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Hydrogen and Oxygen Adsorption on Re/γ-Al_2O_3 Catalyst of Low Metal Content*

by J. Okal

Institute of Low Temperature and Structure Research, Polish Academy of Sciences,
ul. Okólna 2, P.O. 1410, 50-950 Wrocław, Poland

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Selective chemisorption of gases, especially hydrogen at room temperature, has been extensively used to determine the degree of dispersion of group VIII metal catalysts. In the case of supported Re catalysts hydrogen [1–7], oxygen [3–5,8] and CO adsorptions [2] have been used for estimation of the rhenium dispersion. Some controversies exist about the applicability of hydrogen chemisorption because rhenium does not dissociate hydrogen at room temperature [3–6] and chemisorption stoichiometry is not well established: $H/Re_s = 0.5$ [1,3,9] or 1 [6,10]. Oxygen chemisorption at room temperature has been considered as a more suitable method for determination of the dispersion of rhenium in Re/γ-Al_2O_3 catalysts [5] or total (Pt+Re) dispersion in Pt-Re/Al_2O_3 catalyst [11]. However, stoichiometry of oxygen chemisorption on the Re/γ-Al_2O_3 catalyst is not well established also: O/Re = 0.5 [10] or 1 [11] or is higher than one [3].

In this study, a volumetric method of chemisorption of hydrogen and oxygen has been applied for determining the dispersion of rhenium in a low-loaded Re/γ-Al_2O_3 catalyst. The influence of the oxidation-reduction treatment on the dispersion of rhenium was also investigated. In spite of the wide use of rhenium-containing supported catalyst, *e.g.* in catalytic reforming, data on redispersion of Re/γ-Al_2O_3 catalyst caused by oxidation-reduction treatment are still scarce [3,5,12].

The 1.04 wt.% Re/γ-Al_2O_3 catalyst was prepared by wet impregnation of γ-alumina (220 m^2/g) with aqueous solution of NH_4ReO_4, next was dried in air at 100°C and preliminary reduced in H_2 flow at 550°C for 10 h. Then, the catalyst was again reduced by H_2 at 550°C for 20 h, sintered at 800°C for 5 h [12] and subjected to a redispersion procedure by heating in static air at 400 or 600°C for 4 h. Finally, the catalyst was reduced in H_2 flow at 550°C for 20 h. The rhenium content in the samples before and after oxidation was measured by ICP-AES method. No loss of rhenium was observed after heating of the catalyst in air at 400°C, but the amount of rhenium slightly decreased after heating at 600°C. The BET surface area of the catalyst was

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*In memory of Prof. Helena Kubicka.

measured by nitrogen adsorption. Reduction at 800°C caused a decrease of the surface area from 211 to 170 m^2/g, while oxidation up to 600°C did not change the BET surface area.

Volumetric measurements of hydrogen and oxygen chemisorption were performed in a conventional glass apparatus (base pressure 10^{-6} Torr) [13], first for hydrogen and then for oxygen. The pretreated catalyst sample (*ca.* 1.5 g) was subjected to repeated heating at 520°C in H_2 at 300 Torr (1 Torr = 133N/m^2) for 4 h and next under vacuum for 2 h. Finally, the sample was saturated with hydrogen at about 150 Torr from 520°C to room temperature. The time needed for cooling the sample was about 3 h. Then, adsorption isotherms were obtained at room temperature. Chemisorption was also measured after admission of hydrogen at room temperature and keeping it at this temperature for 3 h. The oxygen sorption was measured at room temperature with oxygen pressure of 100–220 Torr. The sample was pretreated *in situ* in hydrogen at 520°C for 4 h, outgassed for 4 h, and cooled under dynamic vacuum to room temperature. Then, oxygen was introduced and the amount of adsorbed oxygen was measured. Typically an equilibration time of 20 min was employed.

On all studied samples, chemisorption of hydrogen at room temperature was very low in agreement with [3–6]. Hydrogen chemisorption isotherms obtained after saturation of the surface with hydrogen from 520°C to room temperature on variously pretreated 1.04 % Re/γ-Al_2O_3 catalyst were linear and parallel to those obtained on γ-alumina. The total amount of chemisorbed hydrogen was determined by extrapolation of isotherms to zero pressure. The uptake, obtained for sample reduced at 550°C, appears to be nearly equivalent to the corresponding value of the monoatomic amount of chemisorbed hydrogen determined for the same catalyst by gravimetric method [6]. Thus, it seems reasonable to assume that the maximum values of the total chemisorption correspond to monoatomic amounts. The chemisorption stoichiometry H:Re = 1:1 was assumed, the same as in gravimetric measurements [6] because the chemisorption conditions, *i.e.* temperature, pressure and equilibration time, were comparable. The oxygen uptake was determined also from a single isotherm, since oxygen was totally irreversibly chemisorbed on rhenium at room temperature. The adsorption of oxygen on all samples increases slightly with the increasing pressure. Since the adsorption isotherms were linear and parallel above 130 Torr, extrapolation of the linear part to zero pressure should give correct oxygen uptakes.

