Role of tungsten in supported Pt-W reforming catalysts
Part I. Modification of platinum activity and selectivity by addition of tungsten

Jean Saturnin M'Boungou, Jean Louis Schmitt, Gilbert Maire
and François Garin *

Laboratoire de Catalyse et Chimie des Surfaces, Institut Le Bel, Université Louis Pasteur,
4 rue Blaise Pascal, 67070 Strasbourg, France

Received 30 October 1990; accepted 24 July 1991

Bimetallic supported Pt-W catalysts are studied for 3-methylhexane reforming. An increase in the activity and selectivity in aromatization is found for Pt-low W/Al_2O_3 catalysts compared to the classical monometallic Pt/Al_2O_3 catalyst. Changes in activity and selectivity, for bimetallic catalysts, are attributed to "tungsten moderator interaction" effects between platinum and support which modify the metallic particle sizes. These changes are observed on Pt-high W/Al_2O_3 and $Pt\text{-}W/SiO_2$ catalysts. Superficial carbide formation and modification of the hydrogen chemisorption may be proposed to explain the reactivity of Pt-W catalysts under low hydrogen pressure.

Keywords: Platinum; supported bimetallic Pt-W catalysts; 3-methylhexane reforming

1. Introduction

The operation of petroleum reforming has been revolutionised in the past two decades by the introduction of bimetallic catalysts [1a–f]. It has been shown that bimetallic catalysts (Pt-Re, Pt-Ir,...) compared to classical hydrocarbon reforming catalysts (Pt/Al_2O_3) have better stability and greater activity and selectivity in skeletal rearrangement of hydrocarbons. As far as we know few studies in skeletal rearrangement of hydrocarbons have been realized on $Pt\text{-}W/Al_2O_3$ catalysts. Yermakov and Boudart [2,3] have studied $Pt\text{-}W/SiO_2$ catalysts, and they have shown that the bimetallic systems exhibit a decrease in selectivity towards isomerization of neopentane but an increase in activity towards hydrogenolysis when compared with the sample containing platinum only.

---

* To whom correspondence may be addressed.

The aim of this paper (Part I) is to analyze the modifications of the catalytic behavior of alumina supported platinum catalysts when tungsten is added, and to show that these modifications are also dependent on the tungsten loading.

In the following paper, Part II, we have focussed our attention on catalyst morphologies and metal-support interactions effect on the reaction mechanisms of 3-methylhexane over of the supported Pt-W catalysts [4].

2. Experimental

SAMPLE PREPARATION

Catalyst samples are prepared by successive impregnation method. WO_3 is dissolved in NH_4OH at 140 ° C (PH = 9) and the support carrier is impregnated with this solution. The pretreatment steps can be summarized as follows:

1–Impregnation of supports. Woelm alumina [5] or Fluka silica with ammonium paratungstate ($WO_3 + NH_4OH$)

2–drying at 60 ° C for 12 h.

3–reduction at 550 ° C for 2 h under H_2.

4–reimpregnation with hexachloroplatine acid, for 1 hour.

5–drying at 120 ° C for 12 h.

6–reduction in-situ at 400 ° C for 2 h under H_2.

The atomic composition of the Pt-W catalysts used in the study and their codes are given in table 1.

APPARATUS AND PROCEDURE

Hydrocarbon reactions are carried out in an apparatus shown schematically in fig. 1 in which it is possible to perform the catalytic reactions under high pressure. In each experiment, a small amount of hydrocarbon is vaporized in a U-tube maintained at a constant temperature so as the hydrocarbon passes over

Table 1
Atomic composition of the catalysts

Catalyst	Actual atomic percent		Other notation
	%Pt	%W	
$10Pt/Al_2O_3$	7	0	–
$5Pt\text{-}5W/Al_2O_3$	4.42	3.79	Pt-low W/support
$5Pt\text{-}5W/SiO_2$	4.78	4.13	
$5Pt\text{-}35W/Al_2O_3$	2.76	21.24	Pt-high W/support

