150 °C, the Re/Al ratio is two times higher than the initial one and remains nearly constant up to 800 °C. This result indicates that the rhenium is strongly redispersed over the alumina surface and all rhenium in the samples is detected by XPS in range of 150–800 °C.

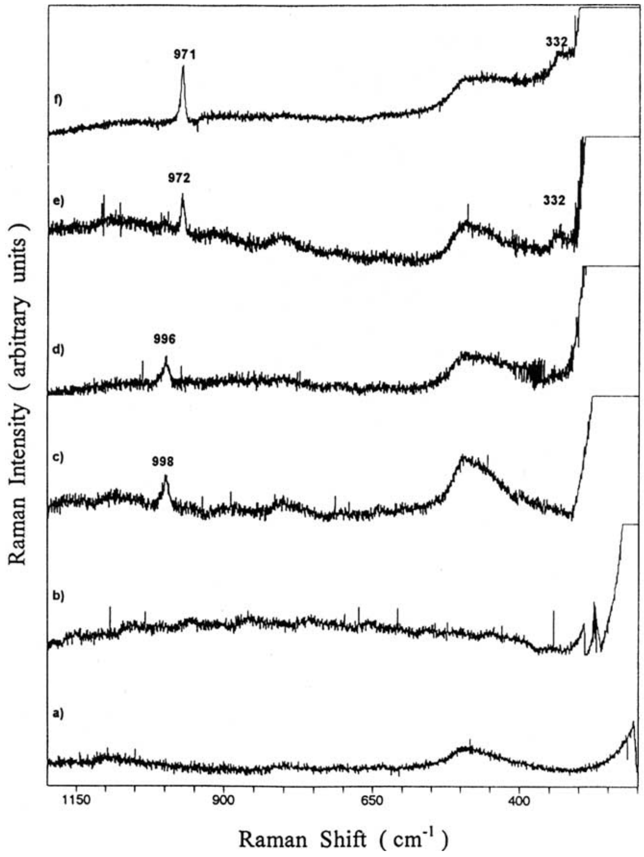

Fig. 6. Raman spectra of γ-alumina (a) and the sintered 1.04% Re/γ-Al_2O_3 catalyst oxidized for 4 h at 400 °C (b), 600 °C (c), and 800 °C (d); dehydration conditions. Spectra e and f were taken after exposing the samples c and d to ambient conditions for 20 h.

3.6. *Raman studies*

Fig. 6 shows the Raman spectra obtained for γ-alumina support (Fig. 6a) and for the oxidized catalyst under dehydrated (Figs. 6b, 6c, and 6d) and hydrated (Figs. 6e and 6f) conditions. The support exhibits only a broad Raman signal at approximately 500 cm^{-1}, which is associated with a defective spinel γ-alumina structure [49]. Also, a weak band at about 800 cm^{-1} observed in some Raman spectra of the catalyst corresponds to γ-alumina structure [35]. The Raman spectrum of the sample oxidized at 400 or at 500 °C for 4 h and recorded under dehydration conditions revealed no evidence of any rhenium oxide species (Fig. 6b). Very similar spectra were observed under hydration conditions (not shown). The Raman spectra of the sample oxidized at 600 or 800 °C for 4 h were similar and exhibited one band at 998 or 996 cm^{-1}, respectively (Figs. 6c and 6d). Increasing the oxidation time at 500 °C to 20 h allowed a similar Raman spectrum with one band at 998 cm^{-1} to be obtained. The band is assigned to the terminal Re=O symmetric stretching vibration of the dehydrated surface rhenium oxide species [32,34,35]. The corresponding antisymmetric stretching and bending modes expected at lower wavenumbers were not visible.

Exposure of the sample oxidized at 600 and 800 °C to atmospheric moisture for 20 h or even 3 h caused a shift of the main Raman band from 998 to 972 cm^{-1} and from 996 to 971 cm^{-1} and appearance of a weak band at 332 cm^{-1} (Figs. 6e and 6f). The band at 332 cm^{-1} is attributed to the O–Re–O bending mode of the surface rhenium oxide species under hydrated conditions [34]. The positions of these bands are similar to those recorded from aqueous ReO^{4-} ions, indicating a tetrahedral rhenium species at the catalyst surface [10].

