Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Catalysis 225 (2004) 498–509

JOURNAL OF CATALYSIS

www.elsevier.com/locate/jcat

XPS study of oxidation of rhenium metal on γ-Al_2O_3 support

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

[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

Received 2 March 2004; revised 29 April 2004; accepted 1 May 2004

Abstract

The oxidation of Re/γ-Al_2O_3 catalysts, containing 1 and 10 wt% of rhenium, sintered in hydrogen was examined in the temperature range of 20–800 °C. The structures of the catalysts were investigated by XPS spectroscopy, TEM, and O_2 uptake measurements. The low-loaded catalyst comprises metallic particles with sizes of 1–4 nm ($d_{av} = 2.1$ nm), while the high-loaded catalyst comprises particles with sizes of 1–9 nm ($d_{av} = 4.9$ nm). Even short exposure to air at room temperature causes complete oxidation of small clusters of metallic Re, while larger particles are covered with very thin ReO_x skin (undetected by TEM). XPS shows that the high-loaded catalyst still contains 94.5% of metallic Re, while the low-loaded catalyst contains only 60.5%. The remaining part of the Re is oxidized to Re^{4+}, Re^{6+}, and Re^{7+} species. Oxidation at 150 °C causes enhanced formation of Re^{4+}–Re^{7+} species and the amount of metallic Re quickly decreases to 33 and 2% for high- and low-loaded catalysts, respectively. This indicates a high affinity of the highly dispersed Re to oxygen. At this temperature, the Re/Al atomic ratio increases 2–4 times, indicating a large spreading of the oxide species on the support surface. Simultaneously, the average size of Re particles decreased as determined by TEM. At 300 °C, whole Re was oxidized mainly to Re_2O_7, though some amount to Re^{4+} and Re^{6+} species remained. The O_2 uptake measurements confirm oxidation of rhenium particles. For the high-loaded catalyst O_2 uptake attained a maximum level ($O/Re = 3.3$) already at 300 °C, while for the low-loaded catalyst even at 500 °C the uptake ($O/Re = 2.98$) is below the maximum level. XPS data showed, however, that at 500 °C, oxidation of rhenium to Re_2O_7 occurs for both catalysts. The Re/Al atomic ratio remains nearly constant after oxidation of both catalysts at 300–800 °C, indicating that Re^{7+} species are firmly bonded to alumina surfaces even at 800 °C. A detailed mechanism of oxidation of Re particles with different sizes is proposed based on a quantitative analysis of the XPS, O_2 uptake, TEM, and previous Raman results.

Keywords: Re/γ-Al_2O_3 catalyst; Oxidation of Re; TEM; O_2 sorption; XPS spectroscopy

1. Introduction

The practical importance of Pt–Re/Al_2O_3-reforming catalysts and recently also Re–Co/Al_2O_3 catalysts [1,2] has created interest in catalytic chemistry on the Re-containing catalysts. Generally, Re addition promotes diesel and gasoline production [3]. Supported rhenium catalysts have been tested for hydrocarbon conversion craking [4–6], hydrogenation of benzene [6,7], *n*-heptane reforming [8], and recently as promising catalysts for methane [9] and ethane [10] aromatization and also for ammonia synthesis [11]. Catalytic hydrocarbon reactions are always accompanied by the catalyst deactivation, which results from the sintering of the catalyst, the presence of poisons in the reagents, and the deposition of carbonaceous species. Thermal treatment in oxygen or in air is usually used to remove the effects of catalyst deactivation, and it is also an important step in the activation or regeneration procedures of rhenium-containing catalysts. Regeneration of the spent (reduced) Re_2O_7/Al_2O_3 catalyst by oxidation at elevated temperatures brings about the redispersion of rhenium crystals and the formation of the well-dispersed oxide phase [12–14].

However, the interaction between supported rhenium and oxygen has not been well characterized and only few studies have reported on the oxidation behavior of the supported Re particles [13–19]. On the contrary, for the Pt–Re/Al_2O_3 catalyst, the effects of oxidation–reduction or oxychlorination–reduction cycles on the structure and activity are often studied [8,20–24]. It is well known that oxidation of the Pt–

---

[*] Corresponding author. Fax: + 48 71 441 029.
E-mail address: jana@int.pan.wroc.pl (J. Okal).

0021-9517/$ – see front matter © 2004 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcat.2004.05.004

Re/Al_2O_3 catalyst above 300 °C leads to segregation of Pt and Re oxide [15,20,21] and as a consequence causes important changes in the catalytic behavior of the system. XANES and TPR studies of a $Pt–Re/Al_2O_3$ catalyst subjected to oxychlorination also showed that redispersion of both active components into their single, monometallic oxides occurs [22,23]. IR study of CO adsorption for calcined, oxidized, and oxychlorinated $Pt–Re/Al_2O_3$ catalysts also confirmed that Re and Pt components were segregated after such treatment [24]. Botman et al. [25] showed that hydrogenolysis activity of the Re/γ-Al_2O_3 catalyst decreased significantly after calcination in air at 450 °C. In contrast, Rochester and co-workers [8] found for Re/Al_2O_3 that oxidation treatments at 550 °C had little effect on activity and selectivity for heptane–H_2 reactions. Prestvik et al. [20] and earlier Isaacs and Petersen [26] found that the reduction temperature of Re in Re/Al_2O_3 catalysts is influenced by the temperature of calcination/oxidation pretreatment. Chądzyński and Kubicka [18] established the increased resistance of the oxidized Re/γ-Al_2O_3 catalyst with low Re content to re-reduction by hydrogen.

On the other hand, Raty and Pakkanen [19] found recently, using temperature-programmed oxidation method (TPO), that at 20–500 °C no oxygen consumption occurred on the 1% Re/γ-Al_2O_3 catalyst and explained this by a strong interaction between reduced rhenium particles and the support. At higher rhenium loading the interaction weakens and oxidation becomes possible. It was proposed [14] that rhenium existing on the surface of γ-alumina as a well-dispersed phase may be oxidized at 500 °C only to Re^{4+} species, whereas three-dimensional particles to Re^{7+} species. Other data demonstrated that ReO_3 is the product of oxidation of Re in Re/γ-Al_2O_3 catalyst above 400 °C [16]. It was also reported that at or above 300 °C rhenium heptaoxide is the main product of oxidation of Re supported on alumina [15,21] as well as rhenium powder [27] and thin Re films [28]. As can be seen, the interaction of oxygen with Re/γ-Al_2O_3 catalyst is a complex process and depends mainly on the temperature and the rhenium loading [13,14, 16,18,19].

Many physical techniques have been employed to study the molecular structures of oxidized rhenium catalysts. Raman and IR spectroscopies [12,29–32] revealed that rhenium in the fully oxidized state on γ-alumina forms a two-dimensional surface phase of monomoleculary dispersed ReO_4 species. Also XANES analysis confirms that after calcination Re is present in an oxidation state close to Re^{7+} [22,23]. Wachs and co-workers suggested additionally that the dehydrated surface ReO_x species may be polymerized [33,34].

X-ray photoelectron spectroscopy (XPS) provides a valuable technique for assigning oxidation states and stoichiometry of the oxides. There are a few XPS studies on various Re oxides, including ReO_2, ReO_3, and Re_2O_7 [27,28]. These oxides could possibly form during oxidation of the Re/γ-Al_2O_3 catalyst. A large chemical shift of about 7 eV occurs between the Re metal and the highest rhenium oxide, Re_2O_7; therefore, rhenium is particularly amenable to this method of analysis. Rhenium–oxygen interactions were studied by XPS mainly in simple systems such as thin films [28,35], foils and ribbons [36], and single crystals [37]. For supported rhenium catalysts, XPS was used to examine the oxidation states of rhenium after reduction [38–40] or more often after oxidation at high temperature [41–46]. Shpiro et al. [38] employed this method to determine differences in the reduction behavior of Re/SiO_2 and Re/γ-Al_2O_3 catalysts. Cimino et al. [43] applied XPS and other techniques to identify the interaction between rhenium species and silica heated in air at 200–750 °C. Yuan et al. [45] used XPS to determine the redox capability of Re oxides supported on α-Fe_2O_3 in order to explain the high performance of this system for the selective methanol oxidation. Similarly, Yide et al. [46] presented XPS evidence for the existence of different valence states of rhenium after propane methatesis over Re_2O_7/Al_2O_3 catalyst.

