Gold Nanoclusters Confined in a Supercage of Y Zeolite for Aerobic Oxidation of HMF under Mild Conditions**

Jiaying Cai,^[a, b] Hong Ma,^[a] Junjie Zhang,^[a, b] Qi Song,^[a] Zhongtian Du,^[a] Yizheng Huang,^[a] and Jie Xu^{*[a]}

Abstract: Au nanoclusters with an average size of approximately 1 nm size supported on HY zeolite exhibit a superior catalytic performance for the selective oxidation of 5-hydroxymethyl-2-furfural (HMF) into 2,5-furandicarboxylic acid (FDCA). It achieved >99 % yield of 2,5-furandicarboxylic acid in water under mild conditions (60 °C, 0.3 MPa oxygen), which is much higher than that of Au supported on metal oxides/hydroxide (TiO₂, CeO₂, and Mg(OH)₂) and channel-type zeo-

lites (ZSM-5 and H-MOR). Detailed characterizations, such as X-ray diffraction, transmission electron microscopy, N_2 -physisorption, and H_2 -temperatureprogrammed reduction (TPR), revealed that the Au nanoclusters are well encapsulated in the HY zeolite supercage, which is considered to restrict

Keywords: 5-hydroxymethylfurfural • biomass • gold • nanostructures • oxidation and avoid further growing of the Au nanoclusters into large particles. The acidic hydroxyl groups of the supercage were proven to be responsible for the formation and stabilization of the gold nanoclusters. Moreover, the interaction between the hydroxyl groups in the supercage and the Au nanoclusters leads to electronic modification of the Au nanoparticles, which is supposed to contribute to the high efficiency in the catalytic oxidation of HMF to FDCA.

Introduction

The catalytic conversion of biomass provides a sustainable alternative opportunity for producing non-fossil-based chemicals and biofuel, etc., and thus could reduce the heavy dependence on unsustainable petroleum-based resource.^[1-4] Among the various conversion routes, the catalytic oxidation of 5-hydroxymethylfurfural (HMF) to 2,5-furandicarboxylic acid (FDCA) is an essential process. Because the starting material HMF and the target product FDCA are both identified as important biomass-based building blocks, and FDCA is also a widely used chemical and medical intermediate.^[5] Moreover, due to its similar structure to terephthalic acid (PTA)—a monomer for the production of polyethyleneterephthalate (PET plastic)—renewable FDCA obtained from biomass has a great potential to replace

- [a] J. Cai, Dr. H. Ma, J. Zhang, Dr. Q. Song, Dr. Z. Du, Dr. Y. Huang, Prof. J. Xu
 Dalian National Laboratory for Clean Energy
 State Key Laboratory of Catalysis
 Dalian Institute of Chemical Physics
 Chinese Academy of Sciences
 Dalian 116023 (P.R. China)
 Fax: (+86)411-84379245
 E-mail: xujie@dicp.ac.cn
- [b] J. Cai, J. Zhang University of Chinese Academy of Sciences Beijing 100049 (P.R. China)
- [**] HMF=5-Hydroxymethylfurfural.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201301735.

PTA.^[6–10] Therefore, the exploration of the efficient oxidation of HMF and production of FDCA is a significant and commercially viable alternative process to the petroleum approach.

Currently, there is considerable interest in the catalytic oxidation of HMF to FDCA. Catalysts such as Pt,^[11] Pd,^[12] and Co/Zn/Br^{-[13]} have been studied to realize this process. But these catalytic systems exhibit relative low selectivity towards FDCA and commonly give mixed products comprising hydroxymethyl-2-furancarboxylic acid (HMFCA) and FDCA. To promote HMF conversion and increase the selectivity for FDCA, various materials have been employed as carriers or supports to increase the reaction activity by regulating the metal-support interaction. For example, activated carbon is a good carrier for noble metals, but here it is not as efficient as expected. Studies have shown that Pt/C and Pd/C only achieved 79 and 71% yields towards FDCA, respectively.^[12] Gold catalysts as promising oxidation candidates have received more attention.^[14-23] Recently, Corma et al. realized the efficient oxidation of HMF to FDCA with high yield by using CeO₂-supported Au nanoparticles (NPs) (3.5 nm) at 130 °C under 1 MPa air pressure.^[14] But in the second run the activity of the catalytic system decreased rapidly under identical conditions. Ebitani et al.^[16] have shown that basic hydrotalcite (HT)-supported Au NP (3.2 nm) catalysts gave an excellent yield to FDCA without the addition of ahomogeneous base, and the Au/HT catalyst can be recycled three times. Subsequent study conducted by Zope et al.^[24] found that Mg²⁺ ions leached from hydrotalcite during the oxidation reaction. On the other hand, increasing the HMF/base ratio can also improve the FDCA

