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Pt–Mo Bimetallic Catalysts Supported on Y-Zeolite

II. Activity and Selectivity in *n*-Butane Conversion

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Pt–Mo bimetallic catalysts prepared by adsorption and decomposition of $Mo(CO)_6$ on 1-nm Pt aggregates supported on Y-zeolite exhibit enhanced hydrogenolysis activity with respect to PtY zeolite in *n*-butane conversion. The activity curve vs Pt/Mo composition is volcano-shaped with a maximum near equiatomic composition. The rate at maximum is 7 and 34 times larger than on PtNaHY and Pt/SiO_2, respectively. The reaction orders with respect to n-C_4 and H_2 are positive in a large range of pressures. The kinetic parameters are interpreted in terms of the participation of both Pt and Mo atoms in the reaction mechanism. Mo atoms act primarily as strong adsorption sites for the hydrocarbon whereas hydrogen atoms dissociated on Pt are required to hydrogenate the hydrocarbon fragments.

INTRODUCTION

The preparation and characterization of Pt–Mo bimetallic catalysts supported on Y-zeolites has been reported in a previous paper (*1*). The molybdenum was introduced into the zeolites by means of adsorption and thermal decomposition of $Mo(CO)_6$ vapor in reduced PtY-zeolites containing 1-nm Pt particles. Upon Mo addition, a slight increase of the particle size and a progressive decrease of the amount of H_2 and CO chemisorbed were observed. It was concluded that some of the Mo atoms freed by $Mo(CO)_6$ decomposition are deposited on the surface, masking progressively the platinum atoms and their chemisorptive properties. Furthermore, it was shown by XPS, X-ray absorption spectroscopy, and ir spectroscopy that the initially electron-deficient Pt particles behave like bulk platinum after Mo addition.

Yermakov *et al.* (*2–4*) have studied the catalytic properties of Pt–Mo bimetallic clusters prepared by successive deposition and reduction of Mo and Pt π-allyl complexes on SiO_2. Rate enhancements of hydrogenolysis reactions with respect to Pt/SiO_2 were attributed to a modification of the electronic structure of platinum induced by low-valent molybdenum. In the present work the catalytic properties of PtMoY catalysts have been studied as a function of Mo concentration. The kinetic parameters of *n*-butane isomerization and hydrogenolysis have been determined and compared with those obtained previously on PtNaHY, PtCeY, and Pt/SiO_2 catalysts (*5*) with the aim of determining how the addition of molybdenum affects the mechanism of the reaction.

EXPERIMENTAL

The preparation and characterization of the catalysts were described in Part I of this work (*1*). The composition and nomenclature of the samples are given in Table 1.

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TABLE 1

Nomenclature and Composition of Catalysts

Samples	Unit cell composition	Pt (wt%)	Mo (wt%)	Pt/(Pt + Mo) (atoms)	H/Pt[a]
PtNaHY	$Pt_{7.6}Na_{30.9}H_{9.9}Y$	10.9	0	1	0.96
PtMoY,I	$Pt_{7.6}Na_{30.9}Mo_{1.7}Y$	10.9	1.2	0.82	0.68
PtMoY,II	$Pt_{7.6}Na_{30.9}Mo_{5.0}Y$	10.6	3.4	0.61	0.45
PtMoY,III	$Pt_{7.6}Na_{30.9}Mo_{8.3}Y$	10.4	5.6	0.48	0.41
PtMoY,IV	$Pt_{7.6}Na_{30.9}Mo_{12.2}Y$	10.1	8.0	0.38	0.39
PtMoY,V	$Pt_{3.2}Na_{29.5}Mo_{8.0}Y$	4.5	5.5	0.29	0.14
PtMoY,VI	$Pt_{0.4}Mo_8Na_{55}Y$	0.5	5.6	0.04	0.03
MoNaHY	$Mo_8Na_{17}H_{39}Y$	0	6.1	0	0
Pt/SiO_2		5	0	1	0.6

[a] H/Pt ratios determined from chemisorption measurements in previous work (*1*).

Measurements of the rates of *n*-butane reactions were performed at low conversion (<5%) in a conventional flow reactor under atmospheric pressure.

