DOI: 10.1002/adsc.200700553

Membrane-Occluded Gold-Palladium Nanoclusters as Heterogeneous Catalysts for the Selective Oxidation of Alcohols to Carbonyl Compounds

P. G. N. Mertens,[a] P. Vandezande ,[a] X. Ye,[b] H. Poelman,[c] D. E. De Vos,[a] and I. F. J. Vankelecom[a,*]

[a] Centre for Surface Chemistry and Catalysis, Faculty of Bioscience Engineering, Katholieke Universiteit Leuven, Kasteelpark Arenberg 23 – box 2461, 3001 Leuven, Belgium
Phone: (+32)-16-321594; fax: (+32)-16-321998
E-mail: Ivo.Vankelecom@biw.kuleuven.be
[b] Department of Metallurgy and Materials Engineering, Faculty of Engineering, Katholieke Universiteit Leuven, Kasteelpark Arenberg 44 – box 2450, 3001 Leuven, Belgium
[c] Department of Solid State Science, Faculty of Sciences, University of Gent, Krijgslaan 281 S1, 9000 Gent, Belgium

Received: December 22, 2008; Revised: February 19, 2008; Published online: April 15, 2008

Abstract: Pre-formed polyvinylpyrrolidone-stabilized gold-palladium clusters, consisting of 80 mol% gold and with a mean size of 1.9 nm, were immobilized quantitatively in a porous polyimide membrane *via* the process of phase inversion, without loss of metal nanodispersion. The obtained gold-palladium/polyimide membrane emerged as a highly active heterogeneous metal catalyst for the amide-phase and solvent-free oxidation of aliphatic, allylic and benzylic alcohols with full selectivity to the corresponding aldehydes and ketones, and could be recycled with excellently preserved catalytic activity and product selectivity. Occlusion of the optimized bimetallic clusters in the polyimide structure proved beneficial in view of their superior catalytic performance compared to the analogous colloidal gold-palladium clusters.

Keywords: alcohol oxidation; bimetallic catalyst; catalytic membrane; gold-palladium; phase inversion; solvent-free oxidation

The selective oxidation of alcohols to aldehydes or ketones is a key process in the production of fine chemicals.[1] Alcohols are traditionally oxidized by stoichiometric amounts of costly metal oxidants like chromate and permanganate, inevitably leading to the formation of environmentally noxious waste products.[2] More benign processes employ O_2 or H_2O_2 as the oxidizing reagent in the presence of a catalyst, with H_2O as the harmless by-product.[3] Both homogeneous and heterogeneous catalysts have already proven their suitability for the liquid-phase alcohol oxidation.[4] Successful homogeneous catalysts based on, e.g., Pd and Ru have been introduced before.[5] Apart from metal-based systems, efficient heterogeneous catalysts such as heteropolyacids, hydrotalcites, mixed oxides and molecular sieves have been proposed.[6] With respect to metal catalysts, mostly Pd- and Pt-based catalysts have been investigated, despite their sensitivity to deactivation through overoxidation and chemical poisoning.[3b,7]

Recently, the suitability of mono- and bimetallic Au clusters deposited on carbon or oxide supports for the liquid-phase oxidation of alcohols has been demonstrated.[8] The advantageous introduction of Au resulted in more active, selective and durable oxidation catalysts. Concurrently, Au clusters immobilized in polymeric structures have been introduced as promising metal catalysts for the aerobic alcohol oxidation.[9] These Au clusters were enclosed by polyvinylpyrrolidone (PVP) polymers,[9a] embedded in microgels with pyridine functional groups,[9b] incarcerated in a polystyrene matrix[9c] or encapsulated by vinyl ether star polymers[9d]. Besides their often tedious synthesis,[9c,d] the predominant disadvantage of such polymer-stabilized Au clusters is their recovery from the reaction mixtures, which involves separation procedures like centrifugation, filtration, decantation, etc.

In recent years, metal clusters have also been immobilized in insoluble polymer matrices to facilitate catalyst recycling. Au clusters supported on, for instance, an ion exchange resin were successfully applied in the oxidative carbonylation of amines,[10] while an amphiphilic resin containing Pd nanoparticles proved useful for the aqueous phase oxidation of alcohols.[11]

