# Hydrotalcite-Supported Gold Catalyst for the Oxidant-Free Dehydrogenation of Benzyl Alcohol: Studies on Support and Gold Size Effects

# Wenhao Fang, Jiashu Chen, Qinghong Zhang,\* Weiping Deng, and Ye Wang<sup>\*[a]</sup>

Abstract: Gold nanoparticles with uniform mean sizes ( $\approx 3$  nm) loaded onto various supports have been prepared and studied for the oxidant-free dehydrogenation of benzyl alcohol to benzaldehyde and hydrogen. The use of hydrotalcite (HT), which possesses both strong acidity and strong basicity, provides the best catalytic performance. Au/HT catalysts with various mean Au particle sizes (2.1–21 nm) have been successfully prepared by a deposition–precipitation method under

### Introduction

Gold catalysis has become an exciting research area since the discovery that Au particles < 3-5 nm in diameter are catalytically active.<sup>[1]</sup> Supported Au nanoparticles have shown unique catalytic properties in many important reactions, such as hydrogenations of alkenes,  $\alpha$ , $\beta$ -unsaturated carbonyl compounds, and nitro compounds, CO oxidation, propylene epoxidation, hydrogen peroxide synthesis, aerobic oxidation of alcohols, and C–C coupling reactions.<sup>[2,3]</sup> The size of the Au nanoparticles and the nature of the support are believed to be pivotal in determining the catalytic behavior of the supported Au nanoparticles, although many other issues (e.g., the chemical state of Au, the morphology of the Au

[a] W. Fang, J. Chen, Prof. Dr. Q. Zhang, Dr. W. Deng, Prof. Dr. Y. Wang State Key Laboratory of Physical Chemistry of Solid Surfaces and National Engineering Laboratory for Green Chemical Productions of Alcohols, Ethers and Esters College of Chemistry and Chemical Engineering Xiamen University, Xiamen 361005 (China) Fax: (+86)592-2183047 E-mail: zhangqh@xmu.edu.cn wangye@xmu.edu.cn

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201002469.

controlled conditions. Detailed catalytic reaction studies with these catalysts demonstrate that the Au-catalyzed dehydrogenation of benzyl alcohol is a structure-sensitive reaction. The turnover frequency (TOF) increases with decreasing Au mean particle size (from 12 to 2.1 nm). A steep rise in TOF

**Keywords:** alcohols • dehydrogenation • gold • heterogeneous catalysis • nanoparticles occurs when the mean Au particle size becomes smaller than 4 nm. Our present work suggests that the acid–base properties of the support and the size of Au nanoparticles are two key factors controlling the alcohol dehydrogenation catalysis. A reaction mechanism is proposed to rationalize these results. It is assumed that the activation of the  $\beta$ -C–H bond of alcohol, which requires the coordinatively unsaturated Au atoms, is the rate-determining step.

nanoparticles, and the Au–support interaction) may also affect catalytic performance.<sup>[3–12]</sup> Undoubtedly, understanding of the effect of Au particle size and the function of the support in various Au-catalyzed reactions will be helpful for the rational design of highly efficient Au catalysts.

The dehydrogenation of alcohols to give carbonyl compounds is one of the most essential transformations in organic synthesis. A number of studies have contributed to the development of efficient heterogeneous catalysts for the oxidative dehydrogenation of alcohols to aldehydes and ketones by  $O_{2}$ ,<sup>[13-24]</sup> which is more environmentally benign and "greener" than stoichiometric oxidation with a metal-containing inorganic oxidant such dichromate or permanganate. Together with Pd- and Ru-based catalysts,<sup>[13]</sup> some supported Au nanoparticles such as Au/CeO2, Au/TiO2, Au/  $Cu_5MgAl_2O_x$ ,  $Au/Ga_xAl_{6-x}O_9$  (x = 2, 3, or 4),  $Au/MnO_2$ , Au/hydrotalcite (HT), Au/PCPs (PCP=porous coordination polymers), and Au-Pd bimetallic nanoparticles have been reported to show excellent catalytic performances for the aerobic oxidation of alcohols.<sup>[14-24]</sup> However, the presence of O<sub>2</sub> may cause problems of overoxidation and explosion, or flammability of organic solvent or alcohol reactants.<sup>[13c]</sup> The safety problem becomes particularly serious for practical large-scale production. In this context, the dehydrogenation of alcohols under anaerobic conditions is desirable.

Chem. Eur. J. 2011, 17, 1247-1256

© 2011 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

WILEY CONLINE LIBRARY

- 1247

Transfer dehydrogenation of alcohols to aldehydes or ketones in the presence of a hydrogen acceptor, such as alkenes (e.g., ethylene, cyclohexene, styrene) or ketones, catalyzed by supported Pd and Cu catalysts has been reported,<sup>[25–27]</sup> but the transfer process consumes the hydrogen acceptor and produces organic byproducts, and thus is not an atom-economical process. With respect to atom economy, the dehydrogenation of alcohols under an inert atmosphere to produce aldehydes or ketones and H<sub>2</sub> is the most desirable process [Eq. (1)]:

$$\begin{array}{ccc} R \xrightarrow{H} & & \\ \searrow & OH & & \\ R' \xrightarrow{} & O & + H_2 \end{array}$$
(1)

The oxidant- and acceptor-free dehydrogenation of alcohols may also provide a novel and promising route for H<sub>2</sub> synthesis and storage.<sup>[28]</sup> By using benzyl alcohol as an example, we made a thermodynamic analysis for this reaction. Our analysis reveals that the standard Gibbs free-energy change ( $\Delta G^{\circ}$ ) for the dehydrogenation of benzyl alcohol to benzaldehyde and H<sub>2</sub> is 33.4 kJ mol<sup>-1</sup> at 298 K, and that this decreases to 20.6 kJ mol<sup>-1</sup> as the temperature rises to 393 K. The equilibrium conversion is estimated to be around 4% at 393 K. Although the dehydrogenation is a thermodynamically limited reaction, the removal of H<sub>2</sub> from the system by an inert gas flow could drive the reaction to the product side, as has been reported several times for the dehydrogenation of alcohols.<sup>[29–35]</sup>

Early studies showed that Ru-based catalysts, including the Shvo-type Ru complex grafted on SiO<sub>2</sub>, Ru/AlO(OH), and  $Ru(OH)_x/Al_2O_3$ , are effective for the dehydrogenation of alcohols without hydrogen acceptors.<sup>[29-31]</sup> Recently, supported Ag and Cu nanoparticles were also shown to catalyze the dehydrogenation of various alcohols.[32-34] In a recent short communication,<sup>[35]</sup> we demonstrated, for the first time, that supported Au nanoparticles could catalyze the oxidantand acceptor-free dehydrogenation of alcohols to aldehydes (or ketones) and H<sub>2</sub>. In particular, HT-supported Au nanoparticles exhibited high activity and selectivity for the oxidant-free dehydrogenation of a wide range of alcohols.<sup>[35]</sup> There is little information about Au-catalyzed dehydrogenation reactions in the absence of an oxidant. Herein, we report our recent studies on the elucidation of the effects of support and Au particle size in the oxidant-free dehydrogenation of benzyl alcohol.

#### **Results and Discussion**

**Support effects**: A deep understanding of the role of the support may lead to significant improvements in supported Au catalysts for alcohol dehydrogenation. Au nanoparticles loaded onto various supports prepared by the conventional impregnation method were examined for the dehydrogena-

tion of benzyl alcohol in our previous communication.<sup>[35]</sup> However, the mean sizes of Au nanoparticles in those catalysts were quite varied and often greater than 5 nm.<sup>[35]</sup> It is clear that a rigorous study of support effects requires the use of catalysts with uniform Au particle sizes.

