Supported Au Catalysts

DOI: 10.1002/anie.200502101

Catalysis by Gold: Isolated Surface Au^{3+} Ions are Active Sites for Selective Hydrogenation of 1,3-Butadiene over Au/ZrO_2 Catalysts**

*Xin Zhang, Hui Shi, and Bo-Qing Xu**

In recent years, there has been an increasing interest in catalysis by nanosized gold catalysts,[1–5] which are active in reactions such as CO oxidation,[1–10] propylene epoxidation,[1–3] hydrogenation of unsaturated compounds,[3,12–15] vinyl chloride synthesis,[5] and others.[2,3,5,11] Despite such a diverse spectrum of reactions, efforts have been mainly devoted to elucidating the catalytically active sites in the oxidation reactions.[1–10] Little attention has been paid to the nature of active gold, especially cationic gold species,[5,11] in the other reactions such as hydrogenation of unsaturated compounds.[12–17] This is surprising, since catalytic hydrogenation is one category of the best studied and industrially most important reactions on conventional transition metal catalysts,[18,19] and Au^{3+} ions in solution can activate carbon–carbon double and triple bonds and are finding applications as efficient homogeneous catalysts in many organic reactions.[20,21] Hydrogenation of 1,3-butadiene has long been a model reaction for the study of active sites on conventional metal catalysts.[18,19] A few preliminary investigations[12,13] on the hydrogenation of 1,3-butadiene with supported gold catalysts showed that small gold nanoparticles were active in the reaction, although theoretical calculations seem to suggest that the surface of metallic gold is chemically inert for hydrogen activation.[22,23]

By using Au/ZrO_2 catalysts with very low loadings of Au ($< 0.1\,\%$), we have now discovered that isolated surface-type Au^{3+} ions are actually the active sites for the selective hydrogenation of 1,3-butadiene. The activity and selectivity of these Au^{3+} ions are comparable to those of conventional precious transition metals such as Pd and Pt. This finding that low loadings of Au^{3+} ions are more active for the hydrogenation reaction than high loadings of Au nanoparticles could raise intensive interest in exploring the potential of surface-type Au^{3+} ions in heterogeneous catalytic reactions. The use of isolated and heterogenized Au^{3+} ions in catalysis and related materials may be the key to using the noble gold in areas usually reserved for conventional precious metal catalysts, for example, to significantly improve the economics and reduce the use of other precious metals.

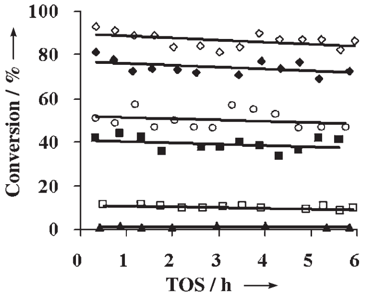

Figure 1. Conversion of 1,3-butadiene at 120 °C over Au/ZrO_2 catalysts (calcined at 200 °C) containing 0.76 (◆), 0.23 (■), 0.08 (◇), 0.05 (○), and 0.01 % Au (□). The (▲) data show the conversion over bare ZrO_2 support. TOS = reaction time on stream.

Figure 1 shows the effect of gold loading on 1,3-butadiene conversion over Au/ZrO_2 catalysts calcined at 200 °C. No butane (i.e., the product of complete hydrogenation) but only butenes were detected as the hydrogenation products over all catalysts used. The conversion was less than 1 % in our blank test with bare ZrO_2 support as catalyst. The activity was enhanced greatly on loading with gold, and only a slight decrease in catalyst activity was observed up to 6 h of reaction time on stream (TOS). Surprisingly, higher conversion (ca. 50 %) is obtained over 0.05 % Au/ZrO_2 than over 0.23 % Au/ZrO_2 catalyst (ca. 40 %). The 1,3-butadiene conversions are converted to show the specific mass activity of gold in the catalysts in Table 1. The catalytic turnover frequencies (TOFs) based on surface gold atoms or nonmetallic Au "atoms" are also given in the table. These catalytic rates decreased sharply when the Au loading was increased from 0.05 to 0.23 % and higher. It is noteworthy that the TOFs are very similar (ca. 0.40 s^{-1}) for the catalysts containing 0.05 and 0.01 % Au, that is, the gold "atoms" in these two samples are equally active for the selective hydrogenation reaction.

