Catalysis Communications 12 (2011) 1260–1264

Contents lists available at ScienceDirect

Catalysis Communications

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

Short Communication

Gold–palladium supported on porous steel fiber matrix: Structured catalyst for benzyl alcohol oxidation and benzyl amine oxidation

Hongfan Guo [1], Marianna Kemell, Afnan Al-Hunaiti, Sari Rautiainen, Markku Leskelä, Timo Repo *

Laboratory of Inorganic Chemistry, Department of Chemistry, University of Helsinki, P.O. Box 55, Helsinki FI-00014, Finland

ARTICLE INFO

Article history:
Received 11 March 2011
Received in revised form 19 April 2011
Accepted 22 April 2011
Available online 29 April 2011

Keywords:
Au-Pd
Sputtering
Benzyl alcohol
Benzyl amines
Oxidation

ABSTRACT

Au, Pd and Au-Pd alloy are deposited on porous steel fiber matrices via sputtering technique. By this technique the preparation of the heterogeneous catalysts is clean, simple and fast as noble metal complexes, solvents or reducing agents are not needed. The studied Au-Pd catalyst exhibits good activity in the aerobic oxidation of benzyl alcohol and benzyl amines. Especially in the oxidation of benzyl amines, the Au-Pd catalyst shows a great synergistic enhancement in the activity.

1. Introduction

The oxidation of alcohols to corresponding carbonyl compounds and the oxidative dehydrogenation of amines to imines are of significance in organic synthesis [1–5]. Traditionally, these oxidations are performed using stoichiometric amounts of oxidants, such as chromate or permanganate, but these reagents have serious toxicity issues [2]. Therefore, being one of the greenest oxidants O_2 has received much attention [2]. On the other hand, promising catalytic activity of Au based catalysts in these oxidations [1–5] by O_2 makes them attractive.

The common Au based catalysts are supported on metal oxide powders [6]. They are usually prepared by various solution synthesis methods. Physical methods, such as thermal evaporation and sputtering, are simple and clean methods, which directly deposit metal to various surfaces without production of waste stream, and without impurities introduced to the catalyst. In comparison, solution synthesis requires solvents, soluble metal precursors and reductants, such as sodium borohydride, hydrazine and hydroxylamine [7].

Here, a new concept for preparation of heterogeneous noble metal catalyst is developed. We employ sputtering method to deposit Au, Au-Pd and Pd directly onto porous steel fiber matrices. This deposition of the noble metals is rather simple, and takes a few minutes. The steel fiber matrix (Fig. 1) is a type of structural and functional material with high specific surface area [8]. Among the Au, Au-Pd and Pd catalysts, the Au-Pd catalyst exhibits most promising activity in the oxidation of benzyl alcohol and benzyl amines by O_2. To the best of our knowledge, this is the first report on the sputtering method applied to preparation of bimetallic Au-Pd catalyst on such special support for catalytic oxidation.

2. Experimental

The deposition of Au by sputtering is described elsewhere [8]. Pd and Au-Pd were deposited by the same technique. The matrix (NV Bekaert SA, Belgium) used as the catalyst support consisted of stainless steel 316 L fibers and was ~0.5 mm thick. Before use, it was annealed in air at 650 °C for 4 h. Noble metals were deposited on the matrices in a high resolution sputter coater (Cressington 208HR, UK; 0.02 mbar under argon; sputtering current: 80 mA). The target materials used were pure Au (99.99%, Cressington), pure Pd (99.95%, Ted Pella. INC, USA) and a Au-Pd alloy (99.99%, 80/20 by weight, Cressington).

The sputter coater is fitted with a MTM-20 high-resolution terminating thickness controller to determine the nominal deposition thickness (NDT) of deposited noble metals. NDT is quantified as a flat metallic film deposited on a flat substrate. The amount of deposited metals can be calculated by the following formula: $m = V \times \rho = 2 \times (A \times \text{NDT}) \times \rho$, where m = mass of the metal, ρ = density of the metal, A = footprint area of the fiber matrix which is multiplied by 2 because metal was deposited on both sides.

