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# Bimetallic Catalysts. VI. Surface Composition of Pt–Mo/$SiO_2$ Catalysts: Influence of Reaction Media

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**Bimetallic Pt–Mo catalysts deposited on silica show unusual behavior when used in reactions of hydrocarbons with hydrogen (hydrogenolysis, isomerization, dehydrocyclization). This can be explained by variations of the surface composition, i.e., the Mo/Pt surface ratio, with the conditions, particularly the temperature and the composition of the gas phase in contact with the catalyst. Two methods for detecting such variations have been used in this work: these are XPS analysis and the product distribution in 3-methylpentane hydrogenolysis which is very sensitive to the surface composition. Both methods have shown that the surface composition of Pt–Mo/$SiO_2$ catalysts is modified in the presence of aromatic hydrocarbons, the molybdenum surface content of metal particles being decreased compared with their original molybdenum content after reduction in hydrogen.** 

## INTRODUCTION

Catalysts containing platinum and molybdenum species supported on silica, alumina, or other solids, prepared in various ways, have been studied for the past two decades by several research groups (1–6). In these studies the catalysts were tested in reactions of hydrogenolysis, hydrogenation, dehydrogenation, or isomerization of hydrocarbons (1–5) and in the synthesis of alcohols from CO and $H_2$ (6).

As the present work concerns Pt–Mo catalysts supported on silica, prepared by impregnation, we shall first sum up the main results obtained in our previous research on such catalysts (3, 4, 8).

*Species present in reduced catalysts (400–700°C).* As expected, platinum is completely reduced, as seen by XPS analysis, and only small shifts of the Pt signals are observed. The XPS signals of molybdenum are more complex, indicating the presence of both metallic molybdenum, even in catalysts reduced at 400°C (in flowing hydrogen), and also higher oxidation states of molybdenum.

*Hydrogen chemisorption and surface composition.* When determined by a classical method used with platinum catalysts (see, e.g., Ref. (7)), the amount of hydrogen adsorbed by 1 g of catalyst decreased rapidly with the atom ratio Mo/(Mo + Pt) in a series with a constant total metal content Pt + Mo (150 $\mu$mol/g). The molybdenum-only catalyst (reduced between 400 and 700°C) did not adsorb any hydrogen. In view of this, we expressed the amount of chemisorbed gas per mole of platinum rather than per gram of catalyst. The diminishing chemisorption with Mo atom fraction could be due to a decrease of platinum dispersion, but since other results strongly suggest a constant size for the Pt crystallites (3, 4), whatever the Mo content, the shape of the curves of hydrogen chemisorption vs composition must be explained by a blocking of Pt surface by some Mo-containing species. This assumption is in good agreement with the results of surface composition analysis by XPS which indicated a large excess of molybdenum in the analyzed layer in comparison with the bulk composition. Moreover, the extent of this molybdenum surface excess strongly depends on the catalyst pretreatment.

*Activities and selectivities in reactions of hydrocarbon.* Activities of our series of catalysts were found to vary strongly with the composition of catalysts in such reactions as the hydrogenation of aromatic hydrocarbons, dehydrogenation, dehydrocyclization, and isomerization of hydrocarbons.

In the dehydrogenation of cyclohexane, the reaction rate decreases linearly (3) when the ratio Mo/(Mo + Pt) increases. Such a linear relationship seems to indicate a constant percentage of platinum at the surface and appears to exclude any important blocking effect as seen, e.g., by hydrogen chemisorption. This apparent contradiction may mean important changes at the surface of the catalyst brought about by changes in the conditions of the reactions (temperature, composition of the gas phase).

In the reactions between hexanes and hydrogen (4, 10) studied at 400°C for *n*-hexane and at 350°C for 3-methyl-

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pentane, the sum of the rates of isomerization and of dehydrocyclization decreases almost linearly when the ratio Mo/(Mo + Pt) increases for *n*-hexane, while for 3-methylpentane it is always slightly lower than that corresponding to linearity. This shows that isomerization and dehydrocyclization probably take place on platinum only and that the blocking effect almost disappears at 400°C with *n*-hexane but partly remains at 350°C with 3-methylpentane. Let us mention that at 350°C the reaction of 3-methylpentane leads to much lower proportions of benzene than that of *n*-hexane at 400°C. Hence the surface composition seems to be influenced by the reacting mixture. The analysis of all our results leads to the idea that the surface composition could be influenced by the partial pressure of benzene; an increase of this partial pressure would induce a decrease of the masking of Pt surface by Mo species visible particularly in hydrogen adsorption.

The aim of the present work was to confirm or invalidate the above hypothesis of variations of catalyst surface composition under the influence of aromatic hydrocarbons by varying the benzene partial pressure in the reaction mixture.

Two methods have been used, namely XPS surface analysis and the reaction probe of variations of selectivity sensitive to the Mo proportion in the catalyst.

## EXPERIMENTAL

### *Preparation of Catalysts*

The support is a non-porous silica, Aerosil 200 from Degussa, having a specific surface area of 200 $m^2/g$ and containing the following impurities: 20 ppm Fe, 180 ppm Ti, and 270 ppm Al.

The total metal content in all catalysts is about 150 $\mu$mol/g of reduced solid. The precursors used are aqueous solution of hexachloroplatinic acid from Johnson Mathey, and ammonium heptamolybdate $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ from Fluka, quality "puriss. p.a."

Two series of catalysts were prepared by impregnation in the following way. Distilled water was added to the support in large excess of the quantity necessary to fill the voids between particles of solid, and the solutions containing calculated amounts of Pt and Mo were added. In the first series, designated as $PMD_x$, the solution containing chloroplatinic acid was added first; then, after stirring the mixture, the solution of heptamolybdate was added. In the preparation of the catalysts of the second series, $PMD^*_x$, the two solutions were mixed together and added to the support with distilled water. In both cases water was evaporated under continuous stirring, and the solids were dried overnight at 110°C. The composition of the catalysts of both series, as determined by the Service Central de Microanalyse du CNRS by atomic absorption, is given in Table 1.

### *Chemisorption of Hydrogen*

The samples of catalysts (0.2 to 1 g) were reduced *in situ* in flowing hydrogen, using the following procedure: heating rate 3 K/min, maximum temperature 500°C maintained for 7 h, hydrogen flow of 3.6 Nl/h. The reduced samples were outgassed overnight in vacuum at 400°C, the final pressure being in the range $10^{-4}$–$10^{-5}$ Torr. The

TABLE 1

**Composition and Hydrogen Chemisorption Capacity of Pt–Mo Catalysts**

| Catalyst | Pt content ($\mu$mol/g) | Mo content ($\mu$mol/g) | Mo/(Mo + Pt) | $H_2$ chemisorption ($\mu$mol $H_2$/g) | H/Pt |
|---|---|---|---|---|---|
| $PMD_0$ | 130.6 | 0 | 0.0 | 44.5 | 0.68 |
| $PMD_{12}$ | 121.4 | 18.2 | 0.13 | 38.7 | 0.64 |
| $PMD_{25}$ | 106.0 | 34.4 | 0.245 | 15.4 | 0.29 |
| $PMD_{37}$ | 88.1 | 51.1 | 0.367 | 8.8 | 0.20 |
| $PMD_{50}$ | 74.8 | 72.1 | 0.491 | 6.7 | 0.18 |
| $PMD_{62}$ | 60.4 | 84.4 | 0.583 | 1.4 | 0.05 |
| $PMD_{75}$ | 40.0 | 105.3 | 0.725 | 1.0 | 0.05 |
| $PMD_{87}$ | 32.8 | 135.5 | 0.805 | 0.8 | 0.05 |
| $PMD_{100}$ | 0 | 150 | 1.0 | 0 | — |
| $PMD^*_{12}$ | 119.9 | 15.6 | 0.115 | 34.7 | 0.58 |
| $PMD^*_{25}$ | 98.9 | 35.4 | 0.264 | 14.7 | 0.3 |
| $PMD^*_{37}$ | 76.8 | 58.4 | 0.432 | 8.9 | 0.23 |
| $PMD^*_{50}$ | 62.5 | 76.1 | 0.55 | 4.1 | 0.13 |
| $PMD^*_{62}$ | 45.1 | 96.9 | 0.682 | 3.2 | 0.14 |
| $PMD^*_{75}$ | 34.3 | 111.5 | 0.765 | 2.1 | 0.12 |
| $PMD^*_{87}$ | 16.4 | 130.3 | 0.888 | 1.3 | 0.16 |
| $PMD^*_{100}$ | 0 | 155.3 | 1.0 | 0 | — |

adsorption isotherm was determined at room temperature between 50 and 300 Torr, by a volumetric method, and the amount of chemisorbed hydrogen was evaluated by extrapolation at zero pressure. The values obtained are given in Table 1.

