

Catalytic influence of bimetallic phases for the synthesis of single-walled carbon nanotubes

V. Brotons, B. Coq^{*}, J.M. Planeix¹

Laboratoire de Matériaux Catalytiques et Catalyse Organique, URA 418 du CNRS, ENSCM, 8 rue de l'Ecole Normale, 34053 Montpellier Cedex, France

Received 29 April 1996; revised 31 May 1996; accepted 9 June 1996

Abstract

Bimetallic systems of Co with Sn, Pd, Ru, Fe, Ni, W and Pt were studied for the metal-mediated synthesis of single-walled carbon nanotubes (SWT), and compared with Co alone. The materials were characterized by TEM, XRD and H₂ chemisorption. Sn, Ru, Fe and Pd decrease the catalytic effect of Co, whereas W or Ni have little effect on Co. By contrast, a synergy exists between Co and Pt for the SWT formation. The highest SWT yield was obtained with Co/Pt = 3/1 (at/at), but the selective catalytic phase is actually the definite CoPt compound identified by XRD. After activation at 673 K under hydrogen, 1/3 to 1/2 of the bimetallic surface becomes accessible for hydrogen. The CoPt(3/1)/SWT composite is active and selective for the liquid-phase hydrogenation of cinnamaldehyde to cinnamyl alcohol.

Keywords: Bimetallics; Cobalt; Nanotubes; Cinnamaldehyde hydrogenation; Cinnamyl alcohol

1. Introduction

Multi-walled carbon nanotubes since their discovery [1] and large scale synthesis [2], have given rise to numerous basic and applied researches. Among the theoretical predictions, those promising original electronic properties are particularly interesting [3–5], which claim that depending on the layers' number and diameter, the electronic structure could look like that of metal, narrow gap semiconductor or semi-

conductor. Moreover, it was recently shown that good selectivity for single-walled carbon nanotubes (SWT) can be obtained by introducing various metals within one graphite electrode [6–13]. In particular, cobalt was claimed to give the best results, pure [7] or associated with Ni [9] or Pt [11]. Moreover, it should be pointed out that PtCo is a commercial catalyst claimed to be active for the catalytic chemical vapor deposition (CCVD) carbon fibre production [14]. On the other hand, in the field of heterogeneous catalysis, carbon materials have been widely used to disperse and stabilize metallic particles of nanometric size [15]. Catalytic properties of these solids are known to be dependent upon the metal–carbon interaction. One might hope that

^{*} Corresponding author. Fax: +33-67144349. E-mail: coq@cit.enscm.fr.

¹ Present address: Laboratoire de Chimie Organique de Coordination, Université Louis Pasteur, 4 bd Blaise Pascal, 67000 Strasbourg, France.

with the nanotubes, the metal–carbon interaction will be different, as suggested by a first study about the catalytic behavior of Ru/carbon-nanotubes for the hydrogenation of cinnamaldehyde [16].

Due to the importance of alloy effects in heterogeneous catalysis and considering the key role of Co in the single-shell carbon nanotubes synthesis, the aim of this study was to investigate the effect of associating Co with Sn, Pd, Ru, Fe, Ni, W and Pt in the carbon nanotubes synthesis; special attention was paid to the bimetallic PtCo couple. The properties of a PtCo/SWT composite were evaluated for the hydrogenation of cinnamaldehyde.

2. Experimental

The synthesis of carbon nanotubes was carried out according to the general procedure described by Ebbesen and Ajayan [2], using a horizontal vessel and composite anodes in a stainless steel chamber under a 500 kPa static pressure of helium. The cathode was a pure graphite rod 16 mm in diameter and 5 cm in length. The anode, 6 mm diameter and 20 cm length, was drilled to obtain a 3.5 mm diameter and 14 cm length core cylindrical cavity. The bore was filled with a metal/graphite powder mixture in order to have a total metal percentage of 10%. The composite anodes were then vaporized in an arc-discharge with a 100 A current and a voltage of 27–29 V. In their macroscopic form, the synthesized carbon materials are soot, deposit and sometimes webs. These collected materials were characterized by elemental analysis, transmission electron microscopy (TEM), X-ray diffraction (XRD) and hydrogen chemisorption. For TEM, a drop of sonicated solution of solid in ethanol was put on carbon films supported on copper grids and examinations were performed using a JEOL 200CX TEM micrograph with accelerating voltage of 100 keV. XRD patterns were obtained

with a Philips theta 60 automated powder diffractometer using Cu K α radiation. Hydrogen chemisorption was carried out in a static volumetric apparatus. After activation of the solid at 673 K under H₂ overnight, the sample was evacuated under 10⁻⁴ Pa at the same temperature. The adsorption isotherm was then determined at room temperature in the 0–3.3 kPa pressure range. The hydrogen uptake at monolayer of the metal particle was calculated by extrapolation to zero pressure. Considering a stoichiometry of unity for hydrogen adsorption, the metal dispersion is given by $D = H/Me$ ($Me = Pt, Co$).