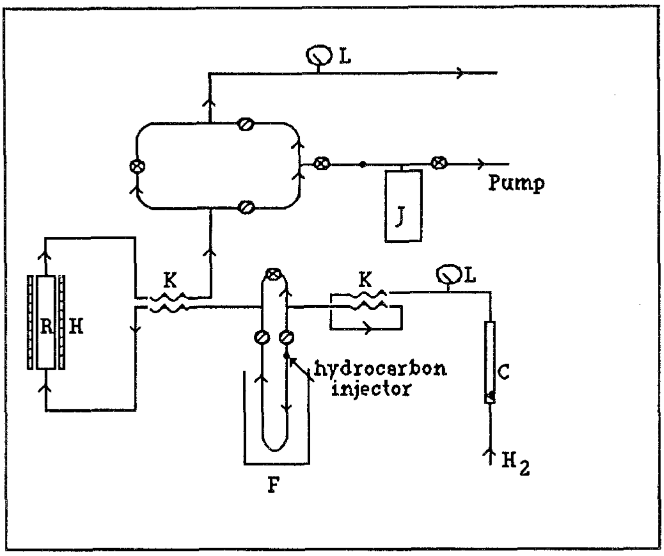


Fig. 1. Apparatus for hydrocarbon reactions. (C) flowmeter, (R) reactor and (H) oven; (F) U-tube; (J) gas expansion to get atmospheric pressure; (K) catharometers; (L) manometer; (⌀) valve opened during reaction; (⊗) valve closed during reaction.

the catalyst at constant pressure. The eluent gas mixture is composed of H_2 and He. The total hydrogen-helium pressure is varied from 0 to 10 bars. Hydrogen-helium mixture (5% H_2) is used to achieve a low H_2 pressure. The reactor is a stainless-steel tube, 240 × 5 mm, in which the position of the catalyst is fixed by means of quartz wool. A uniform reactor temperature is obtained by making use of an oven. The reaction conditions are as follows: temperature in the reactor 375 °C; hydrocarbon pressure 0.5 bar; H_2 pressure varied from 0.01–6 bars; hydrogen flow is 18 cc/min; the amount of catalyst is about 5 mg.

After the catalytic reaction the products stream is analyzed by means of gas-liquid chromatography. The column is a 50 m of fused silic WCOT-Sil 8CB (5.0 μm) tube of 0.53 mm internal diameter, filled with 95% methylsiloxane and 5% phenylsiloxane.

CATALYST CHARACTERIZATION

In the following paper (Part II) we have studied these catalysts by ESCA. In this Part we shall only give the electron microscopy results.

Electron microscopy: A PHILIPS TEM 300G transmission electron microscope operating between 10 and 100 kV is used, with a resolution of about 5 Å. The extractive technique is used which involves separation of the platinum particles by destruction of the alumina or silica carrier in a dilute solution of HF [6,7]. Particle sizes are obtained from measurements of more than 2000 particles after each treatment.

3. Results

CATALYTIC REACTIONS

Starting with 3-methylhexane four parallel reactions pathways may occur at low conversion. The consecutive reactions in such experimental conditions do not occur (for example 7C1 = 0). We have:

–The cracking reactions, where only one carbon-carbon bond breaking occurs.

–the bound shift isomerization reactions

–the isomerization reactions via dimethyl or ethylcyclopentanes adsorbed intermediates which are hydrogenolyzed. These isomers are coming from what we call the cyclic mechanism [8].

–the aromatization reactions occurring either from a direct 1–6 ring closure or via 1–5 ring enlargement.