*XPS Analysis*

The spectrometer used was an A.E.I. ES 200B apparatus with an Al anode, equipped with a dry-box and an electric oven allowing pretreatment of samples before analysis in flowing gases and subsequent introduction of the samples into the chamber of the spectrometer without exposure to air (3).

The samples of catalysts were first reduced as described above at 500°C, transferred with the reduction cell to the dry-box, and deposited on the support grid of the spectrometer after purging of the dry-box with dry nitrogen. The whole of this operation was conducted without exposing the reduced samples to air; however, to eliminate any possible reoxidation by traces of oxygen, the catalyst on the grid was further exposed to hydrogen at 500°C for 1 h. The XPS spectra were measured in the ranges corresponding to signals of Si 2*p*, C 1*s* (contamination), O 1*s*, Mo 3*d*, and Pt 4*f*. The signals of Mo 3*d* and Pt 4*f* were accumulated for 4 h. After the completion of the analyses, the catalyst sample on the grid was transferred into the oven and treated with hydrogen–benzene mixture (benzene mol fraction of about 0.1) at 400° C for 1 h, and the analyses were repeated as above. Finally, the catalyst was treated once again with pure hydrogen at 400°C for 1 h and analyzed.

The binding energies (B.E.) were calculated from the measured kinetic energies taking the B.E. of C 1*s* equal to 285 eV as reference. The integrated intensities were used to calculate atomic ratios in the surface layers, $(n_i/n_j)_{xps}$ by

$$(n_i/n_j)_{xps} = (I_i/I_j)(\sigma_i/\sigma_j)(E_{ci}/E_{cj})^{a+1}, \qquad [1]$$

where $I_i$ is the integrated intensity, $\sigma_i$ is the cross section, and $E_{ci}$ is the kinetic energy corresponding to the element $i$; the $\sigma$ values were those given by Scofield (11), and the exponent $a$ was taken equal to 0.7.

*Catalytic Tests*

The reactions of 3-methylpentane at 350°C with hydrogen were studied in a continuous flow reactor with a fixed bed of catalyst at atmospheric pressure. The catalysts were reduced at 500°C *in situ* as before chemisorption experiments (see above). 3-Methylpentane from Fluka, of "purissimum" quality, was stored in contact with a Pt/13X zeolite catalyst to remove any traces of sulfur-containing impurities. Hydrogen was purified through a Deoxo catalyst and two sorption traps, the first one with silica gel and the second with 13X zeolite. The mole fraction of 3-methylpentane in the initial hydrocarbon–hydrogen mixture was 0.1, and the flow rate and the mass of catalyst were adjusted to keep the conversion lower than 20%.

The product mixture was analyzed by gas chromatography using an automatic injection valve, and a 3-m, 1/8" column with 10% of squalane on Spheron, between 45 and 110°C.

## RESULTS AND DISCUSSION

*Determination by XPS of Variations in Surface Composition Induced by Exposure of the Catalyst to a Hydrogen–Benzene Mixture*

As already described under Experimental, three Pt–Mo catalysts belonging to both series have been reduced at 500°C, analyzed by XPS, exposed at 400°C to hydrogen saturated with benzene at room temperature, and retreated by hydrogen at 400°C, the XPS analyses being repeated after each step. Since the hydrogen–benzene mixture was prepared by passing a flow of hydrogen through liquid benzene at room temperature, the benzene mol fraction in the mixture may be evaluated at about 0.1 (saturated vapor pressure of benzene at 20°C is 0.1 atm). The Pt 4*f* and Mo 3*d* XPS peaks (Fig. 1) are qualitatively the same after the three pretreatments and show that Pt is completely reduced to Pt metal while Mo is only partly reduced to the zero-valent state, as already stated in Ref. (3) ((B.E. = 228.3 ± 0.3 eV (with the binding energy of C1*s* of carbon contamination at 285 eV as reference)), and roughly to the same extent for the three analyses taking into account the margin of error. Concerning the C 1*s* signal, unfortunately we have not been able to see evidence of the coke deposit resulting from benzene exposure of the catalysts since the major part of the carbon arises from pollution in the spectrometer; the ratio C 1*s*/Si 2*p* increases with the time of analysis in the spectrometer as seen, for example, in the case of $PMD^*_{50}$ in Table 2.

The surface compositions are given in Tables 3 and 4. It should be noted that (i) the mol ratio Mo/Pt as seen by XPS, $(Mo/Pt)_{XPS}$, is generally higher than the corresponding bulk values, and (ii) the $(Mo/Pt)_{XPS}$ ratio becomes slightly but significantly and systematically lower after the treatment with $H_2$/benzene mixture. This first result is in agreement with our earlier observations (3, 4) and agrees well with the hypothesis described in the Introduction, explaining some variations in catalyst activity by the elimination of molybdenum-containing species from the surface of platinum under the influence of aromatic compounds.

It is difficult to estimate the importance of the extent of the process in the above experiments, taking into ac-

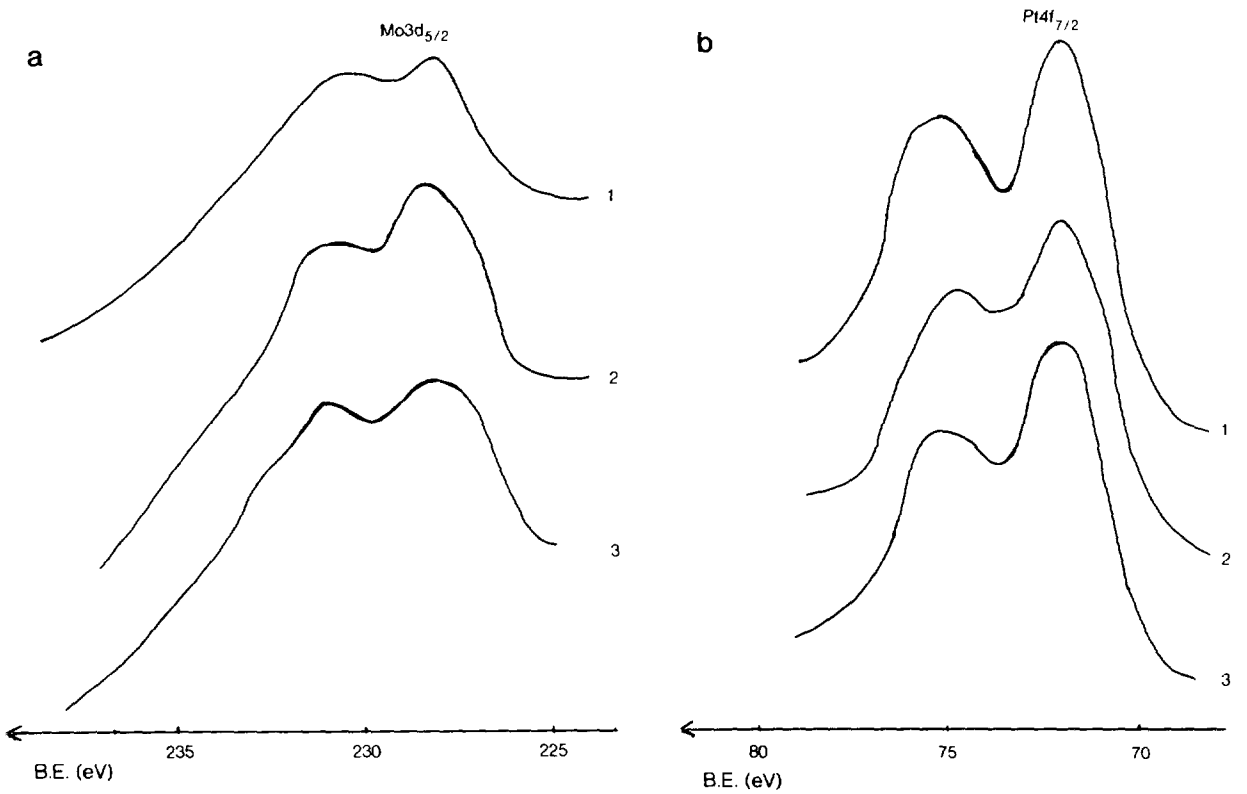


FIG. 1. PMD*$_{50}$ XPS peaks of Mo 3*d* (a) and Pt 4*f* (b) after three pretreatments. (1) $H_2$/500°C; (2) $H_2$ + $C_6H_6$/400°C; (3) $H_2$/400°C.