The experimental procedure to carry out hydrogenation of cinnamaldehyde has been described in detail previously [17]. In short, the reaction was carried out in a 100 cm³ batch reactor. The pre-reduced PtCo/SWT sample (0.26 g) was reactivated in-situ in *i*-propanol (40 cm³) at 383 K and under 4.5 MPa H₂ pressure for 2 h. After cooling to room temperature, the cinnamaldehyde was charged and the reaction started at 383 K under 4.5 MPa H₂ pressure with a reactant concentration of 7.9×10^{-4} mol cm⁻³. Micro-samples were withdrawn and analyzed on a gas chromatograph (Varian 3300 equipped with FID detector) using a DB wax capillary column (30 m \times 0.32 mm i.d.). The calibration was done by using synthetic mixtures of pure components.

3. Results and discussion

High SWT yields are associated with the existence in the reactor of rubbery soots and particularly with ‘spider webs’ joining the chamber walls. In our syntheses, those which did not lead to monotubes or few, always gave crumbly soot. We noted that the crumbly soot on the lower part of the reactor is formed in a very small quantity and that it is more fibrous than the soot in the upper part. In several systems, the metal contents are higher in the soot

than in the fibres, but the differences are particularly important between the soot and the deposit core.

In the absence of any method which gives a bulk quantification of the single-walled nanotubes content, it is not obvious to compare our carbon materials with previous reported studies. Taking as an example the sample prepared with pure cobalt, the soot contains SWT materials but it seems that with our experimental set up, the SWT yield is lower than that reported by Bethune et al. [7] for a similar preparation. Notwithstanding these reserves, we have classified our samples on a comparative basis according to TEM examinations. We used XRD patterns in order to identify the metallic phase formed during the synthesis. Table 1 summarizes the main characteristics of the materials and the SWT contents.

When Co is associated with Sn, Ru or Pd, there is no formation of SWT. XRD shows that for these three associations, unknown metallic phases have been formed. In these cases the presence of a second metal inhibits the catalytic effect of Co.

The composite anode of Co with W and Ni respectively, led to monotubes containing soots and few webs, with a comparable yield as with pure Co. The XRD pattern of the soot obtained with the Co/W system shows the (111) peak of fcc Co, but no peak of W. Instead, the patterns of the deposit core powder show that the Co_3W compound is formed during the process. This is in agreement with the elemental analysis data: 8% Co and less than 1% W in the soot, 3% W and 3.5% Co in the deposit. The identification of the metallic phases formed with the Co/Ni association is difficult due to the very close diffraction peaks of Co, Ni, and CoNi_3 phases. With these bimetallic systems, we can conclude that the presence of a second metal does not really improve the catalytic role of cobalt.

The CoPt bimetallic couple gives by far the most interesting results. When the CoPt ratio is varied from 9/1 to 1/3 (at/at), the composition which gives the highest SWT yield is

Co/Pt = 3/1 (Fig. 1). In the soots and webs prepared from Co/Pt = 1/1 and 9/1, the SWT yield is slightly higher than in the material prepared with pure Co. By contrast, a Co/Pt 1/3 ratio gives only fibrous soot, no webs and SWT are very scarce. In the webs obtained from the Co/Pt 3/1 mixture, the (101), (110) and (111) reflections of tetragonal CoPt and the (111) reflection of fcc Co appeared. On the other hand, the CoPt alloy is not formed with Co/Pt = 1/1 and 9/1 containing anodes. The soots we found in the reactor with these molar ratios give the (111) reflection of both hcp and fcc Co. When we covaporized the Co/Pt:1/3 mixture, the (111), (200), (220) and (311) reflections of the CoPt_3 compound were found but no peak of single Co.

