Contents lists available at ScienceDirect

## **Catalysis Today**

journal homepage: www.elsevier.com/locate/cattod

# Pd on carbon nanotubes for liquid phase alcohol oxidation

Alberto Villa<sup>b</sup>, Di Wang<sup>b</sup>, Nikolaos Dimitratos<sup>a,1</sup>, Dangsheng Su<sup>b,\*</sup>, Valentina Trevisan<sup>c</sup>, Laura Prati<sup>a,\*</sup>

<sup>a</sup> Università di Milano, Dipartimento CIMA "L.Malatesta", via Venezian 21, I-20133 Milano, Italy <sup>b</sup> Department of Inorganic Chemistry, Fritz Haber Institute of the Max Planck Society, Faradayweg 4-6, D-14195 Berlin, Germany

<sup>c</sup> Università di Venezia, Dipartimento di Chimica, Dorsoduro 2137, I-30123 Venezia, Italy

ARTICLE INFO

#### *Article history:* Available online 17 July 2009

Keywords: Alcohol oxidation Palladium on carbon nanotubes Gold–palladium catalyst

## ABSTRACT

Pd nanoparticles supported on carbon nanotubes (CNTs) showed a higher selectivity than Pd nanoparticles supported on activated carbon (AC) in the liquid phase oxidation of benzylic alcohol to benzaldehyde. Under solventless conditions a significant improvement in selectivity was observed for Pd/CNTs, whereas using Pd/AC a considerable over-oxidation of benzaldehyde was observed. Differently from other solvents cyclohexane improved significantly the selectivity to benzaldehyde for both catalysts. Characterisation by means of transmission electron microscopy revealed differences in metal dispersion between Pd/AC and Pd/CNTs that can be ascribed to textural, chemical and physical differences between active carbon and carbon nanotubes. The higher activity in the case of Pd on AC than on CNTs can be attributed to the improved Pd dispersion in the first case.

On recycling Pd/CNTs resulted more stable (activity loss 50% in 7 runs) than Pd/AC (activity loss 70% in 7 runs) even a structural change of catalysts after reaction is observed. The Pd leaching and particle coalescence are the main reasons for the loss of activity. An extraordinary improving of catalyst life has been observed by alloying the Pd nanoparticles with Au, When CNTs are used as support the strong Pd leaching can be greatly limited and the activity/selectivity maintained at least for 8 runs.

© 2009 Elsevier B.V.. All rights reserved.

#### 1. Introduction

Metal catalyzed alcohol oxidation in the liquid phase using oxygen as the oxidant represents a well known interesting process, but its industrial exploitation was limited by the strong deactivation [1]. Several metals (ruthenium, platinum, palladium and gold) have been used as monometallic catalysts, in some cases with modifier (like Bi, Pb) [2–5]. The main requirement for a high selectivity and long durability has not been yet achieved. Moreover, a variety of experimental conditions have been tested: from solventless to organic solvents or aqueous conditions. It has been observed that basic conditions improved the activity and the durability, probably due to a prolonged catalyst life. However, under basic conditions the selectivity to aldehyde in the alcohol oxidation decreased in favour of the corresponding carboxylic acid (carboxylate).

From an industrial point of view carbonaceous supports are preferable because of the facile recovery of precious metals by

\* Corresponding authors.

E-mail addresses: dangsheng@fhi-berlin.mpg.de (D. Su), Laura.Prati@unimi.it (L. Prati). burning off the support. Recently, there is a growing interest in the use of CNTs as catalyst supports for metal nanoparticles in many catalytic applications; for example, CNTs supported platinum nanoparticles are used as electrocatalyst in proton-exchange membrane fuel cells [6,7]. Moreover, Ni [8,9] and Pd [10] nanoparticles decorated CNTs were used for hydrogen storage and for hydrogen sensing. In addition, Pd [11], Pt and Ru [12] metal nanoparticles supported on CNTs show a high catalytic activity in the liquid phase hydrogenation of cinnamaldehyde. However, only few reports on the use of CNTs instead of the widely used AC can be found in the literature. For example, Corma et al. [13] showed that Pd nanoparticles immobilised on CNTs are more active than the one supported on AC in the Heck reaction of styrene and iodobenzene and for the Suzuki coupling of phenylboronic and iodobenzene. They assigned the high activity to the different particle size obtained for the different supports. They showed that the Pd/AC is more active than Pd/CNTs for the aerobic oxidation of cinnamyl alcohol in ethanol. Moreover Karaousis et al. [14] reported higher activity of CNTs supported metal nanoparticles with respect to AC supported ones in the hydrogenation of methyl-9-octadecenoate and 2-methyl-2-pentenal. They concluded that the high catalytic performance of CNTs supported Pd is due to the large active surface of metallic palladium.