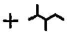
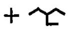
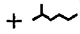
In table 2 are reported the product distributions obtained from 3-methylhexane reacting on these four catalysts. As these reactions were not performed with labeled hydrocarbons it is almost impossible or very difficult and sullied with large errors, to make a distinction between acyclic products formed either via a bond shift mechanism or via a cyclic mechanism. It is the reason why we have regrouped in one column all the acyclic products formed. In the second column is mentioned the sum of the five cyclopentanes desorbed: cis + trans, 1-2 and 1-3 dimethylcyclopentanes and ethylcyclopentane. The third column is relative to the aromatics, toluene and methylcyclohexane. In the last column the cracked products are reported. The experiments have been performed under 0.25 bar of hydrogen and 0.5 bar of hydrocarbon, we shall see later on that these conditions correspond to the maximum rate on Pt-W catalysts.

Under such conditions, it can be observed that cracking reactions are not important except when the tungsten loading is equal to 35%. On the other hand,

Table 2
Product distributions from 3-methylhexane on various catalysts at: $P_{H_2} = 0.25$ bar; $P_{HC} = 0.5$ bar; $T = 375\,°C$.

Catalyst	Activity [a]	Acyclics [b] (%)	C_5-Cyclics [c] (%)	Aromat. [d] (%)	Cracking [e] (%)
$10Pt/Al_2O_3$	13.3	36.0	36.0	13.5	8.5
$5Pt\text{-}5W/Al_2O_3$	92.0	33.5	45.4	11.4	9.7
$5Pt\text{-}35W/Al_2O_3$	23.7	63.6	11.8	4.8	19.8
$5Pt\text{-}5W/SiO_2$	36.9	39.6	37.5	11.3	11.6

[a] Activity is expressed as: 10^7 mole $s^{-1}g^{-1}$ catalyst.

[b] Acyclic products are:  +  +  +  + 

[c] C5-Cyclic products are: 1,3- and 1,2-dimethylcyclopentanes cis + trans + ethylcyclopentane.

[d] Aromatic products are: Toluene and methylcyclohexane.

[e] Cracking is composed of (C6-C1) + (C5-C2) + (C4-C3); (7C1 = 0 no repetitive processes).

