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NOTE

XPS Studies of the Rhenium State in Supported Re Catalysts

Recently it has been found that catalytic (*1*) and adsorptive (*2*) properties of supported Re catalysts are affected by prereduction conditions, and Re reducibility depends on the supports and starting materials (*3*). An assumption has been made to account for it by Re interaction with the support (*3–5*). But information available on the nature of the interaction as well as the information on valence and physical state of Re in supported catalysts is scarce and this complicates interpretation of the results obtained from catalytic studies of Re catalysts. X-ray photoelectron spectroscopy (*6–10*) is known to be an efficient method to study these problems.

The present paper deals with XPS study of Re interaction with various supports (SiO_2, Al_2O_3). Besides the support the influence of starting materials ($HReO_4$, NH_4ReO_4, $KReO_4$, $Ba(ReO_4)_2$) and conditions of pretreatment (chemical environment, temperature, pressure) were studied to determine their effect on the state of Re on those surfaces.

The catalysts containing 3.4 to 4.8 wt% of Re were prepared by impregnation of the supports with aqueous solutions of the corresponding Re compounds followed by drying in air at 120°C. The samples were treated *in vacuo* and at low hydrogen pressure (ca. 10 Torr) in a preparation chamber connected to a spectrometer. Re catalysts were also reduced in a stainless steel reactor either in flowing H_2 at 1 atm or in the mixture of hydrogen with benzene at 30 atm. All operations, including the transfer of the catalyst from the reactor to spectrometer chamber were carried out in a purified Ar atmosphere to avoid any contact with the air. XPS spectra were recorded with an ES-100 spectrometer according to (*6*). The C 1s line (E_b, 285 eV) of the adsorbed diffusion pump oil was used as the standard to calibrate the energetic positions of the peaks. The pressure in the spectrometer was 10^{-7} Torr, which excluded Re^0 oxidation during spectra recording.

To identify the Re state on the support surface one should have spectral data for individual Re compounds of various valencies. Therefore, first the spectra of some Re oxides and complexes were studied. As seen from Table 1, different salts of perrhenic acid show practically equal binding energies of Re $4f$, whereas for Re_2O_7 E_b is 0.5 eV higher. It may be noted that the binding energy of Re $4f_{7/2}$ in the compounds depends upon both the "formal" oxidation state and the nearest neighbors of the Re ions (bond ionicity and coordination). The identification of the intermediate Re^{n+} states is complicated, particularly for $0 < n \leq 4$.

Table 1 and Fig. 1 show that the Re state in the catalysts after impregnation and drying is different from that found in their starting compounds.

All the spectra of the catalysts show a considerable broadening of the lines, and in the case of γ-Al_2O_3 there is a chemical shift of Re $4f_{7/2}$ line. Moreover, due to a strong broadening the splitting of Re $4f_{5/2}$

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TABLE 1

Parameters of Re $4f$ XPS of Re-Containing Samples

Sample[a]	Treatment conditions	E_b, Re $4f_{7/2}$	δ[b] (eV)	State of oxidation
Re_2O_7	Vacuum, 20°C	46.5	—	7
NH_4ReO_4		46.0	1.6	7
$KReO_4$		46.2	1.6	7
$Ba(ReO_4)_2$		46.2	1.6	7
ReO_3		44.3	—	6[c]
ReO_2		43.2	—	4[c]
K_2ReCl_6		44.8	1.8	4
Re_3Cl_9		43.2	3.0	3
Re(metal)	500°C H_2	40.6	1.2	0
$HReO_4/\gamma\text{-}Al_2O_3$	Starting samples	46.7	—	7
$NH_4ReO_4/\gamma\text{-}Al_2O_3$		46.5	3.0	7
$KReO_4/\gamma\text{-}Al_2O_3$		46.4	—	7
$Ba(ReO_4)_2/\gamma\text{-}Al_2O_3$		46.3	—	7
$HReO_4/SiO_2$	Starting samples	45.9	—	7
NH_4ReO_4/SiO_2		46.0	2.0	7
$KReO_4/SiO_2$		45.9	—	7
$Ba(ReO_4)_2/SiO_2$		45.9	—	7
$HReO_4/SiO_2$	500°C, H_2	41.0	—	0
NH_4ReO_4/SiO_2	10 Torr	40.9	—	0
$HReO_4/\gamma\text{-}Al_2O_3$	650°C H_2	41.3	—	0
$NH_4ReO_4/\gamma\text{-}Al_2O_3$	10 Torr	41.0	—	0
$KReO_4/\gamma\text{-}Al_2O_3$		40.5	—	0
$Ba(ReO_4)_2/\gamma\text{-}Al_2O_3$		41.8	—	0
$HReO_4/\gamma\text{-}Al_2O_3$	500°C, H_2, 1 atm	41.1	—	0
$HReO_4/\gamma\text{-}Al_2O_3$	300°C, air	45.7–46[d]	—	
$HReO_4/\gamma\text{-}Al_2O_3$	500°C, vacuum	43.4[e]		

[a] The starting compounds were prepared as described in (*12*).

