THE INFLUENCE OF TIN ON THE ACTIVITY AND SELECTIVITY OF Sn-Pd/HY ZEOLITES, IN THE HYDROCRACKING AND HYDROISOMERIZATION OF n-HEPTANE

C. HENRIQUES[a], P. DUFRESNE[b], C. MARCILLY[b], F. RAMÔA RIBEIRO[a]
GRUPO DE ESTUDOS DE CATÁLISE HETEROGÉNEA, Instituto Superior Técnico, Av. Rovisco Pais, 1096 Lisboa Codex, PORTUGAL (a)
INSTITUT FRANÇAIS DU PÉTROLE, B.P.311, 92 506 Rueil-Malmaison Cédex, FRANCE (b)

ABSTRACT

The hydrocracking and hydroisomerization of n-heptane on Sn-Pd/HY zeolites have been studied, in order to understand the influence of tin on the activity and selectivity of these catalysts.

When the tin content increases, we observe a decrease of the global activity, and a change of the selectivity with a decrease of the molar ratios: isomerization/ /cracking and monobranched/dibranched products.

The influence of tin cannot be explained only by the poisoning of the palladium by tin. In fact, the presence of the second metal will probably induce the production of highly active hydrogen species, which diffuse towards the catalyst surface, by a spillover effect, getting in competition with the n-paraffins in the adsorption over palladium. In consequence, there is a change in the balance between the acidic and hydrogenating functions, with a decrease of the hydrogenating activity.

INTRODUCTION

The hydrocracking of different petroleum cuts, from light naphtas to atmospheric vacuum residue, to produce propane, butane, gasoline, jet fuels and diesel oils [1,2] uses bifunctional catalysts, some of them composed of a noble metal (palladium) on a acidic zeolite.

The hydroisomerization of n-alcanes to upgrade the octane number of the light gasoline fractions also use bifunctional catalysts.

The balance between the acidic and the metallic functions has a great influence on the selectivity and activity of the bifunctional catalysts [3,4].

In the last years, the use of bimetallic-acidic catalysts has had a growing interest, namely for the catalytic reforming [5,6]. Consequently, it is important the clarify the role of the second metal [7,8,9] in the behaviour of the bifunctional catalysts.

The purpose of this work is to study the influence of tin on the activity and

selectivity of Sn-Pd/HY zeolites, in the hydrocracking and hydroisomerization of n-
-heptane.

EXPERIMENTAL

Four tin-palladium HY zeolites were prepared (with different tin contents),
according to the following procedure:

- Preparation of the ammonium Y zeolite, by ion exchange of the NaY with
  ammonium nitrate solutions;
- Dilution of the NH_4Y in an alumina gel (50 wt.%), extrusion and calcination
  in wet air at $500^{\circ}C$ for 2 hrs;
- Introduction of palladium (Pd $(NH_3)_4^{2+}$), by using the technique of ion ex-
  change with competition [10] (the competing ion is NH_4^{+});
- Calcination in dry air at $500^{\circ}C$, for 2 hrs, and reduction with hydrogen 2 hrs,
  at $450^{\circ}C$;
- Introduction of tin, as described in reference [11].

The percentage loadings of tin and palladium on HY zeolite were determined by
X-ray fluorescence.

The metallic phase was characterized by electron probe microscopy and trans-
mission electron microscopy.

The n-heptane transformation was carried out in a fix-bed dynamic reactor, under
the following conditions: total pressure = 60 bar, molar ratio H_2/nC_7 = 6.2, tempera-
ture from 230 to $290^{\circ}C$.

The liquid condensates and the gaseous effluents were analyzed by GLC (100 m
squalane capillary column), with a flame-ionization detector.

RESULTS

Characterization of the metallic phase

The metal contents of the catalysts are presented in Table 1:

Table 1

Metal contents of catalysts

Catalyst	Pd (wt.%)	Sn (wt.%)	Sn/Pd (molar ratio)
Pd HY	0.45	-	-
Sn/Pd HY 0.5	0.45	0.25	0.5
Sn/Pd HY 0.8	0.45	0.38	0.8
Sn/Pd HY 2.2	0.45	1.12	2.2