4. Discussion

Previously, we found for the 10.4% Re/γ-Al_2O_3 catalyst that oxygen uptake at 20 °C was low (O/Re = 0.16) and increased at 300–500 °C to the maximum value of 3.3, only 6% lower than that in Re_2O_7 oxide [45]. Oxygen uptake at room temperature obtained in the present study for the low-loaded Re/γ-Al_2O_3 catalyst sintered in H_2 was also rather low (O/Re = 0.33). A recent study on the same catalyst [27] gave the surface coverage of the rhenium with oxygen (expressed as O/H) as only 0.5, which was consistent with that obtained on a rhenium powder [50]. However, our XPS result for the reduced catalyst exposed for a short time to air at room temperature showed significant reoxidation of rhenium (Table 3), which cannot be considered as only a passivation of the metal particles. It appears, therefore, that O_2 chemisorption should be used with a precaution as a routine method for determination of the Re dispersion in low-loaded Re catalysts.

With increasing temperature, rise of the oxygen uptake was observed but even 1 h oxidation at 500 °C did not cause complete oxidation of rhenium particles to Re_2O_7 (O/Re = 2.98). An average oxidation state of Re was 2 at 150 °C, 4 at 250 °C, and 6 at 500 °C (Fig. 2). Prolonged oxidation at 500 °C (4 h) did not cause any increase in the O_2 uptake. Paryjczak et al. [17] also obtained stoichiometry close to ReO_3 after oxidation of the Re/γ-Al_2O_3 catalyst above 400 °C. However, none of our Raman spectra showed bands characteristic for ReO_3 oxide, i.e., for octahedrally coordinated rhenium, which appear at frequencies much lower than those measured in the present study [32]. In addition, our XPS results show complete oxidation of Re to Re^{7+} in the sample treated at 500 °C for 1 and 4 h (Table 3).

The oxygen uptake lower then expected for oxidation of Re^0 to Re^{7+} may indicate that a certain part of Re exists in a low positive oxidation state before oxidation. This low-valent Re, probably monolayer phase or very small clusters, undergoes the oxidation to Re^{4+}, Re^{6+}, or Re^{7+} during exposure to air at room temperature, as was observed by XPS. Unfortunately, we could not characterize our reduced samples by in situ XPS, i.e., without exposure to air. The remaining part of Re is present as metal particles with sizes of 1–4 nm, easily detected by HRTEM and XPS. We suppose that partial reoxidation of rhenium may occur during the evacuation of the catalyst at 520 °C applied after the H_2 reduction treatment in the procedure used for O_2 uptake measurement. The same process may be present also in procedures used for H_2 chemisorption. Calculated from H_2 chemisorption data metal particle sizes were slightly higher than those from TEM supporting lower H_2 uptake then expected. Solymosi and Bansagi [51] reported that isolated Re species in the reduced 1% Re/γ-Al_2O_3 catalyst could be oxidized to mono or higher valence metal ions by the OH groups of the alumina support. It is known that alumina support even at 500 °C keeps water on its surface for a long time [52,53]. The results of O_2 uptake may also be influenced by polar interactions between reduced rhenium species and oxygen atoms of the support. Fung et al. [54] and Ronning et al. [55] showed by EXAFS study of the reduced 2% Re/γ-Al_2O_3 catalyst, a pronounced Re–O interaction at ca. 2.0 Å, which they associated with the strong interaction between rhenium and oxygen atoms of the γ-Al_2O_3 support.

Our results are consistent with those presented by Yao and Shelef [9] who found that Re at low concentrations on γ-alumina, after reduction at 500 °C, is present as highly dispersed two-dimensional rafts in addition to crystalline three-dimensional particles. EXAFS data obtained by Fung et al. [47] for the 1% Re/γ-Al_2O_3 catalyst prepared from NH_4ReO_4 showed that after reduction at 400 °C, the resulting surface species were highly nonuniform, consisting of surface rhenium oxide and metallic rhenium particles. In other paper, Fung et al. [38] found by TPR that passivation of the reduced 1% Re/γ-Al_2O_3 catalyst had led to a complete oxidation of Re^0 to Re^{7+}. The authors explained the complete oxidation of Re by the high affinity of the supported Re to oxygen. Hence, the oxophilic character of Re may be a problem when O_2 is used to determine the exposed Re surface area in supported Re and Pt–Re catalysts [19,27].