The same high TOFs of the Au/ZrO_2 catalysts containing no more than 0.05 % Au would mean that the active gold species are atomically dispersed and isolated from each other on the surface of the zirconia support. It was shown previously[11,25] that treatment of supported gold catalysts with an aqueous solution of NaCN can dissolve the gold particles and create isolated gold cations on the support surface. Using a similar procedure (Supporting Information), we treated the 0.76 % Au/ZrO_2 sample with an aqueous solution of 2 % KCN. According to measurements of the Au content by inductively coupled plasma atomic emission spectrometry (ICP-AES), such treatment removed about 90 % of the gold from the solid catalyst and gave a 0.08 % Au/ZrO_2 catalyst. The ICP-AES analysis detected no contamination by K^+ or Na^+ of the sample after treatment. The catalytic activity data of this 0.08 % Au/ZrO_2 catalyst in 1,3-butadiene conversion are included in Figure 1 for comparison

---

[*] X. Zhang, H. Shi, Prof. B.-Q. Xu
Innovative Catalysis Program
Key Lab of Organic Optoelectronics & Molecular Engineering
Department of Chemistry
Tsinghua University
Beijing 100084 (China)
Fax: (+86) 10-6279-2122
E-mail: bqxu@mail.tsinghua.edu.cn

[**] We gratefully acknowledge the financial support of this work by NSF of China (grants: 20443008, 20125310, and 20590360) and National Basic Research Project of China (grant: 2003CB615804). We also thank the referees for their insightful comments.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

Table 1: Average Au particle size (TEM), hydrogen consumption (TPR), and 1,3-butadiene hydrogenation rates at 120 °C over Au/ZrO_2 catalysts.

Au loading [wt %]	d_{Au}[d] [nm]	H_2 consumed [mol(H_2)/ mol(Au)]	Au^{3+}/Au^0 ratio[e]	Au^{3+} [μmol g(cat.)$^{-1}$]	Reaction rate [mmol s^{-1} g(Au)$^{-1}$]	TOF [s^{-1}][d]
0.01	nd[e]	1.57	–	0.5	2.08	0.41
0.05	nd	1.49	–	2.5	2.01	0.40
0.08[a]	nd	1.50	–	4.1	2.15	0.42
0.23	2.9	0.68	0.83	5.3	0.34	0.17
0.76	4.1	0.37	0.33	9.6	0.20	0.14
0.76[b]	6.7	0.25	0.20	6.4	0.14	0.13
0.76[c]	11.7	0	0	0	0.02	0.03

[a] Sample obtained by treatment of the 0.76 % Au/ZrO_2 catalyst with 2 % KCN solution. [b] Sample calcined at 300 °C. [c] Sample calcined at 500 °C. [d] The average particle size of Au was determined according to the equation $d = \Sigma n_i d_i / n_i$ by randomly measuring for each sample ca. 200 particles by TEM; the TOF data were calculated on the basis of Au atoms exposed on the surface, which were obtained from the average particle sizes by assuming closed-shell Au particles of spherical shape. All of the nonmetallic Au "atoms" in the catalyst containing less than 0.1 % Au were assumed to be the catalytic sites in calculating the TOF data. [e] nd: no metallic Au particle was found in the high-resolution TEM image.

with the other catalysts of different Au loadings. To our surprise, this 0.08 % Au/ZrO_2 catalyst effected the highest 1,3-butadiene conversion (ca. 85 %). Assuming that every gold "atom" in this 0.08 % Au/ZrO_2 catalyst was active for the reaction, we obtained a TOF of 0.42 s^{-1}, which is basically the same as those of the 0.05 % Au/ZrO_2 and 0.01 % Au/ZrO_2 catalysts (Table 1). This is remarkable, since these rates reveal that the loaded gold "atoms" were 100 % accessible for the reaction at these low loadings. According to references [11,25], the 0.08 % Au/ZrO_2 sample obtained by treatment of 0.76 % Au/ZrO_2 with aqueous 2 % KCN solution should contain only surface-type gold cations. The unchanged TOFs of gold at such low loadings could hint that the catalytic active sites are gold cations rather than gold nanoparticles.