Chem. Eur. J. 2013, 19, 14215-14223

© 2013 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

WILEY CONLINE LIBRARY

- 14215

A EUROPEAN JOURNAL



yield. Davis et al. improved the selectivity for FDCA up to 65% by increasing the NaOH/HMF ratio from 2 to 20 over Au/TiO₂.^[11] The reason may be that the base can facilitate dehydrogenation of hydroxyl, and reduce the amount of carboxylic acid adsorbed on the Au surface, thus more active sites are unoccupied. These recent researches reveal that the oxidation of HMF to FDCA still exhibit problems such as instability, ion leaching, and the need of a high ratio of base, which need to be overcome. Thus, it is still urgent to develop highly active, more selective, and stable heterogeneous catalysts for highly efficient realizing the efficient oxidation of HMF to FDCA.

According to the current research status, construction of new catalyst comprising extremely small nanoclusters $(<2 \text{ nm})^{[25,26]}$ may be a promising method to break through the bottleneck in the

HMF oxidation reaction and achieve high yields of FDCA. The small size endows nanoclusters an extremely high activity, but accompanies with the problem of easy aggregation and instability which become more serious under severe conditions. Recently, various protectors were widely employed to prevent aggregation, including dendrimers,^[27,28] functional polymers,^[29,30] or classic σ -type ligands,^[31–33] such as carboxylic acids, thiols, and amines. Unfortunately, these protectors, typically containing heteroatoms such as S and N, which remarkably influence or even hamper the catalytic performance. As widely industrialized catalyst, zeolites are crystalline aluminosilicates with a diverse morphology and a rigid microporous structure. We notice that the cage-type Y zeolites own a typical supercage with 1.2 nm in diameter and an open aperture of 0.74 nm, which can serve as a natural nanocage to encapsulate the extremely small nanoclusters and prevent the inside nanoclusters from aggregation and deactivation. However, this topic has not yet been extensively addressed.

In the present study, we prepared Au/HY catalysts, in which Au nanoclusters with 1 nm average size were encapsulated within a HY supercage, and applied this catalytic system on HMF oxidation. The Au/HY catalyst exhibited highly efficiency in the oxidation of HMF to FDCA. Special attention has been paid to uncover the function of the supercage and the internal hydroxyl groups in the formation of Au/HY, as well as in the promotion of the activity and the stability of the catalyst. In our previous study on HMF oxidation, several vanadium-based catalytic systems were disclosed, achieving 2,5-diformylfuran (DFF) or maleic an-hydride as main products rather than FDCA.^[34,35] Here, the high efficiency in the oxidation of HMF to FDCA is realized by Au nanoclusters encapsulated in a HY supercage.

Results and Discussion

Comparison of different supports: For comparison, Table 1 lists the common texture of various catalysts and their cata-

Table 1. Oxidative conversion of HMF with Au supported on various zeolites and metal oxides. $\ensuremath{^{[a]}}$

Catalysts	d_{Au}	Structure	Conversion	Yield [%]		
	[nm]	(pore size	[%]	HMFCA	FDCA	others
		[nm])				
Au/Mg(OH) ₂	$\approx 5-7$	disorder	>99	10	76	14
Au/TiO ₂	10	disorder	>99	6	85	9
Au/CeO ₂	10	disorder	>99	25	73	2
Au/H-MOR ^[b]	$\approx 3-5$	channel (0.8)	96	64	15	21
Au/Na-ZSM-5-38 ^[b,c]	20	channel (0.5)	87	85	0	15
Au/Na-ZSM-5-25 ^[c]	15	channel (0.5)	92	90	1	9
Au/HY	1	cage (1.2)	>99	0	>99	0
HY	1	cage (1.2)	30	27	0	3
no catalyst	-	-	25	24	0	1

[a] Reaction conditions: catalyst (0.30 g, Au 1.5 wt%), HMF (0.317 g), H_2O (4.6 g), NaOH (0.4 g), 0.3 MPa O_2 , 60°C, 6 h, molar ratio of Au/HMF=1:110. [b] H-MOR and ZSM-5 = channel-type zeolites. [c] The silica alumina ratio of Na-ZSM-5 was 38 and 25, respectively.