Thus, the first task of this work was to prepare Au nanoparticles on various supports with uniform mean sizes  $(\approx 3 \text{ nm})$  by several different techniques. Haruta has summarized the techniques for preparing Au nanoparticle catalysts.<sup>[3a, f]</sup> We clarified that, for SiO<sub>2</sub> (Cab-O-Sil, a fumed silica), SBA-15 (a mesoporous silica), and carbon nanotubes (CNTs), sonication-aided impregnation was useful for preparing finely dispersed Au nanoparticles. For metal oxide supports, such as Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub>, La<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, and MgO, deposition–precipitation with urea as a homogeneous precipitant was suitable for preparing supported Au nanoparticles with smaller mean sizes (<4 nm). Deposition–precipitation with NaOH as a precipitant could give rise to Au/ HT catalysts containing homogeneously distributed Au nanoparticles with mean sizes less than 4 nm.

By regulating the conditions used in various preparation techniques, we were able to control the mean size of Au nanoparticles on various supports at around 3 nm. Typical TEM micrographs and corresponding Au particle size distributions for the supported Au catalysts are shown in Figure 1. The mean sizes (*d*) of Au nanoparticles for all these samples were in the range of 2.9–3.6 nm. All our catalysts underwent reduction by H<sub>2</sub> at 523 K to ensure the complete reduction of Au to the metallic state. X-ray photoelectron spectroscopy (XPS) showed that the binding energies for Au 4f<sub>7/2</sub> in these catalysts were 83.5–83.8 eV, which confirmed the presence of Au<sup>0</sup> in the samples.

The performances of these catalysts in the dehydrogenation of benzyl alcohols in Ar gas flow are shown in Table 1. The Au loading measured by inductively coupled plasma mass spectrometry (ICPMS), the BET surface area derived from N<sub>2</sub> physisorption, and the mean Au particle size obtained from TEM are also listed in Table 1. No correlations between catalytic performance and the BET surface area could be deduced. Au nanoparticles loaded on SiO<sub>2</sub> (Cab-O-Sil) and SBA-15 were almost inactive, and the Au/CNT also showed a low activity. Medium benzyl alcohol conversions (17-55%) were obtained with TiO<sub>2</sub>, ZrO<sub>2</sub>, La<sub>2</sub>O<sub>3</sub>, or CeO<sub>2</sub> as the support. On the other hand, Al<sub>2</sub>O<sub>3</sub>-, MgO-, hydroxyapatite (HAP)-, and HT-supported Au catalysts showed significantly higher benzyl alcohol conversions (>80%). Benzaldehyde selectivity also depended on the identity of the support. Au/SiO<sub>2</sub> and Au/SBA-15 showed significantly lower selectivity towards benzaldehyde, and the main byproduct was toluene. The formation of toluene was also observed with high selectivity in the dehydrogenation of benzyl alcohol over an Au-Pd/TiO2 catalyst.<sup>[36]</sup> Our calculation reveals that the disproportionation of benzyl alcohol into benzaldehyde and toluene [Eq. (2)] is thermodynamically feasible  $[\Delta G^{\circ}(393 \text{ K}) = -37 \text{ kJ mol}^{-1}]:$ 

$$2 \operatorname{PhCH}_2 \operatorname{OH} \to \operatorname{PhCHO} + \operatorname{PhCH}_3 + \operatorname{H}_2 \operatorname{O}$$
(2)

1248



Figure 1. TEM micrographs and corresponding Au particle size distributions for Au catalysts loaded on various supports: a) Au/SiO<sub>2</sub>, b) Au/ SBA-15, c) Au/CNT, d) Au/Al<sub>2</sub>O<sub>3</sub>, e) Au/TiO<sub>2</sub>, f) Au/ZrO<sub>2</sub>, g) Au/MgO, h) Au/La<sub>2</sub>O<sub>3</sub>, i) Au/CeO<sub>2</sub>, j) Au/HAP, k) Au/HT.

Thus, Equation (2) may proceed simultaneously with the dehydrogenation of benzyl alcohol to benzaldehyde and H<sub>2</sub>. Other catalysts showed higher selectivity towards benzaldehyde, which indicated that dehydrogenation was the main reaction. Among the catalysts examined in this work, Au/HT and Au/MgO demonstrated outstanding benzaldehyde selectivity (>99%). We measured the amount of H<sub>2</sub> formed over the Au/HT catalyst; the molar ratio of H<sub>2</sub> to benzyl alcohol was around 1:1. This further confirms that benzyl alcohol dehydrogenation [Eq. (1)] proceeds over our catalyst in the absence of any oxidant or hydrogen acceptor.

To make a better comparison among Au/Al<sub>2</sub>O<sub>3</sub>, Au/MgO, Au/HAP, and Au/HT catalysts, which gave similarly higher benzyl alcohol conversions (84–89%) after 6 h of reaction (Table 1), we performed the dehydrogenation of benzyl alcohol for 1 h over these catalysts. Au/Al<sub>2</sub>O<sub>3</sub> exhibited the highest benzyl alcohol conversion but the lowest benzalde-hyde selectivity, whereas Au/MgO showed the highest benzaldehyde selectivity but the lowest benzyl alcohol conversion (Figure 2). Similar to Au/MgO, Au/HT also exhibited



Figure 2. Catalytic performances of Au/Al<sub>2</sub>O<sub>3</sub>, Au/HAP, Au/MgO, and Au/HT for the oxidant-free dehydrogenation of benzyl alcohol. Reaction conditions: catalyst 0.20 g (Au amount 4–5  $\mu$ mol); benzyl alcohol 1 mmol; solvent (*p*-xylene) 5 mL; Ar flow rate 3 mLmin<sup>-1</sup>; *T*=393 K; *t*= 1 h.

high benzaldehyde selectivity (99.5%), but its benzyl alcohol conversion was higher than Au/MgO.  $Al_2O_3$  is a typical solid acid, whereas MgO is known as a basic oxide; thus, these results suggest that the acid–base properties of the support influence the catalytic behavior of the supported Au catalysts in the dehydrogenation of benzyl alcohol.

We examined the acid–base properties of some typical supported Au catalysts by temperature-programmed desorption (TPD) of NH<sub>3</sub> and CO<sub>2</sub>. As shown in Figure 3, desorption of NH<sub>3</sub> was observed from Au/HT, Au/Al<sub>2</sub>O<sub>3</sub>, and Au/HAP, which indicates that acidic sites exist on these catalysts. From the temperature and intensity of the NH<sub>3</sub> desorption peak, we can see that Au/HT and Au/Al<sub>2</sub>O<sub>3</sub> possess relatively strong acidity. On the other hand, no desorption of NH<sub>3</sub> was detectable from Au/SiO<sub>2</sub>, Au/La<sub>2</sub>O<sub>3</sub>, or Au/MgO, which suggests that these catalysts have no significant acidity. CO<sub>2</sub>-TPD profiles in Figure 4 suggest that Au/HT

www.chemeurj.org

A EUROPEAN JOURNAL

Table 1. Catalytic performances of Au nanoparticles loaded on various supports for the oxidant-free dehydrogenation of benzyl alcohol.<sup>[a]</sup>

Catalyst	Au content	Surface area	Au size	Conversion	Selectivity <sup>[b]</sup> [%]	
-	[wt %]	$[m^2g^{-1}]$	[nm]	[%]	benzaldehyde	toluene
Au/SiO <sub>2</sub>	0.50	262	2.9	2.1	49	40
Au/SBA-15	0.50	352	3.5	1.8	55	27
Au/CNT	0.50	97	3.0	7.4	94	5.1
Au/Al <sub>2</sub> O <sub>3</sub>	0.44	118	3.2	88	96	3.5
Au/TiO <sub>2</sub>	0.48	7.0	3.6	27	87	8.8
Au/ZrO <sub>2</sub>	0.45	9.0	3.5	17	93	4.1
Au/MgO	0.46	38	3.0	84	>99	0.1
Au/La <sub>2</sub> O <sub>3</sub>	0.47	8.0	3.1	55	97	1.7
Au/CeO <sub>2</sub>	0.46	6.0	2.9	37	97	2.5
Au/HAP	0.43	32	3.3	87	85	2.5
Au/HT	0.40	39	3.1	89	>99	0.1

[a] Reaction conditions: catalyst 0.20 g (Au amount  $4-5 \mu$ mol); benzyl alcohol 1 mmol; solvent (*p*-xylene) 5 mL; Ar flow rate 3 mLmin<sup>-1</sup>; T=393 K; t=6 h. [b] The remaining byproduct was benzene.



