# Solvent-Free Aerobic Oxidation of Alcohols Catalyzed by an Efficient and Recyclable Palladium Heterogeneous Catalyst

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Received: February 8, 2005; Accepted: May 6, 2005

Supporting Information for this article is available on the WWW under http://asc.wiley-vch.de/home/.

**Abstract:** A simple alumina-supported palladium catalyst prepared by an adsorption method is highly efficient and recyclable in the solvent-free oxidation of alcohols with molecular oxygen. The adsorption method results in high dispersion of palladium probably as mononuclear or oligonuclear species on alumina surface. These palladium species are transformed to small Pd nanoparticles (*ca.* 5 nm), which are probably the true active species, during the course of alcohol oxidation.

**Keywords:** adsorption method; aerobic oxidation; alcohols; heterogeneous catalysis; palladium; solvent-free

Selective oxidation of alcohols to the corresponding aldehydes or ketones with molecular oxygen has attracted much attention from the viewpoint of establishing green chemical processes for the synthesis of carbonyl compounds, which are important and versatile intermediates for the production of fine chemicals. Many homogeneous catalysts, especially palladium, ruthenium and copper complexes or compounds, could efficiently catalyze the aerobic oxidation of alcohols.[1–5] Heterogeneous catalysts possess obvious advantages in product isolation and catalyst recycling use, and have thus received growing interest in the past years.[5,6] It has been known for a long time that alcohols can be oxidized with molecular oxygen or air to aldehydes or ketones in aqueous media catalyzed by Pt and Pd metallic catalysts, but the deactivation of these catalysts is a serious problem.[7] Recently, many studies have been devoted to the aerobic oxidation of alcohols using supported or confined monomeric or nano-sized Ru- or Pd-based heterogeneous catalysts.[8–18] Although a lot of progress has been achieved with these catalysts, the reaction rates (expressed as turnover frequency, TOF) are still low (generally lower than 1000 $h^{-1}$).[6] Moreover, for most of the catalysts reported so far, the use of a solvent in the reaction is required, while it is highly desirable to develop a process without a solvent from the viewpoint of green chemistry. Reports on catalysts for the solvent-free aerobic oxidation of alcohols are very scarce and the applicability of the substrates for the reported catalysts is limited.[11,12,15]

Recently, we found that an $Al_2O_3$-supported palladium catalyst prepared by an adsorption method (Pd/$Al_2O_3$-*ads*) was very effective for the solvent-free oxidation of alcohols with molecular oxygen. Pd/$Al_2O_3$ is a simple catalyst and is generally prepared by conventional wet impregnation. A few studies have mentioned the use of Pd/$Al_2O_3$ for the oxidation or dehydrogenation of alcohols,[11,16,17,19] but Pd/$Al_2O_3$ prepared by the impregnation (Pd/$Al_2O_3$-*imp*) exhibits lower activities in the aerobic oxidation of alcohols as compared with Pd/hydroxyapatite or Pd/MgO.[11,16] In this communication, we report the superior catalytic performances of the Pd/$Al_2O_3$-*ads* catalyst prepared by the adsorption method for the solvent-free oxidation of alcohols with molecular oxygen. The results we present herein offer a strategy for the preparation of simple and efficient heterogeneous Pd catalysts for the solvent-free aerobic oxidation of alcohols.

Table 1 shows the catalytic performances of the Pd/$Al_2O_3$-*ads* and the Pd/$Al_2O_3$-*imp* catalysts with a Pd content of 0.32 wt % for the solvent-free oxidation of benzyl alcohol by $O_2$. Both catalysts could catalyze the solvent-free selective oxidation of benzyl alcohol to benzaldehyde with selectivities higher than 90%. However, the Pd/$Al_2O_3$-*ads* exhibited significantly higher activity than the Pd/$Al_2O_3$-*imp*. At a lower temperature (88 °C), a longer reaction time was required for obtaining higher conversions. Benzyl alcohol conversion was 97% for an 8 h reaction with benzaldehyde selectivity of 96% over the Pd/$Al_2O_3$-*ads*, giving a TOF of 1952 $h^{-1}$. At 100 °C, a 4 h reaction could provide a benzyl alcohol conversion of 82% with benzaldehyde selectivity of 97%, showing a TOF of 3300 $h^{-1}$ over the same catalyst. These TOF values are remarkably higher than those reported for many other catalysts for the oxidation of benzyl alcohol such as Ru/$Al_2O_3$ (40 $h^{-1}$), 0.3% Pd/