In this work, we report a detailed study of rhenium oxidation in the sintered Re/γ-Al_2O_3 catalysts over a wide temperature range, 20–800 °C, by using XPS spectroscopy, TEM, and volumetric O_2 uptake measurements. To our knowledge, no XPS results on the formation of the Re-oxide phases occurring during the oxidation of supported rhenium are available in the literature. Especially, the effect of particle size on the progressive oxidation of nanometer size rhenium particles has not been studied. The present XPS studies complete our previous characterization of the Re/γ-Al_2O_3 catalysts by H_2 chemisorption, electron microscopy, XRD, and Raman spectroscopy methods [13,32, 47]. The Re/γ-Al_2O_3 catalysts investigated here were identical to those characterized in Refs. [13,32,47].

2. Experimental

Details of the preparation procedure of the Re/γ-Al_2O_3 catalysts containing 1.04 and 10.4 wt% Re have been given elsewhere [13,47]. The catalysts were obtained by wet impregnation of γ-Al_2O_3 (S_{BET}—220 m^2/g) with an aqueous solution of NH_4ReO_4. After impregnation the samples were dried in air at 100 °C for 24 h and next preliminary reduced in H_2 flow at 550 °C for 10 h.

All oxidation experiments were performed on the samples of sintered catalysts. The sintering procedure consisted of repeated reduction in hydrogen flow (heating rate of 6 °C/min) at 550 °C for 20 h and then reduction at 800 °C for 5 h. After cooling to room temperature, the catalyst was carefully passivated by being exposed to air, closed in a glass vessel, and outgassed to 10^{-2} Torr (1 Torr = 133 N/m^2). Rhenium dispersion in the catalysts was derived from hydrogen chemisorption measurements performed in an all glass volumetric adsorption system [13,47]. The same system was used to determine the oxygen uptake by the sintered catalyst samples. The oxygen uptake was measured in temperature range of 20–500 °C with the oxygen pressure of 100–200 Torr (for details cf. [13,47]). Prior to measurements the sample (0.1 or 1 g) was pretreated in situ in H_2 at 500 °C, for 2–4 h, outgassed at the same temperature for 2 h, and cooled to room temperature. Then, oxygen was introduced and the amount of adsorbed O_2 was determined. The sample was then heated to the desired oxidation temperature, kept at isothermal condition for 1 h, and then cooled under oxygen to room temperature, where the total O_2 uptake was measured. The reproducibility of measurements of the amounts adsorbed was always better than 0.5 µmol.

The BET surface area of the catalysts was measured by nitrogen adsorption on samples dehydrated under vacuum at 300 °C for 3 h.

TEM images were recorded with a Philips CM20 SuperTwin microscope, which at 200 kV provides 0.25 nm resolution. Specimens for TEM were prepared simply by dipping a copper microscope grid covered with perforated carbon into a powder sample.

For XPS studies, the catalyst samples reduced at 800 °C were oxidized with static air in temperature range of 20–800 °C, by heating from room temperature to the desired one, with a heating rate of 5 °C/min, and holding at this temperature for 1 h or in some cases 4 or 20 h. The hot sample was transferred to the glass container and sealed to enable the collection of the XPS spectra under dehydration conditions.

XPS was done using a SPECS PHOIBOS-100 hemispherical analyzer equipped with a Mg source (1253.6 eV) operating at 100 W (wide-range scan) and 250 W (high-resolution spectra). The spectra were acquired at room temperature and narrow scans with rather high 40 eV pass energy for the samples with low Re concentrations were recorded. The base pressure in the UHV chamber was below 1×10^{-9} mbar. The spectrometer energy scale was calibrated with Au $4f_{7/2}$, Ag $3d_{5/2}$, and Cu $2p_{3/2}$ lines at 84.2, 367.9, and 932.4 eV, respectively. 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 catalyst samples as a fine powder were pressed into a molybdenum sample holder using reproducible pressure conditions, and mounted to the sample manipulator of the chamber. The obtained tablets had a smooth and uniform surface. Due to electric charging effects, XPS peaks were shifted toward higher energy. Calibration of the energy positions of peak maxima was done using binding energy of the 1s peak of contamination carbon at 284.6 eV as a reference. The energy resolution was ±0.1 eV. The spectra were collected and curve-fitted by using the SpecsLab (version 1.8.2) software. A nonlinear least-squares fitting algorithm was applied using peaks with a mix of Gaussian and Lorentzian shape and a Shirley baseline. The fitting routine constrained the area ratio for the spin-orbit split Re ($4f_{7/2,5/2}$) lines to be 1.33. Intensities, peak positions, line widths, and Gaussian/Lorentzian mix were all optimized by the fitting routine.

Re powder (Johnson & Matthey) and Re_2O_7 oxide (Aldrich, purity 99.9%) were employed as references for Re^0 and Re^{7+} oxidation states, respectively. Before XPS measurement the Re powder was reduced in hydrogen flow at 400 °C for 5 h, then passivated on air for a few minutes, and finally cleaned by Ar^+ sputtering inside the spectrometer. The Re_2O_7 oxide was used as supplied.

Re content in the catalyst samples was determined by the ICP-AES method, with an accuracy of ±0.1 wt% Re. Concentrations of Na and K, present as impurities in the catalysts, were found to be 0.06 and 0.02 wt%, respectively. Other impurities as Fe, Cu, Mg, and Si were below 10^{-3}%. No impurities except carbon were detected on the surface of both catalysts by XPS.

3. Results

3.1. Overall characteristics of the catalysts

The state of the catalysts before oxidation was characterized by H_2 chemisorption and high-resolution electron microscopy (HRTEM). The hydrogen uptake (H/Re) values obtained on the 10.4% Re/γ-Al_2O_3 and 1.04% Re/γ-Al_2O_3 catalysts after reduction in H_2 at 800 °C were 0.25 and 0.54, respectively. The average particle size of rhenium evaluated by direct observation by HRTEM was 4.9 nm for high-loaded catalysts (particle sizes in range of 1–9 nm), and 2.1 nm for low-loaded catalysts (particle sizes in range of 1–4 nm). TEM results are in good agreement with chemisorption data and are consistent with our previous studies [13,47]. BET surface areas of the 10.4 and 1.04% Re/γ-Al_2O_3 catalysts after reduction at 800 °C amount to 153 or 171 m^2/g, respectively, i.e., about 30 or 20% less than the surface area of the bare support. However, reduction at 800 °C did not cause the support crystallization as was shown by XRD and electron diffraction (SEAD) studies [13,47]. Hence, the loss of the BET surface area of the samples studied is connected with changes in the pore structure of the catalysts. The basic characteristics of the Re/γ-Al_2O_3 catalysts after oxidation treatment are given in Table 1. It appears that oxidation up to 800 °C did not change significantly the BET surface area of both catalysts. The Re content in both catalysts did not change upon oxidation up to 600 °C, but some loss of the Re was detected at higher temperatures. At 800 °C, Re loss of about 33 and 10% occurred for 10.4% Re/γ-Al_2O_3 and 1.04% Re/γ-Al_2O_3 catalysts, respectively.

Change in morphology of the reduced catalysts upon oxidation was studied by HRTEM. Fig. 1 shows representative images of the high-loaded catalyst as reduced at 800 °C (a) and then oxidized at 150 °C (b) and at 500 °C (c), while Fig. 2 presents the evolution of the size distribution of Re particles. It appears that already at 150 °C there is some redispersion of Re that manifests as a decrease of the average particle size and the appearance of very small secondary particles. According to HRTEM, there is, however, no evidence

Table 1
BET surface area, Re content (wt%), and rhenium density for sintered in H_2 Re/γ-Al_2O_3 catalysts after oxidation treatments at various temperatures

Catalyst	Oxidation T (°C)/time	BET (m^2/g)	Re content[b] (wt%)	Surface density[c] (atoms Re/nm^2)
10.4% Re/γ-Al_2O_3[a]	400/4 h	154	10.7	2.2
	600/4 h	153	10.0	2.1
	700/4 h	153	9.2	1.9
	800/4 h	151	7.0	1.5
	800/20 h	150	6.9	1.5
1.04% Re/γ-Al_2O_3	400/4 h	172	1.10	0.21
	600/4 h	170	0.98	0.19
	700/4 h	170	0.97	0.19
	800/4 h	166	0.92	0.18
	800/20 h	163	0.89	0.16

[a] Re content calculated from the amount of NH_4ReO_4 used for impregnation.
[b] Measured by ICP-AES, accuracy ±0.1 wt% Re.
[c] Defined as the number of rhenium atoms per square nanometer of the catalyst.

of bulk or even surface oxidation of larger Re particles since the particles exhibit well-defined, sharp outlines (cf. inset to Fig. 1b). The process of the Re redispersion in oxidative atmosphere accelerates at 200 °C, and at 250 °C only sparse metal particles remain. At even higher temperatures whole Re is uniformly spread over the support (Fig. 1c).