Figure 3.  $NH_3$ -TPD profiles for some typical supported Au catalysts.



Figure 4. CO<sub>2</sub>-TPD profiles for some typical supported Au catalysts.

and Au/MgO possess higher concentrations of basic sites, whereas no basic sites can be observed on Au/SiO<sub>2</sub>. The desorption of CO<sub>2</sub> was also observed from Au/Al<sub>2</sub>O<sub>3</sub> and Au/La<sub>2</sub>O<sub>3</sub>; the latter catalyst must be much more basic according to the higher desorption temperature. Only very weak CO<sub>2</sub> desorption peaks could be discerned in the case of Au/HAP, which suggests that this catalyst has fewer basic sites. In short, our NH<sub>3</sub>-TPD and CO<sub>2</sub>-TPD studies reveal that Au/HT possesses both strong acidity and strong basicity,

whereas neither acidic nor basic sites exist on Au/SiO<sub>2</sub>. Au/HAP also possesses both acidity and basicity, but the strength of the acidity and the number of basic sites are lower. Strongly acidic sites exist on Au/Al<sub>2</sub>O<sub>3</sub>, but its basicity is weaker. On the other hand, Au/MgO and Au/La<sub>2</sub>O<sub>3</sub> have relatively strong basic sites, but they do not possess acidic sites.

In summary, we have observed significant support effects in the Au-catalyzed oxidant-free dehydrogenation of benzyl alcohol, and our studies

suggest that the acid-base properties of the support play pivotal roles in determining both the activity and the selectivity. The catalysts with neither acidity nor basicity (e.g.,  $Au/SiO_2$  or Au/SBA-15) were almost inactive and less selective, whereas that with both strong acidity and strong basicity (i.e., Au/HT) exhibited both high activity and excellent selectivity. Further analysis indicates that catalysts with stronger basicity but lower or no acidity (e.g., Au/MgO) afford higher selectivity towards benzaldehyde, whereas those with stronger acidity but lower basicity (e.g.,  $Au/Al_2O_3$ ) are more active for the conversion of benzyl alcohol.

**Preparation and characterization of Au/HT catalysts with controlled mean Au particle sizes**: The preparation of supported Au catalysts with controlled Au sizes is still a challenge. We found that, by regulating the concentration of Au precursor, the aging temperature and the time used in the deposition–precipitation process could lead to the preparation of Au/HT catalysts with controlled Au particle sizes.

In our previous studies, we found that increasing the Au loading by increasing the concentration of Au precursor (HAuCl<sub>4</sub>) solution, while keeping the volume of solution used for deposition–precipitation constant, increased the mean Au particle size over HT.<sup>[35]</sup> This observation implies that the concentration of the HAuCl<sub>4</sub> solution might be key to changing the Au particle size. Herein, we attempt to prepare Au/HT samples with uniform Au loadings ( $\approx 0.5$  wt%) but varying mean Au particle sizes by changing the concentration of HAuCl<sub>4</sub> solution and the volume of the solution while keeping the total amount of Au constant.

In our experiment, the concentration of  $HAuCl_4$  solution was varied from 0.08 to 3.17 mmolL<sup>-1</sup>, whereas the total amount of Au in the solution was fixed, to provide a target Au loading of 0.5 wt%. The actual Au loadings in the obtained Au/HT catalysts, measured by ICPMS, were 0.40– 0.46 wt% (Table 2), which indicated that most (80–90%) of the Au precursors were deposited on the HT support during the deposition–precipitation process at a pH of 8.0. Figure 5 shows the TEM micrographs and the Au particle size distributions for these Au/HT samples. The mean size of Au

Table 2. Mean sizes and dispersions of Au nanoparticles in Au/HT catalysts prepared by deposition–precipitation with various concentrations of HAuCl<sub>4</sub>.

$[HAuCl_4]$ $[mmol L^{-1}]$	Au loading <sup>[a]</sup> [wt %]	Mean Au size <sup>[b]</sup> [nm]	Au disper- sion <sup>[c]</sup> [%]	Au disper- sion <sup>[d]</sup> [%]
0.08	0.40	2.1	56	51
0.16	0.41	2.5	47	49
0.21	0.43	3.1	38	39
0.32	0.43	4.0	29	28
0.63	0.42	7.4	16	19
1.06	0.46	11	11	14
3.17	0.44	12	10	12

[a] Measured by ICPMS. [b] Obtained from TEM. [c] Estimated from Au particle size. [d] Measured by  $H_2$ -O<sub>2</sub> titration.



Figure 5. TEM micrographs and corresponding Au particle size distributions for the Au/HT catalysts prepared by using various concentrations of HAuCl<sub>4</sub>: a) 0.08, b) 0.16, c) 0.21, d) 0.32, e) 0.63, f) 1.06, and g) 3.17 mmol  $L^{-1}$ .

nanoparticles in these samples increased gradually on increasing the concentration of HAuCl<sub>4</sub>. By varying the concentration in the range of 0.08–3.17 mmol L<sup>-1</sup>, we obtained Au/HT samples with mean Au particle sizes ranging from 2.1 to 12 nm (Table 2). We speculate that a smaller number -----FULL PAPER

of Au precursors per unit volume in the solution would decrease the probability of collision among the particles during particle growth, and would thus lead to smaller Au nanoparticles.

By assuming a spherical model of Au nanoparticles, the dispersion of Au (*D*) can be roughly estimated by using the following relationship,  $D = 1.17/d(\text{nm}) \times 100 \,\%$ .<sup>[3b]</sup> The calculated Au dispersion is listed in Table 2. We also measured the dispersion of Au over the Au/HT catalysts by H<sub>2</sub>–O<sub>2</sub> titration.<sup>[37]</sup> The Au dispersion obtained from the H<sub>2</sub>–O<sub>2</sub> titration decreased with increasing HAuCl<sub>4</sub> concentration (see Table 2). Moreover, the values of Au dispersion evaluated from the H<sub>2</sub>–O<sub>2</sub> titration were quite close to those estimated from the Au size obtained by TEM. This indicates that the average size of Au nanoparticles evaluated by TEM is acceptable.