Reactions were carried out on 30–70 mg batches of zeolites in powder form (0.1–1 μm crystal sizes) loosely packed in a cylindrical bed (1 cm^2 × 0.05 cm) over a quartz frit. The reactant mixtures were made with H_2 and He carefully purified by flowing in a deoxo cell and dried on molecular sieves, and with *n*-butane purchased from Air Liquide (99.95% purity with isobutane as main impurity). The gas flows were controlled with a Brooks regulator and measured by flowmeters. The products were separated with a column of 10% SE30 on Chromosorb P and analyzed by gas chromatography using a flame ionization detector. The catalysts were activated in flowing H_2 at 670 K before reactions conducted within the temperature range 520–590 K.

RESULTS AND DISCUSSION

1. Reaction Rate Data

The *n*-butane conversion under our operating conditions yielded only methane (C_1), ethane (C_2), propane (C_3), and isobutane (i-C_4). The rates of the reactions $n\text{-}C_4 \rightarrow C_1 + C_3$, $n\text{-}C_4 \rightarrow 2C_2$ (2), $C_3 \rightarrow C_2 + C_1$ (3), and $n\text{-}C_4 \rightarrow \text{i-}C_4$ were calculated from the amounts of C_1, C_2, C_3, and i-C_4 formed assuming that the reactions $C_4 \rightarrow 4C_1$ and $C_2 \rightarrow 2C_1$ do not occur with an appreciable rate. Also it is assumed that the secondary hydrogenolysis reactions of i-C_4 do not modify substantially the product pattern.

Possible diffusion limitations were considered. Modification of the contact time and of the catalyst mass indicated the absence of external diffusion limitations under our operating conditions (space velocity 0.3–0.5 mol h^{-1}, sample mass 30–70 mg). The presence of internal diffusion can be ruled out in view of the following observations. (I) The study of PtY zeolites by CTEM and STEM (*1*) has shown that the distribution of the Pt aggregates in the zeolite crystals is homogeneous and that their sizes are within 1 ± 0.3 nm whatever the platinum loading. The same turnover numbers have been measured on PtY samples loaded with increasing amounts of platinum up to 15 wt%, according to Koros and Nowack (*6*) this can be a criterion for the absence of internal diffusion. (II) The Arrhenius plots are linear for all the samples investigated in the temperature range 590 K where the measurements were carried out. (III) The efficiency coefficient determined from the Thiele modulus with the diagrams proposed by Satterfield (*7*) is equal to unity under our reaction conditions. This is true for 1-μm zeolite crystals and provided the diffusion coefficient of *n*-butane is larger than 10^{-8} cm^2 s^{-1} which is likely since this value was found for the diffusion of *n*-butane in 5-Å zeolite (*8*).

It was also checked that the reactions proceed essentially on the metallic phase. Following the suggestions of Weisz (*9*) the reaction rates were measured on different platinum catalysts (5% PtNaY, 5% Pt/SiO_2), pure or mixed with acidic support (25 or 75% of HY or CeY zeolites). The measurements were carried out at 580 K on superimposed beds or on well-mixed powders. Within the experimental errors neither the turnover frequencies nor the selectivities were modified by the addition of the acidic support. Therefore, any contribution of a bifunctional mechanism to the overall reaction rate should be small. This is substantiated by a proportionality between the activity and the total metal surface up to 13 wt% of metal and by the high hydrogenolysis selectivity, whereas a plateau of activity with metal concentration and a high isomerization selectivity would be expected with carbonium ion intermediates. Finally, it has been shown that hydrogenolysis reactions are predominant on high surface area platinum zeolites (Ribeiro *et al.* (*10*)) and in the temperature range below 620 K (Christoffel and Paál (*11*)).

The reaction rates have been measured as a function of the partial pressure of *n*-butane (pressure range 5–100 Torr under a constant 600-Torr pressure of hydrogen) and as a function of the partial pressure of hydrogen (pressure range 150–700 Torr under a constant 40-Torr pressure of *n*-butane).