It appears clearly that the highest SWT yield corresponds to the occurrence of the CoPt compound in the carbon materials. When platinum and cobalt do not form this alloy and remain separated, the cobalt effect is only slightly enhanced by platinum. When they form the CoPt_3 alloy the catalytic effect of Co for SWT formation is suppressed.

The role of metal during the SWT formation is still obscure and remains controversial. Lin et al. [8] proposed that the metal (Cu) modifies the temperature gradient during the arc-discharge and prevents the formation of multilayers buckytubes. By contrast, other authors privilege a catalytic role of the metals in the SWT growth [6,7,9,10]. From our results, we could put forward some hypotheses about the metal action. It is very likely that Co and Pt are atomically dispersed and not associated during the vaporization process in the plasma. In the less hot region of the plasma, the aggregation between Pt and Co atoms can start and the synergistic bimetallic effect can operate. It should be mentioned that SWT are collected in the relatively cold region of the reacting chamber. Thereupon, we privilege a catalytic role of the metals, which will act not at the atomic level where both metals are separated ('homogeneous catalysis'), but at the cluster level where they are associated

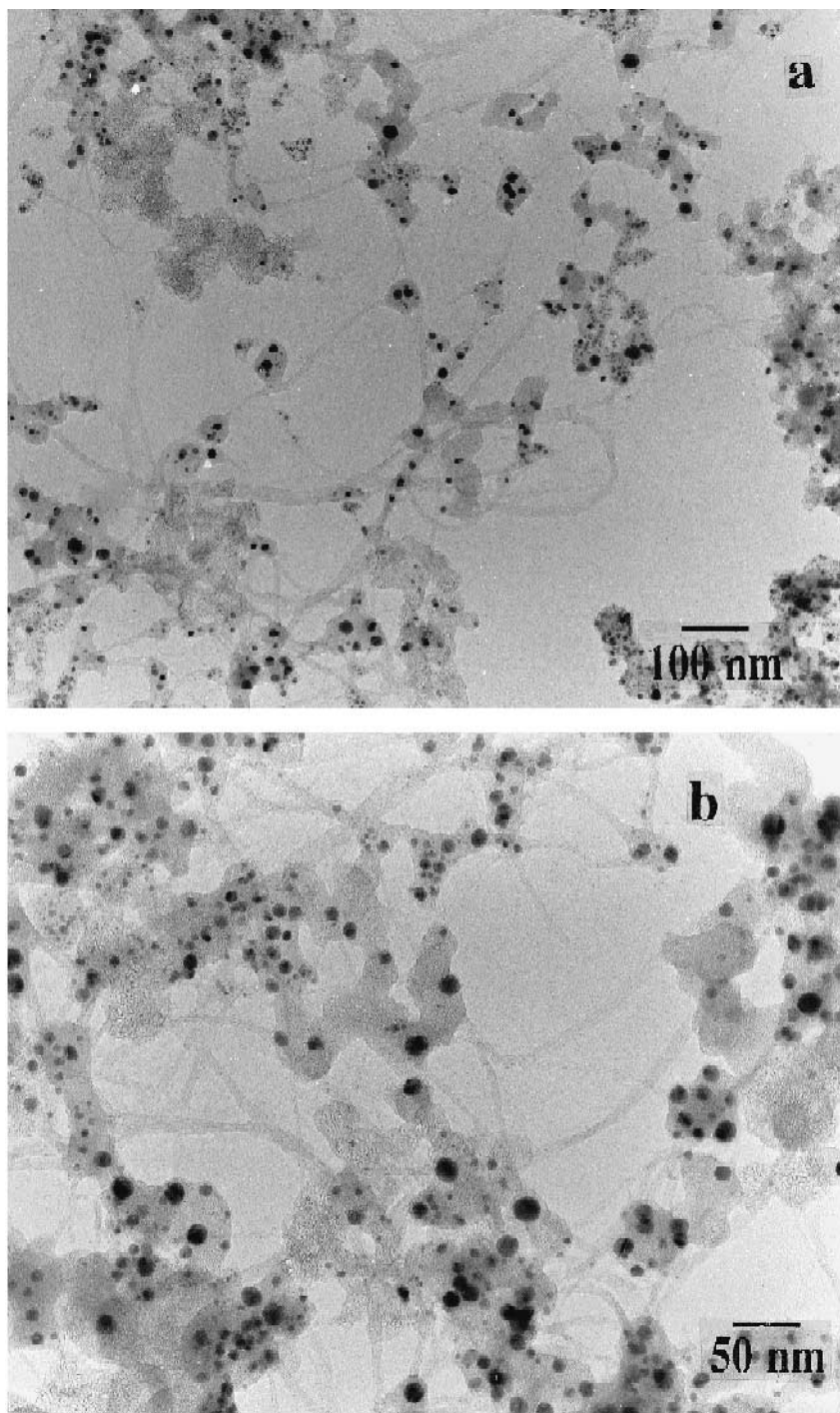


Fig. 1. Transmission electron micrographs, at different magnifications, of the rubbery soots synthesized with the bimetallic powder Co/Pt (3/1, at/at).

(‘heterogeneous catalysis’). It can be pointed out that with the PtCo bimetallic system, the size of the metallic particles ranged from 2 to 20 nm, that is in good agreement with findings of Bethune et al. [7] for the synthesis with pure Co.

Now a second question could be asked about the reactivity of the metal particles with respect to their sizes. It is well known in catalysis by metals that the size of particles affects the reactivity of breaking and formation of C–C bonds [18]. Two hypotheses can be then formulated:

(1) Small metal particles ($\approx 1\text{--}3$ nm) are the most active. The formation rate of SWT goes through a maximum upon coalescence of particles, then decreases with the appearance of large clusters. A similar model was suggested by Kiang et al. [10], where SWT tubules nucleate and grow very rapidly, in a region of high carbon density, on the small metallic particles as soon as they reach a critical size. Lower fullerenes ($C_{60}\text{--}C_{100}$) are formed concurrently in the plasma through a non-catalytic parallel pathway [7]. When the metallic surface becomes less reactive, these fullerenes adsorb on their surface and on some part of formed SWT.