We then studied the effect of calcination temperature of the 0.76 % Au/ZrO_2 catalyst on the selective hydrogenation reaction, since the calcination temperature appears to affect the ratio of Au^{3+}/Au^0 in oxide-supported gold catalysts.[25,26] We found that the conversion of 1,3-butadiene clearly increased with decreasing catalyst calcination temperature in the range of 200–500 °C (Figure 2). We used a combination of temperature-programmed reduction (TPR) and X-ray photoelectron spectroscopy (XPS) to quantitatively characterize the oxidation states of gold. The XPS data (Figure 3) showed that the sample calcined at 500 °C contained only metallic Au^0 showing $4f_{7/2}$ and $4f_{5/2}$ signals at 83.7 and 87.6 eV, respectively.[26] In addition to metallic Au^0, XPS spectra of samples calcined at 300 and 200 °C also contained the $4f_{7/2}$ (86.1 eV) and $4f_{5/2}$ (89.4 eV) signals from Au^{3+} ions. Thus the Au^{3+}/Au^0 ratio increases with decreasing catalyst calcination temperature.

Figure 4 shows the temperature-programmed reduction (TPR) profiles of the bare ZrO_2 support as well as 0.08 % and 0.76 % Au/ZrO_2 catalysts. Bare ZrO_2 showed no consumption of hydrogen up to 800 °C. The TPR profiles of the samples calcined at 200 and 300 °C feature two hydrogen consumption peaks, one at low (210–230 °C) and the other at high temperature (550–580 °C). However, only the high-temperature peak appeared for the sample calcined at 500 °C. With reference to the XPS characterization data, the low-temperature peak should be due to reduction of Au^{3+} ions, while the high-temperature peak can be assigned to partial (< 3 %) reduction of surface Zr^{4+} ions of the zirconia support to Zr^{3+}.[14]

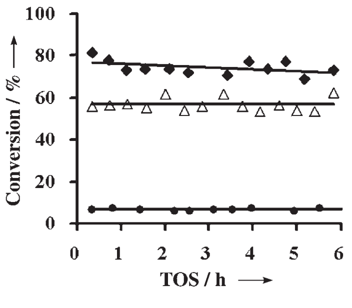

Figure 2. Effect of the catalyst (0.76 % Au/ZrO_2) calcination temperature on 1,3-butadiene conversion: (◆) 200, (△) 300, and (●) 500 °C.

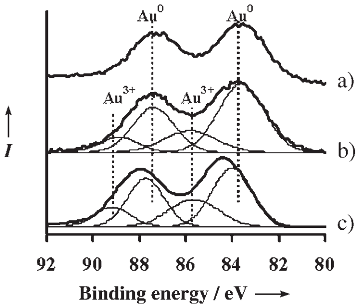

Figure 3. XPS spectra (Au 4f) of 0.76 % Au/ZrO_2 catalysts calcined at different temperatures: a) 500, b) 300, and c) 200 °C.

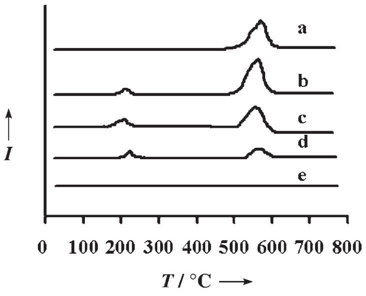

Figure 4. TPR profiles of 0.76 % Au/ZrO_2 catalysts calcined at different temperatures: a) 500, b) 300, c) 200 °C. d) TPR profile for the 0.08 % Au/ZrO_2 catalyst obtained by treatment of sample (c) with 2 % KCN solution. e) TPR profile for bare ZrO_2 support. Intensity *I* was measured with a thermal conductivity detector.