The turnover frequencies on PtMoY catalysts were calculated in two different ways. (I) *N*(*Pt*) *refers to the number of molecules formed per hour and per platinum atom chemisorbing hydrogen.* *N*(Pt) is calculated using the H/Pt ratio determined in Part I of this work (*1*) and given in Table 1. (II) *N*(*Pt* + *Mo*) *refers to the number of molecules formed per hour and per surface atom whatever the nature* (*Pt or Mo*) *of these atoms*. The number of surface atoms is calculated assuming that all the Mo atoms are combined with the Pt atoms in bimetallic aggregates and that the dispersion is 80%. This value is based on the TEM study described previously (*1*) showing that the average particle size is 1.3 ± 0.3 nm in all the PtMoY catalysts.

TABLE 2

Activities and Selectivities of Catalysts in *n*-Butane Conversion at 593 K

Samples	Pt/Pt + Mo	$P_{H_2}/P_{n\text{-}C_4}$	Reaction rates (h^{-1})						Selectivities		
			N_1	N_2	N_3	N_H ($N_1 + N_2$)	N_i	N_T ($N_H + N_i$)	N_H/N_T	N_i/N_T	N_2/N_1
PtNaHY[a]	1	40				20	2	22	0.91	0.09	
PtMoY,I	0.82	20	7.6[b]	3.8[b]	0.8[b]	11.4[b] (14.8)[c]	3.4[b]	14.8[b]	0.77	0.23	0.50
		40	9.8	5.1	1.0	14.9 (18.9)	3.6	18.5	0.80	0.19	0.52
PtMoY,II	0.61	20	27.1	20.0	5.8	47.1 (121.1)	2.6	49.7	0.95	0.05	0.74
		40	26.8	20.0	5.3	46.8 (120.4)	1.1	48.9	0.95	0.04	0.74
PtMoY,III	0.48	20	81.0	53.6	21.8	134.6 (493)	4.6	138.2	0.97	0.03	0.66
		40	64.7	44.6	17.1	109.3 (400)	3.4	112.7	0.97	0.03	0.69
PtMoY,IV	0.38	20	60.4	33.6	19.0	94.0 (429)	3.8	97.8	0.96	0.04	0.66
		40	77.3	47.6	25.0	124.9 (570)	3.0	127.9	0.97	0.02	0.61
PtMoY,V	0.29	20	16.3	10.0	3.1	26.3 (458)	2.6	28.9	0.91	0.09	0.61
		40	13.1	8.0	2.4	21.1 (368)	1.6	22.7	0.93	0.07	0.61
PtMoY,VI	0.04	20	1.0	0.6	0.1	1.6 (856)	0.14	1.74	0.92	0.08	0.60
		40	0.7	0.4	0.1	1.1 (622)	0.10	1.2	0.91	0.08	0.60
MoNaHY	0	40	0	0	0	0	0	0			
Pt/SiO_2[a]	1	40				4	5	11			

[a] From Ref. (*5*).

[b] Turnover frequency *N*(Pt + Mo): number of molecules formed per hour and per Pt or Mo surface atom (see text).

[c] Turnover frequency (*N*(Pt)): number of molecules formed per hour and per Pt atom chemisorbing hydrogen.

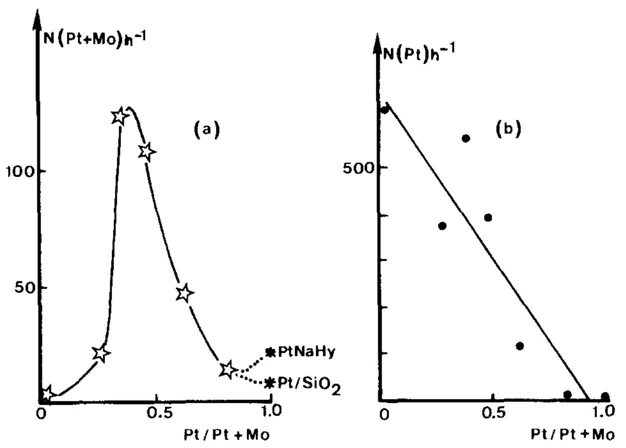

FIG. 1. Influence of Mo content on the total hydrogenolysis rate. (a) Turnover calculated from the total number of atoms: [N(Pt + Mo)] (b) Turnover calculated from the number of Pt atoms chemisorbing H_2: [N(Pt)]. Data on PtNaHY and Pt/SiO_2 are given for comparison.