DOI: 10.1002/adsc.200505081

**Table 1.** Comparison of catalytic properties of the Pd/$Al_2O_3$-*ads* and Pd/$Al_2O_3$-*imp* with a Pd content of 0.32 wt% for the solvent-free oxidation of benzyl alcohol with $O_2$.[a]

| Catalyst | *T* [°C] | Time [h] | Conversion [%] | PhCHO selectivity [%][b] | TOF [$h^{-1}$][c] |
|---|---|---|---|---|---|
| Pd/$Al_2O_3$-*ads* | 88 | 8 | 97 | 96 | 1952 |
| | 100 | 4 | 83 | 97 | 3300 |
| Pd/$Al_2O_3$-*imp* | 88 | 8 | 8 | 96 | 161 |
| | 100 | 4 | 60 | 90 | 2415 |

[a] The reactions were carried out under the following conditions: Pd amount in each catalyst, 3 μmol; benzyl alcohol, 48.5 mmol; $O_2$ flow rate, 3 mL $min^{-1}$.

[b] The by-product was toluene.

[c] TOF was evaluated from the moles of the substrate converted per mole of Pd in the catalyst per hour.

**Table 2.** Effect of Pd content on catalytic properties of the Pd/$Al_2O_3$-*ads* for the solvent-free oxidation of benzyl alcohol with $O_2$.[a]

| Pd content [wt %] | Conversion [%] | PhCHO selectivity [%][b] | TOF [$h^{-1}$][c] |
|---|---|---|---|
| 0 | 0 | – | – |
| 0.084 | 62 | 96 | 1247 |
| 0.19 | 90 | 96 | 1811 |
| 0.32 | 97 | 96 | 1952 |
| 1.03 | 89 | 95 | 1791 |
| 1.68 | 64 | 95 | 1288 |

[a] The reactions were carried out under the following conditions: Pd amount in each catalyst, 3 μmol; benzyl alcohol, 48.5 mmol; $O_2$ flow rate, 3 mL $min^{-1}$; temperature, 88 °C; time, 8 h.

[b] The by-product was toluene.

[c] TOF was evaluated from the moles of the substrate converted per mole of Pd in the catalyst per hour.

hydroxyapatite (500 $h^{-1}$), 10% $RuO_2$/FAU zeolite (8.5 $h^{-1}$) and Co-promoted Ru-hydroxyapatite (78 $h^{-1}$) working with $PhCF_3$ or $PhCH_3$ solvent.[6] They were also higher than that observed for a commercial 0.5 wt % Pd/$Al_2O_3$ (1585 $h^{-1}$) working with supercritical $CO_2$.[17] Only the 0.3 wt % Pd/hydroxyapatite showed a higher TOF (9800 $h^{-1}$) at a relatively higher temperature (160 °C) for the oxidation of 1-phenylethanol but not benzyl alcohol.[11] On the other hand, as shown in Table 1, the corresponding Pd/$Al_2O_3$-*imp* only provided a very low conversion of benzyl alcohol (8%) at 88 °C. The increase in temperature remarkably increased the conversion and TOF over the Pd/$Al_2O_3$-*imp*, but they were still significantly lower than those over the Pd/$Al_2O_3$-*ads*. Moreover, a significant amount of toluene (selectivity 10%) was formed as a by-product over the Pd/$Al_2O_3$-*imp* at 100 °C. It is thus clear that the adsorption method results in a particularly active and selective palladium catalyst for the solvent-free oxidation of benzyl alcohol by $O_2$.

Palladium content in the Pd/$Al_2O_3$-*ads* can be regulated by the concentration of $PdCl_4^{2-}$ in the aqueous solution for adsorption. A typical Langmuir-type curve has been obtained for the Pd content *versus* $PdCl_4^{2-}$ concentration, and the saturated adsorption amount is *ca.* 1.7 wt % of Pd on $Al_2O_3$ (see Supporting Information, Figure S1). The Pd/$Al_2O_3$-*ads* samples with different Pd contents have been examined in detail for the selective oxidation of benzyl alcohol by $O_2$, and the results obtained at 88 °C for 8 h are shown in Table 2. Benzyl alcohol conversion and TOF increased with Pd content and reached a maximum at a Pd content of 0.32 wt %. Further increases in Pd content decreased the conversion and TOF. It is reasonable to speculate that a higher Pd content may lead to the aggregation of Pd species to form PdO particles after the calcination (500 °C used in this work). Thus, mononuclear or oligonuclear Pd species on the surface of $Al_2O_3$ may account for the high catalytic performances of the sample with an appropriate Pd content. The relatively lower TOF at a much lower Pd content ($<0.19$ wt %) probably suggests that the strong interaction existing between the mononuclear Pd species and $Al_2O_3$ might cause the decrease in catalytic performance.