Inspired by these recent findings, the objective of this work was the immobilization of pre-formed, PVP-protected Au^0-Pd^0 clusters in a porous polyimide (PI) matrix, thereby generating a catalytic membrane able to oxidize a wide scope of alcohol substrates in solvent-free oxidation conditions, and easily recoverable from the organic reaction medium. The research approach comprised three successive experimental phases. Firstly, PVP-stabilized Au^0-Pd^0 clusters were evaluated as quasihomogeneous metal catalysts for the benzyl alcohol oxidation in *N,N*-dimethylformamide (DMF), and optimized in terms of cluster composition and size to maximize the oxidation rates. Subsequently, a straightforward procedure was developed for the quantitative immobilization of the optimized Au^0-Pd^0 colloids in a PI matrix *via* the well-known process of diffusion-induced phase inversion where a polymer solution is converted into a solidified porous membrane after immersion in a non-solvent for the polymer, typically water.[13] After synthesis, the obtained membrane was modified by chemical cross-linking to achieve stability in amidic and aromatic media.[14] The potential of the thus developed Au^0-Pd^0/PI catalytic membrane as a heterogeneous catalyst was then assessed in the amide-phase oxidation of various types of alcohols and the solvent-free oxidation of 1-phenylethanol.

PVP-stabilized monometallic Au clusters were synthesized by chemical hydride reduction, using molar vinylpyrrolidone monomer/Au ratios varying between 10 and 200.[9a,12] DMF was selected as the synthesis medium as it facilitates the dissolution of the Au precursor and displays a high affinity for PVP.[15] This favours the unfolding of the PVP chains and the protection of the Au dispersion. X-ray photoelectron spectroscopy (XPS) analysis revealed an Au $4f_{7/2}$ core level at a binding energy of 84.0 eV, proving that all Au species in the various Au sols are in the metallic state. For molar PVP/Au ratios between 10 and 100, the gradual rise in PVP concentration at constant Au content resulted in decreasing Au^0 cluster sizes, as determined by transmission electron microscopy (TEM). For the reddish brown Au^0 nanosols prepared with molar PVP/Au ratios ≥ 100, no further increase in Au nanodispersion was observed. The average Au^0 cluster size of the Au^0 colloids varied between 1.8 nm (PVP/Au = 200) and 6.2 nm (PVP/Au = 10).

These amidic Au^0 nanosols were then tested as quasihomogeneous metal catalysts in the oxidation of benzyl alcohol at 353 K and 2.0 MPa O_2. In contrast to earlier work,[16] promotion of the colloidal nano-Au^0 catalyst with an extra added base was not required to achieve high turnover rates. The weakly basic properties of both the protective polymer and the amide solvent proved sufficient to promote alcohol oxidation. In all experiments, benzaldehyde emerged as the sole reaction product. Typical by-products like, e.g., benzoic acid or benzyl benzoate,[16,17] could not be detected in the product pool.

The Au^0 nanocolloids (Ø 1.8 nm) synthesized with a molar PVP/Au ratio of 100 emerged as the most active catalysts with a turnover frequency (TOF) of 220 h^{-1} after 1 h at a molar benzyl alcohol/Au ratio of 1000. Au^0 sols with similar cluster size but more PVP encapsulation were less active. This can be explained in terms of increased diffusion limitation and active site blocking on the catalytic Au^0 surface as a consequence of the excess PVP. On the other hand, the less protected, more reddish Au^0 sols with distinct surface plasmon resonance (SPR) bands between 515 and 530 nm in the UV-Vis spectrum, displayed lower catalytic activities as a result of their inferior Au nanodispersion.

Next, Pd-doped Au^0 colloids were assessed in view of the recent successes reported with heterogeneous Au-Pd catalysts in alcohol oxidations.[17,18] Bimetallic sols with varying Au/Pd ratios were prepared at a constant PVP/metal ratio of 100 to investigate the potential synergetic effect between Au and Pd. *Via* XPS analysis it was found that the bimetallic sols consisted of zerovalent Au and Pd, with Au $4f_{7/2}$ and Pd $3d_{5/2}$ levels at binding energies of 84.0 eV and 335.8 eV, respectively. Energy dispersive X-ray (EDX) spot analysis upon TEM characterization revealed that the bimetallic sols consisted of Au-Pd clusters as found before.[19]

Using the same evaluation conditions in the benzyl alcohol oxidation as previously applied for the monometallic Au^0 catalyst, a colloidal bimetallic catalyst with molar Au/Pd ratio of 8:2 emerged as the most active, with a TOF of 580 h^{-1}. This sharp turnover rate increase cannot be due to a metal dispersion effect, as the optimal Au^0-Pd^0 colloids had a mean cluster diameter of 1.9 nm (Figure 1 a).

For comparison, the (8:2)Au^0-Pd^0 sols were prepared with varying PVP/metal ratios and thus different sizes of the bimetallic clusters. The ratio of 100 was confirmed to correspond to the most appropriate PVP concentration to maximize the benzyl alcohol oxidation rate. Calculations on the EDX spot data, recorded for individual metal clusters, revealed that the optimized bimetallic clusters consisted of 80.5 mol% Au and 19.5 mol% Pd. The Au/Pd ratio of the clusters thus clearly reflects the ratio applied for the synthesis of the optimal bimetallic sol.