lytic performance in HMF oxidation to FDCA at 60°C under 0.3 MPa O₂ in water, Typical experiments were conducted over a certain amount of catalyst at 60°C under 0.3 MPa O₂ with the addition of NaOH in water. HMF did not convert into FDCA without catalyst or only with the HY support alone. When gold was supported on typical metal oxide/hydroxide materials such as TiO₂, CeO₂, and Mg(OH)₂, the size of Au NPs is non-uniform, as shown by TEM (see the Supporting Information, Figure S8). The diameter of the Au particles in these catalysts was larger than 5 nm, some were even greater than 10 nm. All of them were attached to the oxide surface, consisting with the fact that there is no pore structure in these oxides. These catalysts gave moderate reaction activity, achieving 76, 85, and 73% FDCA yields, respectively. Until now, it is still difficult to synthesize tiny gold nanoclusters, which are uniform and highly dispersed on oxides surface in less than 1.5 nm, because these oxides lack a confined structure and thus cannot restrict the growth of nanoclusters. In our case, even though the oxide supports enable gold to disperse on the metal oxide/hydroxide surface (TiO₂, CeO₂ and Mg(OH)₂) through charge effect, the obtained Au NPs easily aggregate, resulting in large particles.

However, it is remarkable that Au supported on HY zeolite exhibited the top activity in HMF oxidation reaction, achieving >99% conversion and >99% FDCA yield.^[36] Contrasted with Au/HY, other zeolite-supported Au catalysts such as Au/H-MOR and Au/Na-ZSM-5, exhibit lower catalytic performance. For example, when Au was dispersed in H-MOR zeolite featured with a one-dimensional structure or Na-ZSM-5 zeolite characterized by a three-dimensional channel structure, HMF was oxidized into HMFCA rather than the required target FDCA (<3%). The different reaction activity is related to Au particles size effect; the smaller size gives much higher reaction activity.^[37-39]

We carefully checked the Au clusters in the zeolite by TEM. The diameter of gold nanoclusters is calculated by accounting more than 200 clusters. For H-MOR and Na-ZSM-5 carrier, gold particles have a large size of more than 5 nm

1	4216	



Figure 1. a) TEM image of Au/HY (1.5%), the histogram shows the distribution of the diameter of the Au nanoclusters (scale bar = 10 nm). b) HR-TEM image indicating that the Au clusters are confined in the HY supercage (scale bar = 2 nm). c) TEM image of Au/NaY (scale bar = 20 nm). d) TEM image of Au/HY-200 (scale bar = 10 nm). e) TEM image of Au/HY-400 (scale bar = 10 nm). The circles indicate the Au particles.

in average, and these particles were attached on the external surface of the zeolite (see the Supporting Information, Figure S8). However, when Au is supported on HY, the formed Au nanoclusters are observed around 1.0 nm in diameter and highly dispersed (Figures 1a and b). The remarkable difference of the Au size in HY and in other zeolites is most probably caused by the structure of the zeolite. In comparison with H-MOR and Na-ZSM-5, Y zeolite has a unique supercage, which is a spherical cage with a 0.74 nm open aperture and a 1.2 nm inner space. As shown in Figure 1a, the Au nanoclusters have a uniform and narrow distribution centered at 1.0 nm. Such Au size is smaller than the supercage size but larger than the open aperture of the cage, which suggests that the gold nanoclusters may be confined in the supercage of HY zeolite. SEM images of Au/HY show that neither Au particles nor clusters exist on the external surface of HY, indicating that the Au clusters are inside of HY (see the Supporting Information, Figure S7). Both TEM and SEM results suggest that Au clusters are present inside the supercage.