In the present work we report on the catalytic activity of CNTs and AC supported Pd nanoparticles prepared by colloidal method



<sup>&</sup>lt;sup>1</sup> Current address: School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff CF10 3AT, UK.

<sup>0920-5861/\$ –</sup> see front matter @ 2009 Elsevier B.V.. All rights reserved. doi:10.1016/j.cattod.2009.06.009

using PVA as protective agent [15] in the liquid phase oxidation of benzyl alcohol with the aim of preserving a high selectivity to aldehyde but enhancing the catalyst activity and reusability. Different groups showed that adding Au to Pd catalysts has a beneficial effect in the alcohol oxidation, improving not only the catalytic activity and selectivity to the desired product [16], but also the resistance to the deactivation [17–19]. We recently set up a two step methodology allowing the preparation of uniformly alloyed bimetallic Au<sub>60</sub>–Pd<sub>40</sub> catalyst supported on activated carbon [15]. With the same procedure we prepared a bimetallic Au–Pd catalyst supported on CNTs.

## 2. Experimental

#### 2.1. Materials

Na<sub>2</sub>PdCl<sub>4</sub> and NaAuCl<sub>4</sub>·2H<sub>2</sub>O were from Aldrich (99.99% purity), activated carbon from Camel (X40S; SA = 900–1100 m<sup>2</sup>/g; PV = 1.5 ml/g) and carbon nanotubes from Bayern Materials Science AG (Baytubes C150P; SA = 30 m<sup>2</sup>/g; internal diameter 13–16 nm, length 1–10  $\mu$ m). NaBH<sub>4</sub> of purity >96% from Fluka, polyvinylalcohol (PVA) (Mw = 13,000–23,000; 87–89% hydrolysed) from Aldrich were used. Gaseous oxygen from SIAD was 99.99% pure.

## 2.2. Catalyst preparation

#### 2.2.1. Monometallic catalysts

Pd sol:  $Na_2PdCl_4 \cdot 2H_2O$  (0.043 mmol) and PVA solution 2 wt% (880 µl) were added to 130 ml of  $H_2O$ . After 3 min,  $NaBH_4$  solution (860 µl) was added to the yellow-brown solution under vigorous magnetic stirring. The brown Pd(0) sol was immediately formed. An UV–vis spectrum of the palladium sol was recorded for ensuring the complete reduction of Pd(II).

Within few minutes from their generation, the colloids (acidified at pH 2, by sulphuric acid) were immobilised by adding carbon under vigorous stirring. The catalyst has been filtered washed for several times to ensure the removal of the material arising from the reduction treatment. The samples were dried at 353 K for 2 h. The amount of support was calculated to obtain a final metal loading of 1 wt%.