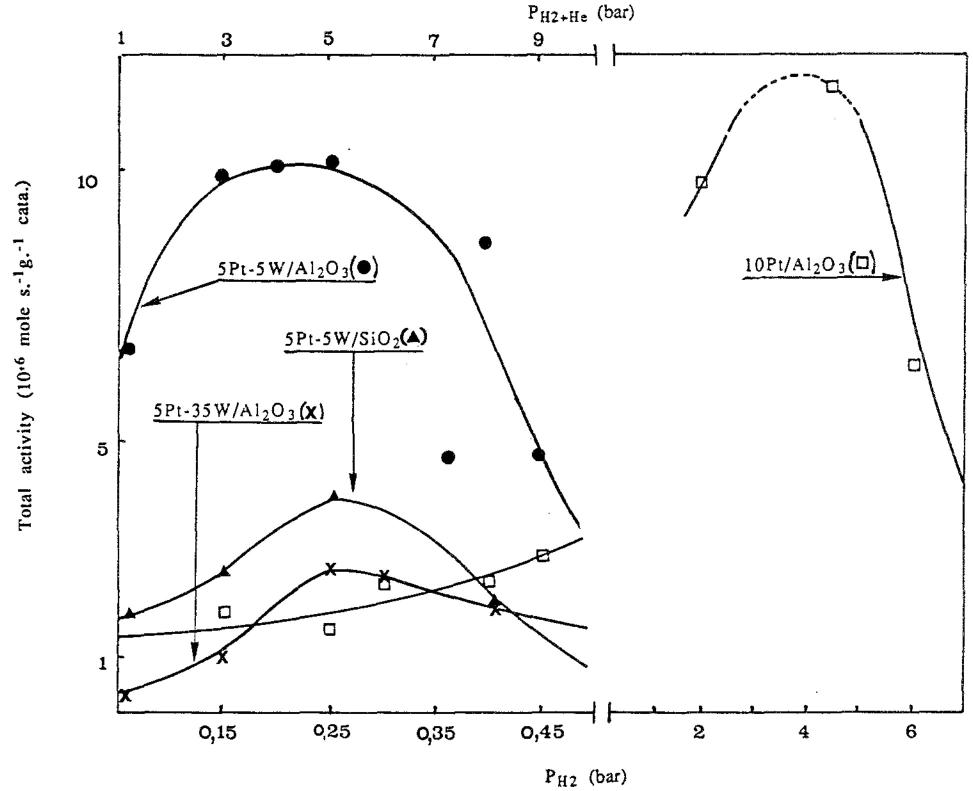


Fig. 2. Total activity of 3-methylhexane as a function of hydrogen pressure over various catalysts. P_{HC}: 0.5 bar; T: 375 ° C.

we may note that the highest activity is obtained on 5Pt-5W/Al_2O_3 catalyst. This activity is divided by a factor 3 and 4 when, respectively, the support is changed from Al_2O_3 to SiO_2 or when on alumina support the tungsten amount is multiplied by 7. The Pt/Al_2O_3 catalyst is about 7 times less active.

The three catalysts 5Pt-5W/Al_2O_3, 5Pt-5W/SiO_2 and 10Pt/Al_2O_3 give nearly the same product distributions. With 5Pt-35W less C5-cyclics and aromatics are formed but cracked and acyclic products are more important. We observed here a very strong influence of tungsten on the selectivity.

As these reforming reactions have not the same hydrogen dependency we are now going to analyze the results obtained when the hydrogen pressure is modified. We shall focuss our interest on the total activity.

The results of the catalytic reaction of 3-methylhexane over the four catalysts as a function of hydrogen pressure are shown in fig. 2 for the total activity. On bimetallic Pt-W catalysts, whatever the support and the tungsten loading the maxima rate values are in the same range of hydrogen pressure, about 0.25 bar, whereas monometallic 10Pt/Al_2O_3 catalyst has its maximum rate value shifted towards higher hydrogen pressure, by about 4 bars.

ELECTRON MICROSCOPY RESULTS

Figs. 3a to 3c are transmission electron micrographs showing the appearance of platinum (and/or tungsten) particles over 5Pt–5W/Al_2O_3, 5Pt-35W/Al_2O_3 and 5Pt-5W/SiO_2 catalysts after heating under hydrogen for 2 hours at 400 ° C. Inspection of these specimens clearly indicates that there are major differences in the growth characteristics of the metals on these various catalysts. The most obvious feature is the wide variation in average metal particle size, which is presented as a function of the catalysts in table 3 . Small mean metallic particle sizes can be seen for platinum (and/or tungsten), of about 16 Å, on 5Pt-5W/Al_2O_3 catalyst. The other three systems show an increase in the mean metallic particle size, about 36 Å for the monometallic catalyst and above 50 Å for the other two.

4. Discussion

Our results point out that: (i) the catalytic activity follows volcano shaped curves versus hydrogen pressure, (ii) total reaction rates depend on the support used and on the amount of tungsten and (iii) maxima of these curves are, for the Pt-W bimetallic systems, shifted towards lower hydrogen pressures compared to the one obtained on monometallic platinum catalyst.

Different approaches may be used to interpret hydrogen effects in these reactions as previously mentioned by Paaàl et al. [9–11]. In the competitive adsorption approach, the rapid dissociation of the C-H bonds is taken into account. The degree of dissociation is governed by the amount of hydrogen present, as explained by Paàl et al. [11]. The concept of reactive chemisorption given by Frennet et al. [12] can also explain these volcano-curves. They found for the isotopic exchange rate of methane a bell-shaped curve as a function of hydrogen pressure. At lower pressures surface carbonaceous species hinder the process, at higher values, sorbed hydrogen hinders the process.

During the catalytic reduction of Pt/WO_3/SiO_2 catalysts, Regalbuto et al. have observed the formation of hydrogen tungsten bronzes [13], which shows that hydrogen chemisorption may induce surface modification.

