Available online at www.sciencedirect.com

SCIENCE DIRECT®

Catalysis Today 89 (2004) 177–182

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Application of a dihydrogen afterglow to the preparation of zeolite-supported metallic nanoparticles

J.-C. Legrand*, A.-M. Diamy, G. Riahi, Z. Randriamanantenasoa,
M. Polisset-Thfoin, J. Fraissard

Laboratoire SIEN (équipe Chimie des Surfaces), CNRS UMR 7142, Université Pierre-et-Marie-Curie (Paris VI),
Case 196, 4 place Jussieu, 75252 Paris Cedex 05, France

Abstract

The afterglow of a microwave plasma (2.45 GHz) of dihydrogen is used for the preparation of zeolite-supported gold-based metallic catalysts. It contains hydrogen atoms at a sufficiently low temperature for the formation of nanoparticles, whereas the conventional reduction of gold at high temperature often leads to large particles.

The study concerns the search for optimal conditions for the preparation of monometallic (Au or Pt) and bimetallic (Pt–Au) catalysts. The following experimental conditions are examined: position of the sample in the afterglow, exposure time, gas pressure, composition of the sample for bimetallics, type of zeolite (NaY or HY).

Direct images of supported metal particles are obtained by transmission electron microscopy (TEM). The sizes and dispersion of the particles are determined from TEM photographs (mean diameter d_m, volumic diameter d_v and dispersion D). The dispersion of platinum atoms is also determined by dihydrogen chemisorption. The particles obtained are less than 5 nm in size, and are stable to thermal treatment.

Keywords: Dihydrogen; Afterglow; Zeolite

1. Introduction

Metallic catalysts are widely used in industry but they are also much studied in research laboratories. The main industrial applications include hydrogenation of oils, petroleum refining to obtain petrol with high octane rating, oxidation, hydrocarbon isomerisation, and processing of vehicle exhaust gases to decrease environmental pollution. These catalysts are efficient when the metal is in the form of very small particles with a high degree of dispersion.

It was found that supported gold can be very selective: this metal can catalyse dioxygen transfer, for example, in the oxidation of pentanol to pentanal by NO_2 [1], dihydrogen transfer, as in the hydrogenation of pentene to pentane [2], as well as isomerisation [3]. The fact that its activity is lower than that of group VIII metals can be explained by the absence of unpaired d electrons in its electronic structure ([Xe] $4f^{14}5d^{10}6s^1$) which prevents it chemisorbing dihydrogen or dioxygen at ambient temperature. A very interesting application of gold in heterogeneous catalysis is its association with group VIII metals, notably platinum [4,5] and palladium [6,7]. Gold is introduced either to increase the dispersion of the more active metal, or increase the turnover number, selectivity or stability [5,8].

However, gold tends to sinter easily and in catalyst preparation conventional reduction of gold in molecular dihydrogen at high temperature very often leads to large particles, especially with zeolites as support [9]; these particles are not active catalysts. A certain number of studies were carried out on the preparation of gold-based catalysts supported on zeolites [10,11] and several patents have been taken out [12–14].

Several recent studies deal with catalyst preparation by means of different kinds of plasmas [15–19], with catalyst activation or catalytic reactions using microwaves [20–24].

In a previous study [25], we explored the possibility of a mild reduction to obtain nanoparticles of pure gold, pure palladium and mixed Au/Pd supported on zeolites. The method consists in using the afterglow of a dihydrogen microwave plasma (2450 MHz) which contains active species (mainly atomic hydrogen) and which makes it possible to work at a kinetic temperature low enough to avoid the formation of

---

* Corresponding author.
E-mail address: jcl@ccr.jussieu.fr (J.-C. Legrand).

0920-5861/$ – see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2003.11.024

large particles. Dihydrogen is dissociated in the plasma to the extent of several tens of percent depending on experimental conditions (pressure, gas flowrate, microwave power, etc.). Since hydrogen atoms have low homogeneous [26] and heterogeneous [27] recombination rates:

$$\mathrm{H} + \mathrm{H} + \mathrm{H_2} = 2\mathrm{H_2},$$
$$k = 2.7 \times 10^{-31} \times T^{-0.6}\,\mathrm{cm^6\,molecule^{-2}\,s^{-1}}$$

$$\mathrm{H} + \text{silica} = 0.5\mathrm{H_2},$$
$$\gamma(300\,\mathrm{K}) \approx 10^{-5}\ \text{up to}\ \gamma(1000\,\mathrm{K}) \approx 10^{-3}$$

they remain in the afterglow well beyond the plasma in our experimental conditions. In the afterglow the gas temperature decreases quickly after the plasma, so downstream the plasma there is a reducing medium at low temperature. This medium seems quite suitable for gold reduction.