count that XPS analysis gives the mean composition of a layer, the thickness of which (3–5 nm) corresponds to several atomic diameters. On the other hand, there are many molybdenum species: there are those on the support and without any interaction with the metal particles, and those on the contrary interacting with the metal particles. We do not know the proportion of this scond type of species which are the only species which could have an effect on the catalytic activity and which are supposed to be driven out of the metal surface. Moreover, if they move away from the platinum surface, they may very well continue to be visible in XPS, e.g., by staying on the very top surface of the silica support. This possibility seems to be quite likely, since it is mostly platinum which becomes more exposed, as can be seen from the intensity ratios $I_{Pt}/I_{Si}$ particularly in $PMD_x$ catalysts; the variations of $I_{Mo}/I_{Si}$ are much less obvious.

Unfortunately, the quality of the XPS spectra was not good enough to elucidate the nature (oxidation state) of the migrating Mo species.

After the last treatment with hydrogen at 400°C, generally the $(Mo/Pt)_{XPS}$ ratios increase slightly. The values do not attain the initial ones; nevertheless, as this variation is observed for all the catalysts studied, we can conclude that this observation cannot be due to experimental uncertainty and that the modifications of the situation at the surface brought about by the treatment with hydrogen/benzene mixture seem to be, at least partially, reversible. Such a reversibility of the surface composition modifications will be confirmed by the catalytic experiments to be reported below.

All these observations are also valid for the PMD*$_x$ catalysts (Table 4), but the variations are markedly attenuated. This can be explained by assuming that in the catalysts prepared by simultaneous introduction of platinum and molybdenum (by coimpregnation: PMD* series) the

TABLE 2

XPS ($I$(C 1*s*)/$I$(Si 2*p*)) Ratio and Time of Analysis in the Case of PMD*$_{50}$

| | ($I$(C 1*s*)/$I$(Si 2*p*)) | |
|---|---|---|
| Pretreatment | 1 h analysis time | 10 h analysis time |
| $H_2$/500°C | 0.09 | 0.30 |
| $H_2$/500°C | 0.15 | 0.35 |
| $H_2$ + $C_6H_6$/400°C | | |
| $H_2$/500°C | 0.27 | 0.38 |
| $H_2$ + $C_6H_6$/400°C | | |
| $H_2$/400°C | | |

TABLE 3

**Variations of the Surface Composition of Three Catalysts of the PMD Series (Prepared by Successive Impregnation)**

| Pretreatment | XPS ratios | Catalyst PMD25 | Catalyst PMD50 | Catalyst PMD75 |
|---|---|---|---|---|
| $H_2$ at 500°C | $I$(Pt)/$I$(Si) | $5.80 \times 10^{-2}$ | $2.40 \times 10^{-2}$ | $0.37 \times 10^{-2}$ |
| | $I$(Mo)/$I$(Si) | $1.65 \times 10^{-2}$ | $3.40 \times 10^{-2}$ | $3.30 \times 10^{-2}$ |
| | $I$(Mo)/$I$(Pt) | 0.29 | 1.40 | 9.0 |
| | $(Mo/Pt)_{XPS}$ | 0.55 | 2.7 | 17.5 |
| $H_2$ + benzene at 400°C (1 h) | $I$(Pt)/$I$(Si) | $6.10 \times 10^{-2}$ | $5.00 \times 10^{-2}$ | $0.63 \times 10^{-2}$ |
| | $I$(Mo)/$I$(Si) | $1.35 \times 10^{-2}$ | $3.65 \times 10^{-2}$ | $4.70 \times 10^{-2}$ |
| | $I$(Mo)/$I$(Pt) | 0.22 | 0.73 | 7.4 |
| | $(Mo/Pt)_{XPS}$ | 0.43 | 1.4 | 14.4 |
| $H_2$ at 400°C (1 h) | $I$(Pt)/$I$(Si) | $6.09 \times 10^{-2}$ | $4.30 \times 10^{-2}$ | $0.56 \times 10^{-2}$ |
| | $I$(Mo)/$I$(Si) | $1.50 \times 10^{-2}$ | $3.55 \times 10^{-2}$ | $4.64 \times 10^{-2}$ |
| | $I$(Mo)/$I$(Pt) | 0.25 | 0.83 | 8.26 |
| | $(Mo/Pt)_{XPS}$ | 0.48 | 1.62 | 16.1 |
| $(Mo/Pt)_{bulk}$ | | 0.32 | 0.96 | 2.6 |

surface enrichment in molybdenum is less pronounced than in those for which platinum was introduced first and molybdenum later (series PMD). Consequently, the modifications of the surface compositions due to the mobility of molybdenum species are of smaller magnitude.

*Hydrogenolysis of 3-Methylpentane; Influence of Benzene Partial Pressure*

As indicated before, the rates and/or the product distributions of some reactions catalyzed by supported Pt–Mo catalysts vary with the Mo/(Mo + Pt) ratio in the catalyst. To select a good reaction probe suitable for the detection of variations in the surface composition, we have discarded the reaction rates, since they are influenced by deactivation due to coking or to poisoning of catalysts; besides, the most dramatic changes in reaction rates observed in the hydrogenolysis of *n*-butane are not a monotonic function of the composition. The selectivities are less influenced by deactivation.

Besides the need for high sensitivity to the surface composition, the obvious condition for using selectivities as a probe is that there should be a sufficiently high proportion of related products in the reaction mixture to give a

TABLE 4

**Variations of the Surface Composition of Three Catalysts of the PMD* Series (Prepared by Coimpregnation)**

| Pretreatment | XPS ratios | Catalyst $PMD^*_{25}$ | Catalyst $PMD^*_{50}$ | Catalyst $PMD^*_{75}$ |
|---|---|---|---|---|
| $H_2$ at 500°C | $I$(Pt)/$I$(Si) | $4.0 \times 10^{-2}$ | $2.3 \times 10^{-2}$ | $0.69 \times 10^{-2}$ |
| | $I$(Mo)/$I$(Si) | $1.2 \times 10^{-2}$ | $2.7 \times 10^{-2}$ | $2.4 \times 10^{-2}$ |
| | $I$(Mo)/$I$(Pt) | 0.31 | 1.17 | 3.44 |
| | $(Mo/Pt)_{XPS}$ | 0.6 | 2.27 | 6.68 |
| $H_2$ + benzene at 400°C (1 h) | $I$(Pt)/$I$(Si) | $4.3 \times 10^{-2}$ | $2.2 \times 10^{-2}$ | $0.76 \times 10^{-2}$ |
| | $I$(Mo)/$I$(Si) | $1.2 \times 10^{-2}$ | $2.3 \times 10^{-2}$ | $2.35 \times 10^{-2}$ |
| | $I$(Mo)/$I$(Pt) | 0.28 | 1.05 | 3.10 |
| | $(Mo/Pt)_{XPS}$ | 0.54 | 2.03 | 6.02 |
| $H_2$ at 400°C (1 h) | $I$(Pt)/$I$(Si) | $4.0 \times 10^{-2}$ | $2.3 \times 10^{-2}$ | $0.88 \times 10^{-2}$ |
| | $I$(Mo)/$I$(Si) | $1.2 \times 10^{-2}$ | $2.4 \times 10^{-2}$ | $2.69 \times 10^{-2}$ |
| | $I$(Mo)/$I$(Pt) | 0.3 | 1.04 | 3.06 |
| | $(Mo/Pt)_{XPS}$ | 0.58 | 2.03 | 5.94 |
| $(Mo/Pt)_{bulk}$ | | 0.36 | 1.21 | 3.25 |

good precision of results. We have shown (10) that on coimpregnated Pt–Mo/$SiO_2$ catalysts the ratio of the quantities of methylbutane (isopentane) and *n*-pentane, obtained among the other products in the reaction of 3-methylpentane with hydrogen, satisfy the above conditions.