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. For the 10.4% Re/γ-Al_2O_3 catalyst oxidized up to 600 °C the Re surface density is close to the monolayer coverage, which according to Ref. [29] amounts to 2.3 Re atoms/nm^2. It can be noted, however, that Re_2O_7 oxide formed by oxidation of the Re at such high temperatures is volatile and monolayer surface coverage of ReO_x species is never achieved on any oxide support [34].

3.2. Uptake of oxygen

The results of the volumetric measurements of the oxygen uptake by the Re/γ-Al_2O_3 catalysts sintered in H_2 at 800 °C are presented in Table 2. The O/H and O/Re given in Table 2 denote the ratios of the number of adsorbed oxygen atoms to the number of hydrogen atoms chemisorbed in the monolayer and to the total number of rhenium atoms in the catalyst, respectively. It appears that at room temperature the O_2 uptake by both catalysts is low and according to literature data it may be attributed to dissociative chemisorption [17]. The coverage of the rhenium surface with oxygen (expressed as O/H) close to 0.60 for both catalysts is consistent with that obtained volumetrically on a rhenium powder [48] and on polycrystalline and single crystals of rhenium [37]. Some authors suggested that difficulties in obtaining the saturation of Re/γ-Al_2O_3 catalysts with oxygen could be due to a penetration of oxygen into the subsurface region of rhenium [18].

Observed rise of the oxygen uptake with increasing temperature (cf. Table 2) points to a bulk oxidation of the Re. Some differences in the oxidation behavior of Re were noted dependent on rhenium loading and thus on particle size of rhenium in the catalyst. For the high-loaded catalyst, with an average particle size of Re about 5 nm, the oxygen uptake reaches a maximum level already at 300 °C and does not change up to 500 °C. The O/Re ratio equal to 3.31 suggests nearly complete oxidation of the Re particles to Re_2O_7 oxide. For the low-loaded catalyst, with an average particle

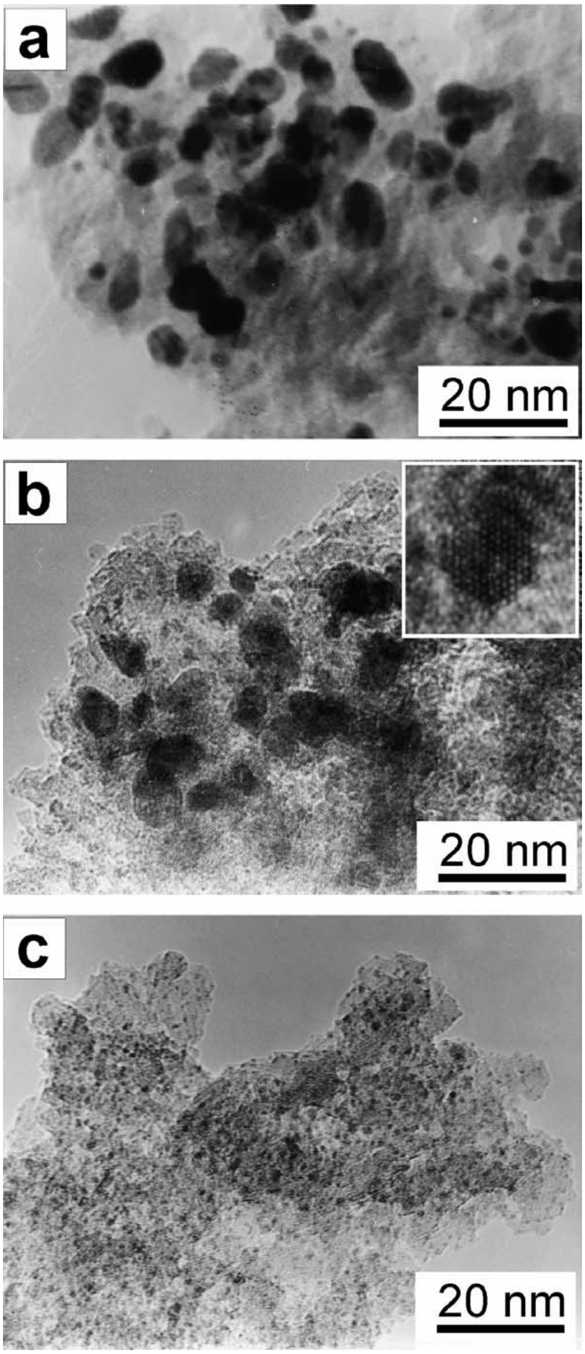

Fig. 1. TEM micrographs of the 10.4% Re/γ-Al_2O_3 catalyst reduced at 800 °C (a), and oxidized at 150 °C (b), and at 500 °C (c). Magnified HRTEM image of Re crystallite with no evidence of the surface oxidation is shown as inset to (b).

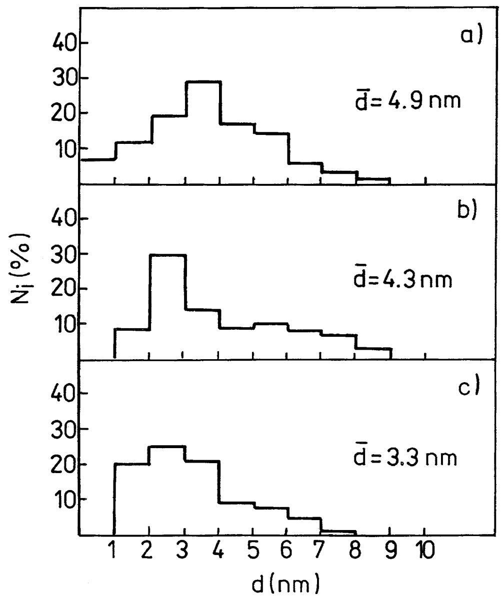

Fig. 2. In the size distribution of the 10.4% Re/γ-Al_2O_3 catalyst after reduction at 800 °C (a), and oxidized at 150 °C (b), and 200 °C (c). Average size of Re particles calculated from the distributions is 4.9, 4.3, and 3.3 nm, respectively.

Table 2
Uptake of oxygen by the reduced at 800 °C Re/γ-Al_2O_3 catalysts as a function of oxidation temperature

Catalyst	Oxidation temperature (°C)	Uptake of oxygen ($\mu mol_{O_2}/g_{cat}$)	O/H[c]	O/Re[d]
10.4% Re/γ-Al_2O_3[a]	20	44.5	0.64	0.16
	150	44.8	0.64	0.16
	200	184.3	2.64	0.66
	250	576.6	8.28	2.07
	300	927.5	13.28	3.32
	400	917.1	13.20	3.30
	500	920.1	13.21	3.31
1.04% Re/γ-Al_2O_3[b]	20	9.1	0.60	0.33
	150	24.35	1.61	0.87
	200	44.88	2.98	1.61
	250	64.65	4.28	2.31
	300	68.88	4.57	2.47
	400	79.85	5.30	2.86
	500	83.20	5.52	2.98

[a] Catalyst with dispersion of rhenium, H/Re = 0.25. Monolayer uptake of hydrogen from H_2 chemisorption at 300 °C amounts to 70.0 $\mu mol_{H_2}/g_{cat}$ [13].

[b] Catalyst with dispersion of rhenium, H/Re = 0.54. Monolayer uptake of hydrogen from H_2 chemisorption at 300 °C amounts to 15.1 $\mu mol_{H_2}/g_{cat}$ [47].

[c] Ratio of the number of O atoms adsorbed to the number H atoms chemisorbed in the monolayer.

[d] Ratio of the number of O atoms adsorbed to the total numbers of Re atoms in the catalyst.

size of Re about 2 nm, the oxygen uptake does not saturate even at 400 °C. The O/Re ratio of 2.98 obtained at 500 °C is still 15% lower than the value of 3.5 expected for oxidation of Re to Re_2O_7. However, prolonged oxidation of both catalysts at 500 °C for 4 h did not result in any increase in O_2 uptake. No loss of rhenium during heating of both catalysts in O_2 up to 500 °C occurred (see Table 1) and could not be responsible for the underestimation of the O/Re ratio.

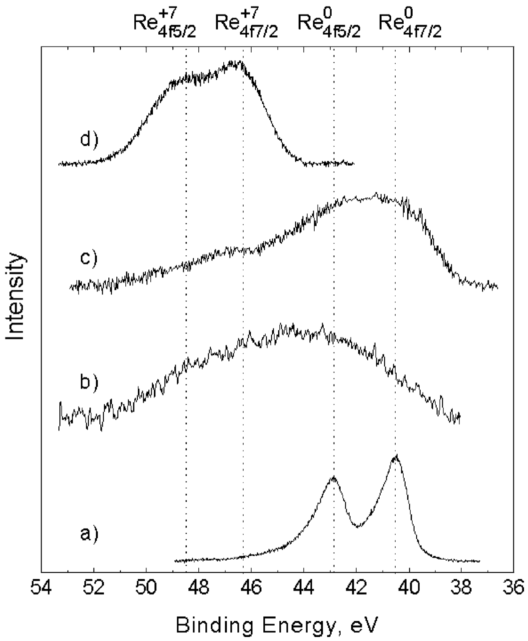

Fig. 3. XPS spectra of the Re 4f region of rhenium powder (a), 1.04% Re/γ-Al_2O_3 catalyst sintered in H_2 and oxidized at room temperature (b), 10.4% Re/γ-Al_2O_3 catalyst sintered in H_2 and oxidized at room temperature (c), and crystalline Re_2O_7 oxide (d).