Immobilization of the Au^0-Pd^0 clusters in a membrane was then realized by adding the optimized bimetallic nanosol to a stirred PI solution. The obtained homogeneous solution was cast on a glass plate, after which the nascent film was solidified in water *via* immersion-precipitation, thus forming a porous PI membrane (Figure 1 b, c) with occluded (8:2)Au^0-Pd^0 clusters. No leaching of dark-coloured bimetallic colloids from the solidifying PI film into the coagulation bath was detected by inductively coupled plasma atomic emission spectrophotometry (ICP-AES), showing that

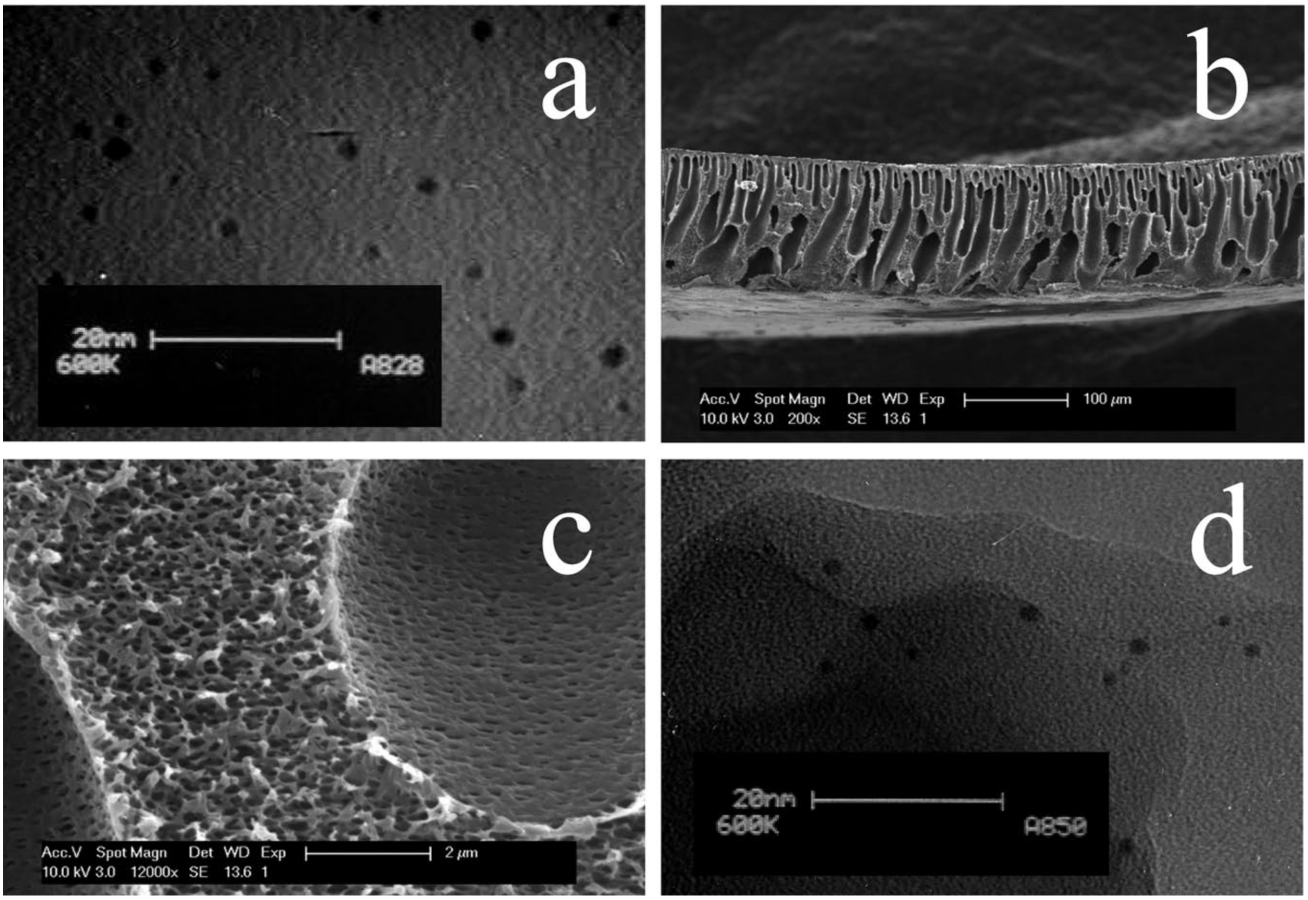

Figure 1. a) TEM picture (8:2)Au^0-Pd^0 nanocolloids; b) SEM picture cross-section catalytic (8:2)Au^0-Pd^0/PI membrane; c) High magnification SEM picture porous matrix structure (8:2)Au^0-Pd^0/PI membrane; d) TEM picture (8:2)Au^0-Pd^0 clusters occluded in PI membrane.