The samples with very low Au loadings (< 0.1 %) were also characterized by the TPR technique. The TPR profile of the 0.08 % Au/ZrO_2 sample is presented as the profile (d) in Figure 4. Calibration of the hydrogen-consumption peak showed that the number of hydrogen molecules (H_2) consumed under the low-temperature peak was just 1.5 times the molar number of gold in the 0.08 % Au/ZrO_2 sample. Since this sample should contain only gold cations after treatment with 2 % KCN solution,[11,25] such stoichiometry ($H_2/Au = 1.5$ or $H/Au = 3.0$) of the reduction proves that the gold cations in the 0.08 % Au/ZrO_2 sample are actually Au^{3+}. The TPR profiles of the samples containing 0.01 and 0.05 % Au were very similar to that of 0.08 % Au/ZrO_2 (not shown in Figure 2). Their reduction stoichiometries (Table 1) also prove that these two samples contain only Au^{3+} ions.

We then measured the Au^{3+}/Au^0 ratios in the 0.76 % Au/ZrO_2 catalysts by calibrating the reduction peaks of their Au^{3+} ions; the ratios were 0.33 and 0.20 for samples calcined at 200 and 300 °C, respectively. For 0.23 % Au/ZrO_2, the measured Au^{3+}/Au^0 ratio was 0.83.

The effects of catalyst calcination temperature and Au loading on the catalyst activity are also compared in Table 1. The 0.76 % Au/ZrO_2 catalyst calcined at 500 °C, which contains only metallic Au particles but no Au^{3+} ions, exhibited a TOF of 0.03 s^{-1}, which is comparable to those of 0.01–0.02 s^{-1} at 150 °C of the most active metallic Au nanoparticles supported on TiO_2 and Al_2O_3 in reference [13]. However, this activity of the metallic gold (0.03 s^{-1}) in the 0.76 % Au/ZrO_2 catalyst is one order of magnitude lower than that of catalysts containing only small amounts of Au^{3+} ions (0.4 s^{-1}). The specific mass activity of the supported metallic Au particles in the 0.76 % Au/ZrO_2 catalyst, as well as in the 1 % Au/TiO_2 and 1 % Au/Al_2O_3 catalysts in ref. [13], is even two orders of magnitude lower. These remarkable differences demonstrate that the surface-type Au^{3+} ions are far more active than the Au^0 atoms at the surface of metal nanoparticles. Earlier, Guzman and Gates[15,16] reported that mononuclear organo-Au^{3+} complexes supported on MgO were active in the catalytic hydrogenation of ethene, while metallic Au^0 particles were inactive. Cationic gold was also found to be responsible for the activity of Au/CeO_2 catalysts in the water-gas shift reaction involving oxygen-containing reactants ($CO + H_2O$).[11] It is noteworthy in the present study that the Au^{3+} ions "fixed" at the ZrO_2 surface are stable and active even under a completely reducing atmosphere (H_2).

The catalytic activity in terms of conversion of 1,3-butadiene (Figures 1 and 2) or mass of gold (Table 1) is apparently not in proportion with the number of Au^{3+} ions in the catalysts containing 0.23 and 0.76 % Au. The numbers of Au^{3+} ions in the 0.23 % Au/ZrO_2 (5.3 $\mu mol\,g^{-1}$) and 0.76 % Au/ZrO_2 (e.g., 9.6 $\mu mol\,g^{-1}$ for the sample calcined at 200 °C) catalysts were much higher than that in the 0.08 % Au/ZrO_2 (4.1 $\mu mol\,g^{-1}$) catalyst, but their activities were significantly lower. This indicates that the highly active Au^{3+} ions are not those with interaction to the metallic gold particles but those independently "fixed" at specific locations of the zirconia surface. The surface density of Au^{3+} ions in the most active 0.08 % Au/ZrO_2 catalyst is 0.02 per square nanometer. This surface density of Au^{3+} ions is sufficiently low to ensure that the most active sites for the hydrogenation reaction are isolated surface-type Au^{3+} ions.

