Interaction of H_2, *n*-butane and cis-2-butene with Pt and Pt In in NaY: a microcalorimetric study

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Pt NaY and Pt In NaY adsorption properties have been compared by using probes like H_2, C_4H_{10}, 2-C_4H_8 and microcalorimetry. It appears that the addition of In to Pt does not change the initial heat of H_2 chemisorption but decreases the initial heat of butane and butene chemisorption.

Keywords: bimetallic Pt In; butane; butene adsorption

1. Introduction

The catalytic dehydrogenation of alkanes is of considerable industrial importance because of the increasing demand for olefins, either long chain linear olefins (C_{10}–C_{14}) for the manufacture of linear alkylbenzenes or short chain olefins like isobutene and propene [1].

It is known that platinum catalysts are active and selective for dehydrogenation reactions but suffer from rapid deactivation with time on stream. By alloying Pt with a metal like Sn, the catalytic properties are considerably enhanced. A large number of fundamental studies have been devoted to the study of Pt Sn supported material [1–6] in order to understand the role of Sn. However, there are very few reports in the literature relative to Pt In bimetallics which have also interesting properties for dehydrogenation reactions [7]. Recently, we have described the preparation and the characterization of Pt In bimetallics in NaY host [8] and we have shown that small Pt In bimetallic particles are formed inside the cavities of the zeolite. These metallic particles (0.8–1 nm) are composed of Pt^0 and In^0 as observed by XPS, but it has not been possible to measure the exact composition since they are heterogeneous as observed by STEM-EDX. The average composition as calculated by using XPS data which show that 40% of the indium is reduced to In^0 can be estimated as Pt_2In.

In this paper we will report some additional characterization results obtained by microcalorimetry studies of H_2, C_4H_{10} and C_4H_8 adsorption, these probes being used to see how the Pt–In interaction could affect Pt adsorption properties.

2. Experimental

The solids utilized in this study have been fully described in a previous paper [8]. Samples were prepared by using NaY zeolite coexchanged with Pt^{2+} and In^{3+}. The Pt loading is 5 wt% and the indium loading is 3.1 wt%. The exchanged samples were calcined under O_2, flushed with N_2, reduced by H_2 at 773 K for 2 h, flushed with N_2 and cooled down to RT.

Before microcalorimetric experiments, samples were placed in a quartz microcalorimetric cell, attached to a vacuum line. Thus, samples were outgassed at 773 K for 8 h, contacted with H_2 ($p = 7$ kPa) in presence of a liquid nitrogen trap and maintained overnight at 773 K before being outgassed at this temperature for 2 h ($p = 0.1$ mPa). Then the microcalorimetric cell was inserted inside the microcalorimeter (Tian Calvet) coupled with a system allowing the introduction of appropriate doses of the adsorbate and the simultaneous measurement of the evolved heat and the pressure [9]. Experiments were performed at 323 K in order to have a basis of comparison with results published in the literature [10,11].

3. Results

3.1. Hydrogen adsorption on Pt_5 NaY and Pt_5 $In_{3.1}$ NaY

Plots of differential heats versus adsorbate coverage are represented in fig. 1 for Pt_5 NaY and Pt_5 $In_{3.1}$ NaY. It is observed that the initial differential heats are not much different for Pt_5 NaY and Pt_5 $In_{3.1}$ NaY samples but, as the hydrogen coverage increased, the decrease in differential heats of adsorption is much more pronounced for the Pt_5 $In_{3.1}$NaY sample than for the pure Pt sample; thus the Pt_5 $In_{3.1}$NaY surface is saturated at lower pressure than the Pt_5 NaY surface. These results indicate that the Pt dispersion is higher for Pt_5 NaY than for Pt_5 $In_{3.1}$NaY solid. If the platinum dispersion is calculated by using the number of H_2 molecules adsorbed with an initial heat larger than 60 kJ/mol [10] the dispersion is

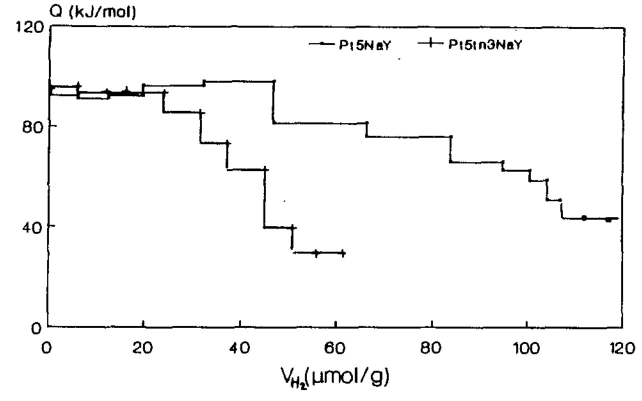

Fig. 1. H_2 chemisorption: plot of differential heat of adsorption versus volume of adsorbed hydrogen.