To develop this original reduction procedure, previous results for the elaboration of gold, palladium and platinum particles were taken into consideration. For example, in chemical reductions it was noted that palladium is more easily reduced when its ions are totally decomplexed by calcination at 300 °C in pure dioxygen [28]. On the other hand, it is impossible to decomplex gold without it being reduced by the ligands, even in a strong current of dioxygen; this autoreduction phenomenon leads to the formation of large particles which migrate out of the zeolite lattice [9]. It is therefore necessary to compromise when the two metals have to coexist in the same sample.

The method developed for gold and palladium was applied to platinum and mixed Pt–Au particles. The influence of the following experimental conditions was studied: sample position in the afterglow, exposure time in the afterglow, H_2 pressure, bimetallic sample composition and support type (NaY or HY zeolite).

Direct images of supported metal particles were obtained by transmission electron microscopy (TEM), carried out with a Jeol JEM 100 CXII apparatus (resolution 0.3 nm and spherical aberration factor 0.7 nm). From these pictures, the size (mean diameter d_m and volumic diameter d_v) and dispersion D of the metallic clusters were obtained.

2. Experimental

2.1. Sample preparation

The support is a synthetic faujasite type Y zeolite ($Na_{52}[(AlO_2)_{52}(SiO_2)_{140}]\cdot 156H_2O$ where $Si/Al = 2.7$) supplied by UOP. Several samples were also prepared using an acidified zeolite as the support (75% of Na^+ ions being replaced by H^+). In what follows the non-acidified zeolite is referred to as NaY and the acidified one as HY.

Metals are introduced into the zeolite by means of cation exchange using metallic complexes. Gold ethylenediamine is introduced onto the support by using the cation $Au(EN)_2{}^{3+}$ where EN is ethylenediamine ($H_2N{-}CH_2{-}CH_2{-}NH_2$), whose synthesis is described by Block and Bailar [29]. Platinum is introduced by means of $Pt(NH_3)_4{}^{2+}$ complexes. The reactions to obtain metallic precursors are schematically represented as follows:

$$2\mathrm{Na}^+_{\mathrm{(zeolite)}} + [\mathrm{Pt(NH_3)_4}]^{2+}_{\mathrm{aq.}} \overset{24\,\mathrm{h},80\,^\circ\mathrm{C}}{\rightleftarrows} 2\mathrm{Na}^+_{\mathrm{aq.}} + [\mathrm{Pt(NH_3)_4}]^{2+}_{\mathrm{(zeolite)}}$$

$$3\mathrm{Na}^+_{\mathrm{(zeolite)}} + [\mathrm{Au(EN)_2}]^{3+}_{\mathrm{aq.}} \overset{24\,\mathrm{h},60\,^\circ\mathrm{C}}{\rightleftarrows} 3\mathrm{Na}^+_{\mathrm{aq.}} + [\mathrm{Au(EN)_2}]^{3+}_{\mathrm{(zeolite)}}$$

For platinum, exchange is followed by calcination under strong dioxygen flow (6 l/h) at 300 °C for several hours. This step allows elimination of the ligand from the cation without causing reduction. Calcination is a crucial step for metallic particle formation: cations without ligands are small enough to migrate partly into the small cages where they are better coordinated [30]. In the case of gold, calcination is not carried out because beyond 60 °C there is formation of large particles which migrate out of the pores.

Bimetallic precursors are elaborated in successive exchanges, first platinum then gold. After filtration under vacuum, the powder is dried and the precursors can be reduced. To assess the suitability of the method, elementary analysis was performed on some samples; results show that cation exchange is complete.

Metallic catalysts are then obtained by reduction under a flowing dihydrogen afterglow as explained below.

The monometallic samples contain about 1% (w/w) of gold and 3% (w/w) of platinum. For the bimetallic samples, different proportions of gold are added to 3% (w/w) of platinum (Pt–Au: 70–30, 60–40, 40–60 and 20–80).