## 2.2.2. Bimetallic catalyst

Solid NaAuCl<sub>4</sub>·2H<sub>2</sub>O (0.072 mmol) was dissolved in 140 ml of water (final  $10^{-4}$  M) and 0.706 ml of PVA (2%, w/w) was added (Au/ PVA 1:1 w/w). The yellow solution was stirred for 3 min and 2.9 ml of 0.1 M NaBH<sub>4</sub> (Au/NaBH<sub>4</sub> 1:3 mol/mol) was added under vigorous magnetic stirring. The ruby red Au(0) sol was immediately formed. An UV-vis spectrum of the gold sol was recorded to check the complete AuCl<sub>4</sub><sup>-</sup> reduction and the formation of Plasmon peak. Within few minutes of sol generation, the gold sol was immobilised by adding carbon nanotubes (acidified until pH 2 by sulphuric acid) under vigorous stirring. The amount of support was calculated as having a gold loading of 0.73 wt% when Au/Pd was prepared. After 2 h the slurry was filtered, the catalyst was thoroughly washed with distilled water (neutral mother liquors). ICP analyses were performed on the filtrate using a Jobin Yvon JV24 to verify the total metal loading on the support. The Au/ CNTs was then dispersed in 140 ml of water; Na<sub>2</sub>PdCl<sub>4</sub> (0.048 mol) and 0.225 ml of PVA solution (0.2%, w/w) (Au/PVA 1:1 w/w) were added. H<sub>2</sub> has been bubbled (50 ml/min) under atmospheric pressure and room temperature for 2 h. After additional 18 h, the slurry was filtered, the catalyst was thoroughly washed with distilled water. ICP analyses were performed on the filtrate using a Jobin Yvon JV24 to verify the metal loading on the support. 1 wt% was the total metal loading.

#### 2.3. Catalytic test

The reactions were carried out in a thermostatted glass reactor (30 ml) provided with an electronically controlled magnetic stirrer connected to a large reservoir (5000 ml) containing oxygen at 2 atm. The oxygen uptake was followed by a mass flow controller connected to a PC through an A/D board, plotting a flow/time diagram. The oxidation experiments were carried out in solventless or in the presence of a solvent (0.0125 mol substrate. substrate/metal = 3000 (mol/mol), 80  $^{\circ}$ C, pO<sub>2</sub> = 2 atm). In the case of organic solvent, periodic removal of samples from the reactor was performed, whereas in the case of water solvent, after the end of the reaction the catalyst was filtered off and the product mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>. Recoveries were always  $98 \pm 3\%$  with this procedure. For the identification and analysis of the products a GC-MS and GC (a Dani 86.10 HT Gas Chromatograph equipped with a capillary column, BP21 30 m  $\times$  0.53 mm, 0.5  $\mu$ m Film, made by SGE), were used by comparison of the authentic samples. For the quantification of the reactant-products the external calibration method was used.

#### 2.4. Characterisation

#### 2.4.1. Sol characterisation

UV-vis spectra of sols were performed on HP8452 and HP8453 Hewlett-Packard spectrophotometers in  $H_2O$  between 190 and 1200 nm, in a quartz cuvette.

#### 2.4.2. Catalyst characterisation

- (a) The metal content was checked by ICP analysis of the filtrate or alternatively directly on catalyst after burning off the carbon, on a Jobin Yvon JY24.
- (b) Morphology and microstructures of the catalysts were characterised by TEM. The powder samples of the catalysts were ultrasonically dispersed in ethanol and mounted onto copper grids covered with holy carbon film. A Philips CM200 FEG electron microscope, operating at 200 kV and equipped with a Gatan imaging filter, GIF Tridiem, was used for TEM observation. EDX analysis was performed in the same microscope using a DX4 analyzer system (EDAX).
- (c) *Z*-potential measurements were performed on Zetasizer nanoZS/MPT-2 from Malvern. 10 mg of support was dispersed in 50 ml of distilled water and sonicated for 10 min. The support was then removed by filtration and the solution was ready for zeta potential measurements. For the colloidal metal solution no pre-treatment was used before the measurement.

## 3. Results and discussion

## 3.1. Catalytic activity of Pd supported on AC and CNTs

AC is a widely used catalyst support for liquid phase reaction. However, recent literature disregards AC as the support for alcohol oxidation; the most used supporting materials are oxides despite their disadvantage in precious metal recovery. We concentrated on benzylic alcohol to benzaldehyde selective oxidation which is an important reaction from an industrial point of view and has been studied under a variety of reaction conditions using different catalytic systems.

We synthesized 1 wt% Pd/AC or CNT via the sol immobilisation method (NaBH<sub>4</sub>/PVA). The palladium metal sol was generated by NaBH<sub>4</sub> reduction of Na<sub>2</sub>PdCl<sub>4</sub> salt in the presence of a protective agent (polyvinyl alcohol, PVA) which provides electrostatic as well as sterical stabilisation of the nanoparticles. Pd-sol appeared negatively charged at any pH of the solution (Fig. 1). The AC and



Fig. 1. Zeta potential measurement.