the heterogenization procedure proceeded quantitatively. TEM characterization confirmed that the bimetallic nanodispersion was unaffected throughout the immobilization (Figure 1 d). A typical membrane had a metal loading of 40 µmol per g, or 0.16 µmol per cm^2 of PI membrane.

After synthesis, the PI membrane with occluded bimetallic clusters was immersed in a methanolic *p*-xylylenediamine solution for cross-linking of the polymer (Figure 2).[14,20] This is required for polymeric membranes to ensure chemical stability in demanding media, such as aromatics or amides that would cause excessive swelling or even full dissolution of the membranes.[13a] After 6 h, a sufficient number of imide groups of the PI chains had been opened and cross-linked to allow complete solvent stability, as proven

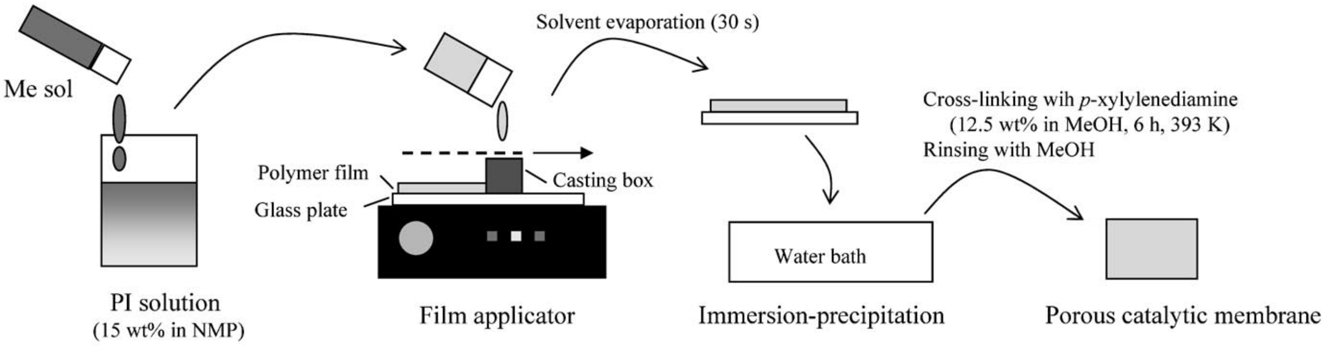

Figure 2. Scheme of the synthesis of the catalytic membrane.

by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). In comparison with a non-cross-linked PI membrane, a gradual increase of the IR signal around 3250 cm^{-1} was observed, characteristic for the N–H stretch vibrations of amidic bonds. The cross-linking procedure did not affect the physical pore structure of the catalytic membrane as confirmed *via* scanning electron microscopy (SEM).

The (8:2)Au^0-Pd^0/PI membrane was then assessed as a heterogeneous metal catalyst in alcohol oxidations. The effects of O_2 pressure (0.5–4.0 MPa O_2) and reaction temperature (353–433 K) were studied for the catalytic oxidation of benzyl alcohol in DMF. A slight decrease in oxidation rate of at most 3% was observed for pressures below the optimum pressure of 2.0 MPa O_2, while higher O_2 pressures did not lead to higher TOF values. While the O_2 pressure had a limited effect, a temperature increase strongly raised the oxidation rate, even though the selectivity somewhat declined at the highest temperatures due to formation of benzene. At 2.0 MPa O_2 pressure and 413 K, the TOF for the benzyl alcohol oxidation amounted to 16520 h^{-1} at 99% conversion (Table 1), meaning a significant improvement as compared to the non-heterogenized (8:2)Au^0-Pd^0 catalyst (12870 h^{-1}), with a maintained full selectivity to benzaldehyde. Under the same conditions, the determined TOF values were 22190 h^{-1}, 20650 h^{-1} and 18830 h^{-1} at, respectively, 25%, 50% and 75% benzyl alcohol conversion. No leaching of Au or Pd species from the catalytic membrane occurred during the oxidation experiments, as determined with ICP-AES. The superior performance of the heterogenized (8:2)Au^0-Pd^0 clusters is probably ascribable to the partial withdrawal of PVP from the bimetallic clusters' surface as a result of the high affinity between PVP and PI, and moreover to the very open structure of the catalytic membrane.