The aging temperature and the time used for depositionprecipitation may also affect the size of the Au nanoparticles. We have clarified that increasing the aging temperature from 273 to 353 K slightly decreased the average size of Au from 3.7 to 2.5 nm (see Figure S1 in the Supporting Information,). In other words, the higher aging temperature resulted in slightly smaller Au nanoparticles. It is known that the size of a particle formed in solution is determined by the rates of nucleation and growth. The decrease in size of Au nanoparticles at higher aging temperature is understandable because the nucleation rate may be higher at increased temperature. On the other hand, increasing the aging time from 1 to 16 h significantly increased the mean size of Au nanoparticles over HT from 2.5 to 21 nm (see Figure S2 in the Supporting Information). This is probably due to Ostwald ripening, which is caused by the dissolved smaller particles precipitating onto the larger particles.<sup>[38]</sup>

Catalytic behavior of Au/HT catalysts with various Au sizes in the oxidant-free dehydrogenation of benzyl alcohol: Table 3 shows the dependence of catalytic performances on the mean size of Au nanoparticles in the Au/HT catalysts prepared by the deposition–precipitation method with various HAuCl<sub>4</sub> concentrations, aging temperatures and times. The loadings of Au in these catalysts were consistent (0.40– 0.46 wt%). Very high selectivity towards benzaldehyde (>99%) was obtained for all these catalysts, which indicates that the Au particle size did not affect product selectivity. Product selectivity is mainly determined by the nature of the support. Table 3 shows that the conversion of benzyl alcohol depends strongly on the mean size of Au nanoparticles. The smaller Au size gave higher benzyl alcohol conversion.

To elucidate the effect of Au particle size on the intrinsic catalytic reactivity of Au sites in the dehydrogenation of benzyl alcohol, we monitored the conversion of benzyl alcohol at the initial reaction stages over Au/HT catalysts. Figure 6 shows the time course for some typical Au/HT catalysts with mean Au sizes ranging from 2.1 to 12 nm. The conversion of benzyl alcohol over HT was zero, which confirms that the Au nanoparticles were the active surface for

www.chemeurj.org

### CHEMISTRY

A EUROPEAN JOURNAL

reaction.

lyzed oxidant-free dehydrogenation of benzyl alcohol is a

structure-sensitive

Table 3. Cataly	tic performance	of Au/HT	catalysts wit	th varying	mean Au nand	oparticle size. <sup>[a]</sup>
-----------------	-----------------	----------	---------------	------------	--------------	--------------------------------

Preparation	Au loading <sup>[c]</sup>	Mean Au size	Conversion [%]	Selectiv	ity [%]
conditions <sup>[b]</sup>	[wt %]	[nm]		aldehyde	toluene
[HAuCl <sub>4</sub> ]=0.08 mм	0.40	2.1	>99	>99	0.1
[HAuCl <sub>4</sub> ]=0.16 mм	0.41	2.5	>99	>99	0.1
[HAuCl <sub>4</sub> ]=0.21 mм	0.43	3.1	89	>99	0.1
T(aging) = 323  K	0.44	3.4	85	>99	0.1
T(aging) = 293  K	0.42	3.5	85	>99	0.1
T(aging) = 273  K	0.41	3.7	78	>99	0.1
[HAuCl <sub>4</sub> ]=0.32 mм	0.43	4.0	78	>99	0.1
t(aging) = 4 h	0.44	5.5	73	>99	0.1
[HAuCl <sub>4</sub> ]=0.63 mм	0.42	7.4	65	>99	0.1
t(aging) = 8 h	0.45	8.5	44	>99	0.2
[HAuCl <sub>4</sub> ]=1.06 mм	0.46	11	38	>99	0.3
[HAuCl <sub>4</sub> ]=3.17 mм	0.44	12	36	>99	0.2
t(aging) = 16 h	0.41	21	11	>99	0.5

[a] Reaction conditions: catalyst 0.20 g; benzyl alcohol 1 mmol; solvent (*p*-xylene) 5 mL; Ar flow rate 3 mLmin<sup>-1</sup>; T=393 K; t=6 h. [b] If not mentioned, conditions used were: [HAuCl<sub>4</sub>]=0.16 mmolL<sup>-1</sup>; aging temperature T(aging)=353 K; aging time t(aging)=1 h.



Figure 6. Time courses for the conversions of benzyl alcohol during the initial stage with Au/HT catalysts with varying mean Au nanoparticle size ( $\odot$ : 2.1,  $\bullet$ : 2.5,  $\triangle$ : 3.1,  $\mathbf{v}$ :  $\Box$ : 7.4,  $\mathbf{u}$ : 11, and  $\diamond$ : 12 nm). Reaction conditions: catalyst 0.10–0.20 g; benzyl alcohol 1–2 mmol; solvent (*p*-xylene) 5 mL; Ar flow rate 3 mL min<sup>-1</sup>; T=393 K.

the dehydrogenation reaction. In all of the runs over Au/HT catalysts shown in Figure 6, benzaldehyde selectivity was always higher than 99%, which further demonstrates that the Au/HT catalyst was highly selective for the oxidant-free dehydrogenation of benzyl alcohol. Figure 6 shows that the conversion of benzyl alcohol increases almost linearly with reaction time over the initial 40 min. Thus, we can calculate the initial reaction rate by using the slope of the straight line for each catalyst. The results are summarized in Table 4. It is clear that the initial reaction rate increases with decreasing mean Au nanoparticle size.

Because only the surface Au atoms contribute to the catalytic reactions, we have evaluated the turnover frequency (TOF), that is, the moles of substrate converted at the initial stage per mole of surface Au atoms per unit time, for each Au/HT catalyst. The TOF was calculated by using the initial reaction rate, and the Au dispersion evaluated by  $H_2$ -O<sub>2</sub> titration. The dependence of TOF on the mean size of Au nanoparticles plotted in Figure 7 suggests that the Au-cata-

When the mean size of Au decreases from 12 to around 4 nm, the TOF increases slightly. However, a further decrease in the mean Au size increases the TOF steeply. Decreasing the mean Au particle size from 4 to 2.1 nm increases the TOF from about 300 to about  $800 h^{-1}$ . The TOF value  $(\approx 800 \text{ h}^{-1})$  with the present catalyst for the oxidant-free dehydrogenation of benzyl alcohol is better than those mea-

Table 4. Initial reaction rates with the Au/HT catalysts for varying mean Au nanoparticle size in the oxidant-free dehydrogenation of benzyl alcohol. $^{[a]}$ 

Au loading [wt%]	Mean Au size [nm]	Initial reaction rate <sup>[b]</sup> [mmol $h^{-1}g^{-1}(\text{cat.})$ ]
0.40	2.1	8.28
0.41	2.5	5.65
0.43	3.1	2.74
0.43	4.0	1.87
0.42	7.4	0.94
0.46	11	0.58
0.44	12	0.50

[a] Reaction conditions: catalyst 0.10–0.20 g; benzyl alcohol 1–2 mmol; solvent (*p*-xylene) 5 mL; Ar flow rate 3 mLmin<sup>-1</sup>; T=393 K. [b] Measured from Figure 6.



Figure 7. Dependence of TOF on the mean Au nanoparticle size for the Au/HT-catalyzed oxidant-free dehydrogenation of benzyl alcohol. Reaction conditions: catalyst 0.10-0.20 g; benzyl alcohol 1-2 mmol; solvent (*p*-xylene) 5 mL; Ar flow rate 3 mLmin<sup>-1</sup>; T=393 K.

sured with many other catalysts such as Ag/HT (590  $h^{-1})$ , Ag/Al<sub>2</sub>O<sub>3</sub> ( $\approx 10 \ h^{-1})$ , Cu/HT (<10  $h^{-1})$ , and Pd/HT (36  $h^{-1})$ .<sup>[32-34]</sup>

We have performed more detailed studies for the 0.40 wt % Au/HT catalyst (with a mean Au size of 2.1 nm), which exhibits excellent performance in the oxidant-free de-

hydrogenation of benzyl alcohol. TEM measurements for this catalyst confirm that the mean Au particle size did not change after the reaction. We measured the Au content in both the filtrate and the recovered solid catalyst after the reaction, and confirmed that no leaching of Au occurred during the reaction.