The characterization of the metallic phase, by electron probe microscopy, ena-
ble us to conclude that tin remains on the external surface of the catalysts   and
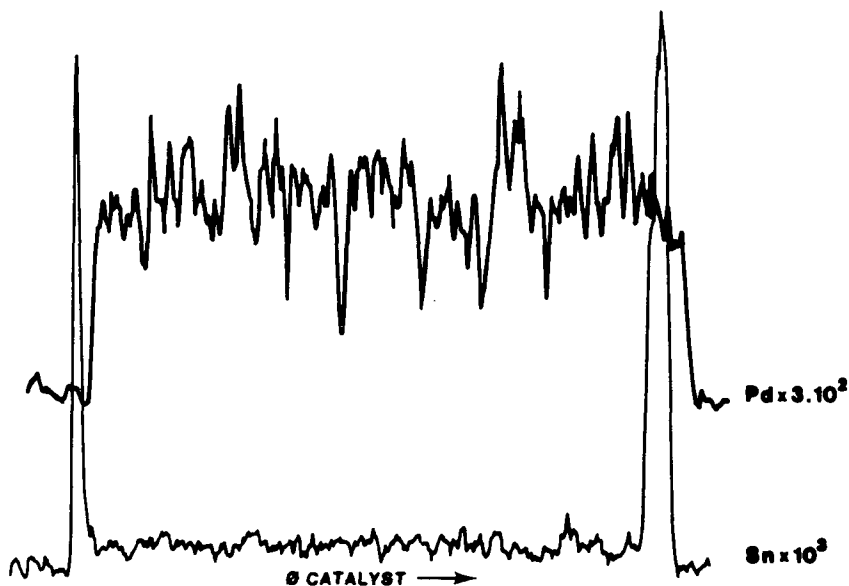palladium is well distributed. As shown in Figure 1, with Sn/Pd HY 0.5 tin   is locali

Fig. 1   Distribution of tin and palladium for Sn/Pd HY 0.5, by electron probe micros
        copy

zed on a thin external layer which represents about 20% of the total surface of the
carrier.

Calculated values from electron microscopy of palladium dispersion and average
particle size were ~ 30% and 14 A°.

Catalytic Results
(i) Effect of the tin content on the activity
Figure 2 shows, for each catalyst, the n-heptane conversion as a function of
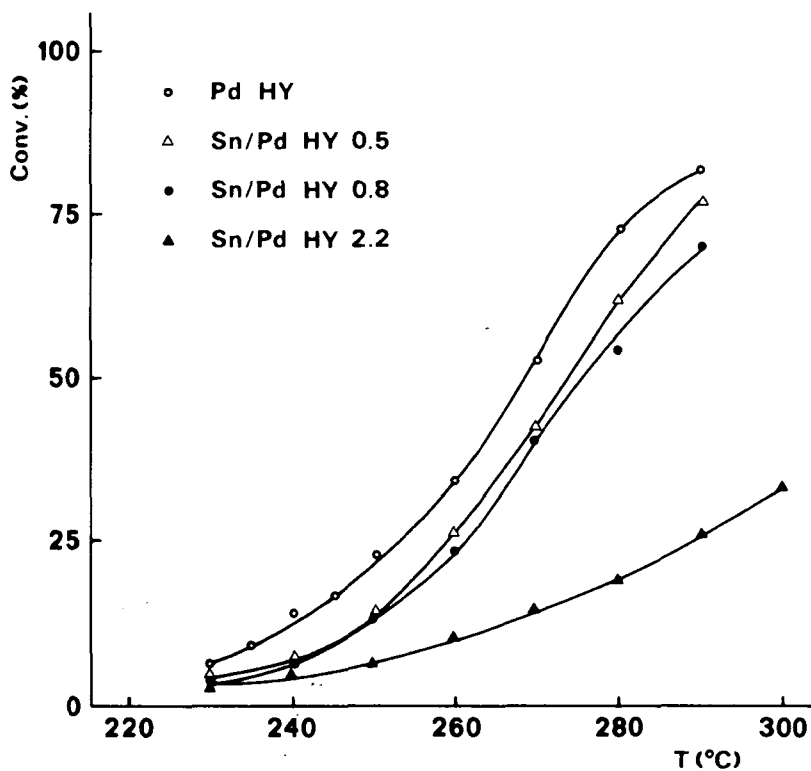the temperature.

Fig. 2 - n-heptane transformation on Sn/Pd HY zeolites: conversion against temperature

We can conclude that the monometallic catalyst is the most active, and the activity, decreases with the tin content.