The rates (turnover frequencies) of the three hydrogenolysis reactions N_1, N_2, N_3, and of the isomerization reaction N_i, together with the selectivities in hydrogenolysis and isomerization, are given in Table 2. The hydrogenolysis rates N_H(Pt) and N_H(Pt + Mo) ($N_H = N_1 + N_2$) are plotted in Fig. 1 (curves a and b, respectively) as a function of the Pt/Pt + Mo ratio. The logarithm of N_H(Pt + Mo) as a function of the partial pressure of n-butane and hydrogen is given for the different catalysts in Fig. 2. The apparent activation energies E_a of the reactions determined from the Arrhenius plots in the temperature range 520–590 K are given in Table 3. From the rate constants and activation energies the frequency factors A have been calculated for the different catalysts. The plot of log A as a function of E_a for the reaction $n\text{-}C_4 \rightarrow C_1 + C_3$ (Fig. 3)

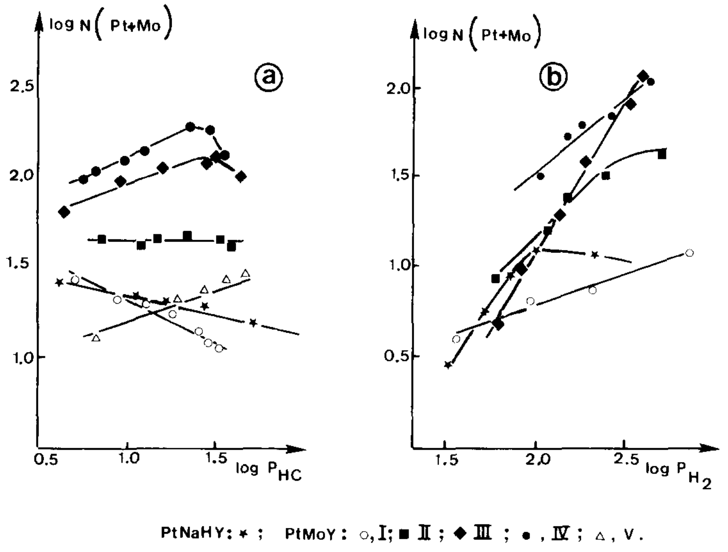

FIG. 2. Variation of hydrogenolysis rate as a function of reactant pressure and Pt/Pt + Mo ratios. (a) log N(Pt + Mo) vs log $p_{n\text{-}C_4}$; (b) log N(Pt + Mo) vs log p_{H_2}.

TABLE 3

Activation Energies E_a (in kJ mol^{-1}) for *n*-Butane Reactions on PtMoY Catalysts

Samples	n-C$_4 \rightarrow$ C$_3$ + C$_1$	n-C$_4 \rightarrow$ 2C$_2$	n-C$_4 \rightarrow$ i-c$_4$
PtNaHY	108.7	125.4	163.0
PtMoY,I	108.7	121.2	133.8
PtMoY,II	141.7	137.1	150.5
PtMoY,III	144.6	141.7	210.7
PtMoY,IV	171.0	168.0	220.5
PtMoY,V	146.3	155.9	191.9
PtMoY,VI	142.1	131.7	181.4

is linear, indicating that a compensation effect occurs between the frequency factors and the activation energies.

2. *Influence of Mo Content*

Reaction rate data given in Table 2 and in Figs. 1 and 2 point to an increase of the hydrogenolysis activity when Mo atoms are added to the 1-nm Pt aggregates. Enhanced hydrogenolysis activities have been reported previously for PtNaHY catalysts in comparison with Pt/SiO$_2$ and for PtCeY in comparison with PtNaHY (*5*). They have been correlated with the electrophilic character of platinum which increases in the series Pt/SiO$_2$ < PtNaHY < PtCeY. This interpretation cannot hold in the case of PtMoY catalysts since it has been shown that the addition of Mo atoms suppresses the electrophilic character of platinum (*1*). Furthermore, the kinetic parameters on PtMoY are, in many respects, different from those observed on PtNaHY and PtCeY. In this section the modifications of the kinetic parameters with Mo content are interpreted in terms of a direct participation of Mo sites in the reaction mechanism.