Significant differences have been observed in diffuse reflectance UV-Vis spectra between the Pd/$Al_2O_3$-*ads* and the Pd/$Al_2O_3$-*imp*. As shown in Figure 1, two absorption bands at 237 and 415 nm were observed for the 0.32 wt % Pd/$Al_2O_3$-*imp*, and these two bands could be attributed to the dπ–pπ charge transfer transition between Pd and O and the d–d transition of small PdO particles, respectively.[20] However, for the 0.32 wt % Pd/$Al_2O_3$-*ads*, the band at 415 nm became almost unobservable. Instead, an additional band at *ca.* 330 nm appeared. Further investigations on the change of the UV-Vis spectra with Pd content for the Pd/$Al_2O_3$-*ads* re-

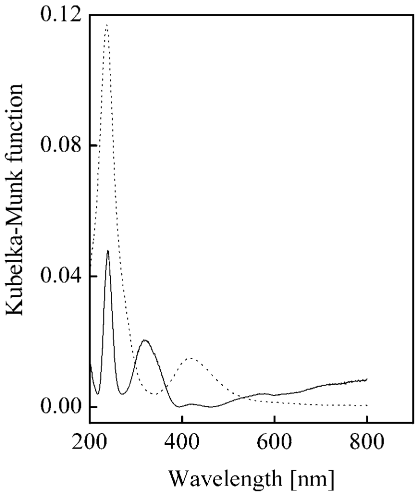


**Figure 1.** Diffuse reflectance UV-Vis spectra of Pd/$Al_2O_3$-*imp* (dotted line) and Pd/$Al_2O_3$-*ads* (solid line) with a Pd content of 0.32 wt %.

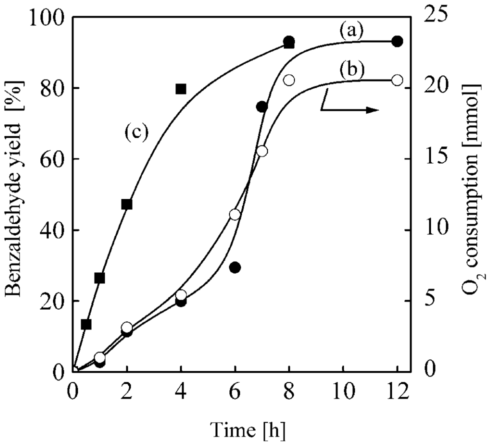


**Figure 2.** Time courses for the solvent-free oxidation of benzyl alcohol over the 0.32 wt % Pd/$Al_2O_3$-*ads* catalyst. (a) Benzaldehyde yield at 88 °C, (b) $O_2$ consumption at 88 °C, (c) benzaldehyde yield at 100 °C. Other reaction conditions were the same with those in Table 1.

vealed that, with an increase in Pd content from 0.19 wt % to 0.32 wt %, the intensity of the band at 330 nm increased significantly, but a further increase in Pd content $>$ 0.32 wt % weakened this band, and caused the appearance of the band at *ca.* 415 nm ascribed to PdO particles. Thus, the band at 330 nm corresponds well to the highest activity observed for the Pd/$Al_2O_3$-*ads* catalyst with a Pd content of 0.32 wt %. We speculate that this band may arise from the highly dispersed Pd(II) species, i.e., mononuclear or oligonuclear palladium species on the surface of $Al_2O_3$.