2.2. Sample reduction

Reduction in the afterglow is shown schematically in Fig. 1. The discharge is produced inside a 10 mm inner diameter fused silica tube. Microwave power (2.45 GHz, 0–1500 W) is transmitted to the flowing dihydrogen by means of a cylindrical cavity connected to a microwave generator. Incident (Π_i) and reflected (Π_r) powers are measured by a powermeter (HP 432 A) connected to thermistors (HP 478 A). Energy losses in the line are assumed to be negligible, so the energy absorbed by the gas is $\Pi = \Pi_i - \Pi_r$. The gas pressure, P, and the gas flowrate, F, are measured by means of a baratron gauge (MKS 122A) and a mass flowmeter (Alfagaz RDM 280), respectively. Research grade dihydrogen (99.995% minimum) is purchased from Air Liquide.

The sample is placed in a silica nacelle which slides inside the reactor in the afterglow zone, and can be positioned at different distances, z, from the plasma. The reduction time τ_r and absorbed microwave power, Π, are also varied, so that the reduction conditions can be changed.

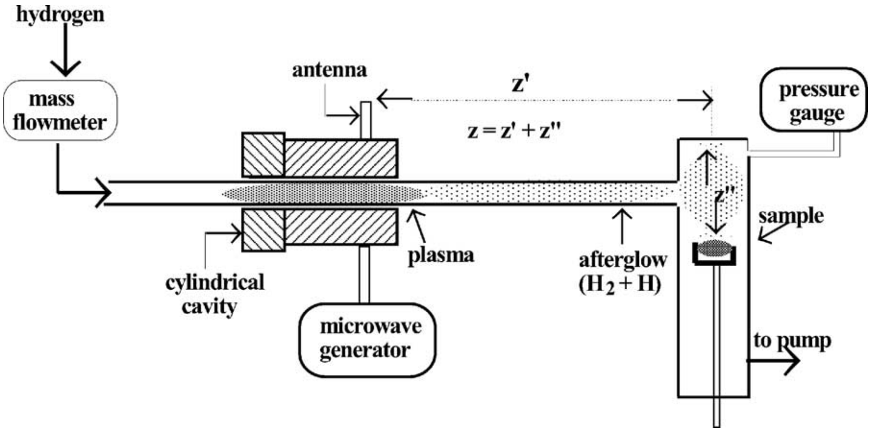

Fig. 1. Experimental setup.

The gas temperature is obtained by means of a Pt–Pt 10% Rh thermocouple coated with a silica sheath. The surface temperature of the silica sheath is not the gas temperature, because there are reactions on the surface, but this temperature gives an idea of the maximum value of the gas temperature, T_g (Fig. 2).

This method was developed with palladium [25] and then applied to platinum and gold and their mixtures. The following parameters were investigated:

- time of reduction (τ_r);
- distance (z) between the sample to be reduced and the cavity;
- microwave power (Π);
- the atomic ratio = mole number of Au/mole number of Pt for mixtures.

A preliminary study showed that the flowrate does not influence the reduction processes and it was kept at 10 or 20 ml/min (measured in standard condition). The pressure was kept constant at 1 mbar for most of the experiments.

2.3. Sample characterisation

(a) *TEM*. The particle sizes are determined from TEM photographs of a very large number of particles (several hundreds) and plotted on histograms so as to calculate the mean diameter, d_m, the volumic diameter d_v and the dispersion, D, for each sample:

$$d_m = \frac{\sum_i n_i d_i}{\sum_i n_i} \quad \text{and} \quad d_v = \frac{\sum_i n_i d_i^3}{\sum_i n_i d_i^2}$$

$$D = \frac{n_s}{n_t}$$

where n_s is the number of atoms on the surface of the particle and n_t the total number of metal atoms.

The dispersion, i.e. the ratio between the number of metal atoms at the surface of the particles and the total number of atoms, is calculated by using the plot of dispersion as a function of volumic diameter. This plot was set up by Anderson et al. [31] for platinum according to the method of Van Hardeveld and Hartog [32] based on the crystalline growth of the metals (ccf) in the particles. We have assumed it can be used also for gold since all the two metals crystallise in the same system (ccf) with about the same metal diameter ($\Phi_{Au} = 0.144$ nm, $\Phi_{Pt} = 0.138$ nm). An example of a histogram is given in Fig. 3.

