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Hydrogenolysis of Ethane on Supported (Mo + Pt)/SiO_2 Catalysts

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The hydrogenolysis of ethane on (Mo + Pt)/SiO_2 catalysts exhibits the following features as compared to hydrogenolysis on a Pt/SiO_2 catalyst: (1) a much higher activity in the temperature range 200–300°C; (2) constant activity in a series of successive runs; and (3) a lower activation energy and a decrease of inhibiting effect of hydrogen. The change in the electronic properties of platinum due to its interaction with molybdenum on the support surface is considered a major reason for these specific features of (Mo + Pt)/SiO_2 catalysts.

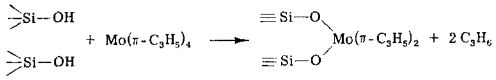
INTRODUCTION

An increase of the platinum activity (both activity per gram of metal and the turnover numbers) in a (Mo + Pt)/SiO_2 system was observed earlier for the structure-insensitive benzene hydrogenation reaction (*1*,*2*). In the present report we give the results from studies of hydrogenolysis of ethane on this catalyst. A detailed investigation of ethane hydrogenolysis by Sinfelt (*3*) shows that this reaction can be considered a structure-sensitive one.

METHODS

Catalyst preparation. The method of preparation and the composition of the catalysts are given in Table 1. Silica gel with a surface area of 300 m^2/g and a pore volume of about 1 cm^3/g was used in all experiments.

Catalyst III was prepared by a technique described elsewhere (*1*). The main features of this technique are: (a) Interaction of tetrakis-π-allyl molybdenum with silica gel proceeding mainly according to the scheme (*4*):



(b) Reduction of the resulting catalyst with hydrogen at 600°C which leads to the removal of organic ligands from the surface organometallic molybdenum compound and the formation of low valent molybdenum ions (*4*).

For the sample employed in the present work after reduction at 600°C, the oxygen uptake at 20°C corresponded to the atomic ratio O:Mo = 1.5; with oxidation at 500°C this ratio was 2.2. Taking into account the fact that oxidation at 500°C results in the formation of Mo(VI) ions (*4*), we may estimate an average oxidation number of molybdenum ions in a sample reduced at 600°C which is ~1.6.

(c) Treatment of the catalyst containing low valent molybdenum ions with a solution of bis-π-metallyl platinum in pentane under conditions eliminating contact of the catalyst with air. Such a technique for supporting platinum was considered to favor the

TABLE 1

Preparation Technique and Compositions of Catalysts

Catalyst No.	Composition	Preparation
I	3.1% Pt on SiO_2	Treatment of calcined SiO_2 under vacuum at 600°C with a solution of Pt(π-metallyl) in pentane, oxidation of catalyst at 200°C
II	3.6% Pt on SiO_2	Impregnation of SiO_2 with an aqueous solution of H_2PtCl_6, drying at 120°C, calcination in air at 500°C
III	1.85% Mo + 4.4% Pt on SiO_2	Treatment of calcined SiO_2 in vacuum at 600°C with a $Mo(\pi\text{-}C_3H_5)_4$ solution in pentane, reduction at 600°C, treatment of reduced catalyst with a $Pt(\pi\text{-}C_4H_7)_2$ solution in pentane
IV	3.4% Mo + 2.3% Pt on SiO_2	Impregnation of SiO_2 with an aqueous solution of $(NH_4)_2MO_4$, drying, calcination at 500°C in air, impregnation with an aqueous H_2PtCl_6 solution, drying, calcining in air at 500°C

interaction between low valent molybdenum ions and platinum in the catalyst.

(d) Reduction of the catalyst before starting the reaction. All catalyst samples (except catalyst II) were X-ray amorphous. X-ray analysis showed the presence of metallic platinum particles in catalyst II with dimension of about 40 Å.

Chemisorption measurements. These were carried out by a pulse technique with chromatographic analysis. After reduction the catalyst was outgassed at the temperature of reduction at $1 \cdot 10^{-3}$ Torr. After oxygen adsorption at 25°C the adsorbed oxygen was titrated with hydrogen.

Catalytic activity. The catalytic activity in ethane hydrogenolysis was measured in a static circulating installation. The activity remained constant with varying circulation rates from 100 to 600 liters/hr and pellet dimensions from 0.1 to 0.7 mm. The catalyst sample was of 0.1–0.5 g with a pellet being 0.25–0.5 mm. The catalyst was preliminarily reduced with hydrogen in the reactor (H_2 pressure was 100 Torr, circulation rate was 400 liters/hr) at 600°C with freezing out the reaction products in a trap cooled with liquid nitrogen. In a standard experiment the initial pressure of the ethane–hydrogen mixture was 100 Torr ($H_2{:}C_2H_6 = 1$). The reaction temperature was varied from 200 to 350°C. The reaction mixture was periodically sampled and analyzed chromatographically. The activities were compared on the basis of the initial rates at the degree of conversion less than 10%.