The 0.32 wt % Pd/$Al_2O_3$-*ads* catalyst, which can provide the best performances for the solvent-free oxidation of benzyl alcohol has been investigated in detail. Figure 2 shows the time courses for benzyl alcohol oxidation at 88 and 100 °C. At 88 °C, the yield of benzaldehyde increased only moderately with time in the initial 6 h, but a big jump of yield from 29% to 93% was observed in the next 2 h. A similar tendency was observed for the change of $O_2$ consumption with reaction time (Figure 2, curve b). The final molar ratio of $O_2$ consumption to benzaldehyde produced was *ca.* 1:2, suggesting the stoichiometric reaction between benzyl alcohol and molecular oxygen yielding benzaldehyde and water. These results indicate that there exists a relatively long induction period (*ca.* 6 h) for the reaction at 88 °C. Such a long induction period was not observed for the reaction at 100 °C, and the steady-state activity could be achieved at a short reaction time (Figure 2, curve c). A very short induction period (*ca.* 10 min) was once reported for the oxidation of 1-phenylethanol in trifluorotoluene (solvent) catalyzed by a Pd-grafted hydroxyapatite.[11b] The transformation of monomeric Pd(II) species grafted on the hydroxyapatite to Pd nanoparticles (*ca.* 4 nm), which were proposed to be the true active species, was observed during the induction period.[11b] To clarify what happened in the induction period in our case, we have carried out TEM observations for the 0.32 wt % Pd/$Al_2O_3$-*ads* catalyst before and after an 8 h reaction at 88 °C. Before reaction, no PdO or Pd particles could be discerned in the TEM images, confirming the high dispersion of Pd species on the surface of $Al_2O_3$ as suggested by the diffuse reflectance UV-Vis result. However, as shown in Figure 3, Pd nanoparticles with sizes of *ca.* 5 nm became observable after the reaction. We thus speculate that these Pd nanoparticles may be the true catalytically active species for the solvent-free oxidation of alcohols with molecular oxygen. It is noteworthy that, for the 0.32 wt % Pd/$Al_2O_3$-*imp* catalyst, which is less active for the selective oxidation of benzyl alcohol, much larger Pd particles (*ca.* 20 nm) have been observed after an 8 h reaction under the same conditions (see Supporting Information, Figure S2).

It has been confirmed that no leaching of Pd from the 0.32 wt % Pd/$Al_2O_3$-*ads* occurs during the aerobic oxidation of benzyl alcohol. The palladium content in the solid sample collected by filtration and drying after the reaction at 100 °C for 4 h was the same as that in the fresh sample. The recycling use of this sample was carried out at 100 °C. As shown in Figure 4, benzyl alcohol conversion, benzaldehyde selectivity and TOF were essentially constant within experimental error, indicating that the Pd/$Al_2O_3$-*ads* could be used repeatedly. Moreover, under the same reaction conditions, the liquid $H_2PdCl_4$ only showed a very low conversion of benzyl alcohol (8%).

The Pd/$Al_2O_3$-*ads* has been confirmed to be effective in the solvent-free oxidation of various alcohols by $O_2$ as shown in Table 3. The selectivity to the corresponding carbonyl compounds was very high for all the alcohols investigated. The reactivities for benzylic alcohols are

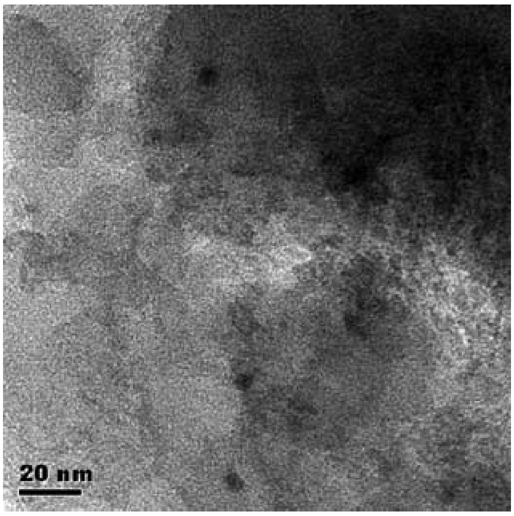


**Figure 3.** TEM image for the 0.32 wt % Pd/$Al_2O_3$-*ads* after the reaction under the conditions in Table 1 (88 °C for 8 h).

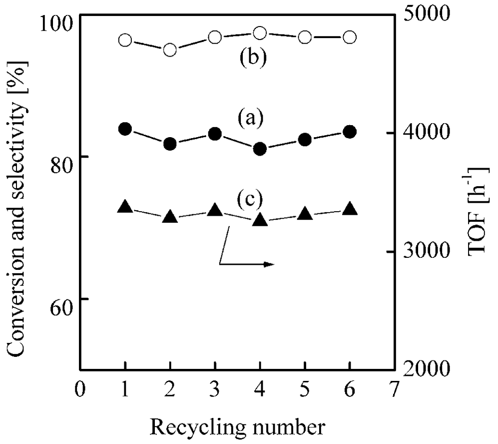


**Figure 4.** Recycling of the 0.32 wt % Pd/$Al_2O_3$-*ads* catalyst for the solvent-free aerobic oxidation of benzyl alcohol. (a) Benzyl alcohol conversion, (b) benzaldehyde selectivity, (c) TOF. Reaction conditions: catalyst, 0.1 g (Pd 3 μmol), benzyl alcohol, 48.5 mmol; $O_2$ flow rate, 3 mL min$^{-1}$, temperature, 100 °C, reaction time, 4 h.

