Infrared and adsorption study of strong metal–support interaction in diluted platinum–alumina catalysts

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Diffuse reflectance IR spectroscopy along with H_2 and CO adsorption measurements were applied to the study of 0.3% Pt/γ-Al_2O_3 catalyst precalcined in an air flow at 1023 K and then reduced at 773 and 973 K in hydrogen. Reduction of the catalyst at 973 K results in formation of supported metallic Pt particles in SMSI (strong metal–support interaction) state, as evidenced by the sharp decrease of Pt ability to chemisorb H_2 at room temperature as well as the significant lowering of thermal stability of linear Pt–CO complexes. Spectroscopically the effect of SMSI is manifested by the slight increase of the singleton frequency of linearly adsorbed CO from 2050 to 2060 cm^{-1} together with the decrease of the dipole–dipole shift from 40 to 15 cm^{-1} and by a large decrease of absorption band extinction.

Keywords: Adsorption of CO; SMSI; infrared frequencies; supported platinum

1. Introduction

The classical example of strong metal–support interaction (SMSI) is represented by transition or noble metals supported on such reducible oxides as TiO_2 [1], Nb_2O_3, V_2O_5, Ta_2O_3 [2,3], CeO_2 [4], etc., treated with hydrogen at temperatures of about 773 K. The evidence of SMSI is the loss of the ability of metals to chemisorb H_2 and CO, which is not connected with the change of metal dispersion.

Several models may account for this phenomenon, for instance, metal particle encapsulation [5], charge transfer from the support to the metal [6] or formation of intermetallic compounds [1]. The examples of SMSI for metals supported on nonreducible carriers such as aluminum oxide are much more limited and are mainly connected with the reduction at higher temperatures. For instance Dautzenberg and Wolters [7] reported that when Pt/Al_2O_3 was reduced in H_2 above 960 K a decrease in hydrogen chemisorption occurred which could not be solely explained by metal sintering. They suggested that under these conditions the formation of Pt_xAl alloy took place. The idea of alloy formation was confirmed later by Kunimori et al. [8]. It is also in agreement with the Knight-shift measurements [9] indicating a change of electron density on the Pt nuclei.

The SMSI phenomenon was also reported for platinum and palladium supported on silica [10,11]. In these cases the formation of platinum or palladium silicides after high temperature reduction was confirmed also by X-ray analysis [10,11].

Noble metals supported on alumina are certainly of much more practical importance than the above model systems. Therefore the elucidation of the SMSI nature in such catalysts is important from both theoretical and practical points of view. It is also obvious, that SMSI effects should be most pronounced for the diluted supported metal catalysts, where the fraction of metal atoms at the metal–support interface is the highest. Low concentration of metal in such systems creates, however, considerable difficulties for the study of the SMSI phenomenon by traditional physical methods.

In this work we applied the highly sensitive diffuse reflectance IR spectroscopic study, which readily allowed us to investigate samples with a metal content as low as several tenths or even hundredths of weight percent [12]. Carbon monoxide adsorption was used as the molecular probe for the state of metal particles.

2. Experimental

The $Pt/\gamma\text{-}Al_2O_3$ catalyst with Pt content of 0.3 wt% was prepared by wet impregnation of IK-02-200 $\gamma\text{-}Al_2O_3$ with an aqueous solution of H_2PtCl_6. (The characteristics of the support were the following: BET specific surface area 180 m^2/g, pore volume 0.50 cm^3/g, mean pore diameter 30 nm. Impurities content: Na_2O 0.03 wt%; Fe_2O_3 0.02 wt%; S 0.009 wt%.) The carrier was preliminary calcined in a flow of dry air at 1023 K for 3–5 h. After impregnation the water excess was evaporated at 353 K and then the catalyst was calcined in a flow of air at 400 K for 4 h. To increase the dispersion of supported Pt the samples were additionally treated at 300 K with a saturated aqueous solution of H_2O_2 containing a small amount of HCl [13]. Then it was again dried at 400 K for 4 h followed by calcination in a flow of dry air at 1023 K for 3 h. The reduction in hydrogen at 773 or 973 K for 1 h was carried out in situ in an IR cell in static conditions ($P_{H_2} = 7 \times 10^3$ Pa). Then the samples were evacuated at reduction temperature for 1 h.