(b) *Dihydrogen chemisorption*. This method is used to determine the metal dispersion by means of adsorption

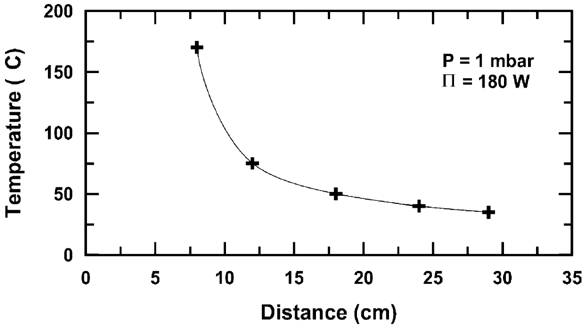

Fig. 2. Temperature along the afterglow.

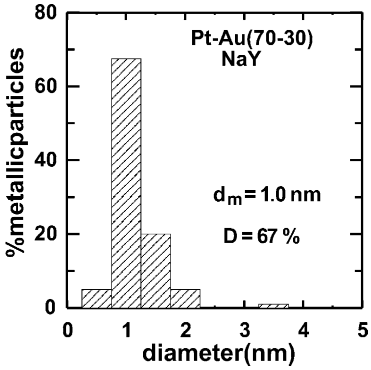

Fig. 3. Electron microscopy analysis of a Pt$_{70}$–Au$_{30}$ on NaY sample (histogram).

Table 1
Size and dispersion of platinum samples

Support	τ_r (min)	z (cm)	Π (W)	d_m (nm)	d_v (nm)	D (%)
NaY	30	12	180	1.7	2.8	43
NaY	30	14	180	1.3	1.7	70
NaY	30	19	180	1.1	1.6	75
NaY	30	27	180	1.7	2.7	44
NaY	60	12	150	1.5	2.2	55
HY	30	12	100	1.8	2.1	58
HY	30	19	150	1.1	1.7	70
HY	30	24	150	1.1	1.4	85

Table 2
Size and dispersion of gold samples

Support	τ_r (min)	z (cm)	Π (W)	d_m (nm)	d_v (nm)	D (%)
NaY	30	12	180	1.7	2.5	48
NaY	30	12	180	1.7	2.8	43
NaY	30	19	180	1.6	2.1	58
NaY	30	30	180	0.8	1.6	75
NaY	30	25	150	1.7	2.4	50
NaY	30	30	100	0.9	1.5	80
NaY	30	30	100	1.2	1.4	87
NaY	60	12	150	1.5	2.2	55
NaY	60	12	180	2.4	3.2	37
HY	30	25	170	1.1	3.1	39
HY	30	30	150	1.8	3.1	39

of dihydrogen on metals. In the case of bimetallic compounds if one of the two components does not adsorb dihydrogen, only the fraction of the metal that chemisorbs can be determined by this method (in this work only platinum is detected since gold does not adsorb).

3. Results

The main results concerning d_m, d_v and D are displayed in Tables 1 and 2 and in Fig. 4a for monometallic samples, and in Figs. 4b–6 for bimetallic samples.

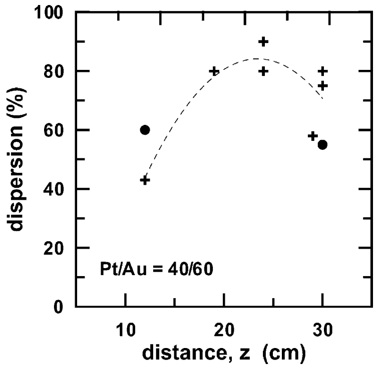

Fig. 5. Dispersion versus z for bimetallic clusters Pt–Au (40/60); support HY (+) and support NaY (●).

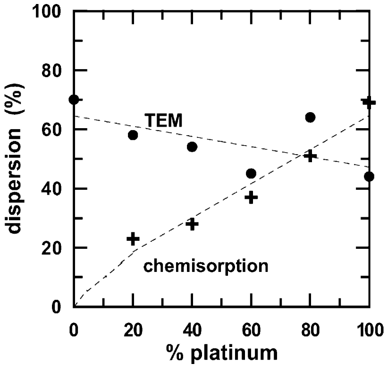

Fig. 6. Dispersion versus % of platinum measured by TEM and chemisorption; support = NaY, $z = 27$ cm, $\tau_r = 30$ min, $\Pi = 180$ W.

3.1. Mean diameters and dispersion

The mean diameter does not exceed 3 nm and the order of magnitude of the dispersion is quite suitable for mono- or bimetallic catalysts [33]. The dispersion increases for gold with the distance downstream the plasma (i.e. as the temperature gets closer to the room temperature) while for platinum dispersion goes through a maximum for a distance of about 20 cm. In Fig. 4b, it is shown that the catalyst with the higher percentage of gold (Pt–Au = 20/80) has the same behaviour with respect to z as pure gold.