The area of the fiber matrix used per catalytic measurement was 4.48 cm^2 in alcohol oxidation and 8.96 cm^2 in amine oxidation.

---

* Corresponding author. Tel.:+358 919150194; fax: +358 919150198.
E-mail address: Timo.Repo@helsinki.fi (T. Repo).

[1] Current address: College of Chemical Engineering, Shenyang University of Chemical Technology, Shenyang 110142, PR China.

1566-7367/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.catcom.2011.04.025

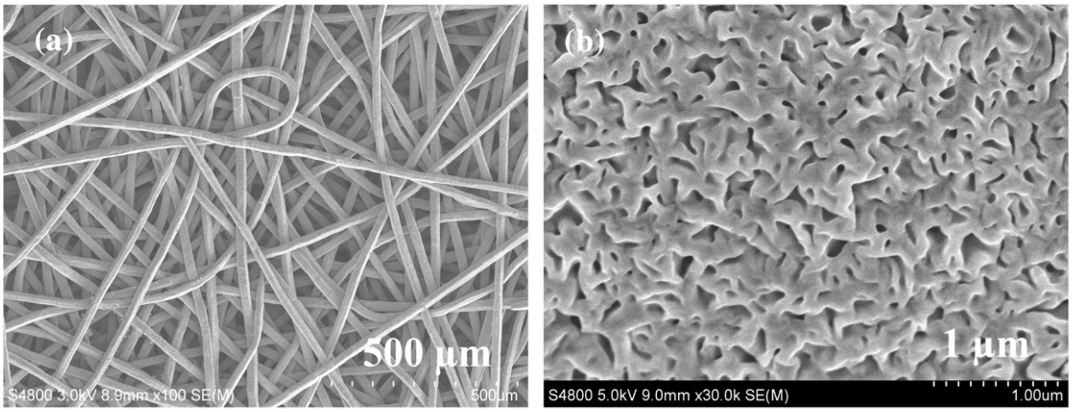


Fig. 1. SEM images with different magnifications of the steel fiber matrix used.

Calculated amounts of noble metals in alcohol oxidation are given in Table 1.

SEM images were obtained by Hitachi S-4800 Field emission scanning electron microscope.

The aerobic oxidation of the alcohols was performed in a stainless steel autoclave loaded with small glass liners and magnetic stir bars. The stirring speed was 1000 rpm. Water and appropriate amounts of alcohol and K_2CO_3 or NaOH were added to the glass liners. The catalyst matrix was cut into small pieces (~2 mm × 2 mm) with scissors before introduced into the reaction mixture. The reactor was then heated up after oxygen pressure was introduced. After reaction, the unreacted alcohol, aldehyde and ester were extracted with toluene. Benzoate (benzoic acid reacted with the base promoter) was transformed to benzoic acid by reacting with HCl, and then the benzoic acid was also extracted with toluene. The combined toluene solutions were analyzed by GC (Agilent 6890 N Gas Chromatograph, HP-Innowax column, FID detector) using acetophenone as the external standard. Every catalytic reaction under the same reaction conditions was measured at least 3 times, and the average values are reported. The catalytic reactions in comparison are measured at the same time. The aerobic dehydrogenation of amines was carried out with the similar reaction setup as used for the oxidation of alcohol. Benzylamine was distilled under reduced pressure before use. Turnover frequency (TOF) was calculated based on the total amount of noble metals applied in the reaction [9–11], because the fraction of surface metal atoms was not available.

3. Results and discussion

The microstructure of the Au on the steel fiber matrices depends on the amount of the deposited Au. The amount of Au is quantified as a NDT (NDT = thickness of a flat metallic film deposited on a flat surface; see Experimental section). SEM studies show that Au exists as isolated nano-islands at low NDTs. The nano-islands are seen as irregularly shaped bright features (Fig. 2a). When the NDT increases, the nano-islands become larger, merge and form a more continuous film (Fig. 2b). The structures of the supported Au-Pd alloys differ from those of Au (Fig. 2c and d). Nano-islands are not formed even at low NDTs as in Fig. 2a nor a discontinuous surface is obtained at high NDTs as in Fig. 2b (two typical discontinuous sites are denoted in Fig. 2b). This indicates that the Au-Pd alloy disperses better than Au alone on the steel fiber matrix. The morphology of Pd on the fiber matrix is similar with that of Au-Pd (pictures not shown).