CNT auto-generates different basic pHs (9.18 and 10.28, respectively) but acidic groups determined by the Boehm method [20] revealed a similar density of carboxylic groups (9.74 and 9.89 mmol/g). Thus the support suspension was previously acidified (pH 2) in order to create a positive electrostatic attraction between the support and the protected metal particles (Fig. 1). In principle the immobilisation of preformed Pd nanoparticles assured a similar particle size distribution on different support.

Fig. 2a and b shows the TEM overview images of the as prepared Pd/AC and Pd/CNTs, respectively. The histograms of the particle size distribution for AC and CNTs supported Pd particles are shown in Fig. 2c and d, respectively. Fitting by Log-Normal function, the Pd/AC was found to have median size of 3.9 nm and the Pd/CNTs of 3.4 nm (Table 1). However, though Pd particles on CNTs have smaller size, Pd particles on AC exhibit a more homogeneous distribution. In fact for Pd/CNTs, some CNTs were found without Pd particles, while many Pd particles are observed in aggregates. This difference could be attributed to a different and inhomogeneous distribution of chemical groups on the CNTs surface respect to AC ones.



Fig. 2. The TEM overview images of (a) Pd/AC and (b) Pd/CNTs, (c) and (d) the Pd particle size distribution of the two catalysts, respectively.

#### Table 1

Statistical median and standard deviation of particle size analysis for Pd and Au/Pd catalysts.





Benzyl benzoate

Scheme 1. Possible reaction scheme for benzyl alcohol oxidation.

The catalysts were tested in the liquid phase oxidation of benzyl alcohol. This reaction has been widely studied in the literature using a variety of experimental conditions. In the present study we tested the most promising solventless reaction, the most benign reaction in water although in the literature toluene represents the most common solvent used [21]. However, as toluene is a possible by-product in the benzyl alcohol oxidation (Scheme 1), we avoided its use and checked a different organic solvent (cyclohexane). Table 2 reports the results of Pd supported on AC and CNT using different amounts of each solvent. The experimental conditions were maintained constant (0.0125 mol substrate, alcohol/metal

## Table 2

Benzyl alcohol oxidation in the presence of supported 1 wt% Pd.

Solvent	Selectivity to toluene <sup>a</sup>		Selectivity to benzaldehyde <sup>a</sup>		TOF $(h^{-1})^b$	
	Pd/AC	Pd/CNT	Pd/AC	Pd/CNT	Pd/AC	Pd/CNT
Neat	33	17	61	78	2980	1412
25% water	25	25	71	73	1485	730
50% water	30	41	67	57	1227	506
75% water	36	37	62	59	840	554
20% cyclohexane	29	24	67	74	2846	1462
50% cyclohexane	23	3	74	92	1482	1340
80% cyclohexane	8	8	88	88	490	493

Reaction condition: alcohol/metal 3000/1 (mol/mol), 80 °C, *p*O<sub>2</sub> 2 atm, 1250 rpm. <sup>a</sup> Selectivity at 90% conversion.

<sup>b</sup> TOF calculated after 15 min of reaction.



Fig. 3. (a) Conversion/selectivity on recycling 1%Pd/AC. (b) Conversion/selectivity on recycling 1%Pd/CNTs.

3000/1 (mol/mol), 80 °C,  $pO_2$  2 atm, 1250 rpm) just varying the amount of solvent.

The screening of activity of Pd on AC (Table 2) revealed that, referring to solventless conditions, water addition causes a decrease in activity. This becomes most significant when 75% of water was added (TOF drops from 2980 to 840  $h^{-1}$ ). The effect on selectivity, however, was negligible. 61-62% selectivity to benzaldehvde at 90% conversion (S90) was obtained in both cases. Here toluene was the main by-product due to a hydrogen transfer process. Indeed Pd is a well known catalyst for this type of reaction [22]. Prior to perform the reaction in organic solvent (cyclohexane) we carried out blank experiment that proved the inertness of cyclohexane under the actual reaction condition. As reported in Table 2, a 20 vol.% addition of cyclohexane did not modified the result of solventless experiment, but when the amount of solvent increased, the expected decreasing of the reaction rate was accompanied by a huge improving in selectivity. By increasing the cyclohexane amount from 50 to 80%, we observed a strong enhancement in aldehyde selectivity and a consistent decreasing in the toluene one.