We also examined the recyclability of this Au/HT catalyst for the oxidant-free dehydrogenation of benzyl alcohol at 393 K. As shown in Figure 8, the conversion of benzyl alcohol and the selectivity of benzaldehyde did not undergo significant changes over repeated usage for at least five cycles, which demonstrates that the present Au/HT catalyst is very stable.



Recycling number

Figure 8. Change in catalytic performance of the 0.40 wt% Au/HT (Au 2.1 nm) catalyst with recycling number, in the oxidant-free dehydrogenation of benzyl alcohol.  $\odot$ : benzyl alcohol conversion, **•**: benzaldehyde selectivity. Reaction conditions: catalyst 0.20 g; benzyl alcohol 1 mmol; solvent (*p*-xylene) 5 mL; Ar flow rate 3 mLmin<sup>-1</sup>; T=393 K; t=4 h.

The size effect and the mechanism of the Au-catalyzed dehydrogenation of benzyl alcohol: The most important feature of Au catalysis is the strong size effect. In CO oxidation, it is well known that the Au particle size exerts a major effect on catalytic activity; the TOF increases sharply with a decrease in Au diameter from around 5 nm.<sup>[1-3]</sup> The combination of catalytic results with the aberration-corrected high-angle annular dark-field-scanning TEM (HAADF-STEM) studies for  $Au/FeO_x$  prepared by coprecipitation suggests that the high catalytic activity for CO oxidation can be correlated with the presence of Au clusters of around 0.5 nm in diameter ( $\approx 10$  Au atoms) on FeO<sub>r</sub>.<sup>[9]</sup> A recent study demonstrated that the Au/FeO<sub>x</sub> catalyst containing Au particles with a mean size of  $(2.1\pm0.54)$  nm prepared by colloidal deposition is also very active for CO oxidation, and it is argued that a size of around 0.5 nm for the Au clusters is not mandatory for achieving the high activity.<sup>[39]</sup> Generally, the unique electronic structure and the high fraction of low-coordinated metal atoms are proposed to account for the specific catalytic properties of small metal nanoparticles,<sup>[3i,7,40,41]</sup> but there is significant debate regarding the origin of the structure sensitivity in Au catalysis.<sup>[3,4,7]</sup>

Several studies have contributed to elucidating the size effect in Au-catalyzed oxidative dehydrogenation of alco-

hols. Tsukuda and co-workers compared the catalytic properties of colloidal Au nanoclusters of varying size (1.3-10 nm) stabilized by poly(N-vinyl-2-pyrrolidone) or poly(allylamine) for the dehydrogenation of benzylic alcohols in the presence of  $O_2$  in water, and found that the smaller Au nanoclusters exhibited higher catalytic activity.<sup>[6]</sup> They further demonstrated, through various spectroscopic investigations, that the higher catalytic activity of the smaller Au nanoclusters was due to the increased negative charge on the Au core surrounded by the organic stabilizer, which facilitated the activation of O2 to superoxo- or peroxo-like species for alcohol dehydrogenation.<sup>[42]</sup> Recently, Tsukuda and co-workers further disclosed that the catalytic activity of Au nanoclusters loaded on SBA-15 decreased monotonically with increasing Au cluster size in the oxidative dehydrogenation of benzyl alcohol to benzaldehyde by H<sub>2</sub>O<sub>2</sub> under microwave irradiation.<sup>[43]</sup> They argued that the activation of H<sub>2</sub>O<sub>2</sub> might be enhanced by the smaller Au nanoclusters. However, with TiO2- or CeO2-supported Au catalysts of various Au particle size (from 1.3 to 11.3 nm), the activity for benzyl alcohol oxidation by O<sub>2</sub> increased with the mean size of Au, and reached a maximum at a mean Au size of 6.9 nm.<sup>[44]</sup> A comparison among Cu-Mg-Al-O mixed-oxide-supported Au catalysts with mean Au particle sizes of 2, 9, and 30 nm also suggested that the catalyst with a medium mean size (9 nm) was the most active for the aerobic oxidation of 1-phenylethanol.<sup>[45]</sup>

We observed a sharp increase in TOF with the decrease in the mean Au particle size from 4.0 to 2.1 nm (Figure 7). In our case, no oxidant was used for the conversion of benzyl alcohol. Therefore, we believe that Au nanoparticles activate the substrate (i.e., benzyl alcohol). Undoubtedly, knowledge about the reaction mechanism would be useful for understanding the size effect observed in our system. It can be expected that the dehydrogenation of benzyl alcohol involves the cleavage of the  $\beta$ -C–H bond. This C–H bond activation, or  $\beta$ -H elimination, has been proposed as the rate-determining step in the oxidative dehydrogenation of alcohols by  $O_2$  over several catalysts such as  $Ru/Al_2O_3$ <sup>[46]</sup> Pd/hydroxyapatite,<sup>[47]</sup> Pd/Al<sub>2</sub>O<sub>3</sub>,<sup>[48]</sup> Pd/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>,<sup>[49]</sup> and the hydrogen-transfer dehydrogenation of alcohols catalyzed by  $Cu/Al_2O_3^{[50]}$  It is reasonable to propose that the  $\beta$ -H elimination also determines the rate in our case. It is well known that the cleavage of  $\sigma$  bonds, including C–H bonds, over metal particles requires coordinative unsaturation of surface atoms (edge and corner atoms).<sup>[51,52]</sup> We speculate that this may result in the size effect observed in Figure 7.

Typically, the fraction of coordinatively unsaturated atoms increases with decreasing metal nanoparticle size.<sup>[53]</sup> By assuming a model of Au nanoparticles (e.g., icosahedron, truncated octahedron, or cubooctahedron), the fraction of higher-coordination-number atoms (face atoms) and lower-coordination-number atoms (edge and corner atoms) can be estimated. Icosahedron and truncated octahedron are typically used as models for unsupported and supported Au nanoclusters.<sup>[7,54-56]</sup> The fractions of coordinatively unsaturated atoms and face atoms estimated by using both icosahe

www.chemeurj.org



A EUROPEAN JOURNAL

Figure 9. Calculated fractions of edge+corner ( $_{\bigcirc}$  and  $_{\bigcirc}$ ) Au atoms and face ( $_{\square}$  and  $_{\blacksquare}$ ) Au atoms on the surfaces of Au nanoparticles with various sizes. Two Au nanoparticle models (icosahedron ( $_{\square}$  and  $_{\bigcirc}$ ) and truncated octahedron ( $_{\blacksquare}$  and  $_{\bigcirc}$ )) were used for the calculations.<sup>[54,56]</sup>

dral and truncated octahedral models<sup>[54,56]</sup> are plotted in Figure 9. Both models show that the fraction of coordinatively unsaturated Au atoms increases with decreasing Au particle size, and such an increase becomes particularly significant as the Au particle size decreases from around 4 nm. Comparison of the trends in Figures 7 and 9 suggests that the variation in TOF for alcohol dehydrogenation with Au particle size corresponds with the estimated fractions of surface-corner and -edge atoms. In other words, the coordinatively unsaturated Au sites on Au nanoparticles play dominant roles in the dehydrogenation of benzyl alcohol.