Table 1
Amount of noble metals in the catalysts with different NDTs per measurement in the oxidation of alcohols.

NDT (nm)	0.5	1.5	3.0	6.0
Au (mmol)	4.39×10^{-5}	1.32×10^{-4}	2.63×10^{-4}	5.27×10^{-4}
Au-Pd (mmol)	4.75×10^{-5}	1.42×10^{-4}	2.85×10^{-4}	5.71×10^{-4}

To study the catalytic properties, aerobic oxidation of benzyl alcohol in water was first chosen as a model reaction. In the absence of a catalyst or with the pure fiber matrix without noble metals no oxidation occurred. However, small amount of Au or Au-Pd (NDT: 0.5 nm) deposited on the fiber matrices gave activity (Fig. 3). Both Au and Au-Pd catalysts were highly selective to benzoic acid when NaOH is used as the promoter (Fig. 3a). On the other hand, when K_2CO_3 is used as the promoter (Fig. 3b) selectivity of Au catalyst turns towards ester formation. Benzoic acid is the main product with Au-Pd catalyst, but its selectivity is reduced. Standard deviations in the measurement of yield in Fig. 3 are given in Table 2. After reaction under O_2 atmosphere, the dispersion form of Au-Pd observed by SEM is the same, and no new Au-Pd nanoparticles formed. Pd alone on the fiber matrix is inert.

The reactivity increases as the NDT increases (Fig. 3a). When NDT is 6 nm and NaOH is used as a base, Au-Pd gives 91% yield of benzoic acid. The relative TOFs are given in Fig. 4. High TOF values towards benzoic acid are noteworthy when comparing to earlier reported catalysts for benzyl alcohol oxidation in water. For example, TOF is up to 400 h^{-1} in Tsukuda's Au catalyst (conversion: ~99%; selectivity to benzoic acid: >90%; H_2O_2 as the oxidant) [12], and is up to 1140 h^{-1} in Prati's Au catalyst (conversion: 57%; selectivity to benzoic acid: 41%; selectivity to benzaldehyde: 32%) [11]. TOF is ~16 h^{-1} in Baiker's Au-Pd catalyst [13], and is up to 57 h^{-1} in Scott's Au-Pd catalyst [1]. Nearly full selectivity to benzaldehyde was reported in these two cases. Incidentally, the oxidation from benzaldehyde to benzoic acid was investigated by some efficient catalytic systems, such as Bi_2O_3 and t-BuOOH as the oxidant [14], β-cyclodextrin and NaClO as the oxidant [15], porphyrin in CH_3CN [16], etc.

Generally, alcohol oxidations over Au based catalysts need a base as a promoter. It is reasonable to assume that base is needed to deprotonate alcohol to initiate the catalytic reaction [17]. Here both Au and Au-Pd catalysts give neglectable conversions without a base. The optimal base to alcohol ratio is ~1:1 (Fig. 5).

To investigate whether the ester is produced via the condensation of benzyl alcohol and the generated benzoic acid, equimolar amounts of alcohol and benzoic acid were introduced to the reaction and K_2CO_3 was selected as a base. Compared to the results in Figs. 3b and 5b, neither the selectivity to ester nor the amount of produced ester is increased. No ester is formed in the absence of a catalyst. Therefore, the ester is most probably produced via a hemiacetal pathway (Scheme 1) [18,19]. Strong base as NaOH may prevent the formation