Comparing the TOFs of Pd/CNTs with that of Pd/AC (Table 2) we could generally observe that Pd on CNTs showed a lower activity than Pd/AC. However, the most interesting point came from the selectivity. In the solventless reaction Pd/CNTs exhibited a considerably higher selectivity to aldehyde with respect to the one obtained with Pd/AC (S90 78% versus 61%). When water was added, a decrease of selectivity to aldehyde was observed. This trend became more serious when water content was at 50–75%. Meanwhile the toluene formation increased. On the contrary, when cyclohexane was added we obtained a remarkable enhancement of benzaldehyde production with selectivity higher than 90% with 50 vol.% solvent. In this latter case it should be noted that the activity of the catalyst is quite good (1340  $h^{-1}$ ) being comparable with the one of Pd/AC (TOF 1482  $h^{-1}$ ).

On the basis of these results we can conclude that performances of both catalysts (Pd/AC and Pd/CNTs) are very sensitive to the



Fig. 4. The TEM overview image for (a) Pd/AC and (b) Pd/CNTs after reaction. Pd particle size distribution of (c) Pd/AC and (d) Pd/CNTs after reaction.

solvent employed and that in both cases the addition of a solvent decreased the catalyst activity compared to solventless conditions. Cyclohexane with respect to water appeared to be more able to preserve the activity. However, the main positive effect of solvent is to improve the selectivity to aldehyde, this effect being slightly higher for Pd on CNTs than on AC.

## 3.2. Catalyst durability (recycling test)

From an applicative point of view, one of the most appreciable properties of a heterogeneous catalyst is its durability. Thus we tested the Pd on AC and on CNTs catalysts on recycling, checking the overall leaching of the Pd or any other modification on the used catalyst after several runs. Each run was carried out under identical conditions (alcohol/metal 3000/1 (mol/mol), 80 °C,  $pO_2$  2 atm, 1250 rpm, cyclohexane 50 vol.%) and reusing the catalyst recovered by filtering off the solution of the previous run after 1 h. After 7 runs, despite the selectivity did not change so far, conversion after 1 h has declined about 70% in the case of Pd/AC (Fig. 3a) and 47% in the case of Pd/CNTs (Fig. 3b). A reason of this behaviour can

be found in the characterisation of the recovered catalysts which have been observed by TEM after washing with water and dried. In both cases a growing in size of Pd particles was observed which are expected to show lower activity than the one of smaller, highly dispersed particles (Fig. 4a and b and Table 1). Fig. 4c and d shows the particle size distribution of the Pd/CNTs and Pd/AC after reaction, in which the median particle sizes are 6.4 and 5.3 nm. respectively (Table 1), considerably larger than those of the corresponding fresh catalysts. Apart from the aggregates, a considerable number of the particles were observed to undergo coalescence to form big and irregularly shaped particles. Moreover, we performed ICP analysis on the used catalysts, after burning off the carbonaceous material, detecting a consistent leaching of Pd (28% for Pd/AC and 25% for Pd/CNTs). All these factors lead to the drastic reduction of the accessible reaction sites on Pd. We can then conclude that these systems are not stable under the reaction conditions used and need to be stabilised for an industrial exploitation. Moreover, considering that the selectivity has not changed during the recycled runs, we also concluded that the selectivity is independent on the particle size range we have



Fig. 5. HRTEM of (a) Au-Pd/AC and AC and (b) Au-Pd/CNTs. Particle size distribution of (c) Au-Pd/AC and (d) Au-Pd/CNTs.

Table 3	
Comparison of mono and bimetallic cataly	yst activities in benzyl alcohol oxidation.