The two products are formed by hydrogenolysis of 3-methylpentane, as a consequence of the rupture of one C–C bond in the molecule

$$C_I-C_{II}-C_{III}(-C_I)-C_{II}-C_I$$

The breaking of a $C_I$–$C_{II}$ bond gives methylbutane, whereas rupture of the $C_I$–$C_{III}$ bond leads to *n*-pentane. If the probabilities of the breaking of the two types of C–C bonds were the same, the ratio of the quantities of the above products, isopentane/*n*-pentane (designated in the following as *i*C5/*n*C5) would be equal to 2. This is indeed observed on Pt-only catalyst $PMD_0$ (and on $PMD_{100}$ catalyst as well), but on all bimetallic catalysts the above ratio is consistently greater than 2, increasing monotonically with the Mo/(Mo + Pt) atomic ratio.

Qualitatively, the same results have been observed on the catalysts of series $PMD_x$ where Pt and Mo have been successively added, as can be seen in Table 5 where we have also reported results obtained with another preparation of coimpregnated catalyst (series $PMD^*_x$) in order to compare the results on the two series. The reproducibility of the values of the ratio *i*C5/*n*C5 for two different preparations of catalysts of the same composition can be appreciated by comparing the results on series $PMD^*_x$ and those reported in Ref (10).

TABLE 5

**Selectivities in the Hydrogenolysis of 3-Methylpentane**
$T = 350°C$, $P_{H_2} = 0.9$ atm, $P_{3MP} = 0.1$ atm

| Catalyst | Mo/(Mo + Pt) | $C_I/C_5$[a] | *i*P/*n*P[b] | MCP/B[c] |
|---|---|---|---|---|
| $PMD_0$ | 0 | 1.02 | 2.31 | 13.5 |
| $PMD_{12}$ | 0.13 | 1.12 | 3.63 | 11.0 |
| $PMD_{25}$ | 0.245 | 1.25 | 6.11 | 11.6 |
| $PMD_{37}$ | 0.367 | 1.36 | 8.45 | 12.2 |
| $PMD_{50}$ | 0.491 | 1.38 | 11.1 | 13.5 |
| $PMD_{62}$ | 0.583 | 1.24 | 9.8 | 42 |
| $PMD_{75}$ | 0.725 | 1.34 | 12.0 | 56.4 |
| $PMD_{87}$ | 0.805 | 1.32 | 13.0 | — |
| $PMD_{100}$ | 1 | 1.45 | 2.33 | — |
| $PMD^*_0$ | 0 | 1.0 | 1.8 | 5.7 |
| $PMD^*_{12}$ | 0.115 | 1.02 | 3.1 | 19.7 |
| $PMD^*_{25}$ | 0.264 | 1.08 | 4.5 | 34.3 |
| $PMD^*_{37}$ | 0.432 | 1.22 | 7.0 | 19.9 |
| $PMD^*_{50}$ | 0.55 | 1.28 | 9.6 | 20.4 |
| $PMD^*_{62}$ | 0.682 | 1.28 | 7.8 | 28.6 |
| $PMD^*_{75}$ | 0.765 | 1.34 | 12.2 | 50.4 |
| $PMD^*_{87}$ | 0.888 | 1.29 | 13.2 | — |
| $PMD^*_{100}$ | 1.0 | 1.4 | 1.7 | — |

[a] $C_I$ is methane; $C_5$ is the sum of pentane isoemers,
[b] *i*P/*n*P is the ratio isopentane/n-pentane,
[c] MCP/B is the ratio methylcyclopentane/benzene.

It should be noted that the variations of the *i*C5/*n*C5 ratio cannot be attributed to perturbations by multiple hydrogenolysis which would become more important for one of the two $C_5$ isomers concerned: the ratios $C_I/C_5$ ($C_I$ is methane; $C_5$ is the sum of both isomers of pentane observed in the products) do not deviate much from 1, and are approximately constant for most catalysts containing the two metals. The values obtained on the $PMD_x$ series are generally higher than on the $PMD^*_x$ series, which is consistent with more Mo at the surface of $PMD_x$ catalysts expected on the basis of the preparation method and confirmed by XPS analysis.

Another selectivity showing fairly dramatic changes with increasing Mo/(Mo + Pt) ratio is the ratio of the amounts of methylcyclopentane and benzene in the products of the reaction of 3-methylpentane with hydrogen. The reproducibility is much worse, however, because of the low contents of benzene and methylcyclopentane among the products of reaction, and the resulting uncertainties of analyses.

For this reason we have taken advantage of the variations of the *i*C5/*n*C5 ratio with the surface Mo/(Mo + Pt) ratio by using it as a chemical probe to provide evidence for the variations of the surface composition induced by exposure of some $PMD_x$ catalysts to different benzene partial pressures. The different partial pressures have been obtained by conducting reactions between hydrogen and 3-methylpentane in the molar ratio 9 : 1 at temperatures varying according to the following sequence: 300–350–400–300–350°C. The duration of each step was 8–12h. In this way, since the proportion of benzene formed is much higher at 400°C than at 300° or 350°C (Table 6), we can test the catalysts at the same temperatures (300 and 350°C) before and after benzene exposure. For three catalysts, $PMD_0$, $PMD_{50}$, and $PMD_{62}$, this sequence was followed by a series of treatments of these catalysts under flowing hydrogen at a few progressively increased temperatures between 350 and 550°C, with some reaction tests performed between these treatments in order to check for the reversibility of changes in catalyst properties occurring during catalytic tests at high temperature (400°C). The results are given in Table 6.

The main products observed, as mentioned in Ref. (10), are those of the hydrogenolysis (C1 to C5), isomerization (mostly 2-methylpentane and smaller amounts of *n*-hexane and 2,2-dimethylbutane), and dehydrocyclization (methylcyclopentane and benzene). Small amounts of hexenes were found as well, mostly at 400°C. In Table 6

**TABLE 6**

**Influence of Temperature and of Exposure to Benzene on the Conversion and Distribution of Products in the Reaction of 3-Methylpentane with Hydrogen. Catalysts reduced at 500°C; PH2 = 0.9 atm, P3MP = 0.1 atm**