In addition to the coordinatively unsaturated sites on Au nanoparticles, we have demonstrated that the acidic and basic sites on the support also play pivotal roles in the dehydrogenation of benzyl alcohol. A base is often added as a promoter into the catalytic system for aerobic oxidation of alcohols.<sup>[13]</sup> For the Au-catalyzed oxidative dehydrogenation of alcohols, a base additive such as K2CO3 also worked as an efficient promoter, especially when the support was not a basic material, or without a support.<sup>[6,16,21,22,42,43]</sup> The base might act to cleave the O-H bond of the alcohol to form an alkoxide intermediate.<sup>[21]</sup> It has been proposed that coadsorbed oxygen atoms on Au surfaces could also act as a Brønsted base, thereby facilitating O-H bond activation.<sup>[57]</sup> The O-H bond was not activated, and no alkoxide was formed, in the absence of such coadsorbed oxygen species on Au surfaces.<sup>[57]</sup> Thus, in the case of oxidant-free dehydrogenation of alcohols (no coadsorbed oxygen species), a base additive or basic support becomes particularly important. In other words, the basic sites on HT support in our case should play a key role in the activation of the O-H bond of the alcohol, to facilitate formation of an adsorbed alkoxide intermediate.

A reaction mechanism that could explain our observations is shown in Scheme 1. The activation of the O–H bond of benzyl alcohol by the basic Mg–OH<sup> $\delta$ -</sup> site on the HT support proceeds in the first step to form the Mg alkoxide intermediate. We speculate that this step may determine the selectivity, although we currently have no information about the conversion path of benzyl alcohol in the absence of



Scheme 1. Possible reaction mechanism for the oxidant-free dehydrogenation of benzyl alcohol over HT-supported Au nanoparticles to give benzaldehyde and  $H_2$ .

basic sites. In the second step, the  $\beta$ -H is eliminated by an Au nanoparticle to produce benzaldehyde. This is expected to be the rate-determining step, and the coordinatively unsaturated Au atoms are more active for the cleavage of this C–H bond. Thus, the catalyst with smaller Au particles exhibits higher activity. The final step is the conversion of Au hydride to H<sub>2</sub>. For the oxidative dehydrogenation of alcohols, the hydride species is believed to be oxidized by O<sub>2</sub>.<sup>[46–48]</sup> In our case, because no oxidant is consumable, we speculate that the Brønsted acid sites (i.e., AlO–H<sup>δ+</sup>) on the HT support might participate in the reaction with the Au hydride to produce molecular H<sub>2</sub>. We will carry out further studies to elucidate this mechanism in our future work.

### Conclusion

We prepared two series of supported Au catalysts; namely, Au nanoparticles with uniform mean sizes (2.9-3.6 nm) loaded onto various supports, and the HT-supported Au nanoparticles with controlled mean sizes ranging from 2.1 to 21 nm. These catalysts were characterized by TEM, H<sub>2</sub>-O<sub>2</sub> titration, NH<sub>3</sub>-TPD, and CO<sub>2</sub>-TPD. It was shown that sonication-aided impregnation was suitable for the preparation of small Au nanoparticles on SiO<sub>2</sub>, SBA-15, and CNTs, whereas deposition-precipitation with urea or NaOH was applicable to the preparation of small Au nanoparticles on many metal oxides, such as Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub>, La<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, MgO, HAP, and HT. We demonstrated that the concentration of the Au precursor (HAuCl<sub>4</sub>) solution, the aging temperature, and the aging time used in the deposition-precipitation process were the main parameters controlling Au particle size in the Au/HT catalysts.

The two series of supported Au catalysts were studied in detail for the oxidant- and acceptor-free dehydrogenation of benzyl alcohol to elucidate the support and Au particle size

effects. Among the supports investigated, HT, which has both strong acidity and strong basicity, provided the best catalytic performance. Excellent activity and very high benzaldehyde selectivity (>99.5%) were achieved with the Au/ HT catalyst. The acid–base properties of the support were proposed to play key roles in the dehydrogenation of benzyl alcohol. Product selectivity, in particular, was strongly affected by the nature of the support.

Studies of the Au/HT catalysts with varying mean Au nanoparticle size demonstrated that the Au-catalyzed dehydrogenation of benzyl alcohol was a structure-sensitive reaction. The TOF for benzyl alcohol conversion increased with decreasing mean Au particle size (from 12 to 2.1 nm), and a particularly steep rise in TOF was observed when the mean Au nanoparticle size was <4 nm. We propose that the dehydrogenation of benzyl alcohol proceeds through the cleavage of the O-H bond to form an adsorbed alkoxide intermediate that undergoes β-H elimination to produce benzaldehyde. The basic sites on the support facilitate the formation of the alkoxide intermediate. The coordinatively unsaturated Au atoms are much more active for  $\beta$ -C-H bond activation, and this is the basis of the Au size effect. Moreover, the Brønsted acid sites may participate in the transformation of Au hydride, formed in the  $\beta$ -H elimination step, to molecular H<sub>2</sub>.

#### **Experimental Section**

Catalyst preparation: The target Au loading for each catalyst used in this work was 0.5 wt %, unless otherwise stated. Au/SiO2, Au/SBA-15, and Au/CNT were prepared by sonication-aided impregnation. The calculated amount of support was suspended in an aqueous solution of HAuCl<sub>4</sub>, and the suspension was placed into the sonication bath with irradiation at 40 kHz and 200 W output power. After sonication, the water was removed by evaporation at 353 K. The solid powder was finally reduced in H2 at 523 K for 2 h. Au/Al2O3, Au/TiO2, Au/ZrO2, Au/MgO, Au/La2O3, Au/CeO2, and Au/HAP were prepared by deposition-precipitation with urea as the precipitant. In brief, urea with a molar ratio of urea/Au of 100:1 was added to an aqueous solution of HAuCl<sub>4</sub>. After addition of the support, the suspension was placed in a water bath at 353 K and was vigorously stirred. After aging for a certain time (6-10 h), the solid product was recovered by filtration followed by thorough washing with deionized water until no Cl- could be detected. The resulting compound was dried in air at 393 K for 1 h, and finally reduced in  $H_2$  at 523 K for 2 h.

HTs are layered materials composed of positively charged two-dimensional sheets of mixed hydroxides with water and exchangeable chargecompensating anions, and their general formula can be expressed as  $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}(A^n)_{x/n}\cdot mH_2O^{.[58]}$  The most popular HT is  $Mg_6Al_2(OH)_{16}(CO_3)\cdot mH_2O$ . We prepared our Mg–Al HT by a simple coprecipitation method with a mixed solution of Mg and Al chlorides as the precursors.<sup>[58]</sup> Precipitation occurred after adding a solution of Na<sub>2</sub>CO<sub>3</sub> and NaOH. The suspension was stirred and aged at 338 K for 18 h. After cooling to room temperature, the resulting material was filtered and washed with deionized water until no Cl<sup>-</sup> could be detected. The solid was dried in air at 393 K overnight, and then calcined in air at 773 K to remove carbonate. Although the crystalline structure was lost during the calcining, it was regained during the subsequent deposition– precipitation process owing to the "memory effect" of HT.<sup>[58]</sup>

The Au/HT catalysts were prepared by deposition–precipitation, as follows: The pH of the aqueous solution of  $HAuCl_4$  was first adjusted to 8.0 by NaOH, and the solution was placed in a water bath at a fixed temper-

ature. Then, the calcined HT (carbonate free) was added, with stirring. Aging for a certain time resulted exclusively in the deposition of Au(OH)<sub>3</sub> precipitates on the HT surfaces.<sup>[3a]</sup> After cooling to room temperature, the solid was recovered by filtration, followed by washing with deionized water until no Cl<sup>-</sup> remained. The resulting compound was dried in air at 393 K overnight, and finally reduced by H<sub>2</sub> at 523 K for 2 h. The concentration of HAuCl<sub>4</sub>, as well as the aging temperature and time, affected the mean Au nanoparticle size. The standard conditions were as follows: [HAuCl<sub>4</sub>]=0.16 mmolL<sup>-1</sup>; aging temperature=353 K; and aging time=1 h.