[b] Half-widths of the lines; see also Fig. 1.

[c] Partially oxidized.

[d] Broadened.

[e] Centroid of the line.

and Re $4f_{7/2}$ lines decreases. Similar spectral changes have been observed for MoO_3/Al_2O_3 (*7*) and WO_3/Al_2O_3 (*8*) and ascribed to the interaction of the supported component with the support and also to the energetic nonequivalency of the transition metal ions on the surface.

On SiO_2 most of the Re retains the form of the initial compound. On $\gamma\text{-}Al_2O_3$ different Re states may arise as a result of ReO_4^- interaction with the acceptor surface sites and also due to the conversion of some Re into Re_2O_7. The Re^{7+} interaction with $\gamma\text{-}Al_2O_3$ is promoted by calcination of the samples in air. For example, the treatment of $HReO_4/\gamma\text{-}Al_2O_3$ at 300°C gives rise to a broad Re $4f$ line so that the doublet is not resolved. Re $4f$ spectra of Re/SiO_2 and Re/Al_2O_3 treated *in vacuo* and in H_2 (p = 10 Torr) at 200 ÷ 500°C have been investigated. In the case of SiO_2, Re 4*f* spectra show new lines (Fig. 1) which are indicative of Re^{7+} transition into lower oxidation states. Increasing the temperature to 300°C results in the appearance of a line due to metallic Re although a shoulder in the high energy side of the Re 4*f* spectrum indicates that some Re remains in cationic form. At 500°C Re is completely reduced in all samples of Re/SiO_2. But at this temperature the spectra of $Re/\gamma\text{-}Al_2O_3$ catalysts are unresolved doublets characteristic of a number of different Re states (Fig. 1).

In the case of $\gamma\text{-}Al_2O_3$, intermediate Re states appear at reduction temperatures as low as 200 to 300°C. In a temperature range of 300 to 600°C no appreciable changes in the energetic position of the spectrum are observed although some alteration in the shape and half-width of the Re 4*f* line occurs. The deconvoluted spectrum of the sample reduced at 600°C reveals that it consists of two doublets of Gaussian form. The positions of the Re $4f_{7/2}$ lines in this spectrum are 43.2 and 40.6 eV, respectively. Since one of the components for Re $4f_{7/2}$ gave E_b of 43.2 eV, which can be ascribed to both $ReO_2(Re^{4+})$ and $Re_3Cl_9(Re^{3+})$ (Table 1), this line does not allow discrimination between these two states of Re. However, a more reliable reference seems to be ReO_2, where every Re atom has oxygens as its nearest neighbors; a similar environment exists in the catalysts. The attribution of the line with E_b of 43.2 eV to Re^{4+} species is more or less speculative and needs additional investigation. The spectra of $HReO_4$, NH_4ReO_4, and $Ba(ReO_4)_2/\gamma\text{-}Al_2O_3$ are similar to the spectrum of massive metallic Re after the treatment of the samples with hydrogen at 10 Torr at temperatures higher than 600°C. An increase in the hydrogen pressure to 1 atm results in the decrease of required reduction temperature to 500°C.

It should be noted that the parameters of the Re 4*f* spectra for the $Re/\gamma\text{-}Al_2O_3$ samples reduced at extreme temperatures

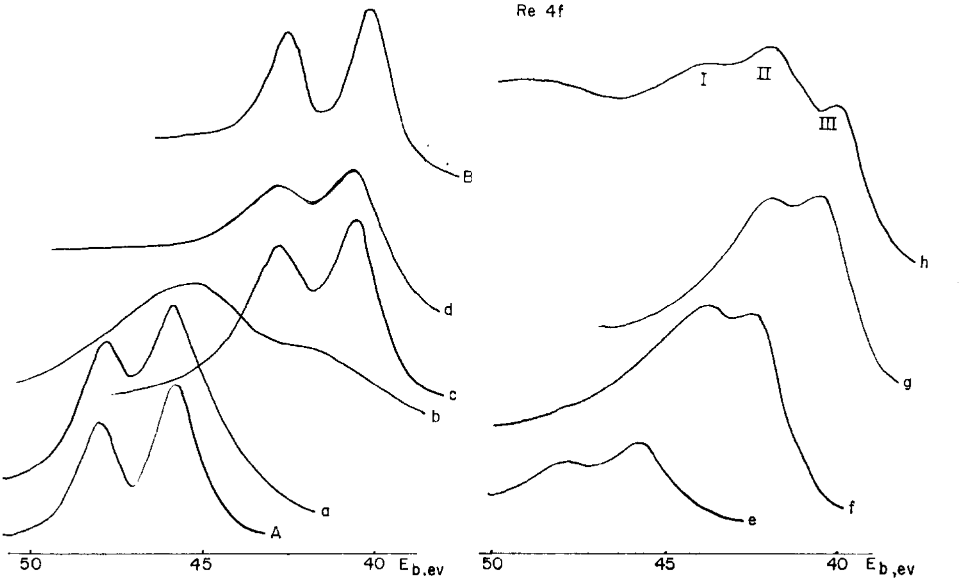

FIG. 1. XPS spectra of Re 4*f* in supported Re catalysts. NH_4ReO_4/SiO_2; (a) initial sample; (b) 200°C, H_2, 10 Torr; (c) 500°C, H_2, 10 Torr; (d) 200°C, C_6H_6 and H_2, 30 atm. $NH_4ReO_4/\gamma\text{-}Al_2O_3$; (e) initial sample; (f) 500°C, H_2, 10 Torr; (g) 650°C, H_2, 10 Torr; (h) 200°C, C_6H_6 and H_2, 30 atm. NH_4ReO_4 powder (A); Re^0 powder, 500°C, H_2(B).