3.3. *XPS studies*

The XPS technique was applied to establish the oxidation states of the surface rhenium atoms in the Re/γ-Al_2O_3 catalysts after various oxidation treatments. A typical wide energy scan of the Re/γ-Al_2O_3 catalyst gave an XPS spectrum with clearly resolved O 1s and 2s, Al 2s and 2p, C 1s, and Re 4d and Re 4f peaks (spectrum is not shown). Impurities other than carbon were not observed in the studied samples. For quantitative measurements of Re the Re 4f doublet was used. Fig. 3 shows the Re 4f region from the Re powder and Re_2O_7 oxide, as references for Re^0 and Re^{7+} oxidation states, respectively, and 1.04% and 10.4% Re/γ-Al_2O_3 catalysts passivated at room temperature. The spectrum of Re powder exhibits two well-resolved 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. 3a). The spectrum of pure Re_2O_7 also exhibits two, but less separated spectral lines at 46.9 and 49.3 eV (Fig. 3d). Observed line broadening may be to some extent due to partial surface reduction of Re_2O_7 oxide [27]. The XPS spectra of both catalysts exposed to air for a short time show strong broadening of the Re 4f peak so that the splitting of Re $4f_{7/2}$ and Re $4f_{5/2}$ lines disappears. However, for the high-loaded catalyst the shape and position of the peak show clearly the presence of metallic rhenium as a major phase with a small amount of the other oxida-

Table 3
Some published Re $4f_{7/2}$ binding energies (eV) for metallic Re, various Re oxides, and rhenium supported on γ-Al_2O_3

Species	Re $4f_{7/2}$	O 1s	Reference energy (eV)	Reference
Re powder	40.5		C 1s = 284.6	This study
	40.7		C 1s = 285.0	[27]
Re foil	40.7		C 1s = 285.0	[27]
	40.5		C 1s = 285.0	[39]
	39.7		Pt $4f_{7/2}$ = 70.9	[28]
	40.0		C 1s = 284.6	[49]
ReO_2	42.5		C 1s = 285.0	[27]
	43.3	531.8	C 1s = 285.0	[39]
	42.5		Pt $4f_{7/2}$ = 70.9	[28]
	43.2		C 1s = 285.0	[38]
ReO_3	44.5		C 1s = 285.0	[27]
	44.9		Pt $4f_{7/2}$ = 70.9	[28]
	44.3		C 1s = 285.0	[38]
Re_2O_7	46.9	532.9	C 1s = 284.6	This study
	46.9		C 1s = 285.0	[27]
	46.8	532.1	C 1s = 285.0	[39]
	46.7		Pt $4f_{7/2}$ = 70.9	[28]
	46.5		C 1s = 285.0	[38]
$HReO_4$/γ-Al_2O_3 (H_2, 500 °C)	41.1		C 1s = 285.0	[38]
$HReO_4$/γ-Al_2O_3 (air, 300 °C)	45.7–46.0		C 1s = 285.0	[38]
2.4 Re/γ-Al_2O_3 (air, 500 °C)	46.3		C 1s = 285.0	[38]
13% Re_2O_7/Al_2O_3 (air, 580 °C)	46.6		C 1s = 285.0	[42]
γ-Al_2O_3 (air, 600 °C)		531.6	C 1s = 284.6	this study
γ-Al_2O_3		531.7	C 1s = 285.0	[39]

tion states of the Re. For the low-loaded sample a mixture of various oxidation states of the Re is observed.

Table 3 contains some literature XPS data for metallic Re, several rhenium oxides, and Re/γ-Al_2O_3 samples subjected to various treatments. It appears that our data for the Re powder and Re_2O_7 oxide are in close agreement with literature data. In Table 3 positions of the O 1s line are also presented when available. However, according to Tysoe et al. [28] O 1s spectra do not yield valuable information on the nature of the rhenium oxide.

Figs. 4 and 5 show Re 4f spectra for the 1.04 and 10.4% Re/γ-Al_2O_3 catalysts after oxidation at 20–800 °C. For the low-loaded catalyst (Fig. 4), each spectrum exhibits only one broad peak, with an apparent shift of the binding energy with the increasing oxidation temperature. Such large spectral broadening previously reported for low-loaded Re/γ-Al_2O_3 catalysts [39,49] was ascribed to the interaction of the rhenium species with the alumina support. The high-loaded catalyst (Fig. 5) generates better spectra, so that even some Re $4f_{7/2}$ and Re $4f_{5/2}$ splitting could be observed for the samples oxidized at 500–800 °C. These spectra resemble that of pure Re_2O_7 oxide, indicating clearly the existence of the Re^{7+} species. For both catalysts, the oxidation states of rhenium increase with the oxidation temperature up to 500 °C and then remain constant.

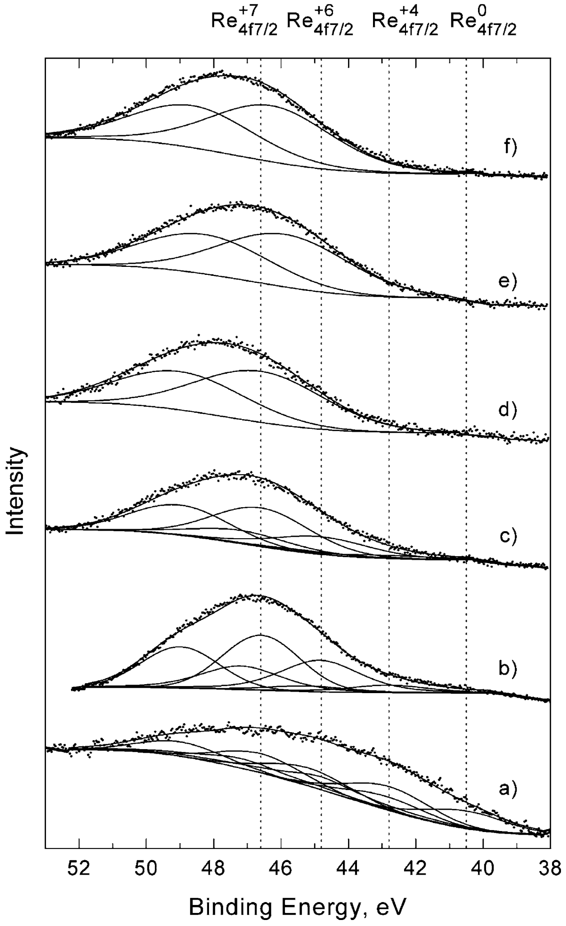

Fig. 4. XPS spectra of the 1.04% Re/γ-Al_2O_3 catalyst oxidized at room temperature (a), 150 °C (b), 300 °C (c), 500 °C (d), 600 °C (e), and 800 °C (f).

The distribution of the Re oxidation states in the oxidized catalysts was estimated by the curve fit of the Re 4f XPS spectra, as is presented in Figs. 4 and 5. In the curve-fitting routine, the relative intensity and separation of the spin-orbit Re $4f_{7/2}$–$Re_{5/2}$ doublet were fixed for each doublet, but linewidth (FWHM) and position were variable to some extent. For both catalysts oxidized at room temperature, the best fitting was obtained assuming four different oxidation states of rhenium. The deconvoluted peaks at 40.5 (or 40.4), 42.8, 44.8, and 46.6 eV (or 46.3 eV) are assigned to Re $4f_{7/2}$ lines and confirm the existence of Re^0, Re^{4+}, Re^{6+}, and Re^{7+} species, respectively (see Table 3). Some amount of the Re may be present also in oxidation states between 0 and 4, but its identification is very difficult or even impossible in the Re/γ-Al_2O_3 system [40]. Treatment at 150 °C leads to enhanced formation of Re^{4+}–Re^{7+} species but a certain amount of metallic rhenium is still observed (as the tail on the low BE side). At 300 °C only Re^{6+} and Re^{7+} species are present. At 500 °C and above, Re^{7+} species are the only