	Selectivity to toluene <sup>a</sup>	Selectivity to benzaldehyde <sup>a</sup>	TOF $(h^{-1})^b$
Pd/AC	23	74	1482
Au/AC	-	-	<1
Au–Pd/AC	9	89	1350
Pd/CNTs	3	92	1340
Au/CNTs	-	-	<1
Au–Pd/CNTs	3	89	1490

Reaction condition: alcohol/metal 3000/1 (mol/mol), 80 °C, solvent: cyclohexane 50 vol.%,  $pO_2$  2 atm, 1250 rpm.

<sup>a</sup> Selectivity at 90% conversion.

<sup>b</sup> TOF calculated after 15 min of reaction.

investigated. Therefore, the difference in selectivity between Pd/AC and Pd/CNTs is expected to relate with the support properties and their influences on the Pd sites.

We already experienced the beneficial effect of alloying gold to Pd nanoparticles [23]. A two step procedure that ensures the formation of uniform alloyed Pd/Au nanoparticles on AC has been published [15] and proved to enhance both activity and durability of the catalyst in glycerol oxidation [23]. As we were interested to improve the catalyst stability, we now extended the same technique to prepare bimetallic Au-Pd nanoparticles on CNTs and thus allowing comparing the behaviour of Au-Pd on AC with that of Au-Pd on CNTs. The resulted catalysts show similar particle size. 3.4 nm for Au-Pd/AC and 3.5 nm for Au-Pd/CNTs (Table 1). even differently distributed (Fig. 5c and d). Preliminary tests for evaluating the real effect of the adding of Au to Pd were performed in cyclohexane (50 vol.%) that, as outlined before, strongly differs from water as solvent and in that also Au-Pd/AC was never used in the past [23]. Table 3 reports the activities of monometallic catalysts compared to bimetallic Au-Pd ones. Under these conditions monometallic gold was inactive both supported on AC and on CNTs. This behaviour did not surprise as gold is expected



Fig. 6. (a) Conversion/selectivity on recycling of 1%Au-Pd/AC. (b) Conversion/ selectivity on recycling of 1%Au-Pd/CNTs.

to be an active catalyst under basic conditions. Moreover, we were quite disappointed to observe that Pd and Au–Pd showed, under these experimental conditions, a similar behaviour from both activity and selectivity point of view. In fact only a slight variation of TOFs was obtained: from 1482 to  $1350 h^{-1}$  for AC and from 1340 to 1490  $h^{-1}$  for CNTs. Selectivity to benzaldehyde only improved in the case of Au–Pd on AC compared to Pd/AC.

On the contrary a completely different catalytic behaviour was highlighted on recycling. Under the same conditions as for the test of monometallic Pd, Au/Pd on AC losses in 8 runs about 50% of its activity whereas CNTs only 4% (Fig. 6a and b). ICP measurements revealed a leaching of palladium of 10% for Au-Pd/AC whereas only 4% in the case of Au-Pd/CNTs. In both cases leaching of Au resulted negligible. Considering the normal loss of the catalyst i.e. the expected decreasing in conversion due to the reduced amount of catalyst recovered from any subsequent run (3-4%), the leaching of Pd is inconsistent with both of catalytic results. However, we already observed that the leaching of Pd depends on particle size [23]. This different leaching could create the presence of different alloy composition that could possibly show different activity. This was already observed in the case of aqueous glycerol oxidation where the maximum of activity was reached for Au<sub>95</sub>Pd<sub>05</sub> composition [24]. At this stage we could only conclude that gold stabilises the palladium more efficiently on CNTs than on active carbon. Further studies are needed to determine the nature of this stabilisation.

#### 4. Conclusions

We compared the activity of Pd nanoparticles supported on AC and CNTs in the liquid phase oxidation of benzylic alcohol to benzaldehyde. Although we used a procedure (sol immobilisation) that in principle assures a similar distribution on different supports, we obtained a slight different metal distribution in the two cases. Pd nanoparticles on CNTs are smaller in size but less dispersed than on AC. Catalytic test revealed that Pd supported on CNTs behaves differently from Pd on AC. In fact, the expected lower activity of Pd/CNTs according to the lower metal dispersion was related to a higher selectivity toward benzaldehyde strongly dependent on the solvent used. The maximum of selectivity (92%) was obtained for a 50% volume of cyclohexane as solvent. The use of Pd on both AC and CNTs is however limited by the high Pd leaching revealed on recycling (28 and 25%, respectively). A consistent improving in the long-term use of the catalysts has been obtained by modifying the monometallic Pd with gold. With this purpose the procedure set up for producing Au-Pd alloyed nanoparticles on AC was extended to CNTs. On recycling this latter catalyst showed limited Pd leaching and stable catalytic performances over 8 runs. Under similar conditions Au-Pd on AC was less stable.