0.85 for Pt_5 NaY and 0.38 for $Pt_5\,In_{3.1}$ NaY, these numbers being close to those obtained earlier [8].

Thus, it is concluded that the main effect of the addition of In to Pt is, for the hydrogen chemisorption, a decrease in the number of Pt centers that are able to chemisorb H_2 with a high heat of adsorption. These results are in line with those for Pt and Pt Sn samples reported by Cortright et al. [10] who concluded that the addition of Sn to Pt does not change much the initial heat of H_2 chemisorption, and with results obtained on Pt(111) and Sn/Pt(111) which have indicated that the temperature of H_2 desorption is slightly higher for tin alloyed Pt than for pure Pt indicating that the Pt–H bond is not deeply modified by tin addition.

3.2. Butane chemisorption

Plots of differential heat versus butane coverage are reported in fig. 2 for Pt_5 NaY and $Pt_5\,In_{3.1}$ NaY samples.

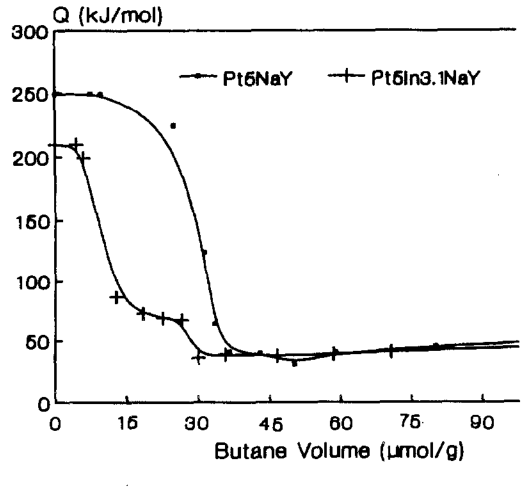

Fig. 2. Butane chemisorption. Differential heat of adsorption versus volume of adsorbed butane.

This figure clearly indicates that the addition of In to Pt has two effects:

(1) A lowering of the initial heat of adsorption for the $Pt_5\,In_{3.1}$ sample: 212 kJ/mol for the Pt In sample compared to 250 kJ/mol for the Pt NaY sample.

The value of 250 kJ/mol obtained for the pure Pt sample is of the same order of magnitude as that reported for the chemisorption of propane over Pt films [11]. The lowering of the initial heat of adsorption due to the addition of In to Pt parallels well that observed for *n*-butane adsorption on Sn/Pt(111) [12] (a decrease of 5–8 kJ/mol is obtained for the desorption energy as compared to Pt(111)). Similar results are reported for cyclohexane desorption [12] on the same solids.

(2) The addition of In to Pt decreases the number of Pt atoms able to chemisorb butane with a high initial heat of adsorption.

From results shown in fig. 2, one can calculate the number of butane molecules adsorbed with a heat of adsorption higher than 100 kJ/mol and, using the number of Pt surface atoms derived from fig. 1, the average number of Pt atoms involved in the adsorption of one butane molecule was calculated. It appears that for the two solids under study, the number of Pt surface atoms needed to chemisorb one butane molecule is almost the same: 7.5 for Pt_5 NaY and 6.8 for $Pt_5\,In_{3.1}$ NaY sample.

Although the exact composition of the bimetallic surface is not known, it can be assumed from hydrogen chemisorption results [8] that only half of the surface atoms are Pt atoms. Since the probability to have 7 (or 6) contiguous Pt atoms in the $Pt_5\,In_{3.1}$ sample is certainly much less than for the Pt_5 NaY solid, the previous result could suggest that the *n*-butane chemisorption does not require 7 (or 6) contiguous Pt atoms but probably a smaller ensemble providing that the other Pt atoms are present.

The high values of the initial heats of adsorption for both samples suggest that the butane molecule is probably dissociatively adsorbed, as it was reported for Pt(110)-(1 × 2) surface [14].

It would be of interest to analyse the gas phase following the calorimetric measurement sequence in order to check if any transformation of the butane has occurred with the possible formation of H_2.