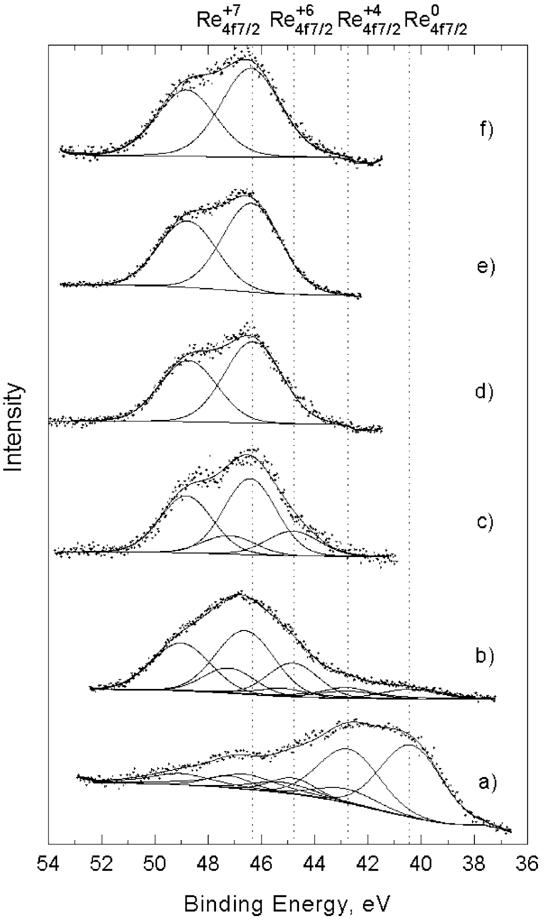

Fig. 5. XPS spectra of the 10.4% Re/γ-Al_2O_3 catalyst oxidized at room temperature (a), 150 °C (b), 300 °C (c), 500 °C (d), 600 °C (e), and 800 °C (f).

product of oxidation, irrespective of the concentration of the Re in the catalyst.

Table 4 summarizes curve-fitting results obtained for the both catalysts oxidized at 20–800 °C. It contains the binding energies of the most intense Re $4f_{7/2}$ component of each doublet, its FWHM (in parentheses), and the distribution of oxidation states of surface Re ions. For the samples oxidized at low temperatures (where large Re particles are present) Table 4 contains also the distribution of oxidation states of Re corrected for the finite "probing depth" of the XPS method. The method of calculation will be explained further in this paper. It should be admitted that the relative accuracy of such quantitative analysis is about 20%, which according to Ref. [50] is quite acceptable for the chemical analysis of the extreme surface. Especially, estimation of the distribution of oxidation states of the rhenium in the low-loaded catalyst bears relatively large uncertainty. Nevertheless, the corrected XPS data for the samples oxidized at low temperatures much better fit the results obtained by HRTEM and O_2 uptake measurements.

In some XPS studies on supported metal particles, the binding energy has been found to be particle size dependent, increasing by ca 0.5 eV as the particle size decreases from 5 to 1 nm [51,52]. Our results demonstrate that the Re $4f_{7/2}$ binding energy for metallic rhenium supported on γ-Al_2O_3 was almost independent of the rhenium particle size (40.4–40.5 eV) and was similar to that determined for rhenium powder (40.5 eV). Biloen et al. [53] reported a similar value of 40.5 eV for reduced rhenium supported on SiO_2. In XPS studies of alumina-supported Pt–Re catalysts reduced at 500 °C, the Re binding energy was found to be greater than 40.5 eV [39,40]. The binding energy of rhenium in Re foil was found to be 40.0 eV [49], while for thin

Table 4
X-ray photoelectron spectroscopy analysis of Re/γ-Al_2O_3 catalysts oxidized at 20–800 °C[a]

Oxidation temperature (°C)	Re $4f_{7/2}$[b]				Re/Al
	Re^0	Re^{4+}	Re^{6+}	Re^{7+}	
			10.4% Re/γ-Al_2O_3		
20	40.4 (2.8) 67.5% (94.5%)[c]	42.8 (2.7) 11.9% (2.0%)[c]	44.8 (2.7) 7.3% (1.2%)[c]	46.3 (2.6) 13.3% (2.3%)[c]	0.008
150	40.4 (2.5) 7.8% (33.3%)[c]	42.8 (2.7) 7.1% (5.3%)[c]	44.8 (2.6) 23.7% (17.1%)[c]	46.3 (2.7) 61.4% (44.4%)[c]	0.034
300			44.8 (2.7) 22%	46.3 (2.3) 78%	0.045
500				46.3 (2.6) 100%	0.047
600				46.4 (2.7) 100%	0.044
800				46.4 (2.8) 100%	0.049
			1.04% Re/γ-Al_2O_3		
20	40.5 (3.3) 21% (60.5%)[c]	42.8 (3.3) 41% (20.5%)[c]	44.8 (3.3) 4% (2.0%)[c]	46.6 (3.3) 33% (16.5%)[c]	0.0024
150	40.5 (3.3) 2%	42.8 (3.3) 24%	44.8 (3.3) 30%	46.6 (3.3) 44%	0.0049
300		42.8 (3.5) 7%	44.8 (3.5) 25%	46.6 (3.5) 68%	0.0050
500				46.6 (4.4) 100%	0.0048
600				46.3 (4.5) 100%	0.0048
800				46.6 (4.6) 100%	0.0050

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

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

[c] Distribution of Re oxidation states corrected for the limited "probing" depth of XPS (see text).

rhenium film deposited on Pt even 39.7 eV [28]. We suppose that higher BE of the Re $4f_{7/2}$ line obtained for our Re/γ-Al_2O_3 catalysts can be partly explained by a change in electronic properties of the rhenium atoms in the particles induced by the interaction with oxygen atoms of the support [47,54].

The Re $4f_{7/2}$ binding energy of Re^{7+} species, formed in our oxidized samples, was always lower by 0.6–0.3 eV than the value for bulk Re_2O_7 oxide (used as the reference for Re^{7+}). Such BE shift may be explained by a different charging of the alumina support as compared to the unsupported Re_2O_7 oxide. It was also found that the BE of Re $4f_{7/2}$ in various compounds depends upon both the "formal" oxidation state and the nearest neighbors of the Re ions [38]. We suppose that increasing oxidation temperature causes some migration of Re^{7+} species over alumina and the environment of the Re ions and/or strength of the interaction with the support, which clearly depends on the amount of the Re in the sample, may be slightly changed. Additionally, rather large FWHM values of the Re 4f doublet components indicate that the Re species may be present in more than one environment in the surface region. Similar broadening of the Re $4f_{7/2}$ peaks was observed by Cimino et al. [43] in silica-supported rhenium catalyst treated in air at 300–750 °C. The authors concluded that Re^{7+} species could be located on SiO_2 support in nonhomogeneous environments. Recently, Daniell et al. [55] proposed on the basis of TPR study of the 9% Re_2O_7/Al_2O_3 catalyst that various Re^{7+} species might exist on the alumina surface. The authors admitted the presence of a small amount of oligomeric rhenium, although in their Raman spectra only one monomeric tetrahedra species was detected [55]. Our recent Raman data for Re/γ-Al_2O_3 catalysts oxidized at 300–800 °C showed that rhenium in the oxidized state is present as two slightly different ReO_4 monomeric species [32]: one occurring for both loadings, and the other, with a weaker Re–O–Al bond, occurring for high loading only. Moreover, we postulated that during oxidation of the high-loaded catalyst at 300–500 °C, ReO_4 monomers may form a kind of surface compound with a Al–O–$(ReO_3)_3$ structure [13,32]. Salvati et al. [56] obtained a XPS spectrum of the bulk $Al(ReO_4)_3$ compound with the Re $4f_{7/2}$ binding energy (46.5 eV) approximately equal to the value reported for Re_2O_7 oxide. Because of this, XPS results of this study could not validate or dismiss our earlier suggestions based on Raman and other data [13,32].

From XPS analysis, the atomic concentrations of Re and Al were obtained and the Re/Al atomic ratios were calculated (last column in Table 4). Atomic ratios were calculated taking into consideration the sensitivity factors of elements. The elemental sensitivity factors for Re $4f_{7/2}$, Re $4f_{5/2}$, and Al 2p were 2.95, 2.21, and 0.249, respectively. In the sample of the 10.4% Re/γ-Al_2O_3 catalyst oxidized at room temperature, the XPS-determined Re/Al atomic ratio is about 4 times lower than the bulk atomic ratio, $(Re/Al)_{bulk} = 0.032$, calculated from the overall chemical composition of the catalyst. It should be noted, however, that atomic ratio given in Table 4 refers to very simple approximation assuming a homogeneous, semi-infinite slab of Re–Al alloy. This approximation is obviously not fulfilled for the high-loaded catalyst where the presence of large Re particles at the surface of alumina is evidenced by TEM. In addition to the very nonuniform Re distribution the inelastic mean free path (IMFP) of Re $4f_{7/2}$ photoelectron with kinetic energy of 1205 keV in Re metal, calculated according to the Seah and Dench formula [57] as 1.73 nm, is much smaller than the mean particle size of Re of about 5 nm so we may assume that not the whole amount of Re is probed by XPS. In the sample of the 1.04% Re/γ-Al_2O_3 catalyst after the same treatment, the Re/Al atomic ratio is closer to the bulk atomic ratio, since Re particles are smaller. It is observed, that after oxidation of the both catalyst at 150 °C or at higher temperatures, the XPS-determined Re/Al atomic ratios are always greater than $(Re/Al)_{bulk}$, what indicates that the rhenium is redispersed over the alumina surface. Additionally, the increase in XPS-determined Re/Al atomic ratio with loading in fully oxidized samples is in accordance with the model proposed by Kerkhof and Moulijn [41] suggesting the presence of well-dispersed surface species.