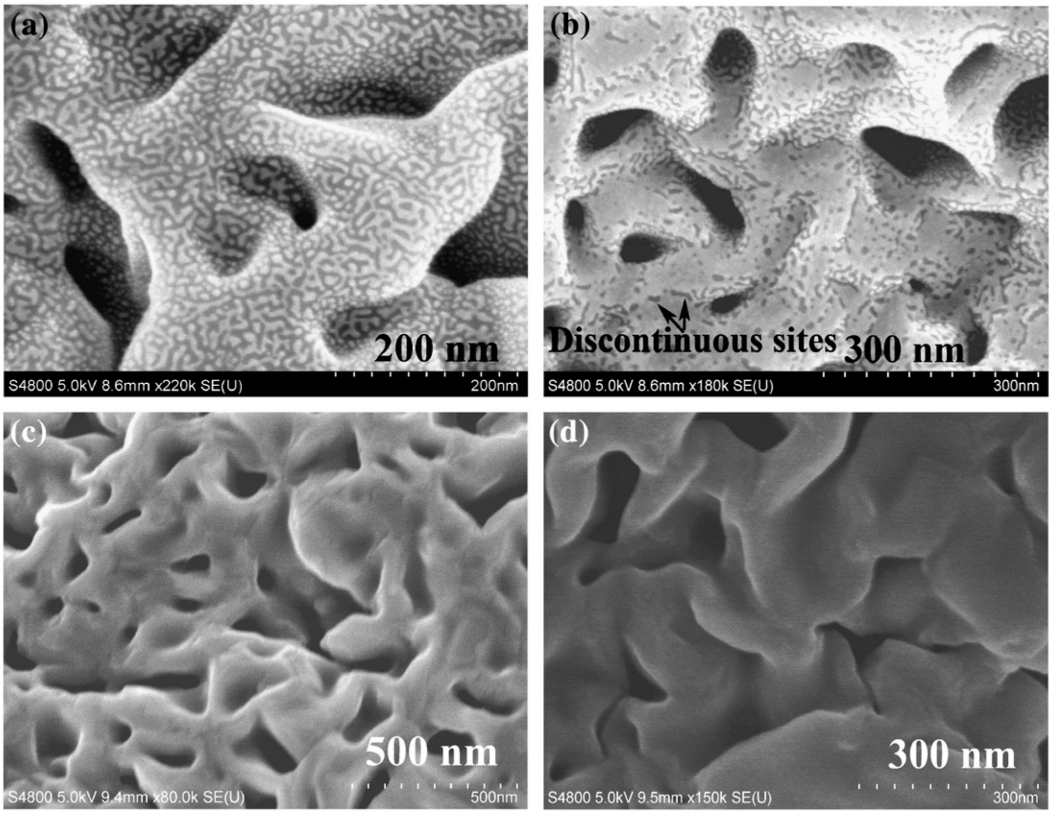


Fig. 2. SEM images of (a, b) Au and (c, d) Au-Pd on the steel fiber matrix. NDT: (a, c)1.5 nm; (b)3.0 nm; (d)6.0 nm.