Thereby, the SWT synthesis process becomes strongly inhibited. However, it should be pointed out that some parts of the metal particles remain free since hydrogen adsorption can occur (Table 1). By applying the empirical relationship between diameter of particle and metal dispersion, $d_p \approx 1/D$ (d_p in nm) it seems that 1/2 to 1/3 of the metal surface remains accessible.

(2) Large metal particles are the most active. Thereby, fullerenes, which are formed from the beginning of the synthesis, accumulated till the appearance of large metal clusters. During this induction period, the fullerene soot can agglomerate around the small metal clusters, slowing down the coalescence process and the particle growth. Such a behavior would not favor the SWT formation.

At present, we would be inclined to privilege the first hypothesis. The promoting role of Pt will be then (i) either to slow down the growth of metal particles, (ii) or to modify the electronic properties of Co in the CoPt compound. The importance of electronic effects in ‘metal-assisted’ synthesis of nanotubes has indeed been pointed out recently [19]. However, by studying the CO adsorption on supported PtCo catalysts

Table 1
Main characteristics of the collected carbon materials

Metal composition in the synthesis medium	Collected carbon materials		Metallic phases in the collected carbon materials					
	aspect	SWT content *	metal content (wt%)	phases (DRX)	H ₂ uptake		metal particle size (nm)	
					H/(Pt + Co)	TEM	XRD	
Co/Sn (2/1)	crumbly soot	0	Co(7.8)/Sn(8.2)	—	—	—	9	15
Co/Ru	crumbly soot	0	Co(0.2%)/Ru(0.4%)	—	—	—	—	—
Co/Pd (2/1)	crumbly soot	0	Co(8.39)/Pd(7.62)	—	—	—	—	—
Co/Ni (1/3)	crumbly soot	++	Co(4.1)/Ni(11.6)	Co + Ni	—	—	—	—
Co/W (3/1)	crumbly soot	++	Co(8.05)/W(0.9)	Co	—	—	8	—
Pd	crumbly soot	0	—	Pd	—	—	—	—
Ni	crumbly soot	0	Ni(15.9)	Ni	—	—	—	—
Fe	crumbly soot	0	—	Fe	—	—	—	—
Co	rubbery soot	++	Co(9.9)	Co	—	—	8	—
Co/Pt (9/1)	rubbery soot	+++	Co(18.3)/Pt(1.8)	Co	—	—	7	—
Co/Pt (3/1)	rubbery soot	+++	Co(6.9)/Pt(5.4)	CoPt	0.05	—	8	20
Co/Pt (1/1)	rubbery soot	+++	Co(3.4)/Pt(10.3)	Co	—	—	9	—
Co/Pt (3/1) 1%	rubbery soot	+++	Co(1.5)/Pt(1.2)	—	0.09	—	—	—
Co/Pt (1/3)	crumbly soot	≈ 0	Co(1.7)/Pt(2.8)	CoPt ₃	0.09	—	10	9
Pt	crumbly soot	0	Pt(3.6)	Pt	—	—	7	14

* According to the TEM observations.