Influence of Mo on hydrogenolysis rates. Figure 1a giving the hydrogenolysis rates (total of reactions C$_4 \rightarrow$ 2C$_2$ and n-C$_4 \rightarrow$ C$_1$ + C$_3$) calculated per surface atom as a function of the amount of Mo is volcano-shaped. At a maximum near Pt/Pt + Mo = 0.5 the rates are 7 and 34 times larger than those on PtNaHY and Pt/SiO$_2$, respectively. The initial drop of activity when Mo

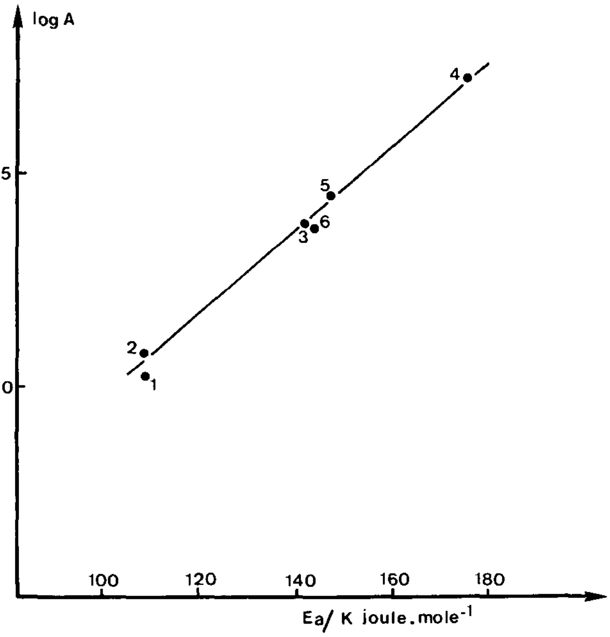

FIG. 3. Compensation effect between the frequency factor and the activation energy of hydrogenolysis reaction n-C$_4 \rightarrow$ C$_1$ + C$_3$. (1) PtNaHY; (2) PtMoY,I; (3) PtMoY,II; (4) PtMoY,IV; (5) PtMoY,V; (6) PtMoY,VI.

is added to PtNaHY (PtY,I → PtMoY,I) can be attributed to the suppression of the electrophilic character of platinum which was invoked to account for the higher hydrogenolysis activity of PtNaHY with respect to Pt/SiO_2 (*5*). Indeed, the platinum aggregates are no longer electrophilic when the first doses of molybdenum are added (*1*). However, the hydrogenolysis rates on PtMoY,I are still twice as fast as on Pt/SiO_2 or PtNaHY + NaOH (*5*).

The hydrogenolysis rate calculated from H_2 chemisorption measurements increases linearly with the Mo content (Fig. 1b). The ratios of the rate on PtMOY,VI with respect to those on PtNaHY and on Pt/SiO_2 are 31 and 56, respectively. This large increase cannot be accounted for with a reaction mechanism involving only the Pt atoms as active sites since they are progressively masked by Mo atoms and their electronic properties are like those of Pt/SiO_2 and PtNaHY + NaOH (*1*) which exhibit little hydrogenolysis activity. Therefore the reaction data given in Figs. 1a and b point to the participation of Mo atoms in the reaction mechanism. On the other hand the MoY zeolite does not exhibit any catalytic activity (Table 2) and physical mixtures of PtY and MoY zeolites behave only like PtY zeolite alone. This suggests that well-defined assemblies of Pt and Mo atoms associated in the aggregates are needed to account for the reaction rate data.

Influence of Mo on the selectivities. The addition of Mo atoms produces essentially an increase of the hydrogenolysis activity. The isomerization is slow and little affected. Therefore, it probably takes place on Pt atoms. The initial increase of isomerization rate from 2 h^{-1} on PtNaHY to 3.4 h^{-1} on PtMoY,I is probably due to the suppression of the electrophilic character when the first increments of Mo are added. A similar increase of isomerization rate concomitant with a drop of hydrogenolysis activity was also observed upon neutralization by NaOH of the PtNaHY acidity (*5*). The isomerization selectivities on PtMoY catalysts are lower than on PtCeY catalysts studied previously (*5*).

The ratios of the reaction rates N_2/N_1 are larger on PtMo catalysts. The probability of central C–C bond rupture has been associated with the presence of strongly adsorbed and dehydrogenated intermediates (*12*). The formation of highly dissociated hydrocarbon fragments on PtMoY catalysts has in fact been observed by the presence of highly deuterated species in the products of the reaction of D_2 with adsorbed species; details of that study will be published elsewhere (*16*).