Different types of substrates were then studied, that is, primary and secondary alcohols of the benzylic, allylic and aliphatic type. In each case, a total chemoselectivity to the derived aldehydes and ketones was observed, and no isomerisation products were discerned for the allylic alcohol substrates, as represented in Table 1. The oxidation rate over the catalytic membrane was found to be highly dependent on the alcohol structure, with a higher reactivity for secondary alcohols in comparison with primary alcohols and moreover a decrease in alcohol reactivity in the order benzylic > allylic > aliphatic.

The catalytic (8:2)Au^0-Pd^0/PI membrane was also applied in solvent-free conditions for the oxidation of 1-phenylethanol (Table 2). Full selectivity to acetophenone was maintained over the temperature range studied. A maximum TOF of 117200 h^{-1} was reached at 433 K, while a value of 49170 h^{-1} was obtained at 413 K (Table 2, entry 4), constituting a 10% increase compared to the 1-phenylethanol oxidation in DMF (Table 1, entry 2). At 353 K an oxidation rate of 2130 h^{-1} was found, corresponding to a 40% increase with respect to the 1-phenylethanol oxidation in DMF over the optimized (8:2)Au^0-Pd^0 nanocolloids which led to a TOF of 1480 h^{-1}.

Finally, recycling experiments were performed to assess the durability of the catalytic membrane at two reaction temperatures (Table 3). In both cases the catalytic membrane retained its activity in the solvent-free oxidation of 1-phenylethanol very well. In the fourth reuse, >97% of the oxidation rate of the first run was still preserved, while total selectivity to acetophenone was maintained.

Table 1. Alcohol oxidation[a] over Au^0-Pd^0/PI.

Substrate (S)	S/Me[b] [mol/mol]	Time[c] [min]	C[d] [%]	TOF[e] [h^{-1}]
benzyl alcohol	50000	32	24	22470
	20000	72	99	16520
1-phenylethanol	50000	12	24	58980
	50000	66	99	45030
crotyl alcohol	2000	15	26	2050
	2000	60	93	1850
1-octen-3-ol	2000	19	25	1610
	2000	78	94	1420
3-octanol	2000	25	24	1140
	1000	60	98	980
1-octanol	2000	53	25	570
	500	60	96	480
1-butanol	2000	30	25	990
	1000	66	95	860

[a] *Conditions:* (8:2)Au^0-Pd^0/PI (PVP/Me = 100); DMF; 413 K; 2.0 MPa O_2.
[b] Me: metal.
[c] Time: reaction time.
[d] C: conversion.
[e] TOF: turnover frequency at reported reaction time and conversion level.

Table 2. Solvent-free 1-phenylethanol oxidation[a] over Au^0-Pd^0/PI.

T (K)	S/Me [mol/mol]	C [%]	TOF[b] [h^{-1}]
353	20000	11	2130
373	20000	33	6540
393	50000	39	19360
413	200000	26	49170
433	200000	59	117200

[a] *Conditions:* (8:2)Au^0-Pd^0/PI (PVP/Me = 100); 1-phenylethanol; 2.0 MPa O_2; 1 h.
[b] TOF: turnover frequency at reported reaction time and conversion level.

Table 3. Recycling experiments in the solvent-free 1-phenylethanol oxidation[a] over Au^0-Pd^0/PI.

T [K]	Run	S/Me [mol/mol]	C [%]	TOF[b] [h^{-1}]
353	1	20000	11	2110
	5	20000	10	2070
433	1	200000	59	116400
	5	200000	57	113300

[a] *Conditions:* (8:2)Au^0-Pd^0/PI (PVP/Me = 100); 1-phenylethanol; 2.0 MPa O_2; 1 h.

[b] TOF: turnover frequency at reported reaction time and conversion level.

The benefits of the developed Au^0-Pd^0/PI membrane in comparison with polymer-stabilized Au nanoclusters described in literature,[9] are obvious in view of its easy synthesis and simple recovery from the reaction mixture and thus its straightforward recycling with preserved catalytic performance in consecutive oxidation runs. Moreover, the significantly higher activity of the membrane-occluded (8:2)Au^0-Pd^0 clusters as compared to the corresponding colloidal bimetallic clusters reveals that the immobilization resulted in a reduced diffusion limitation around the bimetallic clusters. Previous studies with polymer-stabilized Au clusters did also not consider doping with Pd and thus the synergetic effect observed here, which clearly induces a significant increase in oxidation rate.