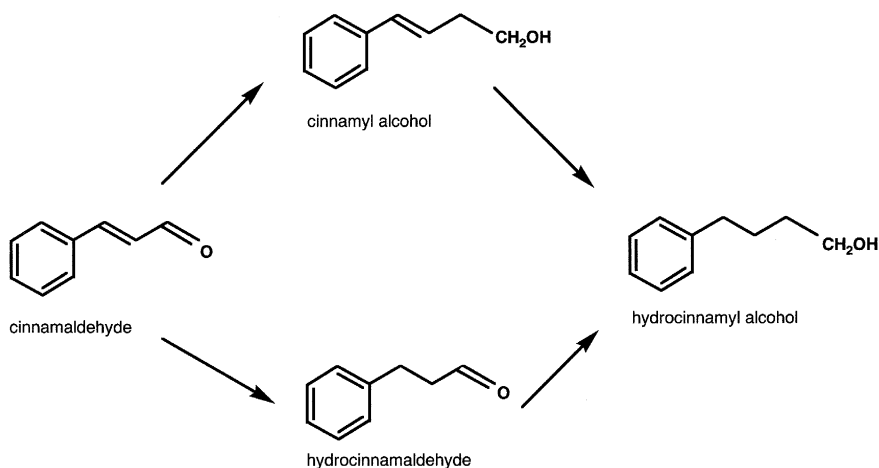


Fig. 2. Scheme of cinnamaldehyde hydrogenation.

by infra-red spectroscopy, Dees et al. [20] concluded that the effect of the added metal can be mainly regarded as a geometric effect (dilution of the Co or Pt layers) without any clear electronic modification of both metals.

On the other hand, a speculative mechanism of SWT growth from metal particles can tentatively be suggested. SWT will be formed starting from lower fullerenes (C_{60} – C_{100}) adsorbed on the bimetallic particles, which will suffer sequences of breaking/formation of C–C bonds, Co being known to favor these processes in alkane hydrogenolysis and Fischer–Tropsch synthesis [21]. Fullerenes, which appeared at the beginning of the arc-discharge synthesis, would thus play the role of a parent phase.

The catalytic properties of one of these new materials, the CoPt(3/1)/SWT sample, were evaluated for the liquid-phase hydrogenation of cinnamaldehyde. Hydrogenation of cinnamaldehyde occurs through the classical pathway illustrated in Fig. 2. Fig. 3 shows the product selectivity as a function of cinnamaldehyde conversion. A high selectivity (80–85 mol%) in cinnamyl alcohol was obtained. Moreover, the initial cinnamyl alcohol selectivity close to 100%, not reported in the case of PtCo/charcoal [22], might indicate that some specific influence of SWT on the properties of PtCo for cinnamaldehyde hydrogenation is occurring. However, this

influence is very likely small since the cinnamyl alcohol selectivity obtained at higher conversion is very close to that reported by Fouilloux [22] on a PtCo/charcoal with similar Co/Pt atomic ratio.

In conclusion, when powdered Co is associated with other metals for the synthesis of SWT, a synergistic effect is only occurring for the PtCo association. The optimal Co/Pt atomic ratio is 3 which yields the higher SWT amount. High SWT yields are always associated with the

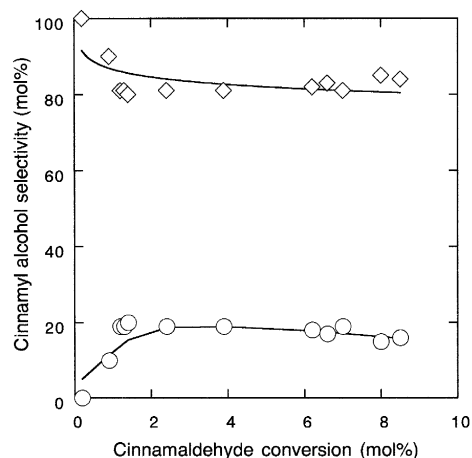


Fig. 3. Selectivity to cinnamyl alcohol (◇) and hydrocinnamaldehyde (○) for the hydrogenation of cinnamaldehyde over a CoPt(3/1)/SWT catalyst as a function of cinnamaldehyde conversion. $T_R = 383$ K, $C_{\text{cinnamaldehyde}} = 7.9 \times 10^{-4}$ mol cm^{-3} , $P_{\text{hydrogen}} = 4.5$ MPa, catalyst weight = 0.26 g.