Influence of Mo on reaction order. Figure 2a shows that the reaction order of the hydrogenolysis reaction with respect to *n*-butane depends upon the composition of the PtMoY catalysts. The Mo-poor sample (PtMoY,I), like the PtNaHY catalysts, exhibits a negative reaction order within the whole range of pressure investigated. This was attributed to a poisoning of the active surface by strongly adsorbed hydrocarbons (*5*). As more and more Mo atoms are added the order becomes zero and then positive. Figure 2b shows that the hydrogenolysis rates as a function of the hydrogen pressure depend also upon the Mo content. On PtNaHY the reaction order, initially positive, becomes negative at 75 Torr of H_2 pressure. On progressive Mo addition the order remains positive and its value increases.

These changes in reaction orders mean that the adsorption equilibrium of the reagents is modified on Mo addition. Since both reaction orders remain positive, one is led to conclude that H_2 and *n*-butane are not competing for the same adsorption sites. This suggests that Mo atoms could act as additional adsorption sites.

Influence of Mo on the activation energy and frequency factor. The addition of Mo atoms produces an increase of the apparent activation energy E_a of reaction 1 from 108.7 kJ mol^{-1} on PtNaHY to 171 kJ mol^{-1} on PtMoY,IV. On further addition E_a decreases to 142 kJ mol^{-1}. The variation of E_a

is compensated by a variation of the frequency factor such that the plot of log A as a function of E_a is linear. Compensation effects can be interpreted in several ways (Cremer (*13*)) so that no definite conclusions as to the participation of Mo atoms in the reaction mechanism can be drawn. However, we note that the initial increase of E_a and A can be understood qualitatively if additional hydrocarbon adsorption sites with higher binding energies are available.

3. Mechanism of n-Butane Hydrogenolysis on PtMoY

The above discussion points to the participation of Mo atoms as active sites in *n*-butane conversion unlike cerium in PtCeY zeolite which induces merely a modification of the platinum sites (*5*). The Mo atoms in PtMo aggregates do not chemisorb hydrogen at 300 K (1); however, they can act as strong adsorption sites for *n*-butane. Smutek and Černý (*15*) have measured by calorimetry very high adsorption heats for saturated hydrocarbons on molybdenum. This was attributed to a high dissociation and fragmentation of the molecules leading eventually to surface carbide. Indeed we have checked that the reaction of D_2 with adsorbed hydrocarbon fragments gives a higher fraction of CD_4 and CHD_3 products on PtMoY than on PtNaHY indicating that the hydrocarbons are strongly dehydrogenated and fragmented (*16*).

Therefore we propose the following mechanism for *n*-butane hydrogenolysis on PtMoY catalysts. Hydrogen is dissociatively adsorbed on the Pt atoms which are not masked by molybdenum atoms. Platinum atoms can adsorb and isomerize *n*-butane but the hydrocarbon molecules are mainly adsorbed by molybdenum atoms. The strongly adsorbed and dissociated intermediates thus formed cannot be hydrogenated in the absence of platinum. The hydrogenation step is made possible by the hydrogen dissociated on neighboring platinum atoms. The specialized role of Mo and Pt sites for the adsorption of reactants accounts for the positive reaction orders with respect to both hydrocarbon and hydrogen pressures. Indeed, there is little or no competition between H_2 and *n*-butane since they do not share the same sites. This mechanism also explains how the hydrogenolysis rate increases with Mo content up to an optimal composition where the fraction of unmasked Pt sites is just enough to yield dissociated hydrogen for hydrogenation of the Mo-bonded intermediates. Beyond that maximum the rate decreases progressively to zero because of the lack of dissociated hydrogen.