Diffuse reflectance IR spectra of adsorbed CO, which was used as molecular probe, were recorded in the range of 1700–2300 cm^{-1} at room temperature with a Perkin-Elmer 580 B spectrophotometer as described in ref. [14]. CO adsorption on reduced samples was carried out at 300 K and residual pressure of 5×10^3 Pa. Lower surface coverages were obtained by successive evacuation at 300, 373, 473, 573 or 673 K for 0.5 h.

The amount of H_2 and CO adsorbed on the reduced catalyst was measured volumetrically at 300 K with equilibrium gas pressure of 50 Pa, when the surface of supported metallic Pt is believed to be saturated by chemisorbed H_2 and CO [13]. Both gases were preliminary purified from traces of H_2O or O_2 by successive passing through the columns filled with 4A molecular sieve and with reduced chromium–silica catalyst.

To distinguish CO adsorption on Pt and that on the aluminum oxide carrier, the successive measurements of amounts of adsorbed gas were carried out for the prereduced samples and those evacuated after CO adsorption at 300 K. The difference was related to CO adsorption on aluminum oxide.

3. Results and discussion

Fig. 1 represents IR spectra of carbon monoxide adsorbed on 0.3 wt% Pt/Al_2O_3 catalyst pretreated in hydrogen at different temperatures. In the presence of gaseous CO the intensive absorption bands of the linear form of CO adsorption on Pt metal particles (2100 cm^{-1}) and the weaker broad bands of two-fold (1850 cm^{-1}) and three-fold (1790 cm^{-1}) [15] bridged species as well as the band at 2210 cm^{-1} characteristic of CO molecules coordinated by aprotic sites on the surface of Al_2O_3 [16] are observed. The latter is easily removed by evacuation at 300 K, whereas the intensities of the rest of the bands remain unchanged. This indicates that after evacuation at room temperature CO molecules are mainly adsorbed by metallic Pt particles.

In the following we will mainly focus our attention on the most intense bands around 2100 cm^{-1} of the linear Pt–CO complexes. For the catalyst reduced at 773 K (fig. 1 upper part) the intense 2090 cm^{-1} band is shifted with the decrease of metal surface coverage to the singleton frequency of 2050 cm^{-1}. The Pt–CO complexes in this sample are very stable and could be decomposed in vacuum only above 600 K. A similar linear form of carbon monoxide adsorption has been earlier reported for polycrystalline Pt particles in Pt/Al_2O_3 catalysts by many authors [17].

The properties of linear Pt–CO complexes in the sample reduced at 973 K (fig. 1 lower part) are quite different. The corresponding absorption band with the maximum at 2075 cm^{-1} is narrower and its intensity is considerably lower. With decrease of metal surface coverage it is shifted to the singleton frequency of 2060 cm^{-1}. Such complexes could be partially (by 30%) removed by evacuation even at room temperature and are completely destroyed in vacuum at 373 K. This indicates their lower thermal stability in comparison with linear Pt–CO complexes on “usual” polycrystalline Pt.

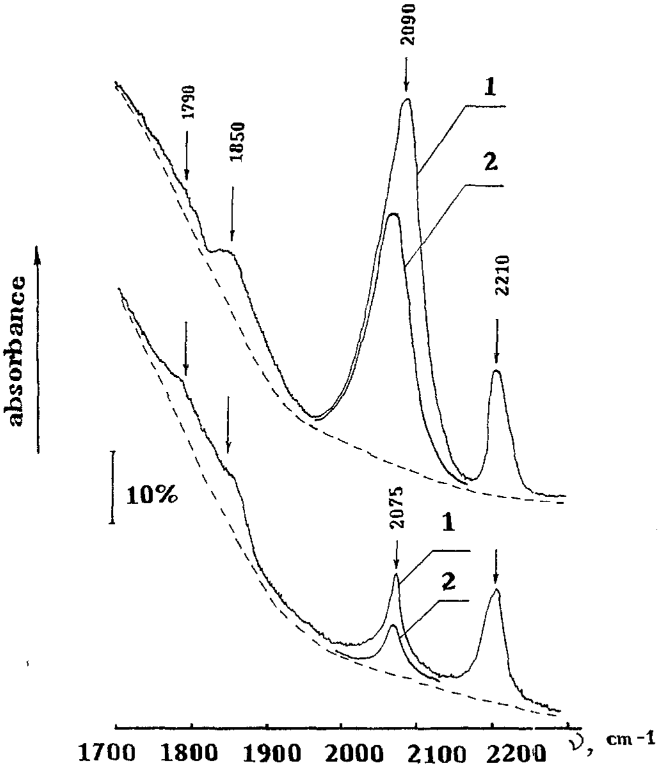

Fig. 1. IR spectra of CO adsorbed on 0.3% Pt/Al_2O_3 prereduced at 773 K (upper part) and at 973 K (lower part). (1) In the presence of gaseous CO and (2) after sample evacuation at 573 K (upper part) and 300 K (lower part).