occurrence of the CoPt crystallographic phase. After hydrogen treatment at 673 K, 1/3 to 1/2 of the bimetallic surface is accessible and active for the hydrogenation of cinnamaldehyde.

Acknowledgements

The authors thank P. Bernier and the G.D.P.C. for the synthesis apparatus and his contribution to the discussion, and the CNRS for supporting this work under the ULTIMATECH Programme (Grant No. 94N89/0067).

References

- [1] S. Iijima, *Nature* 354 (1991) 56.
- [2] T.W. Ebbesen and P.M. Ajayan, *Nature* 358 (1992) 220.
- [3] J.W. Mintmire, B.I. Dunlap and C.T. White, *Phys. Rev. Lett.* 68 (1992) 631.
- [4] N. Hamada, S. Sawada and A. Oshiyama, *Phys. Rev. Lett.* 68 (1992) 1579.
- [5] R. Saito, M. Fujita, G. Dresselhaus and M.S. Dresselhaus, *Phys. Rev. B* 46 (1992) 1804.
- [6] S. Iijima and T. Ichihashi, *Nature* 363 (1993) 604.
- [7] D.S. Bethune, C.H. Klang, M.S. De Vries, G. Gorman, R. Savoy, J. Vasquez and R. Beyers, *Nature* 363 (1993) 605.
- [8] X. Lin, X.K. Wang, V.P. Dravid, R.P.H. Chang and J.B. Ketterson, *Appl. Phys. Lett.* 64 (1994) 181.
- [9] S. Seraphin and D. Zhou, *Appl. Phys. Lett.* 64(16) (1994) 2087.
- [10] C.H. Kiang, W.A. Goddard, R. Beyers and D. Bethune, *Carbon* 33 (1995) 903.
- [11] J.M. Lambert, P.M. Ajayan, P. Bernier, J.M. Planeix, V. Brotons, B. Coq and J. Castaing, *Chem. Phys. Lett.* 226 (1994) 364.
- [12] P.M. Ajayan, J.M. Lambert, P. Bernier, L. Barbedette, C. Colliex and J.M. Planeix, *Chem. Phys. Lett.* 215 (1993) 509.
- [13] S. Seraphin, *J. Electrochem. Soc.* 142 (1995) 290.
- [14] M.S. Dresselhaus, G. Dresselhaus, K. Sugihara, I.L. Spain and H.A. Goldberg, in: *Graphite Fibers and Filaments*, M. Cardona (Ed.) (Springer, Berlin, 1988) p. 18.
- [15] P.N. Rylander, *Catalytic Hydrogenation in Organic Synthesis* (Academic Press, New York, London, 1979).
- [16] J.M. Planeix, N. Coustel, B. Coq, V. Brotons, P.S. Kumbhar, R. Dutartre, P. Geneste, P. Bernier and P.M. Ajayan, *J. Am. Chem. Soc.* 116 (1994) 7935.
- [17] B. Coq, P.S. Kumbhar, C. Moreau, P. Moreau and M.G. Warawdekar, *J. Mol. Catal.* 85 (1993) 215.
- [18] M. Che and C. Bennett, *Advances in Catalysis*, Vol. 36 (Academic Press, London and New York, 1989) p. 55.
- [19] C. Guerret-Piecourt, Y. Le Bouar, A. Loiseau and H. Pascard, *Nature* 372 (1994) 761.
- [20] M.J. Dees, T. Shido, Y. Ywasawa and V. Ponec, *J. Catal.* 124 (1990) 530.
- [21] F.G. Gault, *Advances in Catalysis*, Vol. 30 (Academic Press, London and New York, 1981) p. 1.
- [22] P. Fouilloux, in: *Heterogeneous Catalysis and Fine Chemicals*, M. Guisnet, J. Barrault, C. Bouchoule, D. Duprez, C. Montassier and G. Pérot (Eds.) (Elsevier, Amsterdam, 1988) p. 123.