The nitrogen physisorption and pore width distribution of the Au/HY catalyst further confirms that the Au nanoclusters are settled in the supercage. Figure 2a shows that when Au was introduced in fresh HY, the total adsorbed nitrogen amount by Au/HY (black quadrangle line) decreased comparing with that of fresh HY (black triangle line). The micropore volume of Au/HY is calculated to be 429 m³g⁻¹, which is lower than that of fresh HY (497 m³g⁻¹) based on the *V*-*t* plot method. Especially, those micropore volumes ranged between 1.0 and 1.2 nm pore width, which represent



Figure 2. a) Nitrogen adsorption isotherms obtained at RT. b) Horvath–Kawazoe (HK) method calculation of the pore width for HY (\blacksquare) and Au/ HY (\blacktriangledown).

the supercage volume of HY and Au/HY (Figure 2b). It is obvious that the supercage volume of Au/HY decreased in comparison to that of HY, suggesting that Au clusters occupied some supercages after loading of Au. In addition, the H_2 -temperature-programmed reduction (TPR) result of Au/ HY shows one reduction peak at around 106°C (Figure 3). This peak has been proven to be the typical reduction peak



Figure 3. H_2 -TPR profiles of catalysts Au/HY, Au/HY-200, and Au/HY-400. (TCD = thermal conductivity detector)

Chem. Eur. J. 2013, 19, 14215-14223

© 2013 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

www.chemeurj.org

of gold ions to Au^0 restricted in the supercage of Y zeolite.^[40,41] Taking all the facts above into account, we conclude that Au clusters are located inside the supercage of HY. All these results indicate that gold clusters are presented inside the Y zeolite supercage, which is consistent with the TEM image (Figure 1 a).

Role of acidic –**OH groups in the supercage**: To understand the role of the supercage in the restriction and stabilization of Au nanoclusters, we compared the catalytic performance of Au/HY and Au/NaY by using the same preparation procedure. Although owning a similar supercage structure, to our surprise, these two catalysts exhibited remarkably different performance in FDCA production. Au/HY afforded >99% yield of FDCA, whereas Au/NaY only provided 15% FDCA accompanied with 65% HMFCA (Table 2).

Table 2. Oxidative conversion of HMF with Au supported on various Y zeolites. $\ensuremath{^{[a]}}$

Catalysts	$d_{ m Au}$	Conversion	Yield [%]		
	[nm]	[%]	HMFCA	FDCA	others
Au/NaY	10	>99	65	15	20
Au/HY ^[b]	7	>99	54	21	25
Au/HY ^[c]	1-5	>99	14	63	23
Au/HY-200	1–5	>99	5	81	14
Au/HY-400	5	>99	52	37	11

[a] Reaction conditions: catalyst (0.30 g, Au 1.5 wt %), HMF (0.317 g), H_2O (4.6 g), NaOH (0.4 g), 0.3 MPa O_2 , 60 °C, 6 h, molar ratio of Au/ HMF = 1:110; [b] The HY support was poisoned by pyridine. [c] The HY support was poisoned by 2, 6-di-*tert*-butylpyridine (DTBPy).

The TEM images (Figure 1 c) revealed that Au NPs with a large size around 10 nm exist on the external surface of NaY. These results suggest that the supercage is not the only factor, which is responsible for the formation of the gold nanoclusters.

The difference between HY and NaY lies in the different amount of -OH groups in the structure of the Y-type zeolite, which can be characterized by in situ FTIR spectroscopy. In situ FTIR spectroscopy also conforms this. The in situ FTIR spectra in the $\tilde{v} = 3900-$ 3400 cm⁻¹ region are presented in Figure 4a for HY, Au/HY, and NaY. A strong peak at $\tilde{\nu} =$ 3630 cm^{-1} and a weak broad peak around $\tilde{\nu} = 3550 \text{ cm}^{-1}$ are observed; they are assigned to high-frequency (HF) acidic -OH groups located in the supercage and acidic -OH groups in the sodalite cage respectively.^[42–45] It is obvious that the peak at $\tilde{v} = 3630 \text{ cm}^{-1}$ is strong for the HY sample but weak for NaY, indicating that the –OH groups inside the supercage are abundant in HY but are nearly zero in NaY. In the case of Au/HY, the intensity of the band at $\tilde{v} = 3630 \text{ cm}^{-1}$ decreased, suggesting that the –OH groups are consumed when Au clusters were introduced into the supercage.