Structure sensitivity is an important issue in gold catalysis even in the case of selective hydrogenation.[14,17,27] Since the present work is intended to show the important catalytic implications of Au^{3+} cations at the zirconia surface, it is not clear whether the selective hydrogenation of 1,3-butadiene is structure sensitive or not with respect to the ZrO_2-supported Au particles. We note, however, that in work by Haruta et al.[13] the same reaction was almost insensitive to the size of the Au particles and nature of the support, while an earlier paper by Buchanan and Webb[28] suggested a strong influence of the support materials. Claus et al. found that the same reaction over metallic Au is also sensitive to the nature of the support oxide,[17] but the hydrogenation of acrolein is mainly affected by the percentage of edge/corner atoms relative to the total surface atoms.[14,27]

Due to their ability to activate carbon–carbon double and triple bonds (e.g., alkynes and allenes), Au^{3+} ions (i.e., gold salts) in solution are finding applications as efficient homogeneous catalysts in many organic reactions.[20,21] If the Au^{3+} ions can be properly heterogenized onto a solid surface while still maintaining their catalytic efficiency in the homogeneous systems, the "golden gate"[21] of catalysis by homogeneous gold would be even more useful for advanced heterogeneous catalysis. By reducing the loading of gold to very low levels (< 0.1 % Au), the present work is the first to demonstrate that high loadings of Au nanoparticles are actually not required for the hydrogenation reaction; the very low concentration of Au^{3+} ions (0.02 Au^{3+}/nm^2) heterogenized on zirconia surface from a cheap inorganic gold source ($HAuCl_4$) is enough to grant much higher catalytic activity. Moreover, the present heterogenized Au^{3+} ions were simply prepared from an inorganic gold salt in aqueous solution and were stable in ambient air, which can be very important in practical applications.

The TOF of the isolated Au^{3+} ions (0.4 s^{-1}) is comparable to that of conventional supported precious metals (e.g., ca. 0.2–1.0 s^{-1} for Pd).[18,19] Interestingly, the hydrogenation of 1,3-butadiene over the present Au/ZrO_2 catalysts has 100 % selectivity for butenes; no butane is detected even over the most active 0.08 % Au/ZrO_2 catalyst at high conversions of 1,3-butadiene (80–90 %; see Figure 1). The major component of the product butenes is 1-butene (ca. 60 %), and the *trans*/*cis* ratio of 2-butene is in the range of 0.3–1.0 over all of the Au/ZrO_2 catalysts (Figure 5). This *trans*/*cis* ratio is much lower than that obtained over supported Pd (*trans*/*cis* = 10–14) but close to that over supported Pt and other group VIII metals (*trans*/*cis* = 1.5–2.0).[18,19,29] The comparable activity (TOF) of the surface-type Au^{3+} ions to those of the group VIII precious metals and their unique selectivity in the hydrogenation reaction are of potential for many selective hydrogenations and related reactions. The isolated nature of the active Au^{3+} ions can also have important applications in improving the economics of gold catalysis.

Although this work was successful in demonstrating that the most active sites for the selective hydrogenation reaction are isolated Au^{3+} ions at the surface of zirconia, the mechanism of hydrogen activation by these surface-type

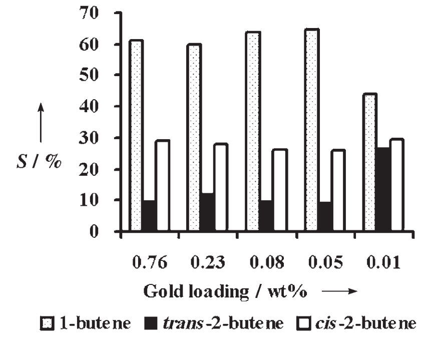

Figure 5. Product selectivity S of 1,3-butadiene hydrogenation over Au/ZrO_2 catalysts of different Au loadings.