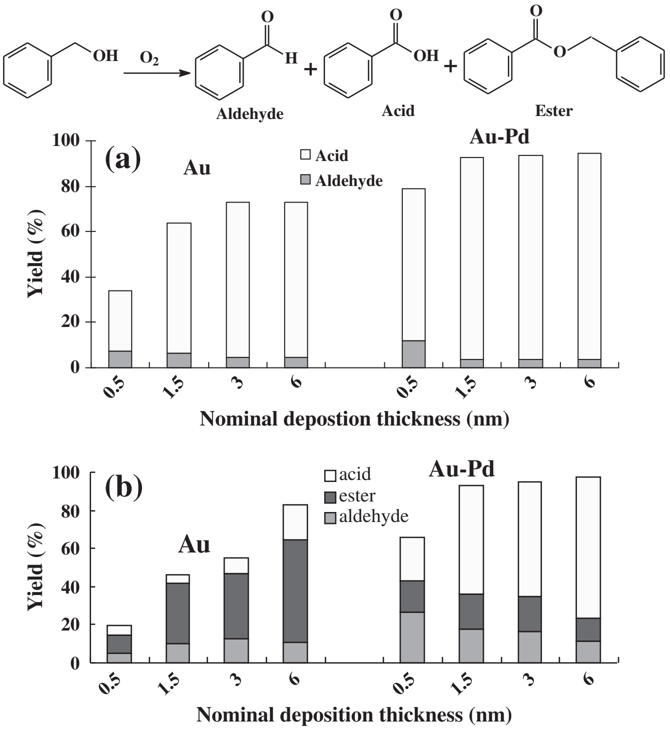


Fig. 3. Yield and selectivity of benzyl alcohol oxidation as a function of NDT when (a) NaOH and (b) K_2CO_3 used as the promoter. Reaction conditions: (a) 1.5 mmol and (b) 0.75 mmol alcohol, 1.5 ml water, 3 h, 80 °C, 5 bar O_2; $\text{base}_{\text{mol}}:\text{alcohol}_{\text{mol}} = 1:1$. Amounts of Au and Au-Pd used in the alcohol oxidation are given in Table 1. Standard deviations in the measurement of yield are given in Table 2.

of the hemiacetal intermediate. This reaction pathway could explain ester formation when K_2CO_3 or very low NaOH:alcohol molar ratio are used (Figs. 3 and 5).

When NaOH is used as a base the catalysts are also very active towards secondary benzylic alcohol. For example, 1-phenyl-1-propanol is oxidized into its relative ketone, propiophenone (Scheme 2), with ~80% yield over Au catalyst and ~90% yield over Au-Pd catalyst, together with excellent selectivity. When K_2CO_3 is used as a base, Au and Au-Pd catalysts give only ~45% yield and ~55% yield, respectively.

Table 2
Standard deviations in the measurement of yield in Fig. 3.

NDT (nm)	0.5	1.5	3.0	6.0
Au in Fig.3a	5.0	4.9	4.7	4.4
Au-Pd in Fig.3a	6.9	6.4	6.9	6.4
Au in Fig.3b	3.9	4.7	3.1	2.7
Au-Pd in Fig.3b	5.5	2.4	4.5	5.1

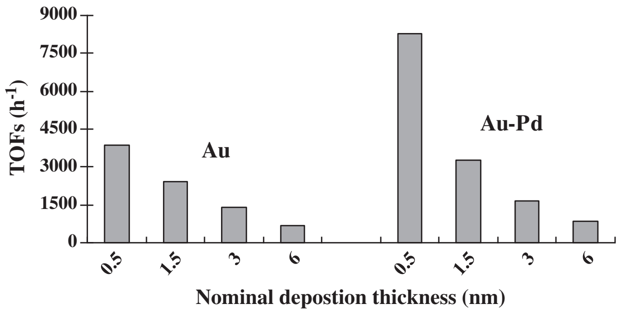


Fig. 4. TOFs at benzyl alcohol oxidation as a function of NDT when NaOH as the promoter (based on Fig.3a and Table 1).

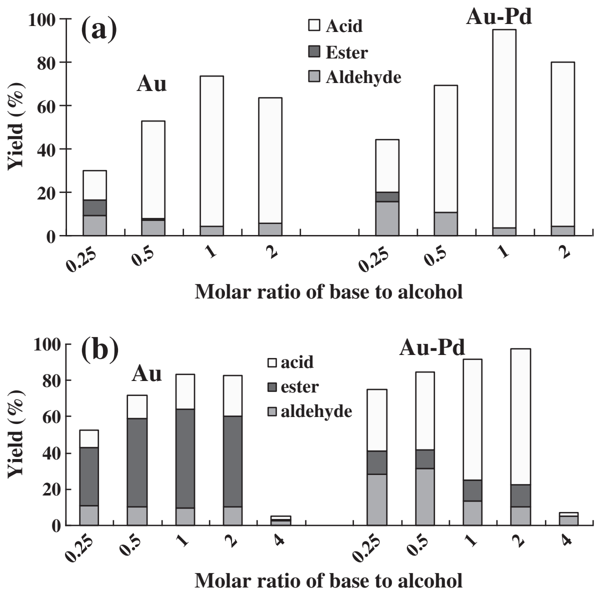
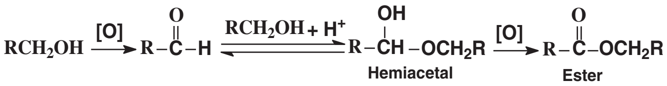


Fig. 5. Yield and selectivity of the benzyl alcohol oxidation as a function of (a) $NaOH_{mol}$:alcohol$_{mol}$ and (b) K_2CO_{3mol}:alcohol$_{mol}$. Reaction conditions are the same as in Fig. 3 and NDT is 6 nm.