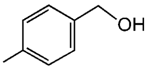
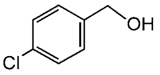
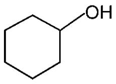
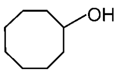
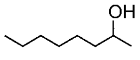
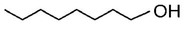
higher than those for aliphatic ones, and those for cyclic aliphatic alcohols are better than those for linear aliphatic ones. To the best of our knowledge, this is the first report to address the solvent-free aerobic oxidation of various alcohols. The result that the addition of a radical scavenger, e.g., butylhydroxytoluene or hydroquinone has not significantly influenced the conversion and selectivity suggests that the radical path is not involved in the reaction.

In conclusion, we have found that the Pd/$Al_2O_3$ catalyst (Pd, 0.32 wt %) prepared by the adsorption method is highly efficient in the solvent-free selective oxidation of various alcohols. The catalyst can be used in recycles. The adsorption method probably results in mononuclear or oligonuclear Pd species stabilized on $Al_2O_3$ surface after calcination. These highly dispersed Pd species are transformed into small Pd nanoparticles (*ca.* 5 nm), which are probably the true catalytically active species, during the course of the alcohol oxidation.

## Experimental Section

The Pd/$Al_2O_3$-*ads* catalysts were prepared by the following procedures. The γ-$Al_2O_3$ support with a specific surface area of 248 m$^2$ g$^{-1}$ was firstly prepared by the precipitation of

**Table 3.** Catalytic properties of the 0.32 wt % Pd/$Al_2O_3$-*ads* for the solvent-free oxidation of various alcohols with $O_2$.[a]

| Entry | Alcohols | Time [h] | Conversion [%] | Selectivity for carbonyl compound [%] |
|---|---|---|---|---|
| 1[b] |  | 4 | 91 | >99 |
| 2 |  | 24 | 16 | >99 |
| 3 |  | 16 | 36 | >99 |
| 4 |  | 48 | 99 | >99 |
| 5 |  | 48 | 80 | >99 |
| 6 |  | 48 | 66 | >99 |

[a] The reactions were carried out under the following conditions: Pd amount, 3 μmol; alcohols, 10 mmol; $O_2$ flow rate, 3 mL min$^{-1}$; temperature, 150 °C.
[b] Temperature, 100 °C.

$Al(NO_3)_3$ with $NH_3 \cdot H_2O$ at pH 9, followed by recovery of the solid powder with filtration, washing, drying at 120 °C and calcination at 500 °C. The $\gamma$-$Al_2O_3$ was added into an $H_2PdCl_4$ aqueous solution with the pH adjusted to 1.2 by 2 M HCl, and the mixture was stirred for 0.5 h at room temperature. Since the point of zero charge for $\gamma$-$Al_2O_3$ was *ca.* 8.0, the surface would be transferred to =Al-$OH_2^+$,[21] and the adsorption of $PdCl_4^{2-}$ would occur on the surface. It was confirmed that the pH of the aqueous solution was an important factor in determining the adsorption. Almost no adsorption took place by adjusting the pH of the aqueous solution above 5. After the adsorption, the powdery solid was separated by filtration and washed with a large amount of water until no $Cl^-$ remained in the filtrate, followed by drying at 120 °C and calcination in air at 500 °C for 6 h. The Pd/$Al_2O_3$-*imp* was prepared by the conventional wet impregnation method. The $\gamma$-$Al_2O_3$ was added into a $PdCl_2$ aqueous solution without pH adjustment and the mixture was evaporated to dryness at 60 °C. The resultant powdery solid was further dried at 120 °C and finally calcined in air at 500 °C for 6 h. The content of palladium in each catalyst was determined by ICP analysis. The UV-Vis spectroscopy and TEM were used for catalyst characterizations, and were performed with a Varian-Cary 5000 spectrometer and an FEI Tecnai 30 electron microscope, respectively.