Table 1 presents the chemisorption capacities and dispersion data for 1.04% Re/γ-Al_2O_3 catalyst. Increase of the temperature of reduction from 550 to 800°C produces some decrease in the uptake of both gases, and heating in air at 600°C (or at 400°C) followed by reduction at 550°C resulted in the increasing uptake of hydrogen and oxygen. Calculated H/Re and O/Re atomic ratios show the same trend indicating the sintering/redispersion of the metallic phase upon the applied treatments. This result suggests that dispersion of rhenium slightly decreases with the temperature of reduction and then, after treatment in air, it increases. Similar conclusion was recently obtained for the 10.4% Re/γ-Al_2O_3 catalyst after similar heat treatments [13].

Table 1. Hydrogen and oxygen chemisorption on 1.04 % Re/γ-Al_2O_3 catalyst after various treatments.

Treatment	H_2 chemisorption			O_2 chemisorption		O/H
T (°C)/time/gas	μmol g^{-1} cat.	H/Re[a]	l (chem.)[b]	μmol g^{-1} cat.	O/Re[a]	
550/20h/H_2	20.7	0.74	1.8	10.7	0.38	0.52
+						
800/5h/H_2	15.1	0.54	2.5	9.1	0.33	0.60
+						
600/4h/air						
+						
550/20h/H_2	25.2	0.90	1.5	13.2	0.41	0.52

[a] Number of hydrogen or oxygen atoms chemisorbed to the total number of Re atoms in the catalyst sample.
[b] Average metal particle size (nm) determined from H_2 chemisorption. It was calculated by using the relation l(chem.) = $6 \times 10^7/a_s\, d$, where a_s is surface area calculated per 1 g of rhenium ($m^2(gRe)^{-1}$ and d = 21.04 g/cm^3.

The amount of irreversibly bound oxygen on all the samples studied is nearly two times lower than the amount of hydrogen chemisorbed at room temperature following saturation from 520°C. Last column of Table 1 shows values of the O/H ratios *i.e.* the number of chemisorbed oxygen atoms to the number of hydrogen atoms chemisorbed in the monolayer. Slightly higher O/H ratio was obtained for the catalyst after reduction at 800°C. Probably, the severe reduction treatment forms oxygen vacancies in the alumina support, which during oxygen chemisorption may be reoxidized. The obtained O/H ratios suggest a surface stoichiometry O/Re_s of 0.5:1 for irreversibly adsorbed oxygen, compared to 1:1, H/Re_s stoichiometry. The coverage of 0.5 obtained for oxygen at room temperature is consistent with that suggested on the basis of UHV studies [14] and with that obtained volumetrically on a rhenium powder [10]. Possible explanation for this effect could be the site pair requirement for immobile, dissociative oxygen adsorption, recently suggested by Vannice *et al.* for chemisorption on Pt/SiO_2 catalyst [15]. Also, a lower adsorption capacity for oxygen on very small Re particles, strongly interacting with the support, can decrease oxygen chemisorption compared to hydrogen chemisorption and/or some volume oxidation even at room temperature cannot be excluded [8]. Our X-ray photoelectron spectroscopy (XPS) data [16] of the sample, reduced at 800°C and passivated in air at room temperature for several minutes, showed very broad Re 4f peak with the binding energy of 43–48 eV. This suggests that a mixture of superficial oxides with oxidation state between Re^{+4} and Re^{+7} was produced in a detectable amount, due to the use of highly dispersed rhenium. Another factor complicating the interpretation of the results of oxygen sorption on metallic Re is dissociative and/or molecular type of adsorption [3,17].

In Table 1 there are also given the average metal particle sizes determined from the H_2 chemisorption results. The small increase of the average particle size of rhenium is observed in the sample reduced at 800°C. This result is in agreement with the high resistance of rhenium to sintering, characteristic for metals of high cohesive energy or melting point. Heating of the sintered sample in air at 600°C (or 400°C) followed by reduction in H_2 at 550°C resulted in the redispersion of rhenium. Small Re particles with an average size of 1.5 nm were obtained by using this procedure. It can be noted that calcination temperature had no influence on final state of the rhenium dispersion. The average particle size obtained for the catalyst reduced at 550°C (1.8 nm) was in good agreement with that observed by high-resolution electron microscopy (HREM), where small particles with diameters *ca*. 2 nm, uniformly distributed over alumina support, were visible [12]. Also X-ray diffraction (XRD) measurement yielded no discernible Re peaks even after reduction of the sample at 800°C.

Summarizing, the results obtained show that the hydrogen chemisorption method may be used for the determination of dispersion of supported rhenium. The rhenium dispersion in Re/γ-Al_2O_3 catalyst with a low Re content can be measured at room temperature following saturation from 520°C. The applicability of oxygen chemisorption at room temperature for estimating the dispersion of Re/γ-Al_2O_3 catalyst is complicated due to incomplete monolayer formation during irreversible dissociative chemisorption as well as to bulk oxidation.

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