Catalyst characterization: Au loadings in all of the catalysts were measured by ICPMS with an Agilent ICP-MS 4500 instrument after dissolving the sample in aqua regia. The Mg/Al ratio of our HT was measured to be 1.80. N2 physisorption at 77 K was carried out with a Micromeritics Tristar 3000 surface-area and porosimetry analyzer to examine the surface area of each sample. XPS was carried out on a Quantum 2000 Scanning ESCA Microprobe instrument (Physical Electronics) with  $Al_{K\alpha}$  radiation. The binding energy was calibrated by using the C<sub>1s</sub> photoelectron peak at 284.6 eV as a reference. TEM measurements were performed on a JEM-2100 electron microscope operated at an acceleration voltage of 200 kV. The mean Au particle size in the Au/HT samples was estimated from TEM micrographs by counting around 150-200 particles. Au dispersions were measured by H2-O2 titration with an ASAP2010C Micromeritics apparatus, according to published procedures.  $^{\left[ 37\right] }$  NH3-TPD and CO2-TPD were performed on a Micromeritics AutoChem 2920 II instrument. Typically, the sample loaded in a quartz reactor was pretreated with highpurity He at 623 K for 1 h. After cooling the sample to 373 K, NH<sub>3</sub> adsorption was performed by switching the He flow to a NH<sub>3</sub>-He (10 vol% NH<sub>3</sub>) gas mixture and then maintaining the sample at 373 K for 1 h. The gas-phase (and/or weakly adsorbed) NH<sub>3</sub>, was purged by high-purity He at the same temperature. NH3-TPD was then performed in the He flow by raising the temperature to 1073 K at a rate of 10 K min<sup>-1</sup>. The desorbed NH<sub>3</sub> molecules were detected by using a ThermoStar GSD 301 T2 mass spectrometer at the signal of m/z 16. CO<sub>2</sub>-TPD was performed by using a similar procedure.

**Catalytic reaction**: The dehydrogenation of benzyl alcohol was carried out by using a batch-type reaction vessel with a reflux condenser. Typically, the powdered catalyst (typically, 0.20 g) was added to the alcohol with the solvent (*p*-xylene), and then high-purity Ar gas (99.999%) was bubbled into the mixture. After purging with Ar gas (flow rate  $8 \text{ mLmin}^{-1}$ ) for 1 h to remove the remaining air in the reaction system, the mixture was heated to the reaction temperature with stirring. The flow rate of Ar was typically kept at  $3 \text{ mLmin}^{-1}$  during the reaction. After the reaction, the catalyst was separated by CC (Shimazu GC-14B) after the addition of an internal standard.

#### Acknowledgements

This work was supported by the National Natural Science Foundation of China (nos. 20625310, 20773099, 20873110, and 20923004), the National Basic Research Program of China (no. 2010CB732303), the Research Fund for the Doctoral Program of Higher Education (no. 20090121110007), and the Key Scientific Project of Fujian Province (2009HZ0002-1). We thank Professors H. B. Zhang and G. D. Lin for providing the CNTs.

[3] For recent reviews on Au catalysis, see: a) M. Haruta, *Catal. Today* 1997, *36*, 153–166; b) G. C. Bond, D. T. Thompson, *Catal. Rev. Sci. Eng.* 1999, *41*, 319–388; c) G. C. Bond, D. T. Thompson, *Gold Bull.* 2000, *33*, 41–50; d) M. Haruta, *CATTECH* 2002, *6*, 102–115; e) M.

a) M. Haruta, T. Kobayashi, H. Sano, N. Yamada, *Chem. Lett.* 1987, 405–408; b) M. Haruta, *Nature* 2005, 437, 1098–1099.

<sup>[2]</sup> Catalysis by Gold (Eds.: G. C. Bond, C. Louis, D. T. Thompson), Imperial College Press, London, 2006.

## CHEMISTRY

Haruta, Chem. Rec. 2003, 3, 75–87; f) M. Haruta, Gold Bull. 2004, 37, 27–36; g) A. S. K. Hashmi, G. J. Hutchings, Angew. Chem. 2006, 118, 8064–8105; Angew. Chem. Int. Ed. 2006, 45, 7896–7936; h) T. Ishida, M. Haruta, Angew. Chem. 2007, 119, 7288–7290; Angew. Chem. Int. Ed. 2007, 46, 7154–7156; i) B. K. Min, C. M. Friend, Chem. Rev. 2007, 107, 2709–2724; j) S. A. K. Hashmi, Chem. Rev. 2007, 107, 3180–3211; k) G. J. Hutchings, Chem. Commun. 2008, 1148–1164; l) G. J. Hutchings, M. Brust, H. Schmidbaur, Chem. Soc. Rev. 2008, 37, 1759–1765; m) A. Corma, H. Garcia, Chem. Soc. Rev. 2008, 37, 2096–2126; n) G. J. Hutchings, J. Mater. Chem. 2009, 19, 1222–1235; o) P. Garcia, M. Malacria, C. Aubert, V. Gandon, L. Fensterbank, ChemCatChem 2010, 2, 493–497.

- [4] a) M. Valden, X. Lai, D. W. Goodman, *Science* **1998**, 281, 1647– 1650; b) M. S. Chen, D. W. Goodman, *Science* **2004**, 306, 252–254.
- [5] T. Hayashi, K. Tanaka, M. Haruta, J. Catal. 1998, 178, 566-575.
- [6] a) H. Tsunoyama, H. Sakurai, Y. Negishi, T. Tsukuda, J. Am. Chem. Soc. 2005, 127, 9374–9375; b) H. Tsunoyama, H. Sakurai, T. Tsukuda, Chem. Phys. Lett. 2006, 429, 528–532.
- [7] a) N. Lopez, T. V. W. Janssens, B. S. Clausen, Y. Xu, M. Mavrikakis, T. Bligaard, J. K. Nørskov, J. Catal. 2004, 223, 232–235; b) B. Hvolbak, T. V. W. Janssens, B. S. Clausen, H. Falsig, C. H. Christensen, J. K. Nørskov, Nano Today 2007, 2, 14–18; c) T. V. W. Janssens, B. S. Clausen, B. Hvolbæk, H. Falsig, C. H. Christensen, T. Bligaard, J. K. Nørskov, Top. Catal. 2007, 44, 15–26.
- [8] T. Ishida, N. Kinoshita, H. Okatsu, T. Akita, T. Takei, M. Haruta, Angew. Chem. 2008, 120, 9405–9408; Angew. Chem. Int. Ed. 2008, 47, 9265–9268.
- [9] A. A. Herzing, C. J. Kiely, A. F. Carley, P. Landon, G. J. Hutchings, *Science* 2008, 321, 1331–1335.
- [10] M. Turner, V. B. Golovko, O. P. Vaughan, P. Abdulkin, A. Berenguer-Murcia, M. S. Tikhov, B. F. G. Johnson, R. M. Lambert, *Nature* 2008, 454, 981–983.
- [11] J. Li, N. Ta, W. Song, E. Zhan, W. She, Gold Bull. 2009, 42, 48-60.
- [12] J. Huang, T. Akita, J. Faye, T. Fujitani, T. Takei, M. Haruta, Angew. Chem. 2009, 121, 8002–8006; Angew. Chem. Int. Ed. 2009, 48, 7862– 7866.
- [13] For recent reviews on heterogeneous aerobic oxidation of alcohols, see: a) T. Mallat, A. Baiker, *Chem. Rev.* 2004, *104*, 3037–3058;
  b) B.-Z. Zhan, A. Thompson, *Tetrahedron* 2004, *60*, 2917–2935; c) T. Matsumoto, M. Ueno, N. Wang, S. Kobayashi, *Chem. Asian J.* 2008, *3*, 196–214.
- [14] A. Abad, P. Concepción, A. Corma, H. García, Angew. Chem. 2005, 117, 4134–4137; Angew. Chem. Int. Ed. 2005, 44, 4066–4069.
- [15] D. I. Enache, J. K. Edwards, P. Landon, B. Solsona-Espriu, A. F. Carley, A. A. Herzing, M. Watanabe, C. J. Kiely, D. W. Knight, G. J. Hutchings, *Science* 2006, *311*, 362.
- [16] N. Zheng, G. D. Stucky, Chem. Commun. 2007, 3862-3864.
- [17] P. Haider, A. Baiker, J. Catal. 2007, 248, 175-187.
- [18] F. Z. Su, Y. M. Liu, L. C. Wang, Y. Cao, H. Y. He, K. N. Fan, Angew. Chem. 2008, 120, 340–343; Angew. Chem. Int. Ed. 2008, 47, 334– 337.
- [19] L. C. Wang, Y. M. Liu, M. Chen, Y. Cao, H. Y. He, K. N. Fan, J. Phys. Chem. C 2008, 112, 6981–6987.
- [20] T. Mitsudome, A. Noujima, T. Mizugaki, K. Jitsukawa, K. Kaneda, *Adv. Synth. Catal.* 2009, 351, 1890–1896.
- [21] T. Ishida, M. Nagaoka, T. Akita, M. Haruta, Chem. Eur. J. 2008, 14, 8456–8460.
- [22] H. Miyamura, R. Matsubara, Y. Miyazaki, S. Kobayashi, Angew. Chem. 2007, 119, 4229–4232; Angew. Chem. Int. Ed. 2007, 46, 4151– 4154.
- [23] N. Dimitratos, A. Villa, D. Wang, F. Porta, D. S. Su, L. Prati, J. Catal. 2006, 244, 113–121.
- [24] D. Wang, A. Villa, P. Spontoni, D. S. Su, L. Prati, Chem. Eur. J. 2010, 16, 10007–10013.