(ii) Influcence of the tin content on the selectivity

In Figure 3, it is represented the molar product distribution, of the transformation of n-heptane at the same conversion (30%).
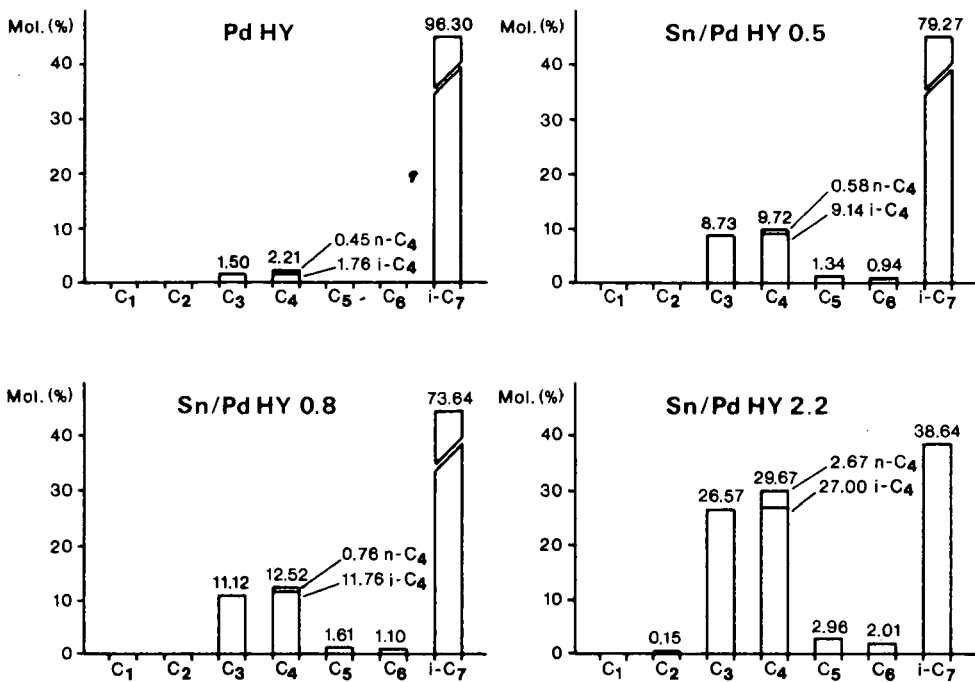
Fig. 3 Distribution of products produced by transformation of n-heptane on Sn/Pd HY
zeolites for the same conversion

We can conclude that, as tin content increases, the production of C_7 isomers decreases and that of cracked products increases. For all the catalysts, the main cracking products are butanes and propane in equimolar quantities with a very high isobutane/n-butane ratio. We observe an increase of C_5 and C_6 products without formation of C_1 and C_2, as tin content increases.

Figure 4 shows for each catalyst, the evolution of the molar ratio of the isomerization/cracking products (I/C) with the conversion. It can be remarked that in all the catalysts, there is a decrease of the I/C ratio, as the conversion increases by increasing the temperature. This decreasing is more pronounced for the lowest tin content.