Furthermore, the catalytic membrane is applicable in amidic media, with the inherent advantage of full selectivity to aldehyde products in the oxidation of primary alcohols. This contrasts with the pronounced formation of acid products reported elsewhere as a consequence of the aqueous reaction medium.[9a,b] Moreover, basic promotion of the membrane-occluded Au^0-Pd^0 clusters proved no pre-requisite to achieve high oxidation rates, contrary to PVP-stabilized Au clusters,[9a] and amphiphilic resin-anchored Pd clusters.[11] The Au^0-Pd^0/PI membrane even affords the opportunity to run the alcohol oxidation in solvent-free conditions, which facilitates product purification and further improves the specific oxidation activity of the bimetallic clusters.

In addition to these benefits, results obtained with the developed (8:2)Au^0-Pd^0/PI membrane in the aerobic alcohol oxidation compare favourably with state-of-the-art metal catalysts in terms of oxidation rates. The solvent-free oxidation of 1-phenylethanol to acetophenone at 433 K was considered as the reference reaction here. With respect to supported monometallic clusters, a Pd/hydroxyapatite catalyst led to a TOF value of 9800 h^{-1},[20] a Au/CeO_2 catalyst resulted in an oxidation rate of 12500 h^{-1},[21] and Au/$Cu_5MgAl_2O_x$ catalyzed the 1-phenylethanol oxidation with a rate of 11750 h^{-1}.[8d] The catalytic membrane introduced here displays a TOF of 117200 h^{-1} (Table 2), which is significantly superior to the results achieved with monometallic catalysts, and in the same activity range as obtained with the PdAu/TiO_2 catalyst (269000 h^{-1})[8b] under identical oxidation conditions.

Summarizing, the evaluation of PVP-stabilized metal clusters as quasihomogeneous catalysts in alcohol oxidations, with experimental control over the cluster composition and size, enabled to discern Au^0-Pd^0 clusters with a mean size of 1.9 nm and consisting of 80 mol% Au as the most active and selective metal clusters. *Via* a straightforward synthesis procedure involving simple immersion-precipitation, a robust solvent-stable PI membrane was obtained, containing occluded Au^0-Pd^0 clusters with fully preserved metal nanodispersion. The bimetallic nanoclusters immobilized in the PI membrane displayed enhanced activity compared to the analogous colloidal Au^0-Pd^0 catalysts. Moreover, the catalytic membrane allowed working in solvent-free conditions leading to an additional increase in alcohol oxidation rates, and could be recycled with excellently preserved performance. These findings clearly demonstrate the potential of porous polymeric membranes as supports for metal clusters.

Experimental Section

Preparation of Quasihomogeneous Metal Catalysts

Mono- and bimetallic sols were prepared by addition of varying amounts of $AuCl_3$ and $PdCl_2$ (total metal (Me) content of 0.1 mmol) to a stirred DMF (8 mL) solution containing PVP (MW = 10000; 0.111–2.220 g with quantity increments of 0.111 g). These variations in PVP content resulted in molar ratios of monomeric vinylpyrrolidone to Me from 10 to 200. The applied variations in the composition of the bimetallic sols led to molar Au/Pd ratios ranging from 10:0 to 0:10 with 10 equal intervals. After 12 h, a DMF solution (2 mL) containing $NaBH_4$ (0.4 mmol; molar ratio $NaBH_4$/$MeCl_x$ = 4) was added to generate the Me sol.

Preparation of Catalytic Membrane

A PI (Matrimid® 9725 US; Huntsman) based catalytic membrane was prepared as schematically shown in Figure 2. First, Me sol (6 mL) was added to a stirred PI solution (10 g; 15 wt%) in *N*-methylpyrrolidone (NMP). After homogenization, this solution was cast (1.2 m min^{-1}) on a glass plate using an automatic film applicator, leading to a wet film thickness of 250 μm. The solvent was allowed to evaporate for 30 s after which the nascent film was immersed in deionized H_2O for 15 min. After synthesis, the obtained catalytic membrane was cross-linked through immersion in a methanolic *p*-xylylenediamine solution (12.5 wt%) for typically 6 h at 393 K. Finally, the modified catalytic membrane was washed with methanol to remove excess cross-linker, after which it was kept in DMF or 1-phenylethanol, depending on its further use. Prior to application in the oxidation experiments, the membrane was cut into pieces of 0.25 cm^2.

Characterization of Catalysts and Catalytic Membrane

Non-diluted monometallic Au sols were characterized by UV-Vis spectroscopy to determine the wavelength position of the SPR band maxima. Colloidal Me clusters were studied with TEM at 200 kV, after deposition of a droplet of a diluted Me sol on a TEM grid. The catalytic membrane was fixated in a resin after which microtome slices of the membrane were characterized with TEM. The mean Me cluster size was estimated as the mean diameter for an ensemble of 200 Me particles. For each Me sol, the composition of 20 individual Me clusters was determined by EDX spot analysis upon TEM analysis. Additionally, the Me sols were immobilized on a glass plate to allow XPS analysis using a monochromated 450 W Al Kα source.

