JOURNAL OF CATALYSIS 56, 468–471 (1979)

NOTE

The State of Re in Pt–Re/γ-Al_2O_3 Catalysts

In our previous studies on Pt–Re/γ-Al_2O_3 catalysts we showed that the complete reduction of Re^{7+} to Re^0 is strongly catalyzed by Pt (*1*) and that there is formation of (Pt, Re) bimetallic aggregates (*2*), the catalytic properties of which differ from the additive behavior of pure Pt and pure Re particles (*3*). Our catalysts were prepared by coimpregnation of the Al_2O_3 support by H_2PtCl_6 and Re_2O_7, followed by drying at 110°C and subsequent hydrogen reduction at 500°C.

Conditions of activation which are closer to the conditions used in industrial processes include calcination in air at 500°C, followed by purging by nitrogen and final reduction by H_2 at 500°C. Therefore we decided to compare the final state of the catalysts prepared in such conditions to that for the preparation conditions used previously. This study was encouraged by a paper of McNicol (*4*) who found the Re to be completely reduced to the metallic state in agreement with us (*1*) but without any catalytic effect of Pt; McNicol explained this discrepacncy by a difference in the degree of hydration of the metal species, a conclusion to which we agree on the basis of our own results published elsewhere (*5*). McNicol calcined his catalysts at 525°C for 2 hr and dried them in nitrogen at 400°C before reduction by hydrogen. This procedure is closer to that used in the present investigation than to the procedure followed in our previous work (*1–3*).

The methods for characterizing the reduced catalysts are:

1. H_2–O_2 titrations at room temperature, as previously (*2*). They allow us to determine the number of Pt and Re atoms exposed, i.e., Pt_s and Re_s, and provide indications about the presence or not of pure Re particles (*2*). For this last purpose profit is taken of the large difference in the reducibility of Re_sO, when Re is alloyed with Pt and when it is not (Pt alloyed to Re promotes the reducibility of Re_sO considerably).
2. Infrared spectroscopy of chemisorbed CO, as previously (*2*). The comparison of the optical density of the CO bands for different modes of activation allows one to corroborate a variation in the dispersion of the metal phase. The values of the ν(CO) frequencies and the variation in the M_2CO bridged species bands allow some insight on the Pt–Re interactions.
3. Hydrogenolysis of cyclopentane (*3*). A sharp maximum in the specific activity for (Pt_s + Re_s) was observed at about 70% Re/(Pt + Re) in the conditions of reduction (*1–3*). A procedure of activation giving rise to little or no interaction between Pt and Re would be expected to provide a much lower intrinsic activity near that composition.

The H_2–O_2 titrations were carried out over sample A, a 2% (Pt + Re)/γ-Al_2O_3 (S = 100 m^2/g)[1] catalyst (percent Re/(Pt + Re) = 60), activated as described

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[1] The support is Al_2O_3 Oxide C Degussa, the same as used for the work in Refs. (*1–3*), where we erroneously indicated 180 m^2/g for its surface specific area.

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TABLE 1

H_2–O_2 Titrations over 2% (Pt + Re)/γ-Al_2O_3[a]

Total number of μat-g (Pt + Re)/g catal. = 102	(Pt_s) μat-g/g	(Re_s) μat-g/g	Percent dispersion (Pt + Re)	(Re_s alloyed to Pt) μat-g/g	(Re_s not alloyed to Pt) μat-g/g
Catalyst A_1 (Direct reduction)	35	36	70	~36	~0
Redispersed Catalyst A_2	29	65	92	~12	~53

[a] Percent Re/(Pt + Re) = 60. All metal contents are expressed in microatom-gram per gram of catalyst. (Pt_s), (Re_s): surface concentration in Pt or Re.

previously (*1–3*) (named catalyst A_1) or activated in the following way: heat treatment at 500°C in O_2 (p = 100 Torr, 4 hr), followed by evacuation in vacuum during 15 hr and finally by H_2 reduction at the same temperature (catalyst A_2). This second state of the catalyst is named "redispersed" in reference to Yao and Shelef (*6*) who showed that such an activation procedure leads to very highly dispersed Re^0 in monometallic Re/Al_2O_3 catalysts. Let us note first that the reduction of the redispersed form A_2 of the catalysts (at $p(H_2) = 50$ Torr, heating rate = 10°C/min, H_2O and HCl being trapped at −198°C) was found to be much more sluggish than the direct reduction of the same bimetallic catalyst. The catalytic effect of Pt on the reduction of Re was reduced very strongly in agreement with previous findings (*4–5*). The data for the H_2–O_2 titrations are reported in Table 1 (for details of the method of calculation, see Ref. (*7*)). They show a significant increase in the percent dispersion of (Pt+Re) and a strong decrease in the Pt–Re interaction for the "redispersed" catalyst A_2 as compared to the directly reduced catalyst A_1.

The surface composition of the bimetallic clusters estimated by the ratio of (Re_s alloy) to (Pt_s + Re_s alloy) should be of the order magnitude of 50% in catalyst A_1 but significantly poorer in Re (~30%) in the redispersed catalyst A_2. The concentration of Re_s in the redispersed catalyst A_2 is found to be very near the total concentration of Re (65 instead of 66 μat-g/g), which suggests that practically all the Re atoms are exposed either in the surface of very small pure Re aggregates or in the surface of the Pt particles in the alloyed state.