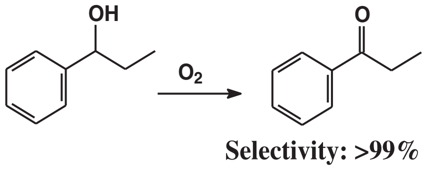
The dehydrogenation of dibenzylamine (secondary amine) and coupling of benzylamine (primary amine) (Scheme 3) were also chosen as the model reactions to study the catalytic properties. These two reactions are very slow. For example, the TOF in dibenzylamine oxidation is 1 h^{-1} in Au/C (reaction time of 17 h and 5 mol% Au related to amine) [2]. The TOF in benzylamine oxidation is 0.001 h^{-1} in Au powder [5], 0.3 h^{-1} in Au/Al_2O_3 (reaction time of 24 h) [5], ~3 h^{-1} in Au$(OAc)_3$/CeO_2 (reaction time of 16 h and 1.74 mol% Au related to amine) [3].

As in alcohol oxidation also in the dehydrogenation of dibenzylamine the Au-Pd catalyst has the highest activity in the series (entries 1–5 in Table 3). The Au and Pd catalysts are significantly less active than the Au-Pd catalyst which gives 60% conversion with a TOF of 3.2 h^{-1}. High selectivity of all catalysts towards imine is noteworthy as benzaldehyde or benzaldoxime as possible by-products [4] is not detected. Also in the coupling reaction of benzylamine, Au-Pd catalyst has a much higher activity than Au and Pd catalysts (entries 8–10 in Table 3). In applied conditions Au-Pd catalyst gives practically 100% selectivity to imine with a TOF of 3.7 h^{-1}.

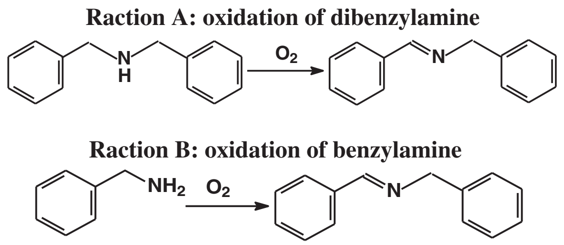
Since Au-Pd gives much higher activity than Au and Pd in the dehydrogenation of amines, synergetic effects in the former catalyst must play an important role. One possibility to the increased activity is that Pd acts as a diluent to improve Au dispersion. Small particle size favors the oxidation of benzyl amines on Au catalyst [4]. Another possibility is related to the stronger ability of Pd catalysts to dehydrogenate C-H bonds than of Au catalysts [20]. As the dehydrogenation of amines to imines involves the cleavage of both C—H and N—H bonds [21], the improved ability of Pd to cleave C—H bonds, together with the fact that Au catalyst is in general active in amine oxidation, might explain the observed synergistic effect.



Scheme 1. Plausible route for the ester formation via hemiacetal oxidation [18,19].



Scheme 2. 1-Phenyl-1-propanol oxidation (reaction conditions are the same as in Fig. 3a and NDT is 6 nm).



Scheme 3. Oxidative dehydrogenation of dibenzylamine and benzylamine.

Table 3
Dehydrogenation of dibenzylamine and benzylamine.