On the other hand, it was shown that there is an important inhibiting effect of hydrogen on the adsorption step whatever the reaction pathways on the surface: exchange only or exchange and hydrogenolysis [14].

Concerning the second point, we can see that the total catalytic activity is a function of the support used and depends also of the amount of tungsten. To explain these points, we have taken into account the TEM results.

On bimetallic 5Pt-5W/Al_2O_3 catalyst, particles of about 16 Å are observed and on monometallic Pt/Al_2O_3 catalyst larger particles are present, of about 36 Å. The total maximum activity (fig. 2) is nearly similar on these two catalysts but

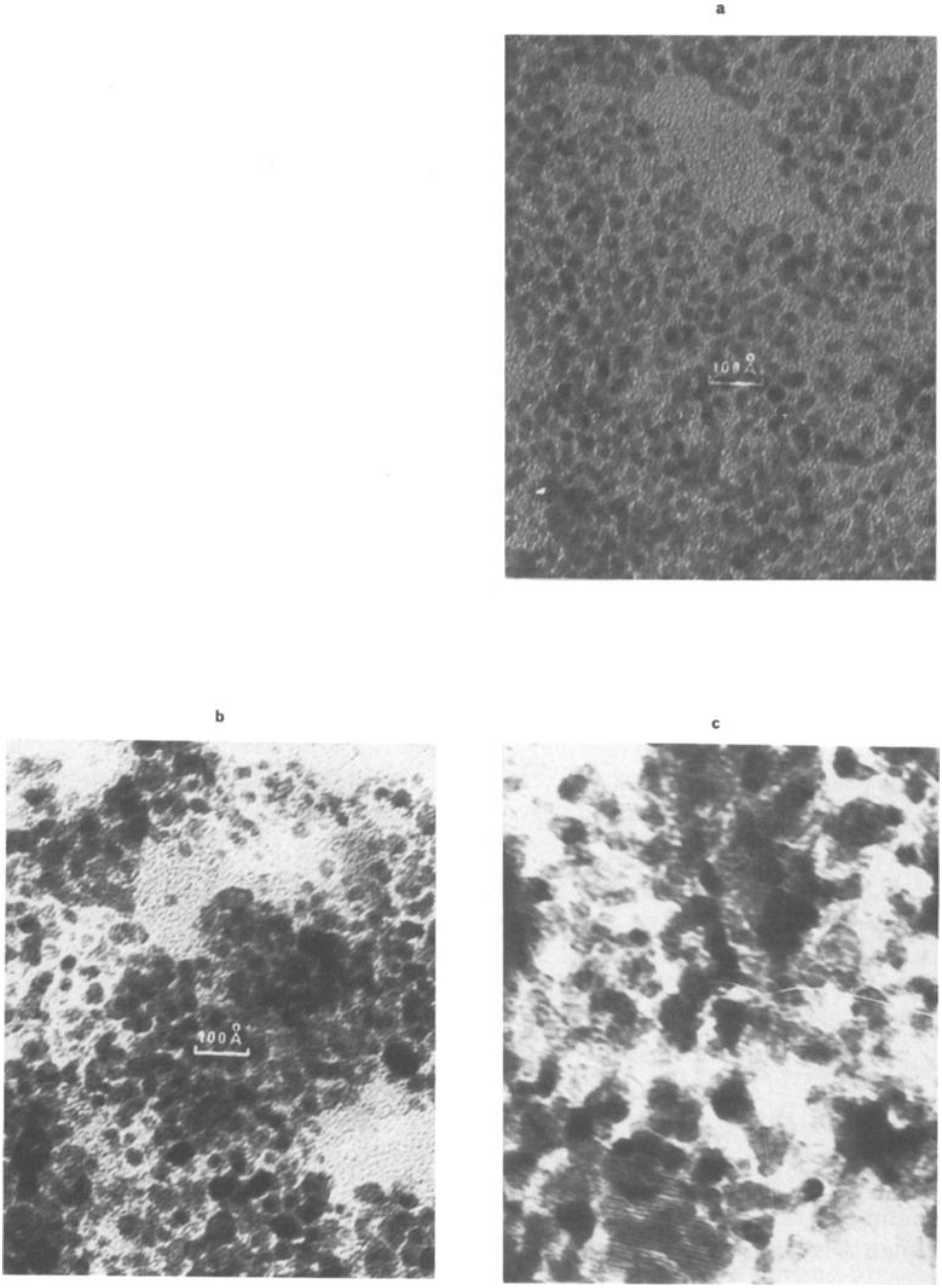
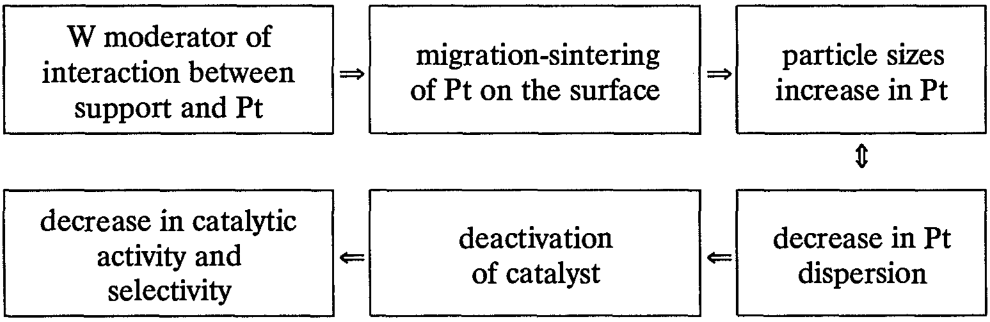