Recently, the linear increase in the surface XPS signal was observed for the 4.1–11.3% Re_2O_7/Al_2O_3 catalysts calcined at 500 °C and for the 0.7–4.8% Re_2O_7/TiO_2 catalysts calcined at 450 °C [44]. The authors assign this behavior to the highly dispersed nature of the supported rhenium oxide phase on the surface of these supports. In our study, after oxidation at 150 °C, the Re/Al atomic ratios are 2–4 times higher in both catalysts than the initial one. For the high-loaded catalyst after oxidation at 300 °C, there is further growth of the Re/Al atomic ratio and then it remains constant for oxidation temperatures up 800 °C. Thus, the XPS results suggest that the rhenium oxide species, formed by oxidation of metallic rhenium particles, is present as a well-dispersed surface phase and all rhenium in our samples is detected in range of 300–800 °C. HRTEM study also shows that under these conditions whole rhenium is uniformly spread over the alumina support. In fact, in supported rhenium catalysts after oxidation at enhanced temperatures, crystallites of rhenium oxide are never produced since Re_2O_7 oxide is volatile just above 150 °C. Our previous Raman study [32] indicates that Re_2O_7 is adsorbed on the surface of the support as ReO_4 tetrahedra. Moreover, the sensitivity of the surface rhenium oxide Raman signal to moisture further confirms that rhenium oxide is present as a two-dimensional phase adsorbed on the alumina support surface [32]. XPS results confirm this observation since for the samples oxidized at 300–800 °C, the measured Re/Al ratio is constant. Under such conditions the model of Kerkhof and Moulijn (KM) [41] should be applicable. In our case the IMFPs for Re $4f_{7/2}$ and Al 2p photoelectrons in Al_2O_3 (kinetic energy 1205 and 1179 eV, respectively) are very close and equal to $\lambda_s = 1.53$ nm [57]. IMFP for the same photoelectrons in Re_2O_7 is 0.9 nm [57] and is much larger than the thickness of the Re_2O_7 overlayer

(0.155 nm as calculated for 10.4% catalyst assuming surface area of the alumina support 153 m^2/g). Attenuation of the XPS signal in the Re oxide overlayer may therefore be neglected. Within the KM model, if no attenuation occurs within the overlayer, the experimentally measured intensity ratio $(I_{Re}/I_{Al})_{exp} = (Re/Al)_b(S_{Re}/S_{Al})z$, where $(Re/Al)_b$ is bulk atomic ratio, (S_{Re}/S_{Al}) is the ratio of atomic sensitivity factors, and z is the correction function depending on the dimensionless geometrical parameter $\beta = t/\lambda_s$ describing the structure of the support ($t = 2/\rho S_0$, where ρ is density and S_0 is surface area). In our case z amounts to 1.38 and 1.30 for high- and low-loaded catalyst, respectively. It means that Re/Al ratios in Table 4 should be divided by z to be compared with $(Re/Al)_b$. For the samples oxidized at 500 °C we obtained therefore values of $0.047/1.38 = 0.034$ and $0.0048/1.30 = 0.0036$ for high- and low-loaded samples, respectively. These values are quite close to 0.032 and 0.0029 ratios calculated from overall chemical composition.

The situation becomes much more complex for the samples oxidized at low temperatures where both metallic and oxidized rhenium is present. Moreover, we have to remember that some Re^0 (within the bulk of larger particles) is probed since IMFP for Re $4f_{7/2}$ photoelectron in Re is 1.74 nm, less than the mean particle size of Re particles (5 nm for high-loaded sample). To tackle the problem we use a very simple approximation. Since in the samples oxidized at 500 °C the whole amount of Re is probed by XPS, then we assume that the ratio $(Re/Al)_T/(Re/Al)_{500}$ gives the fraction of Re probed at lower temperature T. For example, for the high-loaded catalyst oxidized at 20 °C we have $(Re/Al)_{20}/(Re/Al)_{500} = 0.008/0.047 = 0.17$; i.e., only 17% of the whole Re is probed. The remaining part, 83%, is obviously Re^0, because at low temperatures large Re particles may only be oxidized at the surface. Of this 17% of the probed rhenium 67.5% is Re^0 (Table 4 column 2); therefore, the total amount of Re^0 is $83\% + (17\% \times 0.675) = 94.5\%$. It should be admitted that the relative accuracy such "quantitative" analysis is rather poor, especially for the low-loaded catalyst, where estimation of the distribution of oxidation states of Re bears relatively large uncertainty. Nevertheless, the corrected XPS data for the samples oxidized at low temperatures much better fit the results obtained by HRTEM and O_2 uptake measurements.

The values of binding energies of Al 2p and O 1s lines in our samples generally are close to those observed in γ-Al_2O_3 [58]. The Al 2p peak shifted continuously to higher BE with increasing temperature, e.g., from 73.74 to 74.63 eV for high-loaded samples while such dependence was not observed for low-loaded samples. The O 1s feature in our samples was a single symmetric peak occurring at 530.86 to 531.36 eV (spectra for Al and O are not shown). Such BE shift is probably not due to a different charging of the samples, because the separation of the binding energies of Al 2p and O 1s, Δ(Al–O), also undergoes changes as a function of temperature. The Δ(Al–O) values were in the range of 457.12 to 456.76 eV at temperature oxidation of 20–800 °C. Similar Al 2p peak shifts observed in the Au/Al_2O_3 system treated in air at 300–900 °C were explained by an increasing interaction between Au and Al_2O_3 [59]. Zaera and Somorjai [60] found that oxygen chemisorbed on the Re film shows the O 1s peak at 530 eV. However, in our study the O 1s peak could not be used to the analysis of Re–oxygen species because of overlapping with the strong O 1s signal from the alumina support. It is commonly accepted that O 1s peaks at about 531–532 eV are due to adsorbed oxygen species such as O^-, OH^-, or H_2O.

4. Discussion

Our XPS results on oxidation of supported rhenium particles can be compared with existing limited literature data obtained by XPS but only for unsupported rhenium. Ducros et al. [37] reported that at room temperature oxygen is dissociatively adsorbed on Re(0001) single crystal with possible formation of a superficial oxide with composition between Re_2O and ReO. The conclusion was based on the observed shift of 1.1 eV in the Re 4f XPS signal upon oxygen dosage. Similar Re 4f line shifts was observed more recently by Ramstad et al. [35] for the oxidation of thin Re islands on Pt(111). Very recently, Liu and Shuh [36] showed for polycrystalline rhenium, that such small changes in the Re 4f binding energy may be assigned with both molecular and dissociative adsorption of oxygen and that there is little, if any, Re oxide formed on the surface. The authors explained the apparent discrepancies between the previous results by the slow rate of the Re oxidation at room temperature. Zaera and Somorjai [60] found that several oxides of rhenium were formed on thin Re film exposed at room temperature for 1 atm of O_2. Alnot and Ehrhard [61] identified ReO_2, ReO_3, and Re_2O_7 oxides on the surface Re ribbons oxidized at 427 °C in 1 Torr O_2. Oxidation of thin Re film deposited on Pt foil above 200 °C in 1 atm of O_2 caused formation of a mixture of rhenium oxides, and above 300 °C loss of rhenium due formation of the volatile Re_2O_7 was observed [28].