The specificity of Mo for *n*-butane adsorption and of Pt for H_2 adsorption is reinforced by the particular steric configuration of the zeolite cage–aggregate system. Indeed, a 1-nm Pt aggregate almost fills the supercage so that only the atoms facing the four 0.75-nm supercage apertures are accessible. On $Mo(CO)_6$ decomposition, molybdenum deposition should take place on these accessible Pt atoms first. Hydrogen molecules can still be dissociated on the Pt atoms inside the cage but *n*-butane molecules cannot enter the cage and therefore should be chemisorbed by the Mo atoms deposited at the cage aperture. Since about half the Pt atoms are facing the apertures one wonders whether the optimal composition for *n*-butane hydrogenolysis at Pt/Pt + Mo = 0.5 may correspond to the ideal situation where all the Pt atoms at the cage aperture are covered by Mo. Subsequent Mo addition might hamper H_2 chemisorption on platinum without providing additional adsorption sites which account for the progressive decrease of the activity of Mo-rich PtMoY catalysts. It has been shown that H_2 uptake is twice as great at 573 K as at 300 K and that this hydrogen desorbs at high temperatures only (*1*). This could mean that hydrogen chemisorbed on Pt atoms facing the cage walls can be encapsulated because the aperture becomes clogged by deposited Mo atoms. This would explain the decrease of reaction rate because dissociated hydrogen atoms are not available at reaction temperature to hydrogenate the hydrocarbon fragments adsorbed on Mo atoms.

4. Comparison with PtMo/SiO$_2$ Catalysts

Yermakov *et al.* (*2–4*) have studied the hydrogenolysis of ethane (*2*) and of neopentane (*3*) on PtMo/SiO$_2$ catalysts. The hydrogenolysis rates are enhanced with respect to Pt/SiO$_2$ although Mo/SiO$_2$ catalysts are inactive. The reaction orders with respect to hydrogen are larger. In the case of neopentane the order is never negative, unlike on Pt/SiO$_2$. These findings are in agreement with the present reaction data. However, a decrease of the activation energies was observed on PtMo/SiO$_2$, unlike on PtMoY catalysts. Rate enhancement was attributed to an increase of the electron deficient character of platinum induced by the association with Mo atoms. This interpretation cannot hold for PtMoY catalysts since it has been demonstrated that platinum is no longer electron deficient after Mo deposition (*1*). These discrepancies are probably due to the different structure of the PtMo/SiO$_2$ and PtMoY catalysts whose modes of preparation are quite different. The PtMo/SiO$_2$ catalyst is obtained by deposition of Pt atoms (reduction of Pt π-allyl complexes) on low-valent Mo atoms grafted on SiO$_2$. The PtMoY zeolite is prepared in the opposite way since Mo atoms are deposited on encaged Pt aggregates. In the first catalyst one expects that there are mainly Pt atoms exposed on the aggregate surface and the modification of the catalytic properties of platinum can be attributed to the modifications of the electronic properties of platinum induced by molybdenum ions. In the second catalyst the Mo atoms deposited on the platinum act as adsorption sites for the hydrocarbon while Pt atoms dissociate hydrogen. The hydrogenolysis rate enhancement is due to the complementary role of the two components.

CONCLUSION

The Y-zeolite-supported Pt–Mo bimetallic catalyst characterized in detail in previous work (*1*) exhibits enhanced hydrogenolysis activity in *n*-butane conversion. The participation of Pt and Mo sites in the reaction mechanism is supported by the variation of the kinetic parameters with Pt/Mo.

It is suggested that Pt and Mo atoms act primarily as adsorption sites for *n*-C$_4$ and H$_2$, respectively. The specific role of each component is supported both by their adsorption properties and by the steric configuration of the system Pt–Mo aggregate–zeolite cage.

(I) Pt and Mo atoms in the Pt–Mo aggregates have different adsorption properties. Mo atoms do not chemisorb hydrogen whereas Pt atoms do so (*1*). On the other hand, the addition of Mo atoms leads to strong adsorption sites for the hydrocarbon as shown by thermodesorption and surface reaction studies described elsewhere, whereas the Pt atoms having lost their electrophilic character (*1*) cannot account for the enhanced hydrogenolysis properties.

(II) In PtY zeolite the Pt aggregates filling the supercages are accessible to hydrocarbon in the vicinity of the four supercage apertures. In PtMoY, the Mo deposition occurs in the first place on the aggregate surface facing the aperture. Therefore, although H$_2$ can still be adsorbed and dissociated on Pt, the bulky hydrocarbon molecules can only be adsorbed on the Mo atoms deposited at the cage aperture.

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