| Catalyst and weight | Temperature (°C) | Time (h) | Conversion (init.–final) (%) | | | | $iC_5/nC_5$ | $P_{benzene}$ (atm) |
|---|---|---|---|---|---|---|---|---|
| | | | Total | Hydrogenolysis | Isomerization | Dehydrocyclization | | |
| $PMD_0$ | 300 | 12 | 11.7–9.8 | 2.8–2.7 | 8.2–6.5 | 0.7 | 3.8 | 0 |
| 0.813 g | 350 | 10 | 26.5–23.4 | 6.4–5.3 | 17.0–15.3 | 2.9 | 2.2 | $4 \times 10^{-4}$ |
| | 400 | 15 | 35–26.2 | 9.5–6.1 | 15.7–12 | 9.4–7.4 | 1.1 | $2 \times 10^{-3}$ |
| | 300 | 11 | 0.7–0.8 | 0.2 | 0.2 | 0.3 | 3.7 | 0 |
| | 350 | 8 | 9–8.7 | 1.6–1.8 | 4.0–5.0 | 1.8–2.2 | 2.6 | $1 \times 10^{-4}$ |
| 7 h in flowing $H_2$ at 350°C | | | | | | | | |
| | 300 | 15 | 0.9–0.7 | 0.3–0.2 | 0.3–0.2 | 0.3 | 3.9 | |
| | 350 | 8 | 10.2–11.4 | 2.2 | 6–6.7 | 2.5 | 2.2 | |
| 7 h in flowing $H_2$ at 400°C | | | | | | | | |
| | 300 | 8 | 1.4 | 0.4 | 0.8 | 0.4 | 4.0 | |
| | 350 | 14 | 17.2–14.8 | 3.3–2.8 | 11–9.3 | 2.7 | 2.0 | |
| 7 h in flowing $H_2$ at 500°C | | | | | | | | |
| | 300 | 7 | 7.2–5.2 | 2–1.6 | 4.5–3 | 0.7–0.6 | 4.0 | |
| | 350 | 12 | 31–21 | 6.5–4.1 | 21–14 | 3.0–2.4 | 2.0 | |
| | 400 | 21 | 38–24 | 8.5–5.6 | 21–10.0 | 8.0–7.3 | 1.4 | |
| | 300 | 8 | 0.6–0.5 | 0.2 | 0.2–0.1 | 0.3–0.2 | 3.8 | |
| | 350 | 12 | 6.2 | 1.2 | 3.0 | 1.9 | 2.7 | |
| 7 h in flowing $H_2$ at 550°C | | | | | | | | |
| | 300 | 8 | 1.7 | 0.5 | 0.8 | 0.4 | 4.0 | |
| | 350 | 15 | 20–17 | 4.1–3.3 | 13–11.0 | 2.9 | 2.0 | |
| $PMD_{12}$ | 300 | 19 | 8.6–5.1 | 4.4–2.5 | 3.5–2 | 0.7–0.6 | 9.3 | 0 |
| 0.803 g | 350 | 8 | 29–24 | 8.1–5.8 | 17.7–14.8 | 2.8 | 2.6 | $4 \times 10^{-4}$ |
| | 400 | 15 | 37–24 | 7.5–4.5 | 18.4–10.5 | 9.9–7.8 | 1.4 | $2 \times 10^{-3}$ |
| | 300 | 9 | 0.4 | 0.13 | 0.1 | 0.16 | 4.8 | 0 |
| | 350 | 9 | 6.7 | 1.3 | 3.1 | 2.1 | 3.0 | $1 \times 10^{-4}$ |
| $PMD_{25}$ | 300 | 8 | 8.0–6.0 | 5.6–3.9 | 1.9–1.5 | 0.5 | 13 | 0 |
| 0.625 g | 350 | 8 | 23.5–17 | 11–7.0 | 10–7.8 | 2.3 | 4.6 | $2 \times 10^{-4}$ |
| | 400 | 9 | 28–19 | 7.3–4.0 | 12–7.5 | 7.4–6.3 | 2.1 | $1 \times 10^{-3}$ |
| | 300 | 12 | 0.8–0.5 | 0.5–0.3 | 0.2 | 0.1 | 5.9 | 0 |
| | 350 | 8 | 4.2 | 1.1 | 1.5 | 1.3 | 4.3 | $4 \times 10^{-5}$ |
| $PMD_{37}$ | 300 | 21 | 12.5–6.6 | 9.6–5.0 | 2.4–1.2 | 0.6–0.4 | 16 | 0 |
| 1.07 g | 350 | 8 | 22.5–17 | 14–10.0 | 6.4–5.0 | 2.0–1.7 | 6.9 | $2 \times 10^{-4}$ |
| | 400 | 15 | 29–16 | 13–5.1 | 9.5–5.5 | 6.0–4.5 | 3.0 | $1 \times 10^{-3}$ |
| | 300 | 8 | 0.6–0.4 | 0.3–0.2 | 0.1 | 0.13–0.07 | 9.0 | 0 |
| | 350 | 14 | 5 | 1.8 | 1.6 | 1.4 | 6.0 | $6 \times 10^{-5}$ |
| $PMD_{50}$ | 300 | 8 | 6.3–5.1 | 4.8–3.9 | 1.2–0.9 | 0.4 | 19 | 0 |
| 0.935 g | 350 | 14 | 27–14 | 17–7.7 | 7.6–3.9 | 1.9–1.7 | 10 | $1 \times 10^{-4}$ |
| | 400 | 9 | 24–11.0 | 10–3.7 | 6.9–2.9 | 5.3–4.1 | 4.3 | $7 \times 10^{-4}$ |
| | 300 | 8 | 0.3 | 0.15 | 0.15 | 0.02 | 7.5 | 0 |
| | 350 | 11 | 3.3–3.6 | 1.6–1.8 | 0.7–0.9 | 0.9 | 6.9 | $3 \times 10^{-5}$ |
| 7 h in flowing $H_2$ at 350°C | | | | | | | | |
| | 300 | 8 | 0.3 | 0.2 | 0.1 | 0.02 | 11 | |
| | 350 | 15 | 4.7–4.1 | 2.4–2.3 | 1.5–1.0 | 0.8 | 8 | |
| 7 h in flowing $H_2$ at 400°C | | | | | | | | |
| | 300 | 12 | 1.0 | 0.7 | 0.2 | 0.1 | 13 | |
| | 350 | 8 | 9.8–8.1 | 5.3–4.4 | 3.0–2.5 | 1.3–1.2 | 9 | |
| 7 hr in flowing $H_2$ at 500°C | | | | | | | | |
| | 300 | 8 | 8.0–4.0 | 4.9–2.8 | 2.6–1.0 | 0.5–0.3 | 14–16.6 | |
| | 350 | 11 | 23–14 | 11–7.1 | 8.0–5.3 | 3.4–1.6 | 9.2–10.4 | |
| | 400 | 8 | 17–12.0 | 5.5–3.2 | 6.6–4.5 | 4.6–3.9 | 4.2 | |
| | 300 | 5 | 0.3 | 0.13 | 0.1 | 0.03 | 8.1 | |
| | 350 | 10 | 2.6 | 1.0 | 0.8 | 0.7 | 6.3 | |
| 7 h in flowing $H_2$ at 550°C | | | | | | | | |
| | 300 | 9 | 5.5–3.7 | 4.3–2.8 | 0.9–0.7 | 0.3 | 12.8 | |
| | 350 | 11 | 17–11.5 | 10–6.2 | 4.7–3.3 | 2.0 | 8.2 | |

**TABLE 6**—*Continued*

| Catalyst and weight | Temperature (°C) | Time (h) | Conversion (init.–final) (%) | | | | $iC_5/nC_5$ | $P_{benzene}$ (atm) |
|---|---|---|---|---|---|---|---|---|
| | | | Total | Hydrogenolysis | Isomerization | Dehydrocyclization | | |
| | 300 | 15 | 8.1–4.6 | 3.5–2.1 | 4.1–2.2 | 0.6–0.3 | 16 | 0 |
| | 350 | 8 | 23–17 | 7.2–5.0 | 14–10.0 | 2.5–2.2 | 8.6 | $1 \times 10^{-4}$ |
| | 400 | 15 | 25–10.0 | 6.2–2.5 | 13–4.6 | 4.9–2.6 | 4.1 | $7 \times 10^{-4}$ |
| $PMD_{62}$ | 300 | 10 | 0.2 | 0.1 | 0.1 | 0 | | 0 |
| 1.502 g | 350 | 21 | 1.7 | 0.6 | 0.7 | 0.3 | 5.9 | $1 \times 10^{-5}$ |
| 7 h in flowing $H_2$ at 400°C | | | | | | | | |
| | 300 | 15 | 0.6–0.2 | 0.5–0.2 | 0.1 | 0.02 | 10.5 | |
| | 350 | 8 | 5.8–5.2 | 2.3–2.1 | 2.4–2.2 | 0.9 | 7.7 | |
| 7 h in flowing $H_2$ at 500°C | | | | | | | | |
| | 300 | 5 | 2.2–2.1 | 1.5 | 0.5 | 0.2 | 13.5 | |
| | 350 | 15 | 16–10.0 | 6.4–4.0 | 7.6–4.3 | 2.4–1.6 | 8.7 | |
| | 400 | 19 | 24–8.5 | 7.7–2.4 | 10–3.0 | 5.4–2.4 | 4.2 | |
| | 300 | 8 | 0.2 | 0.1 | 0.1 | 0.02 | 6.8 | |
| | 350 | 10 | 1.4 | 0.6 | 0.4 | 0.3 | 5.7 | |
| 7 h in flowing $H_2$ at 550°C | | | | | | | | |
| | 300 | 9 | 3.1–2.0 | 2.1–1.4 | 0.6–0.3 | 0.4–0.2 | 10.6 | |
| | 350 | 12 | 12.9–9.3 | 5.4–3.7 | 5.2–3.6 | 2.2–1.9 | 7.8 | |
| | 300 | 6 | 0.7 | 0.05 | 0.6 | 0.04 | — | 0 |
| | 350 | 15 | 1.7 | 0.2 | 1.1 | 0.35 | 7.3 | 0 |
| | 400 | 7 | 6.3–4.0 | 1.2–1.0 | 3.2–1.1 | 1.9–0.8 | 3.9 | $3 \times 10^{-5}$ |
| $PMD_{75}$ | 300 | 8 | 0.5 | 0 | 0.45 | 0.03 | — | 0 |
| 1.787 g | 350 | 8 | 1.0 | 0.11 | 0.56 | 0.3 | 4.1 | 0 |