From the literature survey and our results obtained for supported rhenium [13,47] it appears that oxidation of rhenium at room or higher temperature depends strongly on the size of rhenium particles, i.e., on dispersion of the Re. At room temperature dissociative or partly molecular chemisorption of oxygen occurs on the surface of Re with very low dispersion [36]. Dissociative chemisorption of oxygen with possible formation of a superficial (few monolayers thick) Re oxide also takes place on large Re particles in our Re/γ-Al_2O_3 catalysts. According to XPS the smallest particles (to 1 nm) and clusters of Re were oxidized to Re^{4+}, Re^{6+}, and even to Re^{7+} species. The amount of these species is particularly large for the passivated low-loaded catalyst, where XPS data showed that only 60% of Re was left in a zero-valence state. This also indicates a high affinity of the highly dispersed Re to oxygen. Fung et al. [40] found that passivation of the 1% Re/γ-Al_2O_3 catalyst prepared from salt precursor (NH_4ReO_4) had led to a complete oxidation of metallic Re to Re^{7+} instead of a partial oxidation to Re^{2+}. The authors explained the complete oxidation of the highly dispersed rhenium by the high affinity of Re for oxygen. Extensive oxidation of small rhenium particles explains the difficulties we encountered in detecting Re in TEM images of a low-loaded nonsintered catalyst [47]. On the contrary, in the sample containing Re particles with an average size of about 5 nm, the majority (94.5%) of rhenium is in the metallic state. Low oxygen uptake at room and at higher temperatures, still lower than expected for total oxidation of Re^0 to Re^{7+} (Table 2), especially in low-loaded catalyst, suggests that part of Re exists in a low positive oxidation state already before oxidation treatment. We found previously [47] that partial reoxidation of rhenium may occur during the evacuation of the catalyst at 520 °C applied after the H_2 reduction treatment. This agrees well with finding of Solymosi and Bansagi [62] that isolated Re species in reduced 1% Re/γ-Al_2O_3 catalyst could be oxidized to mono or higher valence metal ions by the OH groups of the support.

Upon oxidation at 150 °C, enhanced formation of the surface Re^{4+}–Re^{7+} species was observed by XPS and the mount of metallic Re quickly decreased especially in the low-loaded catalyst (only 2% of Re^0 was left). At this temperature, the Re/Al atomic ratio was 2–4 times higher than the initial one, indicating a large spreading of the oxide species on the surface of γ-alumina support. It is evidenced by TEM (Fig. 2) that upon oxidation of the 10.4% Re/γ-Al_2O_3 catalyst at 150 °C and at 200 °C the average particle sizes of Re decreased from 4.9 to 4.3 nm and to 3.3 nm, respectively. This indicates the transport of Re from the surface of the Re particles to the support by volatilization of Re_2O_7 oxide. This dispersed phase is seen in HRTEM images as very small amorphous particles ($\sim$ 0.6 nm) uniformly distributed on the support (Figs. 1b and c), [13]. High volatilization of Re_2O_7 oxide even at 150 °C may explain why we could not found by HRTEM any oxide layer on the surface of supported Re particles as well as in Re powder annealed at 150 °C [13].

At 300 °C, the process of oxidation of Re accelerates, and according to XPS only Re^{4+}, Re^{6+}, and Re^{7+} species are present in both catalysts. Measurements of O_2 uptake suggest nearly complete oxidation of Re to Re_2O_7 for the high-loaded catalyst ($O/Re = 3.31$), while for the low-loaded catalyst O/Re amounts to 2.5 only, indicating that strong interaction of partly oxidized Re with the support prevents its oxidation to Re_2O_7 oxide. This result is in accord with XPS data, where only 68% of Re was in +7 oxidation state (Table 4). Our recent Raman study [32] also showed that oxidation of the 10.4% Re/γ-Al_2O_3 catalyst already at 300 °C for 1 h is enough to obtain a monomoleculary dispersed oxide phase. For the 1.04% Re/γ-Al_2O_3 catalyst the Raman signal was not detected at this temperature. Probably for the low-loaded catalyst, due to diversity of the Re ions, the surface concentration of individual Re ions was to low to be experimentally observed.

For both catalysts oxidized at or above 500 °C, XPS, HRTEM, and our previous Raman data show complete oxidation of Re to Re_2O_7 oxide and its dispersion over alumina support as monomeric ReO_4 species. Large broadening of the Re XPS peaks indicates that this species is present on the surface in various environments. A similar conclusion was drawn from the Raman spectra, showing that depending on the Re loading, ReO_4 monomer species of slightly different kind could form [32]. Moreover, we found previously that high-temperature treatment caused some diffusion of ReO_4 groups over the surface of the alumina [32]. Such temperature-induced surface diffusion of the rhenium surface oxide may be facilitated by an extensive dehydroxylation of the alumina support during prolonged calcination at high temperature as was proposed by Spronk et al. [63]. Since the rhenium oxide is mobile at higher oxidation temperatures a nearly random distribution of ReO_4 units over all types of sites on the alumina surface occurs [63]. Hardcastle et al. [64] and also Spronk et al. [63] showed that rhenium does not react with alumina at temperatures as high as 950 or 1000 °C and is still present as stabilized, surface-coordinated ReO_4 groups.

A large influence of the heat treatment in air on the intensity of XPS Re 4f peak was found in the Re/SiO_2 system [43]. The authors observed a decline of Re 4f peak with increasing temperature and explained this by the Re_2O_7 loss due to volatilization. It is well known that the surface rhenium oxide species supported on SiO_2, in contrast to that on the Al_2O_3, are not thermally stable. In physical mixtures of the Re_2O_7/SiO_2 system with other oxide supports, nearly complete migration of the surface rhenium oxide species from SiO_2 to other oxide support (e.g., Al_2O_3) upon thermal treatment was observed [65]. Our XPS data indicate that the Re/Al atomic ratios do not change for both catalysts even after oxidation at the highest temperatures. This is a surprising result because chemical analysis showed that some loss of rhenium was observed especially at 800 °C (see Table 1). It can be noted that the surface area of the samples remained nearly constant in the temperature range 400–800 °C, although surface structure of the alumina support has probably been modified slightly. An extensive dehydroxylation of the alumina support during prolonged calcination at high temperatures was found by Spronk et al. [63] for the 6% Re_2O_7/Al_2O_3 catalyst. The authors found by hydrogen consumption in a TPR study that all rhenium oxide remained in the catalyst up to 900 °C as stabilized surface-coordinated ReO_4 groups. We suppose that in our case, slightly different treatment procedures of the samples before chemical analysis and XPS measurements, as well as limitations of quantitative XPS analysis of porous samples with high surface area [66], would partly explain our results. Another explanation for the apparent contradiction between XPS and ICP results could be some encapsulation of the small Re particles in micropores of the support during high-temperature reduction. BET surface area of the both catalysts after H_2 treatment at 800 °C was about 30–20% lower than that after reduction at 550 °C. This support-encapsulated rhenium, not accessible to chemical analysis made in our case by the procedure given in [67], could be detected by XPS. In this procedure rhenium is extracted from the catalyst by contact with H_2O_2 solution, without dissolution of the support. It is known that H_2O_2 can oxidize to Re_2O_7 both metallic rhenium and rhenium oxide with oxidation number less than 7. It is also possible that after high-temperature oxidation/reduction treatment a small part of rhenium so strongly interacts with the surface of γ-Al_2O_3 support that is not available to further oxidation by H_2O_2 to water-soluble Re_2O_7 oxide. It should be noted, however, that the EDX analysis of the support after extraction of Re from the sample of the 10.4% Re/γ-Al_2O_3 catalyst oxidized at 800 °C did not detect the presence of Re. This result demonstrates that the amount of Re could be eventually below 1 wt%, because the EDX analysis of Re in 1.04% Re/γ-Al_2O_3 catalyst gave reasonable results. Further, more detailed and well-controlled experiments are needed to resolve the problem of the apparent discrepancy between the results of XPS and chemical analysis of the samples oxidized at the highest temperatures.

5. Conclusions

Oxidation of rhenium in the sintered 1.04 and 10.4% Re/γ-Al_2O_3 catalysts was studied from 20 to 800 °C. Rhenium in these catalysts is present as a highly nonuniform phase, consisting of very small clusters and metallic particles with the size from 1 to 9 nm. Extent of oxidation of rhenium depends strongly on temperature and on particle size of Re. At room temperature clusters and small particles of Re (below 1 nm) are completely oxidized to Re^{4+}–Re^{7+} species, indicating on high affinity of highly dispersed Re to oxygen. On larger Re particles dissociative chemisorption of oxygen occurs with the formation of a superficial Re oxide. At 150 °C, spreading of the rhenium oxide species over the alumina support accompanied with a decrease of the average particle size of Re was observed. Particles of rhenium with sizes of 1–4 nm undergo nearly complete redispersion forming a surface oxide phase detected by XPS. At 300 °C, the process of oxidation accelerates and all rhenium transforms into a highly dispersed surface phase with chemical composition between Re^{4+} and Re^{7+}. At or above 500 °C rhenium undergoes complete oxidation to Re^{7+} species. These rhenium oxide surface species are probably mobile at higher oxidation temperatures and are located on the surface in nonequivalent positions.

Acknowledgments

The authors thank Mrs. L. Krajczyk for taking TEM micrographs and Mrs. A. Cielecka for skillful technical assistance.