Fig. 3. Transmission micrographs of catalysts. a) 5Pt-5W/Al_2O_3; b) 5Pt-5W/SiO_2; c) 5Pt-35W/Al_2O_3. After reduction under H_2 at 400 °C for 2 h.

Table 3
Average metal particle size for bimetallic catalysts

Catalyst	mean diameter (Å)
$10Pt/Al_2O_3$	36 (ref [6])
$5Pt\text{-}5W/Al_2O_3$	16
$5Pt\text{-}35W/Al_2O_3$	60
$5Pt\text{-}5W/SiO_2$	50

at different hydrogen pressures. And, on the bimetallic one the aromatization reaction, at 0.25 bar of H_2 (table 2) is nearly ten times faster than on the monometallic catalyst. When the amount of tungsten is increased (we have Pt-high W/Al_2O_3 catalysts) or when the support is silica, the total activity and aromatization rate decrease on these Pt-W catalysts [15]. We observed, from TEM, large metallic particle sizes of about 60 Å and 50 Å for $5Pt\text{-}35W/Al_2O_3$ and $5Pt\text{-}5W/SiO_2$ catalysts respectively. This increase in metallic particle sizes may be due to the presence of weaker Pt-support interactions, either by increasing the tungsten loading or by changing the support, in fact, silica exhibits less interactions with metals than alumina [16,17]. Two explanations can be given: either tungsten acts as a poison and blocks the Pt reactivity or it plays an "interaction-moderator" role between platinum and support. Alerasool et al. [18] have shown that in the case of weak support-metal interaction, the dispersion and the surface composition of the catalysts may be affected by the diffusion of precursors accross the surface of the support. Taking into account this point and the Ruckenstein-Pulvermacher crystallite migration model [19], we propose for the last two catalysts the following model:



To explain the shift of the "volcano curve maxima" towards lower hydrogen pressures when the catalytic reactions are performed on the bimetallic Pt-W catalysts, we have pointed out that the total carbon coverage can be broken down into three types of carbon atoms [20]: (i) a small carbon coverage due to impurities (about 4%), (ii) carbon atoms existing in the form of chemisorbed hydrocarbon active intermediates reversibly adsorbed, and (iii) carbon atoms in the form of highly dehydrogenated and irreversibly adsorbed species, the coverage of which increases slowly with time. From the results obtained on the Pt-W catalysts, we may think that these systems are able to suppress the formation of the irreversibly adsorbed carbon either by an adaptation of the surface to the gas phase in erecting superficial carbides which are catalytically active under our conditions, as shown by Boudart [21] or by improving the hydrogenation of the residues linked to a modification of the hydrogen chemisorption. We know that hydrogen-tungsten bronzes can be formed. These two arguments may explain why at lower hydrogen pressure these Pt-W catalysts are active.