are given the total conversion of 3-methylpentane (the initial one and the conversion after 8–12 h on stream), its conversions into the three above-mentioned main groups of products, the ratio methylbutane/*n*-pentane (*i*C5/*n*C5), and the benzene partial pressure in the product gas mixture, together with the amount of catalyst used in the experiments. As usual, the total conversion and the conversion into the main groups of products diminish monotonically with the time on stream, especially at 400°C (Fig. 2, Table 6). If we compare the corresponding values at 300 and 350°C before and after the step at 400°C, the hydrogenolysis and the isomerization are very affected, while the dehydrocyclization is slightly less modified (Table 6). The treatments with hydrogen *in situ* progressively restore the initial values of conversion, almost totally if the treatment is at 500°C. A still higher temperature (550°C) leads to lower conversions, probably because of the onset of sintering and/or of poisoning of the catalyst by impurities from the support.

In order to visualize the influence of coking (deactivation) on the ratio *i*C5/*n*C5 we have plotted in Figs. 2a and 2b the changes of the total conversion and of the ratio *i*C5/*n*C5 as a function of the reaction time for $PMD_0$ and $PMD_{37}$. For the Pt-only catalyst, $PMD_0$, one can see that the ratio *i*C5/*n*C5 is hardly affected by the deactivation of the catalyst (at 350 and 400°C it may very slightly increase with the deactivation of the catalyst) or by exposure to benzene (steps at 300°C before and after the step at 400°C). As a matter of fact, at 350°C, the ratio *i*C5/*n*C5 seems to have slightly increased after the step at 400°C: the values are 2.2 and 2.6, respectively, before and after the step at 400°C. This could be related to changes in the proportions of isomers in the products of reaction. This proportion is 65% (with 62% of 2-methylpentane in the isomers) before the step at 400°C and 55% (with 58% of 2-methylpentane). Since the ratio *i*C5/*n*C5 in the products of the hydrogenolysis is likely to be lower for 2-methylpentane ($2C_I$–$C_{III}$ and 1 $C_I$–$C_{II}$ bonds) than for 3-methylpentane, one can understand why the ratio *i*C5/*n*C5 is slightly higher after the step at 400°C than before, in relation with the lower proportion of 2-methylpentane. Nevertheless, at a given temperature, the ratio *i*C5/*n*C5 is not very different for the fresh, the heavily coked, or the regenerated catalyst. For $PMD_{37}$ (Fig. 2b) at 300°C, the ratio *i*C5/*n*C5 first increases when the deactivation increases rather sharply, and then it slowly decreases when deactivation slows down. During the further steps at 350, 400, 300, and 350°C it is fairly constant, but the values obtained for the steps at 300 and 350°C following the 400°C step are now lower than those for the corresponding steps preceding that at 400°C.

We can rationalize these observations if the ratio *i*C5/*n*C5 increases when deactivation is important (first hours in the first step at 300°C), then at 300°C the low benzene partial pressure induces surface composition modifications resulting in a slow decrease of the ratio *i*C5/*n*C5.

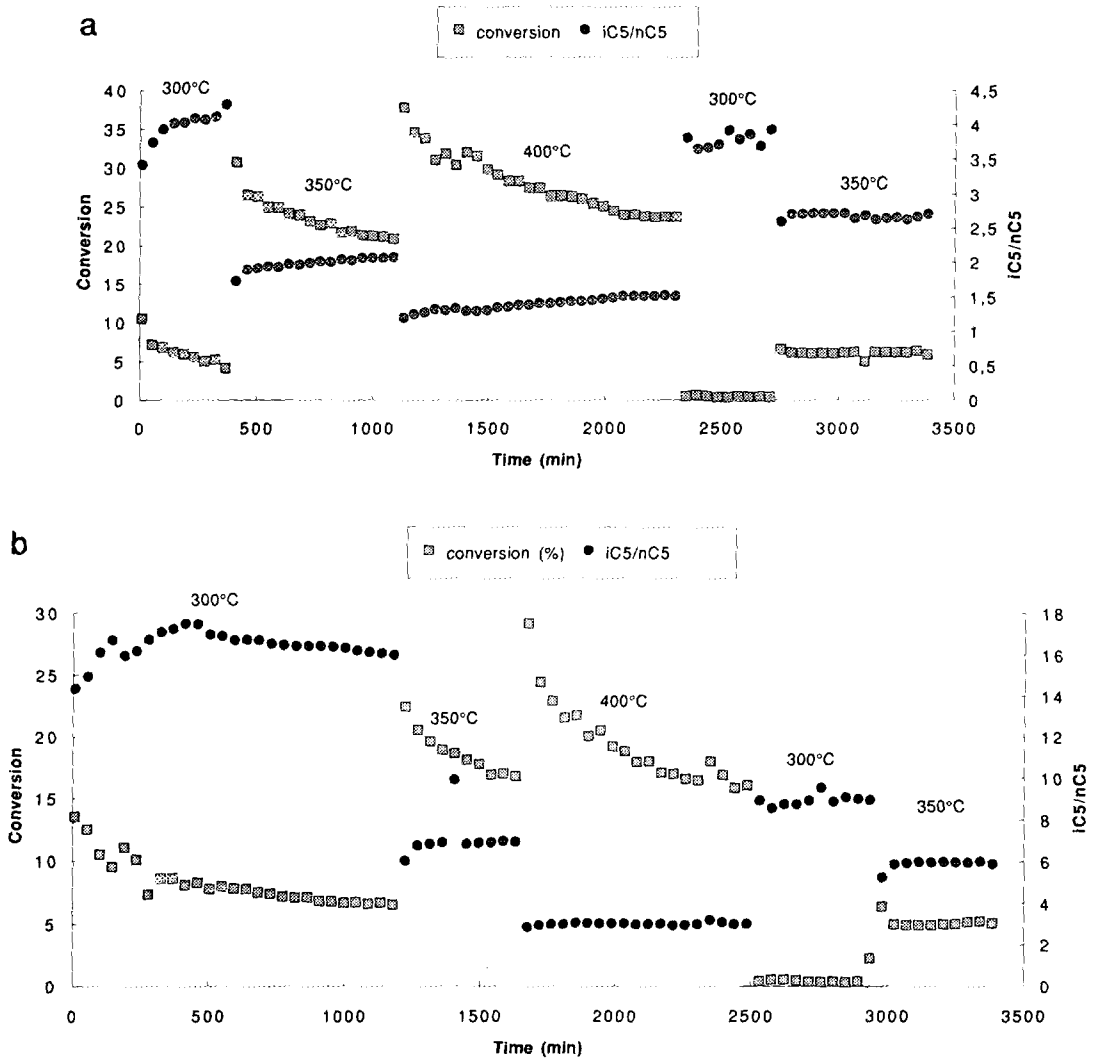


FIG. 2. Total conversion and $iC_5/nC_5$ vs the reaction time for $PMD_0$ (a) and $PMD_{37}$ (b). Reactions between $H_2$ and 3-methylpentane, $P_{H_2}$ = 0.9 atm, $P_{3MP}$ = 0.1 atm.