- Q. Zhang, Y. Wang, et al.
- [25] M. Hayashi, K. Yamada, S. Nakayama, H. Hayashi, S. Yamazaki, Green Chem. 2000, 2, 257–260.
- [26] C. Keresszegi, T. Mallat, A. Baiker, New J. Chem. 2001, 25, 1163– 1167.
- [27] F. Zaccheria, N. Ravasio, R. Fusi, Chem. Commun. 2005, 253-255.
- [28] A. Friedrich, S. Schneider, *ChemCatChem* **2009**, *1*, 72–73.
- [29] J. H. Choi, N. Kim, Y. J. Shin, J. H. Park, J. Park, *Tetrahedron Lett.* 2004, 45, 4607–4610.
- [30] W. H. Kim, I. S. Park, J. Park, Org. Lett. 2006, 8, 2543-2545.
- [31] R. Karvembu, R. Priyarega, *React. Kinet. Catal. Lett.* 2006, 88, 333– 338.
- [32] T. Mitsudome, Y. Mikami, H. Funai, T. Mizugaki, K. Jitsukawa, K. Kaneda, Angew. Chem. 2008, 120, 144–147; Angew. Chem. Int. Ed. 2008, 47, 138–141.
- [33] T. Mitsudome, Y. Mikami, K. Ebata, T. Mizugaki, K. Jitsukawa, K. Kaneda, *Chem. Commun.* 2008, 4804–4806.
- [34] K. Shimizu, K. Sugino, K. Sawabe, A. Satsuma, Chem. Eur. J. 2009, 15, 2341–2351.
- [35] W. Fang, Q. Zhang, J. Chen, W. Deng, Y. Wang, Chem. Commun. 2010, 46, 1547–1549.
- [36] S. Meenakshisundaram, E. Nowicka, P.J. Miedziak, G.L. Brett, R. L. Jenkins, N. Dimitratos, S. H. Taylor, D. W. Knight, D. Bethell, G. J. Hutchings, *Faraday Discuss.* **2010**, *145*, 341–356.
- [37] H. Berndt, I. Pitsch, S. Evert, K. Struve, M.-M. Pohl, J. Radnik, A. Martin, Appl. Catal. A 2003, 244, 169–179.
- [38] F. Schüth, M. Hesse, K. K. Unger in *Handbook of Heterogeneous Catalysis, Vol. 1* (Eds.: G. Ertl, H. Knözinger, F. Schüth, J. Weitkamp), WILEY-VCH, Weinheim, **2008**, pp. 100–119.
- [39] Y. Liu, C. J. Jia, J. Yamasaki, O. Terasaki, F. Schüth, Angew. Chem. Int. Ed. 2010, 49, 5771–5775.
- [40] C. N. R. Rao, G. U. Kulkarni, P. J. Thomas, P. P. Edwards, *Chem. Eur. J.* 2002, 8, 28–35.
- [41] E. Roduner, Chem. Soc. Rev. 2006, 35, 583-592.
- [42] H. Tsunoyama, N. Ichikuni, H. Sakurai, T. Tsukuda, J. Am. Chem. Soc. 2009, 131, 7086–7093.
- [43] a) Y. Liu, H. Tsunoyama, T. Akita, T. Tsukuda, J. Phys. Chem. C 2009, 113, 13457-13461; b) Y. Liu, H. Tsunoyama, T. Akita, T. Tsukuda, Chem. Lett. 2010, 39, 159-161.
- [44] D. P. Haider, B. Kimmerle, F. Krumeich, W. Kleist, J. D. Grunwaldt, A. Baiker, *Catal. Lett.* 2008, 125, 169–176.
- [45] P. Haider, J. D. Grunwaldt, A. Baiker, *Catal. Today* 2009, 141, 349– 354.
- [46] K. Yamaguchi, N. Mizuno, Chem. Eur. J. 2003, 9, 4353-4361.
- [47] K. Mori, T. hara, T. Mizugaki, K. Ebitani, K. Kaneda, J. Am. Chem. Soc. 2004, 126, 10657–10666.
- [48] a) C. Keresszegi, D. Ferri, T. Mallat, A. Baiker, J. Phys. Chem. B 2005, 109, 958–967; b) D. M. Meier, A. Urakawa, A. Baiker, J. Phys. Chem. C 2009, 113, 21849–21855.
- [49] J. Chen, Q. Zhang, Y. Wang, H. Wan, Adv. Synth. Catal. 2008, 350, 453-464.
- [50] F. Zaccheria, N. Ravasio, R. Psaro, A. Fusi, Chem. Eur. J. 2006, 12, 6426–6431.
- [51] R. A. van Santen, Acc. Chem. Res. 2009, 42, 57-66.
- [52] J. Wei, E. Iglesia, J. Phys. Chem. B 2004, 108, 4094-4103.
- [53] R. van Hardeveld, F. Hartog, Surf. Sci. 1969, 15, 189-230.
- [54] R. E. Benfield, J. Chem. Soc. Faraday Trans. 1992, 88, 1107-1110.
- [55] M. J. Yacamán, J. A. Ascencio, H. B. Liu, J. Gardea-Torresdey, J. Vac. Sci. Technol. B 2001, 19, 1091–1103.
- [56] A. Carlsson, A. Puig-Molina, T. V. W. Janssens, J. Phys. Chem. B 2006, 110, 5286–5293.
- [57] M. K. Weldon, C. M. Friend, Chem. Rev. 1996, 96, 1391-1411.
- [58] D. P. Debecker, E. M. Gaigneaux, G. Busca, Chem. Eur. J. 2009, 15, 3920–3935.

Received: August 26, 2010 Published online: December 10, 2010

1256 -