5. Conclusion

These results show tungsten plays a very important role. It disperses the platinum particles and allows the catalyst to be active in low hydrogen pressure range.

Acknowledgement

One of us (J.S. M'B.) gratefully acknowledges financial support from the Congo Education Ministry.

References

[1] a) R.L. Jacobson, H.E. Kluksdahl, G.S. McCoy and R.W. Davis, Proc. Div. Ref. Amer. Petr. Inst. 49 (1969) 504;
b) U.S. Pat. 3, 415, 737 (1968) 3, 537, 980 and 3, 617, 520 to H.E. Klusksdahl;
c) U.S. Pat. 2, 848, 377/3, 839, 194/3, 867, 280/3, 953, 368;
d) British Pat. 1, 364, 875;
e) Fr. Pat. 1, 567, 900;
f) Ger. Offen. 2, 006, 414/2, 1001, 740.
[2] B.N. Kuznetsov, Yu.I. Yermakov, J.P. Collmann and M. Boudart, J. Mol. Catal. 4 (1978) 49.
[3] M.S. Ioffe, B.N. Kuznetsov, Yu.A. Ryndin and Yu.I. Yermakov, *Proc. VIth Int. Congr. Catal.*, London, 1976.
[4] J.S. M'Boungou, L. Hilaire, G. Maire, F. Garin, Catal. Lett. (Part II) 10 (1991) 401.
[5] J.M. Dartigues, A. Chambellan, S. Corolleur, F.G. Gault, A. Renouprez, B. Moraweck, P. Bosch-Giral and G. Dalmai-Imelik, Nouv. J. Chim. 3 (1979) 591.
[6] J.L. Schmitt, Thesis, Strasbourg, 1980.
[7] G. Dalmai-Imelik, Ch. LeClercq and I. Mutin, J. de Microscopie 20 (1974) 123.
[8] F. Garin and G. Maire, Acc. Chem. Res. 22 (1989) 100.
[9] H. Zimmer, Z. Paál and P. Tetenyi, Acta Chimi. Acad. Sci. Hung. 111 (1982) 531.
[10] H. Zimmer, M. Dobrovlszky, P. Tetenyl and Z. Paál J. Phys. Chem. 90 (1986) 20.
[11] Z. Paál, Adv. Cat. 29 (1980) 273.
[12] A. Frennet, G. Lienard, A. Crucq, L. Degols, J. Catal. 53 (1978) 150.

[13] J.R. Regalbuto, C.W. Allen and E.E. Wolf, J. Catal. 108 (1987) 304.
[14] A. Frennet, A. Crucq, L. Degols and G. Lienard, Acta Chimi. Acad. Sci. Hung. 124 (1987) 1.
[15] J.S. M'Boungou, Thesis, Strasbourg, 1990.
[16] P. Biloen and G.T. Pott, J. Catal. 30 (1973) 169.
[17] F.E. Massoth, J. Catal. 30 (1973) 204.
[18] S. Alerasool and R.D. Gonzalez, J. Catal. 124 (1990) 204.
[19] E. Ruckenstein and B.J. Pulvermacher, J. Catal. 37 (1975) 416.
[20] F. Garin, G. Maire, S. Zyade, M. Zauwen, A. Frennet and P. Zielinski, J. Mol. Cat. 58 (1990) 185.
[21] R.B. Levy and M. Boudart, Science 181 (1973) 547.