Au^{3+} ions remains to be elucidated. Hydrogen chemisorption on supported gold was occasionally detected, but sometimes it has not been detectable at all.[3,27] The remarkable activity difference discovered between surface-type Au^{3+} ions and metallic Au^0 atoms could mean a different mechanism for hydrogen activation. Comprehensive in situ spectroscopic studies will be needed to understand the mechanistic aspect of the surface-type Au^{3+} cations in the hydrogen activation.

In conclusion, we have shown that isolated Au^{3+} ions on a zirconia support are obtained by loading very small amount ($< 0.1\,\%$) of gold with simple methods. These heterogenized Au^{3+} ions are highly active for the selective hydrogenation of 1,3-butadiene to butenes. Further exploration of the potential of the surface-type Au^{3+} ions in heterogeneous catalysis may be the key to using the noble metal gold in areas usually reserved for conventional precious metal catalysts such as Pt and Pd.

Experimental Section

A conventionally prepared $ZrO(OH)_2$ hydrogel was calcined at 400 °C to produce a ZrO_2 support with BET surface area of $120\,m^2\,g^{-1}$.[24] Samples of Au/ZrO_2 were prepared by loading the support with appropriate amounts of Au by the deposition–precipitation method with $HAuCl_4$ precursor,[8] the concentration of which was adjusted to yield catalysts containing 0.76, 0.23, 0.05, and 0.01 wt % Au (ICP-AES analysis). The 0.76 % Au/ZrO_2 sample was treated with an aqueous solution of KCN in a process similar to that reported by Fu et al.[11] to give 0.08 % Au/ZrO_2 catalyst. The Au/ZrO_2 catalysts were dried and calcined at 200 °C in flowing air. We also prepared 0.76 % Au/ZrO_2 catalysts at different calcination temperatures, that is, 200, 300, and 500 °C. TPR was used in combination with XPS measurements to quantitatively characterize the oxidation state of gold. TEM/HRTEM images were recorded on a JEM-2010F (200 kV) transmission electron microscope.

Hydrogenation of 1,3-butadiene was conducted at 120 °C in a fixed-bed stainless steel reactor (i.d. 4 mm) at atmospheric pressure. The reaction feed (2.15 vol % 1,3-butadiene in H_2) was introduced to the catalyst at a flow rate of $13.5\,mL\,min^{-1}$ (gas hourly space velocity (GHSV) $= 8100\,mL\,h^{-1}\,(g\,cat.)^{-1}$. Before reaction all samples (ca. 80–120 mesh, 0.1 g diluted with 0.45 g quartz powder) were pretreated in situ in $30\,mL\,min^{-1}$ Ar at 200 °C for 2 h. The selected reaction conditions precluded any significant mass-transfer limitation in a series of pre-experiments at fixed space velocity (GHSV $= 8100\,mL\,h^{-1}\,(g\,cat.)^{-1}$) so that the conversion of butadiene (ca. 75 %) over the 0.76 % Au/ZrO_2 catalyst (calcined at 200 °C) was not significantly affected by changing the flow rate of the reaction feed and the catalyst pellet size (40–120 mesh). The reactor effluent was analyzed in situ by gas chromatography. Experimental details and representative TEM images of the Au/ZrO_2 catalysts can be found in the Supporting Information.

