Diffuse reflectance IR-spectroscopy evidence of the unusual properties of platinum in Pt/Mg(Al)O catalysts for the selective aromatization of *n*-alkanes

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Diffuse reflectance IR spectra of CO adsorbed on Pt/Mg(Al)O catalysts were studied at room temperature and different surface coverages of metallic Pt. They show the existence of two types of metallic Pt particles. One type has a normal behavior toward the adsorption of CO, which is probably related to the lower dispersion of Pt. The other type probably corresponds to smaller negatively charged clusters like those found for Pt-loaded alkaline and alkaline-earth forms of zeolites. They are characterized by the very low frequency of the singletone corresponding to the linear form of adsorbed CO and high thermal stability of the bridging complexes of CO with metallic Pt. Such by metal–support interaction modified platinum is likely responsible for high activity and selectivity of Pt/Mg(Al)O catalyst in *n*-alkanes aromatization.

Keywords: Aromatization of *n*-alkanes; Pt/Mg(Al)O catalyst; IR-spectroscopy

1. Introduction

A high activity and selectivity for the aromatization of hexane was recently reported for highly dispersed platinum and palladium supported on aluminum-stabilized magnesium oxide Pt/Mg(Al)O and Pd/Mg(Al)O catalysts [1–3]. This finding is surprising and important because the mechanism of their action certainly differs from the bifunctional route widely accepted for alumina-supported platinum catalysts promoted by treatment with HF or HCl.

Such catalysts are probably closer to the alkaline and alkaline-earth forms of Pt-containing L and faujasite type zeolites which were found to have a high aromatization activity [4,5]. However, the aluminum-stabilized magnesium oxide support is essentially non-microporous [3]. Therefore, the high aromatization selectivity of Pt/Mg(Al)O and Pd/Mg(Al)O catalysts cannot be explained by molecular shape selectivity effects. Instead, it could be rather connected with some unusual properties of supported noble metal particles due to a modification of their electronic properties because of an interaction with the basic Mg(Al)O support.

Indeed, the properties of small platinum clusters incorporated in the basic forms of zeolites are known to be somewhat unusual. An electron transfer from zeolite crystal lattice to Pt particles was supposed for platinum L zeolites loaded with alkaline [5,6] and alkaline-earth cations [7]. Similar metal–support interaction was also postulated from IR spectra of adsorbed CO molecular probe for Pt incorporated in NaX and NaY zeolites [8].

For Pt supported on Mg(Al)O such data are absent. Therefore in the present note, we report diffuse reflectance IR spectra of CO adsorbed on Pt/Mg(Al)O catalysts.

2. Experimental

Two samples of Pt/Mg(Al)O catalysts were studied in this work. One of them with 0.88 wt% Pt content, Mg/Al = 5 and BET surface area 210 m^2 g^{-1} was the same as studied previously in refs. [1–3], where the details of its preparation are also reported. The second sample with Pt content of 0.9 wt% was specially prepared by impregnation of Mg(Al)O synthesized according to ref. [9] (Mg/Al = 3) with aqueous solution of H_2PtCl_6.

Before spectral measurements, both catalysts were reduced at 750 K in hydrogen (P_H = 100 Torr) under static conditions for 2 h, and subsequently evacuated at 750 K for 1 h. Diffuse reflectance IR spectra of adsorbed CO were recorded in the range of 1700–2300 cm^{-1}, using a Perkin-Elmer spectrophotometer as previously described [10]. The amounts of H_2 and CO adsorbed on the reduced catalyst at different pressures and surface coverages were measured volumetrically. Both gases were purified to be free of H_2O and O_2 traces by passing through columns filled with 4A molecular sieves and with reduced chromia–silica catalyst.

The experimental results obtained for both of the above catalysts were essentially similar. Therefore in the following we will concentrate on the sample (I) for which the data on catalytic activity are available.

3. Results and discussion

After reduction in static conditions, the Pt dispersion in sample (I) was 0.6

(H_2 chemisorption at 300 K and equilibrium pressure of 0.2 Torr). This value compares to 0.49 as reported earlier, but measured following reduction in flowing hydrogen [1,2]. It is close but slightly higher, may be because some H_2 has spilled over onto the Mg(Al)O support [2].

Fig. 1 shows the evolution of the IR spectra of adsorbed CO, obtained after evacuation at progressively increasing temperatures. At room temperature and a CO pressure of 0.5 Torr corresponding to $CO/Pt = 0.5$ (fig. 1a), two bands are observed: one of higher intensity with the maximum at 2080 cm^{-1}, and a shoulder at 1990 cm^{-1}. Both lines are representative of linear forms of adsorbed CO. They are similar to those previously reported for alkaline and alkaline-earth forms of Pt-loaded zeolites [5–8]. In addition, a very weak band corresponding to the bridged form of adsorbed CO is also noticed at 1835 cm^{-1}.