At higher temperatures, the surface composition modifications are very fast and the equilibrium surface composition corresponding to the benzene partial pressure at the reaction temperature is obtained very quickly, explaining the good stability of the ratio. The influence of the benzene partial pressure is seen by comparing the ratio *i*C5/*n*C5 at steps before and after the step at 400°C where the benzene proportion is the highest (Fig. 2b and Table 6). It is clear that an increase in the amount of benzene leads to lowering of *i*C5/*n*C5. Taking into account the behavior of the *i*C5/*n*C5 ratio as a function of the molybdenum content we can conclude that, even in the presence of a relatively low partial pressure of benzene in the products, some molybdenum species are driven away from the surface of the metal particles. It is interesting to note that heating the catalysts in flowing hydrogen brings about an increase of the *i*C5/*n*C5 ratio (Table 6, results for $PMD_{50}$ and $PMD_{62}$) which becomes equal to the initial value at 350°C and remains slightly lower at 300°C, after the treatment at 500°C. This observation confirms the result obtained by XPS analysis concerning the at least partial reversibility of the catalyst modification in the prevailing pressure of benzene at high temperature.

The variations of the conversion of 3-methylpentane in hydrogenolysis on the one hand and in isomerization and dehydrocyclization on the other with the ratio Mo/(Mo + Pt) at various temperatures support also the idea of a decrease of the masking of Pt surface by Mo species. In fact, at 350°C as already reported (10) the rate of hydrogenolysis goes through a maximum at about 40% Mo, while the sum of the rates of isomerization and dehydrocyclization does not strictly obey a linear law but is only slightly lower. These phenomena have been explained (3, 9, 10) by the formation of an intermediate species on

mixed sites composed of Mo and of Pt atoms of the same composition whatever the global catalyst composition in the hydrogenolysis of alkanes, these species being much more reactive than those adsorbed on Pt only. The rate of this reaction is maximum when the number of these mixed sites is maximum. After the maximum, all Pt atoms are included in mixed sites. Before that maximum, Pt is in excess and afterwards Mo is in excess. The maximum rate corresponds to the optimum surface composition. On the contrary, isomerization and dehydrocyclization would occur via a common intermediate adsorbed on Pt only, and hence the sum of the rates of these two reactions would be proportional to the Pt surface area. In Figs. 3 and 4 we have reported the changes of the rate of hydrogenolysis and of the sum of the rates of isomerization and dehydrocyclization extrapolated to zero time on stream vs the ratio Mo/(Mo + Pt). It is clear that, taking into account the uncertainty due to the assessing of the deactivation curves, the position of the maximum is shifted towards higher Mo/(Mo + Pt) ratios at higher temperatures (position of the maxima respectively around 30, 38, and 42% at 300, 350, and 400°C), and hence at higher benzene partial pressures. This shows that, at higher temperature, the optimum surface composition is obtained at higher nominal Mo/(Mo + Pt) ratios, and that consequently for a given catalyst an increase in the proportion of benzene in the reacting mixture results in lower Mo content at the active metal surface, in good agreement with the other results in XPS and with changes in the ratio *i*C5/*n*C5. Concerning the isomerization and the de-

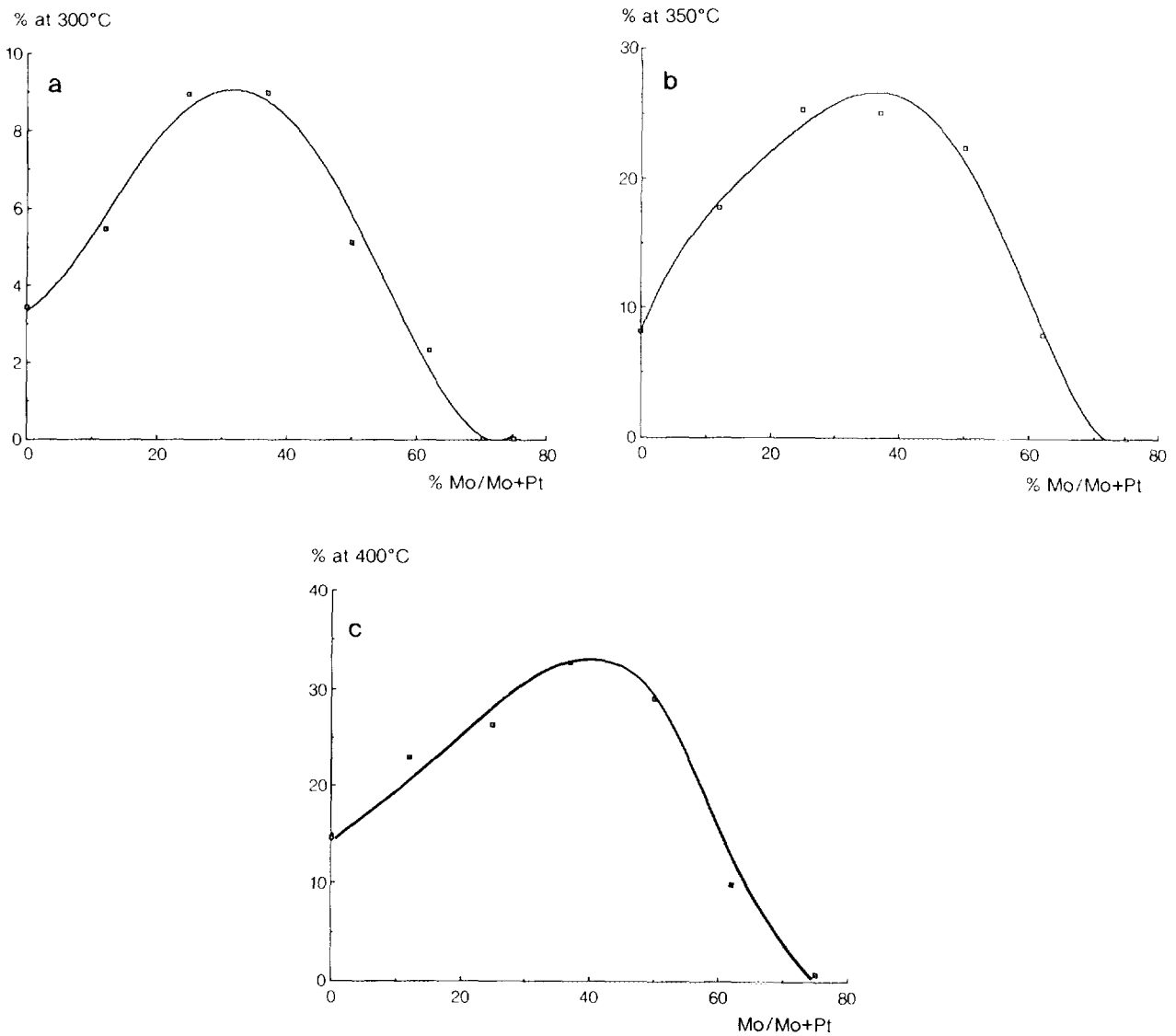


FIG. 3. Rate of hydrogenolysis of 3MP at (a) 300°C, (b) 350°C, and (c) 400°C on $PMD_1$ vs the ratio Mo/(Mo + Pt). Reactions between $H_2$ and 3-methylpentane, $P_{H_2}$ = 0.9 atm, $P_{3MP}$ = 0.1 atm, total flow rate = 0.154 mol × $h^{-1}$.