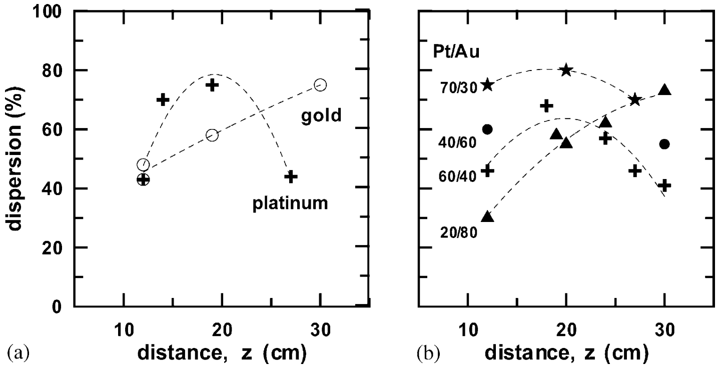

Fig. 4. Dispersion versus z; support = zeolite NaY, $\tau_r = 30$ min, $\Pi = 180$ W.

Table 3
Size and dispersion of bimetallic samples before and after thermal treatment

Pt–Au	Gas stream	τ_r (min)	z (cm)	Before thermal treatment		After thermal treatment	
				d_m (nm)	D (%)	d_m (nm)	D (%)
70–30	Noxal	30	12	1.3	55	1.2	62
60–40	O_2	30	18	1.1	67	1.3	60
40–60	O_2	30	19	1.6	37	1.7	45
20–80	O_2	30	20	1.2	58	1.2	55

The non-acidified NaY zeolite gives the best results (better dispersed metal, smaller metal particles of more homogeneous size) for pure gold as for pure palladium [25]; it is the contrary for platinum. Fig. 5 shows the dispersions of bimetallic Pt–Au (40–60) particles on HY and on NaY versus distance z. The dispersions with the two supports are in the same order of magnitude.

The role of microwave power and the time of exposure in the afterglow are not significant in the range used.

3.2. Comparison of dispersion measured by TEM and chemisorption

Fig. 6 shows the dependence of the dispersion D on the percentage of platinum measured by TEM and chemisorption. D measured by chemisorption increases with the platinum ratio. When TEM is used, the dispersion seems to be roughly constant. TEM measures all the atoms on the surface while chemisorption gives results only for platinum (gold does not absorb dihydrogen). These results show that mixed clusters were obtained, i.e. the particle surface consists of gold and platinum atoms. For pure platinum, the dispersions obtained by both methods agree within the limits of experimental accuracy.

3.3. Thermal stability of samples

Since the reduced samples are to be used as catalysts, it is essential to check their thermal stability. The thermal treatment of samples consists in heating them in a stream of Noxal (mixture of 5% H_2 and 95% Ar, 100 ml/min) or in a stream of O_2 with a small temperature gradient (24 °C/h) up to 300 °C and keeping them at this temperature for 15 h. The effect of this operation can be to sinter the metal. The results are shown in Table 3.

Given the accuracy of the particle diameter determination (about 20%), d_m and D are in the same order of magnitude before and after thermal treatment; consequently, the thermal stability of these samples is quite good.

4. Conclusion

The afterglow of a dihydrogen plasma was used to reduce metallic precursors and obtain mono- (Pt or Au) and bimetallic (Pt–Au) nanoparticles supported on Y zeolite. This afterglow is a medium where reducing species (H atoms) are found at low temperature. The mean diameter of the particles obtained is less than 3 nm and the particles are quite well dispersed in the pores. Moreover the thermal stability of the samples is satisfactory, in that the particle sizes are of the same order of magnitude before and after thermal treatment. For bimetallic samples (Pt–Au), the dispersion obtained by means of dihydrogen chemisorption shows that the surface of the particles consists of a mixture of gold and platinum atoms. Consequently, the afterglow of a dihydrogen plasma appears to be a suitable medium for preparing dispersed gold-based metallic catalysts.

References

[1] S.A. Nyarady, R.E. Sievers, J. Am. Chem. Soc. 107 (1985) 3726.

[2] P.A. Sermon, G.C. Bond, P.B. Wells, J. Chem. Soc., Faraday Trans. I 75 (1979) 385.