For a given conversion, the I/C molar ratio decreases with the tin content.
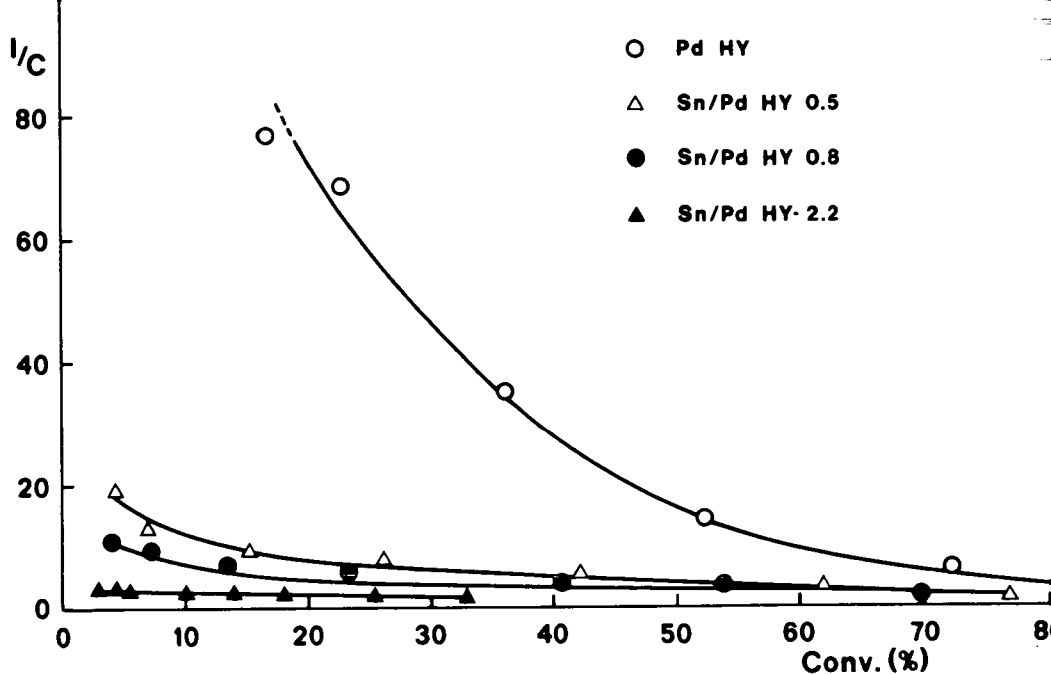
Fig. 4   Isomerization/cracking molar ratio against the conversion for the transfor-
mation of n-heptane on Sn/Pd HY zeolites

In respect of the distribution of the hydroisomerization products, Figure 5
shows the evolution of the molar ratio of the monobranched/dibranched isomers (M/D)
with the conversion. As the conversion increases, there is a decrease of the M/D
ratio, which is more pronounced for the lowest tin content. For a given conversion,
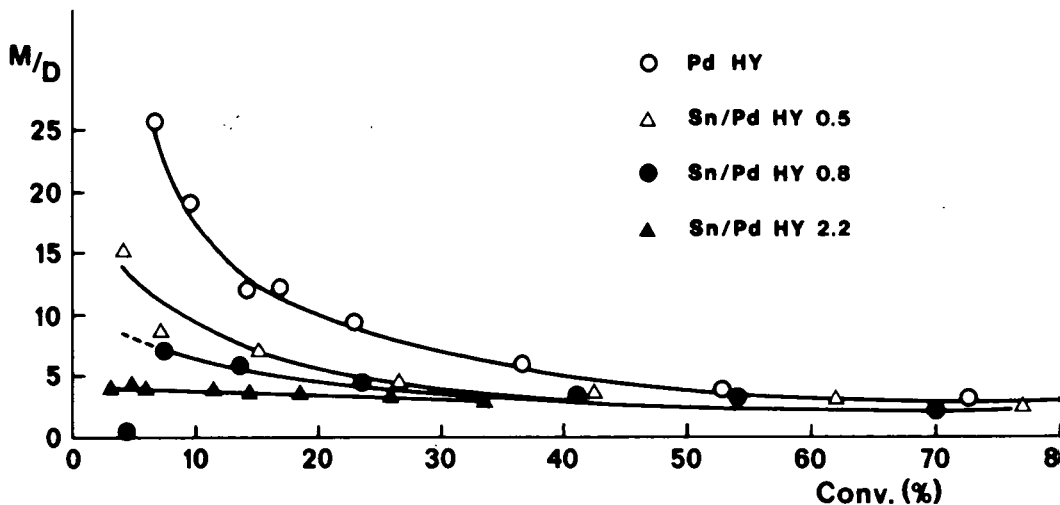the M/D ratio decreases as the tin content increases.

Fig. 5   Monobranched/dibranched isomers molar ratio against the conversion for the
transformation of n-heptane on Sn/Pd HY zeolites