Taking the above results together, the -H groups within the supercage may play a crucial role in forming gold nanoclusters. It has been evidenced that pyridine can easily penetrate through the aperture of the supercage and completely poison the -OH groups of the supercage, whereas 2, 6-ditert-butylpyridne can only block the external surface -OH groups because it is too large to penetrate through the micropore of Y zeolite.^[46-54] Poisoning experiments with pyridine and DTBPy were carried out to further confirm the influence of the -OH groups of the supercage. By this method, the location of effective -OH groups can be distinguished. Before the preparation of the catalysts fresh HY was treated with pyridine and DTBPy, respectively. The amount of poison reagents (pyridine or DTBPy) used here is two times to that of the hydroxyl groups. The poisoned HY-pyridine and HY-DTBPy were subsequently used to synthesize Au/HY-pyridine and Au/HY-DTBPy catalysts. When HMF was oxidized over Au/HY-pyridine (Table 2), the yield of FDCA only reached 14%. Whereas over Au/ HY-DTBPy, the FDCA yield achieved 54%,^[55] which is nearly three times to that of Au/HY-pyridine. In the case of Au/HY-pyridine, due to the deficiency of -OH groups, we



Figure 4. a) FTIR spectra of HY, Au/HY, and NaY. b) TEM image of Au-pyridine. c) TEM image of Au-DTBPy. (scale bars = 10 nm)

© 2013 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

14218 -

envision that Au^0 cannot chemically anchor with acid -OH groups of the supercage and thus form large Au particles, resulting in a low FDCA yield. In contrast, the hydroxyl groups inside the supercage of Au/HY-DTBPy are mostly kept and can be used to stabilize Au nanoclusters, which is responsible for the high FDCA yield. These results are consistent with the TEM images (Figure 4b, obvious aggregation on the external surface for the Au/HY-pyridine). All these results further confirm that the -OH groups in the supercage indeed influence the gold size and distribution, thus generate an improvement in the catalytic activity compared to other oxides or zeolites.

Next, we prepared a series of HY supports containing different OH amounts to provide direct insight into the mutual interactions among the -OH groups and the Au clusters. For HY zeolites, control of the amount of -OH groups can be realized by changing the treatment temperature for the zeolite; thus, the effect of the amount of -OH groups on the gold size can be studied. HY supports were pretreated at 200 and 400 °C for 3 h prior to catalyst synthesis. The obtained catalysts were denoted as Au/HY-200 and Au/HY-400, respectively. The XRD patterns and ²⁹Si NMR spectra show that the zeolite framework structures are well maintained. No characteristic XRD peak belongs to Au due to its tiny size (see the Supporting Information, Figures S10 and S11). XPS reveals that the Au clusters exist in zero valences and that the Au particles in Au/HY have the best dispersion compared to the other two catalysts (see the Supporting Information, Part 13).

We employed in situ FTIR spectroscopy to study the acidic –OH groups in HY, HY-200, and HY-400 (Figure 5 a).

ΗY

3630

It was observed that elevating the calcination temperature (200 and 400°C) results in decreasing intensity of the peak at $\tilde{\nu} = 3630 \text{ cm}^{-1}$, suggesting a decreasing amount of -OHgroups in the supercage. Because the internal hydroxyl groups within the supercage are Brønsted acids, the concentration of acidic -OH groups inside the supercage can be measured by pyridine. Figure 5b shows the FTIR spectra after pyridine adsorption and subsequent evacuation. In all the Au/HY-n samples, pyridine interacts with the acidic OH groups inside the supercage and forms pyridine ions (PyH⁺), showing an intensely characteristic band at $\tilde{\nu} = 1545 \text{ cm}^{-1}$ (see Figure 5b).^[44] It can clearly be seen that this band decreases with an increase of the HY pre-treatment temperature, indicating that the amount of -OH groups in the supercage decreased after heat treatment. For more precise comparison, the -OH group amount is calculated based on the PyH⁺ peak by using Equation (1):

C(pyridine on Brønsted acidic sites $) = 1.88IA(B)R^2W^{-1}$ (1)

where *C* represents the PyH⁺ concentration in $[mmol g^{-1}]$, *IA*(*B*) is the peak area of the Brønsted acidic site band in $[cm^{-1}]$, *R* is the radius of the catalyst disk (0.65 cm), and *W* is the weight of the disk (18 mg).

The amount of -OH group calculated by PyH⁺ in Au/ HY, Au/HY-200, and Au/HY-400 was 0.27, 0.23, and 0.19 mmol g⁻¹, respectively, decreasing with the elevated calcinations temperature. This result indicates that the -OH amount in the supercage decreased after heat treatment,

which is consistent with the trend of the peak at $\tilde{v} = 3630 \text{ cm}^{-1}$.