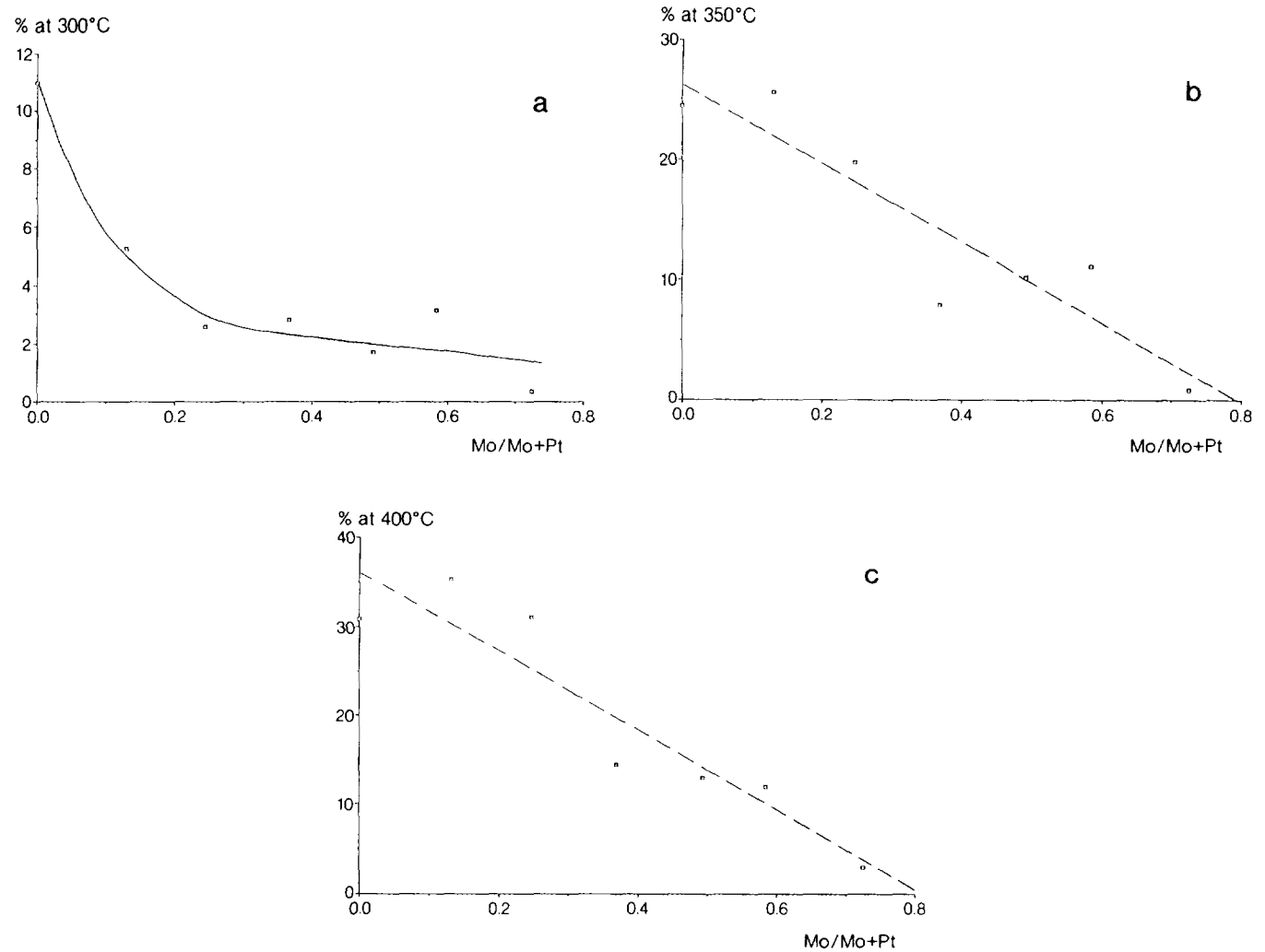


FIG. 4. Sum of the rates of isomerization and of dehydrocyclization of 3MP at (a) 300°C, (b) 350°C, and (c) 400°C on $PMD_x$ vs the ratio Mo/Mo + Pt). Reactions between $H_2$ and 3-methylpentane, $P_{H_2}$ = 0.9 atm, $P_{3MP}$ = 0.1 atm, total flow rate = 0.154 mol × $h^{-1}$.

hydrocyclization, the sum of their rates is noticeably lower than the ones corresponding to linearity at 300°C, while it is roughly scattered around a straight line at 350 and 400°C. These results are very well consistent with a lowering of Mo content at the metal surface.

*Discussion*

It follows from the above results that the two methods used here confirm the hypothesis proposed in the Introduction to explain the behavior of Pt–Mo/$SiO_2$ catalysts in different test reactions, and the variations of their properties with their composition. These methods are largely complementary since the advantage of the reaction probe is the possibility of detecting changes in catalyst surface compositions directly in reaction conditions, while the XPS analysis requires at least an evacuation of the catalyst which can modify its surface. The chemical probe, moreover, is sensitive to the situation on the very top surface of the catalyst, in contrast with the averaging of the composition over a few surface layers taking place with the method of XPS surface analysis. On the other hand, the use of reaction probes is more qualitative than quantitative. Moreover, the partial pressure of benzene which could be attained in the conditions of the reforming of 3-methylpentane was considerably lower than that which was used in the treatment of the catalysts between XPS analyses.

The results obtained by the two methods show that some species at the surface of the catalysts are mobile and can undergo a redistribution under the influence of changing conditions, e.g., temperature or the composition of the gas phase. Any large variations concerning the platinum particles seem improbable, so it is the molybdenum species which appear to be responsible for the observed changes in the surface composition. The exact

nature of these mobile species cannot be determined on the basis of our results only; however, we can apply a model similar to that proposed by Mériaudeau *et al.* (6), which seems to agree with our results even though the catalysts used by those authors were prepared in a different way. According to this model, platinum is present in particles of approximately constant mean diameter, independent of the molybdenum content (and roughly independent of the reduction temperature between 400 and 700°C). During the reduction of the catalysts, molybdenum ($Mo^{x+}$) species are distributed between the surface of (already-formed) metal particles and the silica support. Mériaudeau *et al.* (6) have shown that, at least for small additions of molybdenum precursor (molybdate), it is preferentially adsorbed on the platinum surface rather than on silica. After reduction and outgassing *in vacuo* or in the conditions of butane hydrogenolysis, the molybdenum species seem to stay at the surface of platinum. It should be mentioned that the position of the maximum rate of this reaction does not shift when the reduction temperature is raised from 400 to 500 and 700°C (4).

Our results do not allow an unambiguous identification of the driving force inducing the mobility of the Mo species away from the metal surface. However, the well-known high strength of aromatic hydrocarbon adsorption on metals could result in moving away $Mo^{x+}$ from the metal surface. Some analogies may be drawn with the phenomenon known as strong metal-support interactions (SMSI):

—the interaction involves platinum (reduced metal) and partly reduced oxide species ($Mo^{x+}$, instead of, e.g., $TiO_2$).

—the surface of the reduced metal is in certain circumstances invaded by the partially reduced oxide giving rise to modifications of adsorption and catalytic properties.

Now, when benzene (or maybe other aromatic hydrocarbons) are present in the gas phase in contact with the catalyst, the distribution of the mobile molybdenum species changes in favor of the support until, in some extreme cases, these species may be entirely driven out of the metal surface. This seems to be the case in the cyclohexane dehydrogenation. It can be supposed, therefore, that some bonding interaction exists between metal atoms and Mo ($MoO_x$) species, which is sufficient to induce the covering of the metal surface with these species but is less strong than the adsorption of aromatics on Pt, since aromatics are able to drive away Mo species. A new and interesting element is the reversibility of the observed changes: this means that the reduced Mo species displaced presumably towards the silica support do not lose their mobility and therefore their irreversible fixation, if any, is of lesser importance.

## CONCLUSIONS

XPS analyses have shown that the ratio Mo/Pt in reduced Pt–Mo/$SiO_2$ catalysts is lower after exposure of these catalysts to a benzene/hydrogen mixture at 400°C. This result has been confirmed by reaction tests, using a surface-composition-dependent selectivity known for Pt–Mo catalysts, namely the isopentane/*n*-pentane ratio obtained in the hydrogenolysis of 3-methylpentane. In both cases the modifications of the surface composition were found to be at least partially reversible. The concept of some mobile Mo ($MoO_x$) species invading the surface of Pt particles in the catalyst but subject to being driven away by aromatic hydrocarbons at sufficiently high temperature allows us to explain satisfactorily the adsorption and reaction behavior of reduced Pt–Mo/$SiO_2$ catalysts.

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