in H_2(650°C, static system; 500°C, flow) are different from those of the massive Re^0. The spectral lines of the catalysts are broader, and for $HReO_4/\gamma\text{-}Al_2O_3$ there is a positive shift in the Re $4f_{7/2}$ spectrum by 0.5 eV with respect to that of the metal. The spectra of the reduced supported Re can differ from those of metallic Re for a number of reasons: (a) incomplete reduction of Re, (b) Re nonhomogeneity on the surface, (c) Re^0 interaction with the support and electron structure of the metallic clusters. The chemical analysis data show that Re in $HReO_4/\gamma\text{-}Al_2O_3$ is reduced completely to Re^0. X-ray diffraction indicates that Re, both in the initial samples and after reduction at 500°C in H_2, is highly dispersed, i.e., there is no Re phase. Hence, the observed changes of spectral patterns do not seem to be due to incomplete reduction or nonhomogeneity of Re on the surface. Thus, XPS data suggest that the conclusion made for other metals (Ir, Pd, Pt (*9–11*)), when studied over $\gamma\text{-}Al_2O_3$ by XPS, is also valid for $Re/\gamma\text{-}Al_2O_3$: A strong interaction of the dispersed metal with the support occurs, which results in electron density transfer from Re^0 to $\gamma\text{-}Al_2O_3$. This interaction is less pronounced for Re/SiO_2 the spectrum of which is very close to that of Re^0.

It is of principal importance to study the Re state in the catalyst surfaces which are formed during catalytic processes. The effect of reduction conditions on the Re state in catalysts has already been mentioned. Changing from static to flow conditions results in a decrease from 650 to 500°C in the temperature required for complete reduction of Re supported on $\gamma\text{-}Al_2O_3$.

Reduction of $Re/\gamma\text{-}Al_2O_3$ catalysts under the conditions of benzene hydrogenation (30 atm, $H_2:C_6H_6 = 10$) results in partial formation of the metal at a temperature as low as 200°C. The XPS spectrum from $HReO_4/\gamma Al_2O_3$ reduced under the above conditions shows three broad lines resulting from the overlapping of at least two Re $4f$ doublets (Fig. 1). The high energetic doublet (I, II) is characteristic of Re with an intermediate state of oxidation (possibly, Re^{4+}), whereas the doublet (II, III) may be assigned to Re^0. The analysis of the spectra shows that the extent of Re reduction in the reaction mixture for both $KReO_4/\gamma\text{-}Al_2O_3$ and all Re/SiO_2 samples is much greater than that for the other $Re/\gamma\text{-}Al_2O_3$ samples.

To conclude, the study of Re-supported catalysts by XPS shows that the state of the initial and reduced rhenium on SiO_2 surface is greatly different from that on $\gamma\text{-}Al_2O_3$ and is dependent on the Re compound used to prepare the catalysts. The reducibility of Re on $\gamma\text{-}Al_2O_3$ is much less than that of Re on SiO_2. This is due to a stronger interaction of Re^{7+} with the $\gamma\text{-}Al_2O_3$ surface. After drying and calcination, some of the Re over $\gamma\text{-}Al_2O_3$ is likely to form a surface complex. Reduction at relatively low temperatures (200–300°C) results in transition of some Re^{7+} into an intermediate oxidation state. It has been suggested (*5*) that thermal treatment of $Re/\gamma\text{-}Al_2O_3$ *in vacuo* gives rise to a two-dimensional dispersed phase of Re^{4+}, which interacts with the support surface. In those authors opinion (*5*) it is this phase which is responsible for stabilizing Re over $\gamma\text{-}Al_2O_3$ under oxidizing conditions at high temperatures. Our experiments with $HReO_4/\gamma\text{-}Al_2O_3$ treated *in vacuo* at 500°C also show that the treatment results in transition of some Re into an intermediate oxidation state, possibly to Re^{4+}. But unlike previous results (*5*), subsequent treatment of the catalyst in air at 400°C results in Re reoxidation to Re^{7+}.

It should be noted that the electronic properties of the dispersed metal over supports, in particular over $\gamma\text{-}Al_2O_3$, are different from those of the massive metal, i.e., Re species bear an effective positive charge. The studies of the influence of the physical and valence state of Re on the catalytic activity of supported catalysts are in progress.

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