In order to understand the influence of tin on the activity and selectivity of the bimetallic Sn/Pd HY zeolites, it is important to present the bifunctional mechanism [12,13] scheme for the hydroisomerization and hydrocracking of n-heptane, proposed by Guisnet [14].
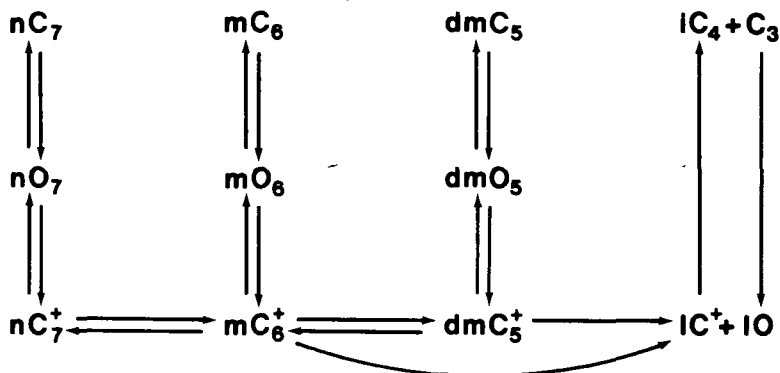
$$nC_7 \qquad mC_6 \qquad dmC_5 \qquad IC_4+C_3$$
$$nO_7 \qquad mO_6 \qquad dmO_5$$
$$nC_7^+ \rightleftharpoons mC_6^+ \rightleftharpoons dmC_5^+ \longrightarrow IC^+ + IO$$

Fig.6 Bifunctional transformation of n-heptane (n C_7);m C_6: methylhexanes;d m C_5: dimethylpentanes; C^+: carbocations; O: olefins; ℓ: light products

For high hydrogenating activity, the skeletal isomerization and the cracking of carbocations are, respectively, the rate limiting steps of the hydroisomerization and hydrocracking of n-alcanes [15,16].

For low hydrogenating activity, the dehydrogenation reactions limit the bifunctional process, and the n-heptane transformation rate is proportional to the metal surface area [16,17].

The evolution of I/C and M/D molar ratios, with the conversion

The decrease of the I/C molar ratio, as the conversion increases by increasing the temperature, can be explained by the fact that the activation energy of cracking reactions is higher than the activation energy of isomerization reactions. So, at higher temperatures, the cracking reactions become more important, and the molar ratio I/C decreases.

Moreover, as cracking products are obtained mainly from dibranched carbocations we must wait a similar behaviour for the evolution of I/C and M/D molar ratios as the conversion increases [18].

The evolution of the activity and selectivity of Pd/Sn HY zeolites with the tin content

The analysis of Figure 2, indicates that the activity of the catalysts, for the same temperature, decreases, as tin content increases. For the same conversion, the I/C and M/D molar ratios (Figures 4,5) also decrease as tin content increases.

The bifunctional mechanism described above, offers a good explanation for the change in the activity and selectivity with the tin content: the behaviour of the Sn/Pd HY zeolites can be explained by a change in the equilibrium of the hydrogenating-dehydrogenating/acidic functions, caused by a decrease of the strength of the

metallic function.

In fact, the decrease of the activity of the hydrogenating-dehydrogenating function, in a bifunctional catalyst, will give rise to the decrease of the formation of the intermediate olefins and carbocations and consequently to a decrease of the catalyst activity.

Moreover, we can also explain the decrease of the I/C and M/D molar ratios with the decrease of the hydrogenating-dehydrogenating function, in agreement with the mechanism of n-heptane transformation on bifunctional catalysts. In fact, with a higher hydrogenating activity the rate of carbocation formation will be greater than carbocation skeletal isomerization and/or carbocation cracking; so we will obtain more isomers products and they will be mainly monobranched products [14].

These modifications in the catalytic behaviour of the Sn/Pd HY zeolites, by the presence of tin, cannot be explained only by the poisoning of the palladium by tin. In fact, as referred above, only a small fraction of palladium is recovered by tin. So, we proposed that the presence of tin will induce the production of highly active hydrogen species, easily desorbed from tin and rapidly adsorbed on palladium particles, displacing the equilibrium (a) to the left:

$$\dot{H}_{M_2}$$
$$\Big\updownarrow \quad \text{fast} \qquad\qquad (a)$$
$$\dot{H}_{M_1} \rightleftharpoons \dot{H}_S \rightleftharpoons H_{2_G}$$
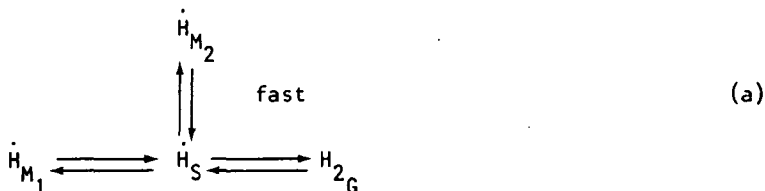
M_1 - Palladium; M_2 - Tin; S - Support; G - Gaz-phase; $\dot{H}$ - Adsorbed hydrogen species.