Thus, in catalyst reduced at 973 K the metallic Pt exists in an unusual state. Its interaction with CO results in weaker linear Pt–CO complexes. Spectroscopically they differ from those on "usual" polycrystalline Pt by a slightly higher value of the singleton frequency (2060 in comparison with 2050 cm^{-1}) and by a smaller dipole–dipole shift ($\Delta\nu_{d-d} = 15$ cm^{-1} in comparison with 40 cm^{-1}). These unusual properties of supported Pt after reduction at high temperature are likely caused by SMSI and are not solely connected with the sintering of metallic particles. This follows from the data on H_2 and CO adsorption by the samples pretreated at different temperatures (table 1).

Indeed, reduction of the catalyst at 973 K results in a sharp decrease of hydrogen adsorption on Pt, whereas the quantity of adsorbed CO is constant or becomes even slightly higher than that for the catalyst reduced at 773 K. The latter indicates that reduction at high temperature does not change the number of surface Pt atoms capable to adsorb CO. Therefore the decrease of the H/Pt ratio should be connected with a considerable lowering of the Pt ability to chemisorb H_2 at room temperature. This is the actual manifestation of SMSI in Pt/Al_2O_3 which is likely connected with the formation after high temperature

Table 1
Adsorption of H_2 and CO on the catalysts reduced at different temperatures

Treatment conditions	H/Pt	CO/Pt
H_2, 773 K	0.51	0.31
H_2, 973 K	0.08	> 0.31 [a]
reoxidation at 923 K followed by reduction at 773 K	0.18	0.17

[a] This is the lower limit of CO adsorption on platinum, since after high temperature reduction carbon monoxide could partially desorb from metal particles even at room temperature.

reduction of the surface intermetallic Pt–Al compounds similar to Pt_xAl alloys as proposed in refs. [7,8].

Comparison of IR spectra intensities (fig. 1 upper and lower spectra 1) with the CO/Pt ratios (table 1) leads also to the conclusion that SMSI sharply reduces (by a factor of about 10) the extinction coefficient of the linear form of the CO absorption band.

The reoxidation of the catalyst at 923 K followed by its reduction at 773 K partially restores the ability of platinum to chemisorb H_2. At the same time the number of surface Pt atoms accessible for CO adsorption is markedly reduced. After reoxidation they probably transform to the surface species containing oxidized Pt which is either not completely reduced at 773 K in hydrogen or may be a source of less dispersed metallic particles.

In IR spectra of adsorbed CO such irreversible transformation of supported Pt is identified by the less intense absorption in the range of 2100 cm^{-1} compared to the catalyst prereduced at 773 K as well as by appearance of an additional narrow band at 2100 cm^{-1}. According to ref. [18] this band could be assigned to CO molecules adsorbed in linear form on thin epitaxial Pt film formed on the partially crystallized support surface.

4. Conclusion

We demonstrate that the characterization of the state of supported metal particles only by the stretching frequency of adsorbed $C\equiv O$ molecules may sometimes be misleading. Indeed, the differences in these frequencies for "usual" supported platinum and for Pt in SMSI state are rather small whereas the thermostability and the extinction coefficients of CO molecules adsorbed on these types of metal particles are quite different. This should be taken into account when using carbon monoxide adsorption as the molecular test for the state of supported metals.

The above results also show, that the reduction of diluted Pt/Al_2O_3 catalysts at 973 K results in formation of supported metallic Pt particles in SMSI state which is probably connected with the formation of intermetallic Pt–Al compounds. This state is characterized by the sharp decrease of the Pt ability to chemisorb H_2 as well as by significant lowering of the thermal stability of linear Pt–CO complexes. Spectroscopically the effect of SMSI is manifested by the increase of the singleton frequency of linearly adsorbed CO from 2050 to 2060 cm^{-1} together with the decrease of the dipole–dipole shift from 40 to 15 cm^{-1} and by a drastic decrease of absorption band extinction.

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