Received: June 17, 2005

Keywords: gold · heterogeneous catalysis · hydrogenation · supported catalysts

[1] M. Haruta, M. Daté, *Appl. Catal. A* **2001**, *222*, 427.
[2] M. Haruta, *CATTECH* **2002**, *6*, 102.
[3] G. C. Bond, D. T. Thompson, *Catal. Rev. Sci. Eng.* **1999**, *41*, 319.
[4] G. C. Bond, D. T. Thompson, *Gold Bull.* **2000**, *33*, 41.
[5] G. J. Hutchings, *Gold Bull.* **2004**, *37*, 3.
[6] M. Valden, X. Lai, D. W. Goodman, *Science* **1998**, *281*, 1647.
[7] B. Yoon, H. Häkkinen, U. Landman, A. S. Wörz, J.-M. Antonietti, S. Abbet, K. Judai, U. Heiz, *Science* **2005**, *307*, 403.
[8] X. Zhang, H. Wang, B.-Q. Xu, *J. Phys. Chem. B* **2005**, *109*, 9678.
[9] H. H. Kung, M. C. Kung, C. K. Costello, *J. Catal.* **2003**, *216*, 425.
[10] J. Guzman, B. C. Gates, *J. Am. Chem. Soc.* **2004**, *126*, 2672.
[11] Q. Fu, H. Saltsburg, M. Flytzani-Stephanopoulos, *Science* **2003**, *301*, 935.
[12] G. C. Bond, P. A. Sermon, *Gold Bull.* **1973**, *6*, 102.
[13] M. Okumura, T. Akita, M. Haruta, *Catal. Today* **2002**, *74*, 265. We found that the TOF data in Table 1 of this paper were erroneous by one order of magnitude. We communicated with the authors (Drs. Okumura and Haruta) who confirmed that TOF ($\times 10^{-3}\,s^{-1}$) in the table was a mistyping of TOF ($\times 10^{-2}\,s^{-1}$) and kindly allowed us to make the correction herein.
[14] P. Claus, A. Brücker, C. Mohr, H. Hofmeister, *J. Am. Chem. Soc.* **2000**, *122*, 11430.
[15] J. Guzman, B. C. Gates, *Angew. Chem.* **2003**, *115*, 714; *Angew. Chem. Int. Ed.* **2003**, *42*, 690.
[16] J. Guzman, B. C. Gates, *J. Catal.* **2004**, *226*, 111.
[17] S. Schimpf, M. Lucas, P. Claus, *Proceedings of DGMK-Conference, Creating Value from Light Olefins—Production and Conversion*, Hamburg, Germany, October 10–12, **2001**, pp. 97–102.
[18] H. Arnold, F. Doebert, J. Gaube in *Handbook of Heterogeneous Catalysis, Vol. 5* (Eds.: G. Ertl, H. Knözinger, J. Weitkamp), VCH, Weinheim, **1997**, pp. 2165–2186.
[19] G. C. Bond, P. B. Wells, *Adv. Catal.* **1964**, *15*, 91.
[20] A. Stephen, K. Hashmi, *Gold Bull.* **2004**, *37*, 51.
[21] A. Hoffmann-Röder, N. Krause, *Org. Biomol. Chem.* **2005**, *3*, 387.
[22] B. Hammer, J. K. Norskov, *Nature* **1995**, *376*, 238.
[23] J. Li, X. Li, H.-J. Zhai, L.-S. Wang, *Science* **2003**, *299*, 864.
[24] B.-Q. Xu, J.-M. Wei, J.-L. Li, Q.-M. Zhu, *J. Phys. Chem. B* **2003**, *107*, 5203.
[25] J. T. Calla, R. J. Davis, *Catal. Lett.* **2005**, *99*, 21.
[26] E. D. Park, J. S. Lee, *J. Catal.* **1999**, *186*, 1.
[27] P. Claus, *Appl. Catal. A* **2005**, *291*, 222, and references therein.
[28] D. A. Buchanan, G. Webb, *J. Chem. Soc. Faraday Trans.* **1975**, *71*, 134.
[29] J. Massardier, J. C. Bertolini, A. Renouprez in *Proc. 9th Int. Cong. Catal.*, *Vol. III* (Eds.: M. J. Philips, M. Ternan), Calgary, **1988**, pp. 1222–1229.