So, the concentration of H_{M_1} species will increase, favouring the displacement of the equilibrated reaction (b) to the left:

$$P_G + M_1 \rightleftharpoons \dot{O}_{M_1} + 2\,\dot{H}_{M_1} \qquad\qquad (b)$$

P_G - Paraffins in gaz-phase; O_{M_1} - Olefin adsorbed on Palladium.

Therefore, there will be a decrease of the hydrogenating-dehydrogenating function, induced by the presence of tin. As we have seen above, this explains not only the decrease of the activity of the Pd/Sn HY zeolites, with the tin content, but also the decrease of the I/C and M/D molar ratios: the occupation of an important number of palladium sites by active hydrogen species, will increase the relative acidity of the bifunctional catalysts.

So, there is a change in the rate limiting step of the bifunctional mechanism and the adsorption of the intermediate iso-olefins on the acidic sites will be favoured, with the consequent increase of the formation of dibranched carbocations and

their consecutive cracking.

This interpretation is also supported by the results of the product distribution in isoconversion conditions (Fig.3): the increasing of C_5 and C_6 products, with the tin content, without formation of C_1 and C_2, are in compliance with a mechanism where the hydrogenation of the intermediate iso-olefins has become the rate limiting step. There is an increase of the carbocations concentration, which can dimerise and, by consecutive cracking, can originate C_5 and C_6 products (without the production of C_1 and C_2).

CONCLUSION

The decrease of the activity and the change of selectivity for the Sn/Pd HY zeolites with the tin content, on the transformation of n-heptane can be explained by a change in the balance between the acidic and metallic functions.

The presence of tin will induce the production of highly active hydrogen species which diffuse towards the catalyst surface, by a spillover effect getting in competition with the n-paraffins in the adsorption over the palladium. In consequence, the hydrogenating-dehydrogenating rate of n-paraffins slows down, becoming the rate limiting step for the bifunctional mechanism.

REFERENCES

1. Marcilly, C., Franck, J.P., in "Catalysis by Zeolites", B.Imelik et al., Eds., Elsevier Sci. Pub. Co., Amsterdam (1980), pg. 93.
2. Jacobs, W.L., Thornton, D.P., Chem. Eng., 77, (25), 79 (1970).
3. Coonradt, M.L., Garwood, W.E., Ind. Eng. Chem., Proc. Res. Dev., 3, (1), 38 (1964).
4. Ribeiro, F., Marcilly, C., Guisnet, M., Proc. 9th Iberoam. Symp. Catalysis, Lisboa (1984), pg. 1237.
5. Rice, R.W., Kang Lu, J. Catal., 24, 367 (1972).
6. Sittig, M., Handbook of Catalysis Manufacture, Noyes Press Ed., Park Ridge N.Y. (1978), pg. 432.
7. Verbeek, H., Sachtler, W.M.H., J. Catal.. 42, 257 (1976).
8. Kuznetzov, B.N., Ermakov, Yu, I., Ryndin, Yu. A., Lorent, J., Duplyakin, V.K., Pentenero, A., Kinet. Katal., 22, (3), 1200 (1981).
9. Burch, R., Mitchell, A.J., Appl. Catal., 6, 121 (1983).
10. Ribeiro, F., Marcilly, C., Rev. Inst. Fr. Pétrole, 34, 405 (1979).
11. US PATENT 4,456,775 (June, 1984).
12. Mills, G.A., Heineman, H., Milliken, T.M., Oblad, A.G., Ind. Eng. Chem., 45, (1), 143 (1953).
13. Sinflet, J.M., Adv. Chem. Eng., 5, 37 (1964).
14. Giannetto, G., Perot, G., Guisnet, M., CNRS International Symposium, Catalysis by Acids and Bases, Sept. 1984, in press.

15. Weisz, P.B., Adv. Catal., $\underline{13}$, 137 (1962).
16. Guisnet, M., Perot, M., in "Zeolites Science and Technology", F. Ramõa Ribeiro et al., Eds., Martinus Nijhoff Publishers, The Hague (1984), pg. 397.
17. Ribeiro, F., Marcilly, C., Guisnet, M., J. Catalysis, 78, 267 (1982).
18. Giannetto, G., Perot, G., Guisnet, M., Proc. 9th Iberoam. Symp. Catalysis, Lisboa (1984), pg. 1661.