Indeed, when comparing the Pt NaY and Pt In NaY samples, it has to be considered that both supports are not exactly identical since the Pt and In elements have been introduced by ionic exchange: by consequence $Pt_5\,In_{3.1}$ NaY samples contain less Na^+ ions (In^{3+} is exchanged with 3 Na^+); after reduction protons will be generated by the reduction of Pt^{2+} and of In^{3+} at the zero state.

Thus, the corresponding number of protons so created in Pt_5 NaY and $Pt_5\,I_3$ NaY will be different. Nevertheless, since it is known that the acidity of NaY is always weak until the major part of Na^+ is removed, it can be assumed that the difference in support acidities can be neglected.

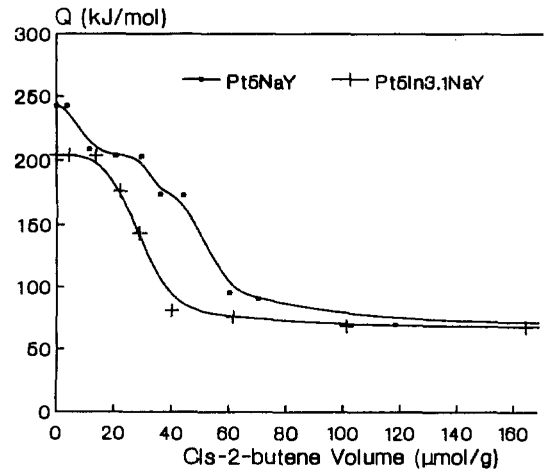

Fig. 3. Butene chemisorption. Differential heat of adsorption versus volume of adsorbed butene.

3.3. *Cis 2-butene chemisorption*

Plots of differential heat versus coverage are represented in fig. 3.

For butane, it is observed that the initial heat of adsorption is higher for Pt_5 NaY (~ 250 kJ/mol) than for $Pt_5 In_{3.1}$ NaY sample (~ 210 kJ/mol). The value of the initial heat of adsorption of butene on Pt or Pt In samples is higher than that reported for C_2H_4 adsorption on Pt/SiO_2 (150 kJ/mol [10]) or on Pt films for C_3H_6 [11] (175 kJ/mol). The higher heat of butene adsorption observed in this work could be explained by suggesting that small Pt particles in NaY are more reactive towards dissociative adsorption of C_4H_8 into $(C_4H_7)_{ads}$ and H_{ads}. Such dissociative adsorption is supported by the formation of H_2 at nearly 300 and 380 K during TPD measurements of adsorbed butene on Pt(111) surface [16].

Another possibility is that the initial heat of adsorption could increase with the carbon chain length as reported for C_1, C_2, C_3 alkanes and for C_2, C_3 olefins on Pt films [11].

As pointed out for butane adsorption it will be of interest to study the TPD of butene in order to know if the decomposition (if any) of the olefin occurs at the same temperature and involves the same number of Pt atoms on Pt and Pt In samples.

As previously, one can calculate by using hydrogen chemisorption results and data of fig. 3 the average number of Pt atoms required to adsorb one butene molecule. This number is 4.9 for Pt_5 NaY. For the pure platinum sample, the value is in reasonable agreement with that reported for ethylene adsorption on Pt (6 Pt atoms for one ethylene molecule [10]) or on Bi Pt(111) [15]. For $Pt_5 In_{3.1}$ NaY, the number is 3.5, a value which is definitely lower than for the pure Pt sample.

A similar trend (decrease of number of Pt atoms/alkene molecule) has been reported for bimetallic Pt Sn deposited on silica [10] (6 Pt atoms/ethylene molecule for pure Pt compared to 4 Pt atoms in Pt Sn).

The decrease in the number of Pt atoms required to chemisorb one butene molecule when Pt is alloyed with In can be understood by assuming, as mentioned in ref. [17], that the olefin molecule is adsorbed in a different manner for Pt and Pt In surfaces. As indicated previously, TPD of butene and measurement of H_2 formation will be of help to understand the adsorption properties and the catalytic properties of these materials.

4. Conclusion

H_2, butane and butene adsorption on Pt_5 NaY and $Pt_5 In_{3.1}$ NaY samples have been studied by using microcalorimetry. For H_2, the initial heat of adsorption is the same for Pt and Pt In, the number of Pt surface atoms decreasing with In addition. By contrast, for butane and butene, the initial heat of adsorption is larger for the pure Pt sample and the number of Pt atoms required to chemisorb one butene molecule is lower for Pt In compared to Pt. These changes in adsorption stoichiometry could be explained by assuming that different species are existing on Pt and Pt In solids.

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