The catalytic oxidation of alcohols was carried out with the following procedures. A certain amount of catalyst was added into the alcohol, and the mixture was then heated to the reaction temperature with vigorous stirring. Then an $O_2$ gas flow was bubbled into the mixture to start the reaction. After the reaction, the solid catalyst was filtered off and the liquid products were analyzed by GC after the addition of an internal standard.

## Acknowledgements

*This work was supported by the Program for New Century Excellent Talents in University of China (No. NCET-04-0602), the NSF of China (No. 20021002), the National Basic Research Program of China (No. 2003CB615803).*

## References

[1] a) G.-J. ten Brink, I. W. C. E. Arends, R. A. Sheldon, *Science* **2000**, *287*, 1636–1639; b) R. A. Sheldon, I. W. C. E. Arends, G.-J. ten Brink, A. Dijksman, *Acc. Chem. Res.* **2002**, *35*, 774–781; c) G.-J. ten Brink, I. W. C. E. Arends, R. A. Sheldon, *Adv. Synth. Catal.* **2002**, *344*, 355–369; d) P. Gamez, I. W. C. E. Arends, R. A. Sheldon, J. Reedijk, *Adv. Synth. Catal.* **2004**, *346*, 805–811.

[2] J. Muzart, *Tetrahedron* **2003**, *59*, 5789–5816.

[3] S. S. Stahl, *Angew. Chem. Int. Ed.* **2004**, *43*, 3400–3420.

[4] a) D. D. Caspi, D. C. Ebner, J. T. Bagdanoff, B. M. Stoltz, *Adv. Synth. Catal.* **2004**, *346*, 185–189; b) B. M. Stoltz, *Chem. Lett.* **2004**, *33*, 362–367.

[5] B.-Z. Zhan, A. Thompson, *Tetrahedron* **2004**, *60*, 2917–2935.

[6] T. Mallat, A. Baiker, *Chem. Rev.* **2004**, *104*, 3037–3058.

[7] M. Besson, P. Gallezot, *Catal. Today* **2000**, *57*, 127–141.

[8] K. Kaneda, T. Yamashita, T. Matsushita, K. Ebitani, *J. Org. Chem.* **1998**, *63*, 1750–1751.

[9] K. Yamaguchi, K. Mori, T. Mizugaki, K. Ebitani, K. Kaneda, *J. Am. Chem. Soc.* **2000**, *122*, 7144–7145.

[10] T. Nishimura, N. Kakiuchi, M. Inoue, S. Uemura, *Chem. Commun.* **2000**, 1245–1246.

[11] a) K. Mori, K. Yamaguchi, T. Hara, T. Mizugaki, K. Ebitani, K. Kaneda, *J. Am. Chem. Soc.* **2002**, *124*, 11572–11573; b) K. Mori, T. Hara, Y. Mizugaki, K. Ebitani, K. Kaneda, *J. Am. Chem. Soc.*, **2004**, *126*, 10657–10666.

[12] K. Yamaguchi, N. Mizuno, *Angew. Chem. Int. Ed.* **2002**, *41*, 4538–4542.

[13] B.-Z. Zhan, M. A. White, T.-K. Sham, J. A. Pincock, R. J. Doucet, K. V. Rao, K. N. Robertson, T. S. Cameron, *J. Am. Chem. Soc.* **2003**, *125*, 2195–2199.

[14] Y. Uozumi, R. Nakao, *Angew. Chem. Int. Ed.* **2003**, 42, 194–197.

[15] V. R. Choudhary, P. A. Chaudhari, V. S. Narkhede, *Catal. Commun.* **2003**, *4*, 171–175.

[16] U. R. Pillai, E. Sahle-Demessie, *Green. Chem.* **2004**, *6*, 161–165.

[17] M. Carravati, J.-D. Grunwaldt, A. Baiker, *Catal. Today* **2004**, *91–92*, 1–5.

[18] Z. Opre, J.-D. Grunwaldt, M. Maciejewski, D. Ferri, T. Mallat, A. Baiker, *J. Catal.* **2005**, *230*, 415–428.

[19] C. Keresszegi, T. Mallat, A. Baiker, *New. J. Chem.* **2001**, *25*, 1163–1167.

[20] Z. Zhang, G. Mestl, H. Knözinger, W. M. H. Sachtler, *Appl. Catal. A* **1992**, *89*, 155–168.

[21] J. A. Schwarz, C. Contescu, A. Contescu, *Chem. Rev.* **1995**, *95*, 477–510.