Entry	Substrate	Catalyst	Conversion (%)
1	Dibenzylamine	No catalyst	Trace
2	Dibenzylamine	Support	3
3	Dibenzylamine	Pd	4.5
4	Dibenzylamine	Au	9
5	Dibenzylamine	Au-Pd	59
6	Benzylamine	No catalyst	15
7	Benzylamine	Support	25
8	Benzylamine	Pd	26
9	Benzylamine	Au	29
10	Benzylamine	Au-Pd	67

Reaction condition: 100 °C, 0.15 mmol amine in 3.0 ml toluene, 5 bar O_2, 24 h; NDT: 6 nm for Au, Pd and Au-Pd catalysts; 1.142 μmol Au-Pd (~0.75 mol% Au-Pd related to the amine).

4. Conclusions

As shown here, a very clean and simple process of preparing heterogeneous noble metal based catalysts is achieved via sputtering technique. Au, Pd and Au-Pd were directly deposited from the corresponding metal targets onto the steel fiber matrix with high specific surface area. The Au-Pd structured catalyst exhibits good activities in the oxidation of benzyl alcohol and benzyl amines and shows a great synergistic enhancement in the reactivity especially in the oxidation of benzyl amines. This green route deserves further development. For example, choosing a matrix with an even larger surface area as the support, optimizing the Au/Pd ratio as well as examining different solvents may further improve the catalytic activity.

Acknowledgment

Financial support by the Academy of Finland (Project No. 124187) is gratefully acknowledged.

References

[1] W. Hou, N.A. Dehm, R.W.J. Scott, J. Catal. 253 (2008) 22–27.
[2] M. So, Y. Liu, C. Ho, C. Che, Chem. Asian J. 4 (2009) 1551–1561.
[3] L. Aschwanden, T. Mallat, F. Krumeich, A. Baiker, J. Mol, Catal. A 309 (2009) 57–62.
[4] A. Grirrane, A. Corma, H. Garcia, J. Catal. 264 (2009) 138–144.
[5] B. Zhu, M. Lazar, B.G. Trewyn, R.J. Angelici, J. Catal. 260 (2008) 1–6.
[6] M. Haruta, Chem. Rec. 3 (2003) 75–87.
[7] T. Premkumar, D. Kim, K. Lee, K.E. Geckeler, Gold Bull. 40 (2007) 321–327.
[8] H. Guo, M. Kemell, M. Heikkilä, M. Leskelä, Appl. Catal. B 95 (2010) 358–364.

[9] T. Ishida, M. Nagaoka, T. Akita, M. Haruta, Chem. Eur. J. 14 (2008) 8456–8460.
[10] F. Su, M. Chen, L. Wang, X. Huang, Y. Liu, Y. Cao, H. He, K. Fan, Catal. Commun. 9 (2008) 1027–1032.
[11] A. Biffis, S. Cunial, P. Spontoni, L. Prati, J. Catal. 251 (2007) 1–6.
[12] Y. Liu, H. Tsunoyama, T. Akita, T. Tsukuda, J. Phys, Chem. C 113 (2009) 13457–13461.
[13] S. Marx, A. Baiker, J. Phys, Chem. C 113 (2009) 6191–6201.
[14] P. Malik, D. Chakraborty, Tetrahedron Lett. 51 (2010) 3521–3523.
[15] D.P. Shi, H.B. Ji, Chinese Chem. Lett. 20 (2009) 139–142.
[16] M. Hajimohammadi, N. Safari, H. Mofakham, A. Shaabani, Tetrahedron Lett. 51 (2010) 4061–4065.
[17] M. Conte, H. Miyamura, S. Kobayashi, V. Chechik, J. Am. Chem. Soc. 131 (2009) 7189–7196.
[18] A. Abad, P. Concepción, A. Corma, H. García, Angew. Chem. Int. Ed. 44 (2005) 4066–4069.
[19] G. Li, D.I. Enache, J. Edwards, A.F. Carley, D.W. Knight, G.J Hutchings, Catal. Lett. 110 (2008) 7–13.
[20] N.F. Dummer, S. Bawaked, J. Hayward, R. Jenkins, G.J. Hutchings, Catal. Today 154 (2010) 2–6.
[21] R.J. Angelici, J. Organomet. Chem. 693 (2008) 847–856.