The TEM image (Figure 1d) for Au/HY-200 shows that the smaller Au clusters around 1 nm exist in the supercage and the larger ones arranged in 3-5 nm are located on the external surface. However, no Au nanoclusters can be observed on Au/HY-400 (Figure 1e), only larger Au NPs ($\approx 5 \text{ nm}$) are present on the external surface. The gold size becomes larger in the order of Au/HY, Au/HY-200, and Au/HY-400, as observed by TEM. This finding is also confirmed by H2-TPR experiments (Figure 3). As mentioned above, H2-TPR can be used to determine the Au location by measuring its reduction temperature. As shown in Figure 3, the TPR profile of Au/HY displays a reduction



Figure 5. a) FTIR spectra of HY, HY-200, and HY-400. b) FTIR spectra of Au/HY, Au/HY-200, and Au/HY-400 after pyridine adsorption and subsequent evacuation, all the samples were treated in vacuum to remove adsorbed water.

Chem. Eur. J. 2013, 19, 14215-14223

а

© 2013 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

1545

www.chemeurj.org

CHEMISTRY

peak at 106 °C, corresponding to the reduction of Au species inside the supercage to Au^{0.[40,41]} Au/HY-200 displays a reduction peak around 120 °C, which may be a combination of the peaks at 106 and 150 °C. Those peaks can be ascribed to the reduction of gold ions located in the supercages and on the exterior surface of HY zeolite, respectively. For the Au/ HY-400 catalyst, there is only one reduction peak at 150 °C observed, which is attributed to the reduction of Au³⁺ species to Au⁰ on the external surface of the catalyst.

The relationship between PyH^+ and the Au particle size is presented in Figure 6. The concentration of PyH^+ represents the total amount of acidic –OH groups in the supercage. It is clearly shown that the decrease of the acidic –OH groups inside the supercage leads to an increase of the Au



Figure 6. Comparison of the catalytic performance (bars) and the PyH⁺ concentration (\bullet) for Au/HY, Au/HY-200, and Au/HY-400. Reaction conditions: catalyst (0.30 g, Au 1.5 wt%), HMF (0.317 g), H₂O (4.6 g), NaOH (0.4 g), 0.3 MPa O₂, 60 °C, 6 h, molar ratio of Au/HMF=1:110. Yield of HMFCA=dark gray bars, yield of FDCA=black bars.

particle size. Meanwhile, these gradually particles transfer from the supercage to the external surface of the Y zeolite. The above results strongly suggest that the -OH groups can interact with and stabilize Au, thus confining the Au nanoclusters in the supercage (Scheme 1 A). Similar interactions also have been observed. For example, hydroxyl groups on MgO(001) or on TiO_2 surfaces favor formation of small and stable Au particles by chemical interaction between Au and -OH groups.^[56-58] In our case, we believe that a similar interaction indeed exists.



To further elucidate this interaction, we performed X-ray

14220

Scheme 1. A) A schematic representation of Au nanoclusters synthesized in the supercages of HY zeolite induced by –OH groups. B) Catalytic oxidation process.



Figure 7. XPS spectrum of the $Au4f_{7/2}$ electron region of Au/HY, Au/HY-200, and Au/HY-400 samples.

photoelectron spectroscopy measurements. Figure 7 shows the XPS spectra of Au/HY, Au/HY-200, and Au/HY-400. The Au4f_{7/2} apparent binding energies of these samples are 83.8, 83.9, and 84.2 eV, respectively. For the Au/HY-400 sample without available -OH groups in the supercage, the Au4 $f_{7/2}$ binding energy is slightly higher than the value of the bulk (84.0 eV) by 0.2 eV, which is consistent with the fact that the SiO₂ surfaces shift the Au peaks by 0.2 eV to higher energy.^[59] Such shift of binding energy is common for very small metal particles (including Au) on various materials. Numerous studies have found that the binding energy of metal clusters decreases with an increase of the cluster size, and it finally converges to the bulk value at large particle sizes.^[60-63] For example, gold clusters with a particle size of approximately 0.6 nm show a binding energy that is +0.8 eVhigher than the one of bulk gold,^[61] whereas clusters greater than 10 nm exhibit a binding energy that is < 0.1 eV compared to bulk gold. Following this trend, the binding energy

www.chemeurj.org © 2013 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

of Au nanoclusters in Au/HY and Au/HY-200 should present at the position larger than 84.2 eV. However, they exhibit negative shifts (-0.6 and -0.4 eV, respectively) compared to Au/HY-400, and also negative compared to bulk Au. This results clearly show that negative charges are deposited on Au, which is ascribed to the closely interaction between Au and the hydroxyl groups of the supercage.