The efficiency of the Me immobilization in the PI membrane matrix and the degree of Me leaching from the catalytic membrane during the oxidation experiments were investigated with ICP-AES (Au: 267.6 nm, Pd: 340.5 nm) with metal detection limits below 1 ppm. DRIFTS allowed us to investigate the post-synthesis modification of the catalytic membrane. The presence of N−H stretching vibrations around 3250 cm^{-1} was monitored since the cross-linking procedure results in the substitution of imide groups (no N−H bond) by amidic bonds (N−H bond). For SEM, membrane cross-sections were obtained by breaking the catalytic membrane under liquid N_2. The samples were then coated with a Au layer to reduce sample charging under the electron beam.

Alcohol Oxidation Experiments

For the oxidations with quasihomogeneous Me^0 catalysts, DMF (0.6 mL), Me^0 sol (0.4 mL; equivalent with 4 μmol of Me) and alcohol substrate (S; 4 or 8 mmol) were mixed, leading to molar S/Me ratios of 1000 and 2000. Reaction mixture for heterogeneously catalyzed amide-phase oxidations consisted of DMF (5 mL), the appropriate amount of S and pieces of the cross-linked Au^0-Pd^0/PI membrane, constituting a total surface of 1.25 cm^2 (0.2 μmol Me; S/Me = 50000, 20000) or 5.0 cm^2 (0.8 μmol Me; S/Me = 2000, 1000, 500). For the solvent-free oxidation of 1-phenylethanol, the solvent was replaced by S (4.89 g; 40 mmol), with an S/Me ratio of 20000 for the oxidations performed at $353\,K \leq T \leq 383\,K$, 50000 for the oxidations at $393\,K \leq T \leq 403\,K$ and 200000 for the oxidations at $T \geq 413\,K$. For the recycling experiments, the reaction was analyzed after 1 h, and the membrane pieces were washed three times in pure 1-phenylethanol. Fresh 1-phenylethanol was then added and the next oxidation run was started. The oxidation experiments were performed at reaction temperatures between 353 and 433 K and O_2 pressures from 0.5 to 4.0 MPa, with continuous O_2 supply and magnetic stirring at 1000 rpm. All oxidation and recycling experiments were performed in triplicate. A blank experiment in the absence of the metal catalysts was always performed to evaluate potential product formation as a result of autoxidation.

For product analysis, a FID-equipped GC with a Chrompack CP-WAX 58 CB stationary phase was used. The retention times of all possible oxidation products were compared with those of commercial reference compounds. Peak assignment was corroborated by analysis of the reaction samples by GC-MS. The TOF (h^{-1}) represents the molar ratio of converted alcohol substrate and Me, divided by the reaction time.

Acknowledgements

PGNM thanks K.U.Leuven for a postdoctoral fellowship grant. This research was done in the framework of an I.A.P.-P.A.I. grant (IAP 6/27) on Supramolecular Catalysis sponsored by the Belgian Federal Government, and of a G.O.A. grant from the Flemish Government.

References

[1] a) R. A. Sheldon, J. K. Kochi, *Metal-Catalyzed Oxidations of Organic Compounds*, Academic Press, New York, **1981**; b) M. Hudlicky, *Oxidations in Organic Chemistry*, American Chemical Society, Washington, DC, **1990**.

[2] G. Cainelli, G. Cardillo, *Chromium Oxidations in Organic Chemistry*, Springer-Verlag, Berlin, **1984**.

[3] a) R. A. Sheldon, I. W. C. E. Arends, G. J. ten Brink, A. Dijksman, *Acc. Chem. Res.* **2002**, *35*, 774; b) T. Mallat, A. Baiker, *Chem. Rev.* **2004**, *104*, 3037.

[4] B. Zhan, A. Thompson, *Tetrahedron* **2004**, *60*, 2917.

[5] a) G. J. ten Brink, I. W. C. E. Arends, R. A. Sheldon, *Science* **2000**, *287*, 1636; b) I. Marko, P. R. Giles, M. Tsukazaki, I. Chelle-Regnaut, C. J. Urch, S. M. Brown, *J. Am. Chem. Soc.* **1997**, *119*, 12661.