[3] G. Parravano, J. Catal. 24 (1972) 233.

[4] V. Bertin, P. Bosch, G. Del Angel, R. Gomez, J. Barbier, P. Maricot, J. Chim. Phys. Fr. 92 (1995) 120.

[5] D. Rouabah, J. Fraissard, Catal. Lett. 34 (1995) 321.

[6] R.J. Davis, M. Boudart, J. Phys. Chem. 98 (1994) 5471.

[7] W. Juszczyk, Z. Karpinski, D. Lomot, J. Pielaszek, W. Sobczak, J. Catal. 151 (1995) 67.

[8] M.C. Demicheli, L.C. Hoang, J.C. Menezo, J. Barbier, M. Pinabiau-Carlier, Appl. Catal. 97 (1993) L11.

[9] M. Boudart, G. Meitzner, in: K.O. Hodgson, B. Hedman, J.E. Penner-Halm (Eds.), Exafs and Near Edge Structure III, Springer Proceedings 2, Springer, Berlin, 1984, p. 217.

[10] G. Riahi, D. Guillemot, M. Polisset-Thfoin, D. Bonnin, J. Fraissard, Stud. Surf. Sci. Catal. 135 (2001) 1594.

[11] J.-N. Lin, J.-H. Chen, C.-Y. Hsiao, Y.-M. Kang, B.-Z. Wan, Appl. Catal. B 36 (2002) 19.

[12] B.S. Uphade, M. Okumura, N. Yamada, S. Tsubota, M. Haruta, Stud. Surf. Sci. Catal. A 130 (2000) 833.

[13] B. Bertsch-Frank, I. Hemme, L. Von Hippel, S. Katusic, J. Rollman, German Patent 19 912 733 (2000).

[14] J.R. Zoeller, A.H. Singleton, G.C. Tustin, D.L. Carver, US Patent 6 506 933 (2003).

[15] M. Boutonnet Kizling, S.G. Järas, Appl. Catal. A 147 (1996) 1.

[16] J.P.S. Badyal, Top. Catal. 3 (1996) 255.

[17] L. Rouleau, R. Bacaud, M. Breysse, J. Dufour, Appl. Catal. A 104 (1993) 137.

[18] C. Laure, P. Brault, A.-L. Thomman, R. Boswell, B. Rousseau, H. Estrade-Szwarckopf, Plasma Sources Sci. Technol. 5 (1996) 510.

[19] O.Y. Ostoshevskaya, S.I. Serdyukov, M.F. Safonov, Kinet. Catal. 6 (1996) 927.

[20] G. Roussy, S. Hilaire, J.M. Thiébaut, G. Maire, F. Garin, S. Ringler, Appl. Catal. A 156 (1997) 167.

[21] J.R. Thomas, Catal. Lett. 49 (1997) 137.

[22] J. Ma, M. Fang, P. Li, B. Zhu, X. Lu, N.T. Lau, Appl. Catal. A 159 (1997) 211.

[23] C. Chen, P. Hong, S. Dai, J. Kan, J. Chem. Soc., Faraday Trans. 91 (1995) 1179.

[24] J.K.S. Wan, Res. Chem. Intermed. 19 (1993) 147.

[25] A.-M. Diamy, Z. Randriamanantenasoa, J.-C. Legrand, M. Polisset-Thfoin, J. Fraissard, Chem. Phys. Lett. 269 (1997) 327.

[26] D.L. Baulch, C.J. Cobos, R.A. Cox, C. Esser, P. Frank, Th. Just, J.A. Ker, M.J. Pilling, J. Troe, R.W. Walker, J. Warnatz, J. Phys. Chem. Ref. Data 21 (1992) 411.

[27] Y.C. Kim, M. Boudart, Langmuir 7 (1991) 2999.

[28] S.T. Homeyer, W.M.H. Sachtler, J. Catal. 117 (1989) 91.

[29] B.P. Block, J.C. Bailar, J. Am. Chem. Soc. 73 (1951) 4722.

[30] T. Rades, C. Pak, M. Polisset-Thfoin, R. Ryoo, J. Fraissard, Catal. Lett. 29 (1994) 91.

[31] J.R. Anderson, K. Foger, R.J. Breakspere, J. Catal. 57 (1979) 458.

[32] R. Van Hardeveld, F. Hartog, Surf. Sci. 15 (1969) 189.

[33] G.C. Bond, Acc. Chem. Res. 26 (1993) 490.