RESULTS

Adsorption Data

The amount of chemisorbed oxygen and the quantity of hydrogen consumed in its titration are given in Table 2. In the hydrogen titràtion of Pt/SiO_2 catalysts used in this study a stoichiometry $H{:}O = 3$ is observed which is in accord with Boudart *et al.* (*5,6*).

For a $(Mo + Pt)/SiO_2$ catalyst obtained by using organometalic compounds, the O:Pt ratio calculated from hydrogen titration data is near unity; the dispersion of platinum (the ratio of surface atoms to the total content of Pt atoms in the catalyst (in percent)) therefore approximates 100%. For a $(Mo + Pt)/SiO_2$ catalyst prepared by impregnating silica with aqueous solutions, the dispersion of platinum was similar to that of a catalyst prepared using bis-π-

TABLE 2

Adsorption Data for Catalysts Reduced at 600°C

Catalyst	Amounts of adsorbed O_2 and H_2 quantities consumed in titration					
	O_2 (mmol O_2/g catalyst)	H_2 (mmol H_2/g catalyst)	Molar ratios (O:(Mo + Pt) for catalyst III and IV or O:Pt for catalyst I and II)	H:Pt in hydrogen titration	O:Pt[a] according to hydrogen titration data	O:Mo[b]
I	0.040	0.122	0.50	1.52	0.50	—
II	0.022	0.069	0.24	0.75	0.25	—
III	0.315	0.320	1.50	2.87	0.96	2.11
IV	0.142	0.106	0.60	1.80	0.60	0.60

[a] Calculated assuming an H:O ratio of 3 for hydrogen titration (*5,6*).

[b] Amount of oxygen consumed in oxidation of Mo is calculated as the difference between the amount of O_2 adsorbed by the catalyst and that adsorbed on Pt according to hydrogen titration data.

metallyl platinum which contains no molybdenum.

Catalytic Activity

The results of measuring the catalytic activity are presented in Fig. 1 and Table 3. The (Mo + Pt)/SiO_2 catalysts retained their activity in a series of successive runs; after each run the catalyst was treated with hydrogen at 600°C. The activity of the Pt/SiO_2 catalyst decreased from run to run, in spite of the fact that the catalyst was treated with hydrogen after each run, and after several runs achieved a constant level, an order lower than the initial one.

The activity per gram of platinum for a (Mo + Pt)/SiO_2 catalyst was 10^4–0.4×10^2 higher (depending on temperature within the range 205–350°C) than the activity of a Pt/SiO_2 catalyst. The samples prepared by using organometallic compounds were more active than catalysts prepared by the conventional technique. The activity of (Mo + Pt)/SiO_2 catalysts increased as their reduction temperature was increased from 200 to 600°C.

The activity of SiO_2-supported molybdenum catalysts with no platinum which were reduced at 400–600°C was immeasurably small at 350°C (below 0.001 mol of C_2H_6/g of molybdenum/h).

Table 4 gives the activation energies and reaction orders with respect to C_2H_6 and

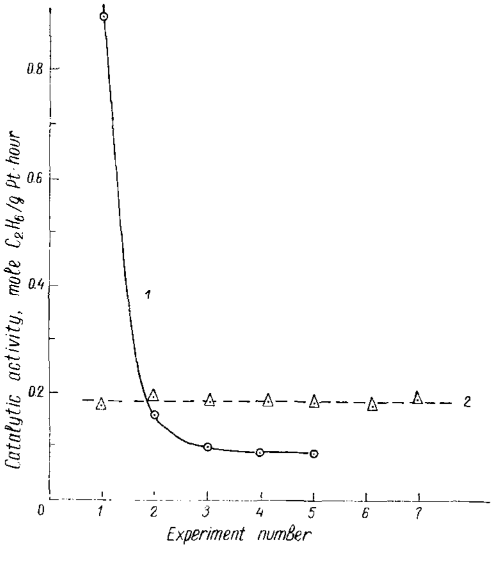


FIG. 1. Change in initial activity of the catalysts in successive hydrogenolysis reactions. The experiments were run at an initial pressure of C_2H_6 of 50 Torr and of H_2 of 50 Torr to 90% conversion degree. After each run the catalyst was treated with hydrogen at 600°C 1. (⊙) Pt/SiO_2 (catalyst I), 350°C reaction temperature. 2. (△) (Mo + Pt)/SiO_2 (catalyst III), 250°C reaction temperature.