[6] a) W. Turek, M. Lapkowski, J. Debiec, A. Krowiak, *Appl. Surf. Sci.* **2005**, *252*, 847; b) V. R. Choudhary, D. K. Dumbre, B. S. Uphade, V. S. Narkhede, *J. Mol. Catal. A: Chem.* **2004**, *215*, 129; c) H. G. Manyar, G. S. Chaure, A. Kumar, *J. Mol. Catal. A: Chem.* **2006**, *243*, 244; d) V. D. Makwana, L. J. Garces, J. Liu, J. Cai, Y. Son, S. L. Suib, *Catal. Today* **2003**, *85*, 225.

[7] M. Besson, P. Gallezot, *Catal. Today* **2000**, *57*, 127.

[8] a) D. Wang, A. Villa, F. Porta, D. Su, L. Prati, *Chem. Commun.* **2006**, *18*,1956; b) D. I. Enache, J. K. Edwards, P. Landon, B. Solsona-Espriu, A. F. Carley, A. A. Herzing, M. Watanabe, C. J. Kiely, J. D. W. Knight, G. J. Hutchings, *Science* **2006**, *311*, 362; c) A. Abad, C. Almela, A. Corma, H. Garcia, *Chem. Commun.* **2006**, *30*, 3178; d) P. Haider, A. Baiker, *J. Catal.* **2007**, *248*, 175.

[9] a) H. Tsunoyama, H. Sakurai, Y. Negishi, T. Tsukuda, *J. Am. Chem. Soc.* **2005**, *127*, 9374; b) A. Biffis, S. Cunial, P. Spontoni, L. Prati, *J. Catal.* **2007**, *251*, 1; c) H. Miyamura, R. Matsubara, Y. Miyazaki, S. Kobayashi, *Angew. Chem.* **2007**, *119*, 4229; *Angew. Chem. Int. Ed.* **2007**, *46*, 4151; d) S. Kanaoka, N. Yagi, Y. Fukuyama, S. Aoshima, H. Tsunoyama, T. Tsukuda, H. Sakurai, *J. Am. Chem. Soc.* **2007**, *129*, 12060.

[10] F. Shi, Y. Deng, *J. Catal.* **2002**, *211*, 548.

[11] Y. Uozumi, R. Nakao, H. Rhee, *J. Organomet. Chem.* **2007**, *692*, 420.

[12] P. G. N. Mertens, H. Poelman, X. Ye, I. F. J. Vankelecom, P. A. Jacobs, D. E. De Vos, *Catal. Today* **2007**, *122*, 352.

[13] a) P. Vandezande, L. E. M. Gevers, I. F. J. Vankelecom, *Chem. Soc. Rev.* **2008**, doi:10.1039/b610848m; b) I. F. J. Vankelecom, K. De Smet, L. E. M. Gevers, P. A. Jacobs, in: *Nanofiltration. Principles and Applications*, (Eds.: A. I. Schäfer, A. G. Fane, T. D. Waite), Elsevier, Oxford, **2005**, pp 33–65.

[14] Y. H. See Toh, F. W. Lim, A. G. Livingston, *J. Membr. Sci.* **2007**, *301*, 3.

[15] C. Comuzzi, P. Di Bernardo, P. Polese, P. Portanova, M. Tolazzi, P. L. Zanonato, *Polyhedron* **2000**, *19*, 2427.

[16] N. Dimitratos, J. A. Lopez-Sanchez, D. Morgan, A. F. Carley, L. Prati, G. J. Hutchings, *Catal. Today* **2007**, *122*, 317.

[17] D. I. Enache, D. Barker, J. K. Edwards, S. H. Taylor, D. W. Knight, A. F. Carley, G. J. Hutchings, *Catal. Today* **2007**, *122*, 407.

[18] N. Dimitratos, A. Villa, D. Wang, F. Porta, D. Su, L. Prati, *J. Catal.* **2006**, *244*, 113.

[19] H. Liu, G. Mao, S. Meng, *J. Mol. Catal.* **1992**, *74*, 275.

[20] a) C. E. Powell, X. J. Duthie, S. E. Kentish, G. G. Qiao, G. W. Stevens, *J. Membr. Sci.* **2007**, *291*, 199; b) X. Y. Qiao, T. S. Chung, *AIChE J.* **2006**, *52*, 3462; c) P. S. Tin, T. S. Chung, Y. Liu, R. Wang, S. L. Liu, K. P. Pramoda, *J. Membr. Sci.* **2003**, *225*, 77.

[21] K. Mori, K. Yamaguchi, T. Hara, T. Mizugaki, K. Ebitani, K. Kaneda, *J. Am. Chem. Soc.* **2002**, *124*, 11572.

[22] A. Abad, P. Concepción, A. Corma, H. García, *Angew. Chem.* **2005**, *117*, 4134; *Angew. Chem. Int. Ed.* **2005**, *44*, 4066.