References

[1] D. Bazin, L. Borkó, Zs. Koppány, I. Kovács, G. Stefler, L.I. Sajó, Z. Schay, L. Guczi, Catal. Lett. 84 (2002) 169.
[2] L. Guczi, G. Stefler, L. Borkó, Zs. Koppány, F. Mizukami, M. Toba, S. Niwa, Appl. Catal. A 246 (2003) 79.
[3] F. Mendes, F.B. Noronha, R.R. Soares, C.A.C. Perez, G. Marcheti, M. Schmal, Stud. Surf. Sci. Catal. 136 (2001) 177.
[4] G.C. Bond, M.R. Gelsthorpe, Catal. Lett. 2 (1989) 257.
[5] D.J.C. Yates, I.H. Sinfelt, J. Catal. 14 (1969) 182.
[6] C. Betizeau, G. Leclercq, R. Maurel, C. Bolivar, H. Charcosset, R. Frety, L. Tournayan, J. Catal. 45 (1976) 176.
[7] J. Okal, H. Kubicka, Appl. Catal. A 171 (1998) 351.
[8] F.K. Chong, J.A. Anderson, C.H. Rochester, Phys. Chem. Chem. Phys. 2 (2000) 5730.
[9] L. Wang, R. Ohnishi, M. Ichikawa, J. Catal. 190 (2000) 276.
[10] A. Krogh, A. Hagen, T.W. Hansen, C.H. Christensen, J. Schmidt, Catal. Commun. 4 (2003) 627.
[11] R. Kojima, H. Enomoto, M. Muhler, K. Aika, Appl. Catal. A 246 (2003) 311.
[12] A.A. Olsthoorn, C. Boelhouwer, J. Catal. 44 (1976) 207.
[13] J. Okal, L. Kępiński, L. Krajczyk, M. Drozd, J. Catal. 188 (1999) 140.
[14] H.C. Yao, M. Shelef, J. Catal. 44 (1976) 392.
[15] N. Wagstaff, R. Prins, J. Catal. 59 (1979) 434.
[16] T. Paryjczak, D. Gebauer, A. Kozakiewicz, J. Colloid Interface Sci. 70 (1979) 320.
[17] B.H. Isaacs, E.E. Petersen, J. Catal. 85 (1984) 1, 8.
[18] G.W. Chądzyński, H. Kubicka, Termochim. Acta 158 (1990) 369.
[19] J. Raty, T.A. Pakkanen, J. Mol. Catal. A 166 (2001) 275.
[20] R. Prestvik, K. Moljord, K. Grande, A. Holmen, J. Catal. 174 (1998) 119.
[21] S.M. Augustine, W.M.H. Sachtler, J. Catal. 116 (1989) 184.
[22] F. Hilbrig, C.G. Michel, G.L. Haller, J. Chem. Phys. 96 (1992) 9893.
[23] M. Fernandez-Garcia, F.K. Chong, J.A. Anderson, C.H. Rochester, L. Haller, J. Catal. 182 (1999) 199.
[24] F.K. Chong, J.A. Anderson, C.H. Rochester, J. Catal. 190 (2000) 327.
[25] M.J.P. Botman, K. de Vreugd, H.W. Zandbergen, R. de Block, V. Ponec, J. Catal. 116 (1989) 467.
[26] B.H. Isaacs, E.E. Petersen, J. Catal. 77 (1982) 43.
[27] A. Cimino, B.A. De Angelis, D. Gazzoli, M. Valigi, Z. Anorg. Allg. Chem. 460 (1980) 86.
[28] W.T. Tysoe, F. Zaera, G.A. Somorjai, Surf. Sci. 200 (1988) 1.
[29] M.A. Vuurman, D.J. Stufkens, A. Oskam, I.E. Wachs, J. Mol. Catal. 76 (1992) 263.
[30] I.E. Wachs, Catal. Today 27 (1996) 437.
[31] J.C. Mol, Catal. Today 51 (1999) 289.
[32] J. Okal, J. Baran, J. Catal. 203 (2001) 466.
[33] B.M. Weckhuysen, J.-M. Jehng, I.E. Wachs, J. Phys. Chem. B 104 (31) (2000) 7382.
[34] Y. Chen, I.E. Wachs, J. Catal. 217 (2003) 468.
[35] A. Ramstad, F. Strisland, S. Raaen, A. Borg, C. Berg, Surf. Sci. 440 (1999) 290.
[36] P. Liu, D.K. Shuh, J. Electron Spectrosc. Relat. Phenom. 114–116 (2001) 319.
[37] R. Ducros, M. Alnot, J.J. Ehrhardt, M. Housley, G. Piquard, A. Cassuto, Surf. Sci. 94 (1980) 154.
[38] E.S. Shpiro, V.I. Avaev, G.V. Antoshin, M.A. Ryashentseva, K.M. Minachev, J. Catal. 55 (1978) 402.

[39] P.S. Kirlin, B.R. Strohmeier, B.C. Gates, J. Catal. 98 (1986) 308.

[40] A.S. Fung, M.R. McDevitt, P.A. Tooley, M.J. Kelley, D.C. Koningsberger, B.C. Gates, J. Catal. 140 (1993) 190.

[41] F.P.J.M. Kerkhof, J.A. Moulijn, J. Phys. Chem. 83 (1979) 1612.

[42] R.M. Edreva-Kardieva, A.A. Andreev, J. Catal. 94 (1985) 97.

[43] A. Cimino, D. Gazzoli, M. Inversi, M. Valigi, Surf. Interface Anal. 10 (1987) 194.

[44] B. Mitra, X. Gao, I.E. Wachs, A.M. Hirt, G. Deo, Phys. Chem. Chem. Phys. 3 (2001) 1144.

[45] Y. Yuan, T. Shido, Y. Iwasawa, Chem. Commun. (2000) 1421.

[46] X. Yide, H. Jiasheng, L. Zhiying, G. Xiexian, J. Mol. Catal. 65 (1991) 275.

[47] J. Okal, L. Kępiński, L. Krajczyk, W. Tylus, J. Catal. 219 (2003) 362.

[48] H. Kubicka, Roczniki Chem. 47 (1973) 599.

[49] A.S. Fung, A.A. Tooley, M.J. Kelley, D.C. Koningsberger, B.C. Gates, J. Phys. Chem. 95 (1991) 225.

[50] P. Beccat, P. Da Silva, Y. Huiban, S. Kasztelan, Oil Gas Sci. Technol. Rev. IFP 54 (1999) 487.

[51] T. Huizinga, H.F.J. Van't Blik, J.C. Vis, R. Prins, Surf. Sci. 135 (1983) 580.

[52] B.L. Mojet, J.T. Miller, D.E. Ramaker, D.C. Koningsberger, J. Catal. 186 (1999) 373.

[53] P. Biloen, J.N. Helle, H. Verbeek, F.M. Dautzenberg, W.M.H. Sachtler, J. Catal. 63 (1980) 112.

[54] A.S. Fung, M.J. Kelley, D.C. Koningsberger, B.C. Gates, J. Am. Chem. Soc. 119 (1997) 5877.

[55] W. Daniell, T. Weingand, H. Knozinger, J. Mol. Catal. A 204–205 (2003) 519.

[56] L. Salvati Jr., G.L. Jones, D.M. Hercules, Appl. Spectrosc. 34 (1980) 624.

[57] M.P. Seah, W.A. Dench, Surf. Interf. Anal. 1 (1979) 2, www.lasurface.com/imfp.

[58] N.E. Bogdanchikova, S. Fuentes, M. Avalos-Borja, M.H. Farias, A. Boronin, G. Diaz, Appl. Catal. B 17 (1998) 221.

[59] T. Ishizaka, S. Muto, Y. Kurosawa, Opt. Commun. 190 (2001) 385.

[60] F. Zaera, G.A. Somorjai, Surf. Sci. 154 (1985) 303.

[61] M. Alnot, J.J. Ehrhardt, J. Chim. Phys. 79 (1982) 735.

[62] F. Solymosi, T. Bansagi, J. Phys. Chem. 96 (1992) 1349.

[63] R. Spronk, J.A.R. van Veen, J.C. Mol, J. Catal. 144 (1993) 472.

[64] F.D. Hardcastle, I.E. Wachs, J.A. Horsley, G.H. Via, J. Mol. Catal. 46 (1988) 15.

[65] M. Sibeijn, J.C. Mol, Appl. Catal. 67 (1991) 279.

[66] A. Cimino, D. Gazzoli, M. Valigi, J. Electron Spectrosc. Relat. Phenom. 104 (1999) 1.

[67] M. Valigi, G. Minelli, J. Less-Common Metals 51 (1977) 271.