TABLE 3

Activities of Different Catalysts in Ethane Hydrogenolysis[a]

Catalyst	Activity ($mol\ C_2H_6/gPt \cdot hr$)		Turnover numbers at 350°C[b] ($molecules\ C_2H_6/atom\ Pt \cdot sec$)
	At 205°C	At 350°C	
I	—	0.90 (0.09)[c]	0.098
II	0.15×10^{-6}[d]	0.084 (0.006)[c]	0.019
III	1.1×10^{-2}	36[d]	2.04
IV	0.19×10^{-2}	—	—

[a] Initial pressure of C_2H_6 was 50 Torr and of H_2, 50 Torr. Catalysts were reduced at 600°C.

[b] Calculated on the assumption that the O:Pt ratio in Table 2 characterizes dispersion of Pt.

[c] Initial activity of a freshly reduced catalyst (enclosed in parentheses is the activity after four runs).

[d] Obtained by extrapolation using activation energy data cited in Table 4.

H_2 for hydrogenolysis on an $(Mo + Pt)/SiO_2$ catalyst. The known data (*3*) for a Pt/SiO_2 catalyst are given for comparison.

DISCUSSION

Platinum Dispersion

The dispersion of platinum in $(Mo+Pt)/SiO_2$ catalysts was calculated assuming that the H:O stoichiometry of 3 obtained for supported platinum is valid also for these catalysts (which has not been rigorously proved). Under this assumption, the results obtained may indicate that all supported platinum in a catalyst prepared by using organometallic compounds of Pt and Mo is accessible for oxygen adsorption. Similar results were obtained in our earlier work (*1*).

TABLE 4

Kinetic Characteristics of Ethane Hydrogenolysis on Different Catalysts

Catalyst	Activation energy	Reaction order with respect to hydrogen	Reaction order with respect to ethane
$(Mo + Pt)/SiO_2$ (catalyst III)	33[a]	−1.0[b]	+0.95[c]
Pt/SiO_2[d]	54	−2.5	+0.90

[a] Determined over the range 200–280°C.

[b] Determined over a hydrogen pressure range of 50–200 Torr.

[c] Determined over an ethane pressure range of 50–150 Torr at P_{H_2} of 50 Torr.

[d] Data taken from Ref. (*8*), activation energy in Ref. (*8*) was determined for the range 344–385°C.

The adsorption of oxygen on catalyst III at 25°C leads to the oxidation of molybdenum ions. If one assumes that after reduction catalyst III retains the same oxidation state of molybdenum as the catalyst Mo/SiO_2 used for supporting $Pt(\pi - C_4H_7)_2$, the adsorption of oxygen will increase the mean oxidation state of molybdenum ions to 5.82 $(1.6 + 2 \times 2.11)$. Thus, in the presence of platinum the major portion of molybdenum ions is oxidized even at room temperature. A low O:Mo ratio in the case of catalyst IV indicates that molybdenum is present mainly as clusters in which only surface molybdenum ions undergo oxidation.

Catalytic Properties in Ethane Hydrogenolysis

In the ethane hydrogenolysis on $(Mo + Pt)/SiO_2$ catalysts there is a substantial reduction in activation energy along with a decrease of inhibiting effect of hydrogen compared to platinum catalysts. Sinfelt (*3*) interpreted the kinetic data on ethane hydrogenolysis in terms of the following reaction scheme:

$$C_2H_6 \rightleftharpoons C_{2}H_{5(ads)} + H_{(ads)} \qquad (1)$$

$$C_{2}H_{5(ads)} + H_{(ads)} \rightleftharpoons C_{2}H_{x(ads)} + aH_2 \qquad (2)$$

$$C_{2}H_{x(ads)} \rightarrow CH_{y(ads)} + CH_{z(ads)} \xrightarrow{H_2} CH_4 \qquad (3)$$

where (ads) denotes the adsorbed state, $a = (6 - x)/2$ Step (3) of the scheme was assumed to be rate determining; this gave the following expression for the reaction rate (*3*):

$$W = K\cdot P_{C_2H_6}{}^{n}\cdot P_{H_2}{}^{m},$$

where $P_{C_2H_6}$ and P_{H_2} are ethane and hydrogen pressures, respectively, n is the reaction order with respect to ethane, $m = -na$ is the reaction order with respect to hydrogen, and K is the rate constant. According to Sinfelt (*3*), for platinum on SiO_2 the experimentally determined reaction orders with respect to ethane and hydrogen are 0.9 and −2.5, respectively, which corresponds to $x = 0$ in $C_2H_{x(ads)}$. The increase in the reaction order with respect to hydrogen for the $(Mo + Pt)/SiO_2$ catalyst may point to the fact that surface compounds with a higher hydrogen content serve as intermediate products of the reaction ($x = 4$ for reaction orders of about of +1 and −1 with respect to ethane and hydrogen, respectively).