Figure 1 reports the infrared spectroscopic data for CO chemisorbed on catalysts A_1 and A_2. The spectra (I) were recorded after *in situ* cooling of the reduced catalysts in hydrogen, followed by H_2 evacuation at 25°C, displacement of the chemisorbed hydrogen by CO (p = 50 Torr), and evacuation of CO. The spectra (II) were recorded after a subsequent O_2 treatment at 25°C (p = 100 Torr, 15 hr) and evacuation of the oxygen. Comparison of spectra I for the two samples A_1 and A_2 corroborates the above conclusion that the overall dispersion of the metal phase (Pt + Re) is increased very significantly following the redispersion; in fact the optical density of the whole spectrum is multiplied by a factor of ~1.8. Spectrum I for the redispersed catalyst A_2 further shows clearly a band at 1940 cm^{-1} which corresponds to bridged or multicentered forms of CO adsorbed on Re (*2*), while only a small shoulder is observed in the same spectral range (1945 cm^{-1}) over the directly reduced catalyst A_1. It has been shown previously that the alloying effect leads to a strong decrease of the multicentered forms of adsorbed CO (*8*). The appearance to a large extent of Re_2CO

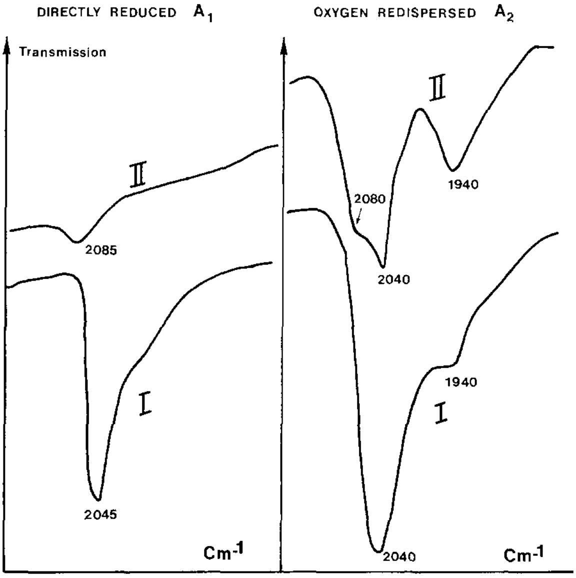

FIG. 1. νCO infrared absorption bands from CO adsorbed on 2% (Pt + Re)/γ-Al_2O_3 (percent Re/(Pt + Re) = 60) reduced by H_2 either directly (A_1) or after (O_2 plus vacuum) heat treatment at 500°C (A_2) (I) for CO irreversibly chemisorbed at 25°C, (II) after a further treatment with O_2 at 25°C.

species confirms then the presence of unalloyed Re in the oxygen redispersed catalyst.

The spectra (II) recorded after oxygen treatment of the CO-covered surface of both catalysts agree with this scheme. Spectrum II for the catalyst A_1 shows mainly a band at 2085 cm^{-1}, which corresponds to Pt_s–CO species in interaction with Pt_sO species (*2*). Spectrum II for the redispersed catalyst A_2 shows two strong bands at 2040 and 1940 cm^{-1} which correspond to the linear and bridged forms, respectively, for CO chemisorbed on pure Re particles (*2*); identification of the 2085-cm^{-1} band is the same as for the directly reduced catalyst A_1. Since catalyst A_2 includes much more Re as pure Re particles than the directly reduced one, the Re content in the bimetallic particles has to be smaller. Hence a difference should be expected in the ν(CO) frequency for CO chemisorbed on Pt in the two catalysts A_1 and A_2, according to our earlier considerations (*2*). This is not observed since the frequency (2040–2045 cm^{-1}) is about the same for the two modes of activation and is smaller than the value previously reported (*2*) (2066 cm^{-1}) where the catalyst was outgassed at 500°C before adsorption of CO at 25°C. In the spectra reported here there is an additional effect of chemisorbed water (identified by a band at 1640 cm^{-1}) on the ν(CO) frequencies for CO chemisorbed on Pt; the shift in ν(CO) frequencies due to water was previously shown and discussed for monometallic Pt/Al_2O_3 catalysts (*9*). The effect of the adsorbed water could overcome the alloying effect shown in Ref. (*2*).

The influence of the redispersion on cyclopentane hydrogenolysis (*T*: 240°C) was also studied. The redispersed form B_2 of the 2% Re/γ-Al_2O_3 monometallic catalyst was found to have approximately the same activity per Re_s as the directly reduced form B_1 of the same catalyst. The catalytic activity of the redispersed form C_2 and of the directly reduced form C_1 of a bimetallic catalyst was measured over the

67.5% Re/(Pt + Re) catalyst, a composition which is very close to that found for the maximum in activity detected in our previous study (*3*). The activities were approximately equal to 0.08 and 0.45 mole/h/g, respectively. The smaller activity of the redispersed form C_2 in spite of its larger percent dispersion of (Pt + Re) is to be ascribed to the segregation of Pt and Re. Assuming the redispersed catalyst to be composed of a mixture of Pt (percent dispersion ~50) and of Re (percent dispersion ~100) particles, its activity would be at best nearly equal to 0.002 mole/h/g, taking into account the intrinsic activities for Pt and for Re, respectively, given in Ref. (*3*). The difference between that value and the experimental one (~0.08 mole/h/g) supports the idea that in the redispersed catalyst the segregation between Pt and Re is not complete.

As a whole, the present results show that the ($Pt + Re/\gamma\text{-}Al_2O_3$) catalysts may be stabilized under various states, according to the procedure followed during their activation. Two extreme situations should be homogeneous bimetallic aggregates on the one hand, and separate particles of pure Pt and of highly dispersed pure Re on the other one. The extent to which Re is alloyed to Pt is certainly highly dependent on the details in the experimental procedures, and therefore the state in which it is present in industrial conditions may not be inferred accurately from the present data obtained in laboratory scale conditions.

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Received: May 10, 1978