When the sample is successively evacuated at 300, 420, 500 and 570 K for 0.5 h at each step, a decrease of the amount of adsorbed CO is observed together with a shift to lower frequencies of the maxima of the high intensity band and of the shoulder. The latter observation is a common feature for CO adsorption on

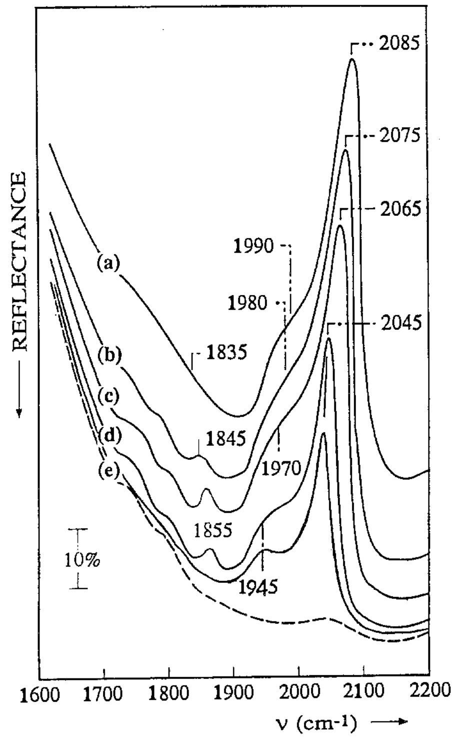

Fig. 1. IR diffuse reflectance spectra of CO adsorbed at 298 K on Pt/Mg(Al)O. (a) In the presence of 0.5 Torr gaseous CO, (b) after evacuation for 30 min at 420 K, (c) after evacuation for 30 min at 500 K, (d) after evacuation for 30 min at 570 K, (e) after evacuation for 150 min at 570 K. Dashed curve, after evacuation for 30 min at 620 K.

metallic Pt. It is connected to the decrease of dipole–dipole coupling between the adsorbed molecules at lower coverage [11]. After more prolonged evacuation at 570 K the two bands are well resolved (spectrum e). The bands of adsorbed CO disappeared completely only after sample evacuation for 0.5 h at 620 K (fig. 1, dashed line).

The positions of the bands at the lowest surface coverages (those of the singletones) are characteristic of isolated CO molecules and can be used to compare different supported Pt catalysts. For the sample under consideration, they peak at 2045 and 1945 cm^{-1}, the separation between the singletone maxima being about 100 cm^{-1} (fig. 1e).

For diluted Pt/Al_2O_3 catalysts, such a position of the high frequency band has been reported many times [11]. The second band, however, is strongly shifted toward lower frequencies as also observed in Pt-loaded alkaline forms of zeolites. The bathochromic shift equal to about 100 cm^{-1} observed in this work is considerably larger than the value of 80 cm^{-1} reported for Pt-loaded NaX zeolite [8]. It indicates that the unusual properties of Pt in Pt/Mg(Al)O are expressed even stronger.

An additional argument for this conclusion stems from the thermal stability of the bridging form of adsorbed CO. For diluted Pt/Al_2O_3 catalysts, the corresponding band at about 1850 cm^{-1} is removed after sample evacuation at 373 K [12]. On the contrary, for the present Pt/Mg(Al)O sample, this band is observed up to an evacuation temperature of 570 K (fig. 1e). This indicates unambiguously the much stronger binding of the bridging form of adsorbed CO and also confirms the unusual properties of small Pt particles in Pt/Mg(AL)O. With respect to CO adsorption, they resemble more Pd or transition metals, for which the bridging form of CO is more stable than for Pt.

Infrared study of CO adsorption on charged electrodes [13] together with quantum chemical analysis of the electrostatic potential influence on CO adsorption [14,15] evidence that negative charging of metallic Pt results in the decrease of vibrational frequency of the C=O bond for linearly adsorbed molecules due to the larger contribution of the back donation effects as well as to the marked increase of bridging species stability. The negative charging of Pt particles incorporated in basic NaY and NaX zeolites was also proposed for explanation of very low singletone frequencies (up to 1963 cm^{-1}) of adsorbed CO by an increase in extent of back donation in such systems [8].

Accordingly we also suppose that "unusual" metallic Pt in Pt/Mg(Al)O characterized by the CO singletone frequency of 1945 cm^{-1} and the high thermal stability of the bridging form of CO adsorption represents strongly negatively charged clusters due to severe electron transfer from basic oxygen anions of the support to small Pt particles. This conclusion is in agreement with our results on CO adsorption on sample (II) with less basic Mg(Al)O (Mg/Al = 3) support. In this case the position of low frequency singletone becomes at least by 15 cm^{-1} higher indicating a decrease in the extent of electron transfer from less basic oxygen anions to metallic Pt.

4. Conclusions

Two different kinds of Pt particles exist on the surface of Pt/Mg(Al)O catalysts. One type has a normal behavior toward the adsorption of CO, which is probably related to the lower dispersion of Pt. The other type probably corresponds to smaller clusters and has unusual properties like those found for Pt-loaded alkaline and alkaline-earth forms of zeolites.

The latter particles are believed to possess an excess negative charge as in zeolites [5,7,8] that results in a red shift of CO singletone frequency due to an increase in the extent of back donation. Because of the very low frequency of the singletone corresponding to the linear form of adsorbed CO, a similar conclusion should also hold for the small Pt particles supported on Mg(Al)O. This finding is additionally supported by the unusual stability of the bridging form of adsorbed CO that has also been proved experimentally and theoretically to be favored by negative charging of Pt [13–15]. Such by metal–support interaction modified platinum similar to that incorporated in basic zeolites is likely responsible for high activity and selectivity of Pt/Mg(Al)O catalyst in *n*-alkanes aromatization.

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