#### Acknowledgements

Authors thank DAAD, Programma Vigoni and Fondazione Cariplo for financial support.

#### References

- [1] T. Mallat, A. Baiker, Chem. Rev. 104 (2004) 3037.
- [2] M. Besson, P. Gallezot, Catal. Today 57 (2000) 127.
- [3] R.A. Sheldon, I.W.C.E. Arends, G.J. ten Brink, A. Dijksman, Acc. Chem. Res. 35 (2002) 774.
- [4] B.A. Steinhoff, S.R. Fix, S.S. Stahl, J. Am. Chem. Soc. 124 (2002) 766.
- [5] T. Nishimura, Y. Maeda, N. Kaikiuchi, S. Uemura, J. Chem. Soc., Perkin Trans. 1 (2000) 4301.
- [6] Z. Liu, X. Lin, J.Y. Lee, W. Zhang, M. Han, L.M. Gan, Langmuir 18 (2002) 4054.
- [7] Y. Xing, J. Phys. Chem. B 108 (2004) 19255.

- [8] H.-S. Kim, H. Lee, K.-S. Han, J.-H. Kim, M.-S. Song, M.-S. Park, J.-Y. Lee, J.-K. Kang, J. Phys. Chem. B 109 (2005) 8983.
- [9] J.-Y. Lee, H. Lee, H.-S. Kim, Mater. Sci. Forum 475-479 (2005) 2463.
- [10] Kong, M.G. Chapline, H. Dai, Adv. Mater. 13 (2001) 1384.
- [11] J.P. Tessonier, L. Pesant, G. Ehret, M.J. Ledoux, C. Pham-Huu, Appl. Catal. A 288 (2005) 203.
- [12] H. Vu, F. Goncalves, R. Philippe, E. Lamouroux, M. Corrias, Y. Kihn, D. Plee, P. Kalck, P. Serp, J. Catal. 240 (2006) 18.
- [13] A. Corma, H. Garcia, A. Leyva, J. Mol. Catal. A 230 (2005) 97.
- [14] N. Karaousis, G. Tsotsou, F. Evangelista, P. Rudolf, N. Ragoussis, N. Tagmatarchis, J. Phys. Chem. C 112 (2008) 13463.
- [15] D. Wang, A. Villa, F. Porta, D. Su, L. Prati, Chem. Commun. (2006) 1956.

- [16] S. Demeril, K. Lehnert, M. Lucas, P. Claus, Appl. Catal. B 70 (2007) 637.
- [17] D.I. Enache, J.K. Edwards, P. Landon, B. Solsona-Espriu, A.F. Carley, A.A. Herzing, M. Watanabe, C.J. Kiely, D.W. Knight, G.J. Hutchings, Science 11 (2006) 362.
- [18] N. Dimitratos, A. Villa, D. Wang, F. Porta, D. Su, L. Prati, J. Catal. 244 (2006) 113.
- [19] W. Hou, N.A. Dehm, R.W.J. Scott, J. Catal. 253 (2008) 22.
- [20] H.P. Boehm, Advances in Catalysis, 16, Academic Press, New York, 1966.
- [21] C. Della Pina, E. Falletta, L. Prati, M. Rossi, Chem. Soc. Rev. 37 (2008) 2077 (and references cited therein).
- [22] J.M. Thomas, W.J. Thomas Principles, Practice of Heterogeneous Catalysis, VHC Ed, Weinheim, Germany, 1997.
- [23] L. Prati, A. Villa, F. Porta, D. Wang, D. Su, Catal. Today 122 (2007) 386.
- [24] D. Wang, A. Villa, F. Porta, L. Prati, D. Su, J. Phys. Chem. C 112 (2008) 8617.