The present study shows that in the oxidized 1.04% Re/γ-Al_2O_3 catalyst Re species could be observed by Raman spectroscopy only after oxidation at 500 °C for 20 h or at 600 °C and above for 4 h, i.e., for samples where only Re^{7+} species were found by XPS (see Table 3). For high-loaded catalyst we observed Raman peaks already at 300 °C [35]. Probably for low-loaded catalyst, due to diversity of Re ions, the surface concentration of individual Re ions was too low be experimentally observed, or the presence of water molecules on the surface of the γ-alumina precluded the observation of the Re species. Chan et al. [56] found that the removal of water from various supported transition metal oxide systems decreases the disorder on the surface and improves the Raman spectra. Raman spectra (Fig. 6) show that under dehydrated conditions only one kind of surface rhenium oxide species corresponding to ν_s(Re=O) of 996–998 cm^{-1} is present. This result is in accord with our previous study [35] and the literature data obtained for low-loaded Re_2O_7/Al_2O_3 catalysts calcined at 500 °C [32,34]. Hence, the dehydrated rhenium oxide exists as an isolated, four-coordinated species with three terminal Re=O bonds and one bridging Re–O–Al bond [32–34]. For 10.4% Re/γ-Al_2O_3 we found that ReO_4 monomers exist as two slightly different species [35,45]. The strength of the bridging Re–O–support bond is not influenced by the temperature of oxidation up to 800 °C, as is evidenced by small changes in the bond strength of the terminal Re=O bonds. The rhenium oxide formed at 500–800 °C is firmly bonded to alumina support as distorted ReO_4 tetrahedra. Strong interaction between the rhenium oxide and the alumina surface in the low-loaded catalyst is also confirmed by low loss of rhenium at 800 °C evidenced by chemical analysis and XPS (see Tables 1 and 3). Exposure of the dehydrated low-loaded catalyst to ambient air at room temperature caused hydration of the surface rhenium oxide species (ν_s(Re=O) in the range 972–971 cm^{-1}).

Results of H_2 chemisorption and TEM showed that oxidation of the sintered catalyst at 400 or at 600 °C for 1 h followed by reduction in H_2 at 550 °C leads to about 40% growth of the Re dispersion. Issacs and Petersen obtained similar enhancement of the Re dispersion for the 0.33% Re/γ-Al_2O_3 catalyst calcined at 300–500 °C [18]. The redispersion effect obtained in this work for the low-loaded catalyst is not as large as observed earlier for the sintered 10.4% Re/γ-Al_2O_3 catalyst, where we found a 3-fold decrease of the mean particle size of Re [45]. Okal and Kubicka [3] reported a significant increase in hydrogenation activity of both catalysts after redispersion procedures similar to those used in the present study.

We suppose that the mechanism of oxidation and redispersion of rhenium, proposed for high-loaded Re/γ-Al_2O_3 catalyst in Ref. [45], is generally valid also for the low-loaded catalyst studied in this work. In the 1.04% Re/γ-Al_2O_3 catalyst sintered at 800 °C, Re is present as a highly nonuniform phase, consisting of very small clusters and particles with sizes of 1–4 nm. Upon oxidation at room temperature dissociative chemisorption of oxygen occurs on the Re particles with the possible formation of a superficial Re oxide, while small clusters of rhenium were oxidized to Re^{4+}, Re^{6+}, or even Re^{7+} as found by XPS. Only 21% of Re was left in a zero valence state. This indicates a high affinity of highly dispersed Re to oxygen. At 150 °C only a trace amount of Re (2%) was not oxidized. At temperatures 200–300 °C, the process of oxidation was also detected by measurements of oxygen uptake. At 500 °C, XPS and Raman results confirm complete oxidation of Re to Re_2O_7. At this or even lower temperatures, Re_2O_7 sublimes and is adsorbed on the support as ReO_4 monomers. At 500–800 °C, ReO_4 species are firmly bound at γ-alumina surface and form a kind of a surface compound with Al–O–ReO_3 structure. Reduction of the oxidized catalyst in H_2 at 550 °C causes a 40% increase in Re dispersion. The particles of Re with an average size of 1.5 nm as determined by H_2 chemisorption could not, however, be detected by HRTEM.

5. Conclusions

Rhenium in the sintered in H_2 1.04% Re/γ-Al_2O_3 catalyst is present as a highly nonuniform phase, consisting of very small clusters and metallic particles with the size of 1–4 nm. The interaction of oxygen with this catalyst is a complex process, which depends strongly on temperature. At room temperature a superficial Re oxide is formed on Re particles, whereas small clusters are completely oxidized to Re^{4+}–Re^{7+} species. At 150 °C, nearly all Re is in an oxidized (cationic) state. At 200–300 °C, the oxidation process accelerates and the rhenium is redispersed over the alumina surface. At 500 °C complete oxidation of Re to Re_2O_7 takes place with its simultaneous sublimation and adsorption on γ-alumina as ReO_4 species. At 500–800 °C, ReO_4 monomers are firmly bonded to the support. Mild reduction of the oxidized low-loaded Re/γ-Al_2O_3 catalyst caused redispersion of the metallic phase.

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