A large increase in platinum activity was also observed for a $(W + Pt)/SiO_2$ catalyst. In the hydrogenolysis of ethane on this catalyst there was also a decrease in activation energy of the reaction and a change in the reaction order with respect to hydrogen to −0.5 compared with a Pt/SiO_2 catalyst. The results of the $(W + Pt)/SiO_2$ catalyst investigations will be reported later (*7*).

When explaining the specific properties of bimetallic catalysts in ethane hydrogenolysis, two reasons can be considered for the effect of the second component (for example, molybdenum) on the activity of the main component (platinum): (a) a change in catalytic activity in a structure sensitive reaction due to the change of the platinum dispersion and (b) a change in the electronic properties of a platinum cluster due to the interaction of platinum with molybdenum.

For Pt/SiO_2 catalysts some increase of turnover number in ethane hydrogenolysis with decreasing size of platinum particles was observed, approximately fivefold for catalyst I compared with catalyst II.

However, it is difficult to explain the sharp rise in the activity of the $(Mo + Pt)/SiO_2$ catalyst (and also of the $(W + Pt)/SiO_2$ catalyst (*7*)) in ethane hydrogenolysis merely by the change in platinum dispersion upon addition of molybdenum. It should be noted that the catalyst Pt/SiO_2 prepared by the conventional technique (Sample I) and $(Mo + Pt)/SiO_2$ catalyst (Sample IV) have approximately the same dispersion of platinum but differ essentially in their catalytic activity. It appears that the major reason for the specific catalytic properties of $(Mo + Pt)/SiO_2$ catalysts is the change in electronic properties of the platinum particles.

This change is confirmed by the data of the ESCA measurements (*9*). For a $(Mo + Pt)/SiO_2$ catalyst the energy of the $4f\,\frac{7}{2}$ level is 72.0 eV compared to 71.5 eV for a Pt/SiO_2 catalyst. This may be related to a decrease in electron density in the platinum particles of $(Mo + Pt)/SiO_2$ catalysts (in the *d*-zone in particular). It is noteworthy, that the decrease in electron density due to the interaction between platinum and molybdenum leads to the same catalytic effect that is observed when varying the nature of the transition metal, namely, the catalytic activity increases while the activation energy and the reaction order with respect to hydrogen decrease. A similar effect is observed for the following series of transition metals: Pt → Ir → Os (*3*). At 205°C there is a 10^4- fold change in turnover numbers when passing from a $(Mo + Pt)/SiO_2$ to a Pt/SiO_2 catalyst; it should be noted that according to Sinfelt's data (*3*) there is a

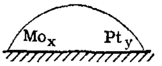
10^5- fold change in activity when passing from Pt to Ir at the same temperature.

The diminishing electron density of Pt clusters has already been pointed out as a possible reason for the increase of the catalytic activity of platinum in zeolites (*10*).

Possible Reasons for the Change in Platinum Properties in Pt–Mo Catalysts

In explaining the effect of additives on the electronic properties of platinum in supported catalysts, two extreme models can be considered.

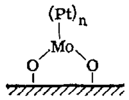
A. Formation of "bimetallic" clusters. In our case this means the formation of dispersed particles of a (Mo + Pt) alloy on the silica:



A

The formation of "bimetallic" clusters has been proposed by Sinfelt (*11*) to be the reason for the decrease in activity of binary Ru–Cu and Os–Cu catalysts supported on SiO_2 in ethane hydrogenolysis.

B. Formation of platinum clusters that react with the transition metal ion bound to the support surface as was assumed in Ref. (*1*) and (*2*):



B

Such a surface structure implies the formation of a molybdenum–platinum bond. At the present time, numerous complex compounds are known containing a metal–metal bond, the strength of such a bond approaching tens of kilocalories/mole (*11*). The formation of a molybdenum–platinum bond with a strength of tens of kilocalories/mole can account for both the high stability of dispersed platinum and an appreciable change in its electronic properties in type-B structures.

The catalyst prepared by supporting platinum on a support containing low valent molybdenum ions (catalyst III) has a higher activity than that prepared by co-impregnating the support with a solution of Mo and Pt compounds (catalyst IV). However, this fact cannot be considered decisive evidence for the formation of a type-B structure. A more uniform distribution of the components over the surface of the support when preparing a catalyst using organometallic compounds may also favor the formation of "bimetallic" clusters.

More detailed studies on the two-component systems obtained by supporting metal on catalysts containing low valent transition metal ions will provide more unambiguous evidence to distinguish between the above extreme models that can be considered to explain the effect of the second component on the properties of supported platinum.

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