The catalytic performances of Au/HY, Au/HY-200, Au/ HY-400, and Au/NaY were carried out in the oxidation of HMF (Table 2). As expected, the catalytic efficiency changed remarkably, and the FDCA yields reduced from 99 to 81, 37, and 15%, respectively. This trend is consistent with the order of the Au particle size in these catalysts (Figure 6). Further studies on the relationship of the PyH⁺ concentration, the Au size, and the reaction yield demonstrated that the improvement of the catalytic activity is related to an increase of the amount of acidic -OH groups inside the supercage (Figure 6). As XPS revealed, the -OH groups of the supercage strongly interact with gold by closely contact, leading to the occurrence of charge transfer between them. This charge transfer makes the gold cluster more electronegative, which facilitate the HMF oxidation. It is reported that the presence of negative charge on the Au core would enhance the catalytic activity of Au for aerobic oxidations.^[64-66] Recent theoretical calculations also confirm that this interaction can increase the reaction activity.^[67] Therefore, we conclude that these strong interactions transfer the charge to the Au cluster and lead to the high performance of the reaction (Scheme 1B), besides protecting the gold nanoclusters against sintering.

HMF oxidation to FDCA: The catalytic oxidation of HMF was carried out over the Au/HY catalyst in water with addition of NaOH at 60 °C under 0.3 MPa oxygen pressure. In order to gain information of the reaction course, we detected the products variation with the reaction time. Figure 8 shows the formation of products as a function of the reaction time. HMF is nearly quantitative converted into HMFCA with a conversion higher than 90% in less than



Figure 8. Time course of the oxidative conversion of HMF. Reaction conditions: catalyst (0.30 g, Au 1.5 wt%), HMF (0.317 g), H_2O (4.6 g), NaOH (0.4 g), 0.3 MPa O₂, 60 °C, 6 h, molar ratio of Au/HMF=1:110 (\bullet =yield of FDCA, \bullet =yield of HMFCA, \blacktriangle =conversion).

one hour, indicating that HMF is firstly transformed into HMFCA at the beginning of the reaction. After that, FDCA gradually generates in the next 5 h, whereas the amount of HMFCA gradually decreased accordingly. The total yield to HMFCA and FDCA is 95%, it is nearly constant during this course. This suggests that the FDCA is transferred from further oxidation of HMFCA, which consists with the fact that the activation of HMFCA is the rate-determining step for the production of FDCA. After 6 h of reaction, the yield of FDCA achieved 98%, and decreased when the reaction time was prolonged to 9 h. The decrease of the yield of FDCA may be caused by the over oxidation or coke formation of FDCA under such oxidative conditions.

The stability of the Au/HY catalyst was tested by evaluating the catalytic activity during the recycling runs on the oxidation reaction of HMF at 60 °C under 0.3 MPa O_2 pressure. After each reaction, the catalyst was washed with distilled water and then dried in air at 60 °C for the next catalytic run. The results show (see Figure 9) that the yield of FDCA of the second, third, and fourth cycle reached 92, 89, and



Figure 9. Stability tests for the Au/HY catalyst. Reaction conditions: catalyst (0.30 g, Au 1.5 wt%), HMF (0.317 g), H_2O (12.0 g), NaOH (0.4 g), 0.3 MPa O_2 , 60 °C, 6 h, molar ratio of Au/HMF = 1:110.

88%, respectively, which suggested that the Au/HY catalyst can be re-used at least four cycles without obvious activity loss. After that the re-used Au/HY catalyst was characterized by XRD (see the Supporting Information, Figure S13) and TEM (see the Supporting Information, Figure S15). The mean diameter of the Au nanoclusters was essentially unaltered after the re-used test and the amount of acidic –OH groups in the supercage of the re-used Au/HY catalyst is lower than that of the fresh Au/HY catalyst (see the Supporting Information, Figure S14). Because the Au/HY catalyst still performed high activity in the recycling test, this means that the –OH group has no impact on the reaction process, whereas is plays an important role in stabilizing the Au nanoclusters during the catalyst preparation.

Chem. Eur. J. 2013, 19, 14215-14223

www.chemeurj.org

Conclusion

In summary, gold nanoclusters of 1 nm in average are encapsulated within the HY zeolite supercage. These confined Au nanoclusters show remarkably high efficiency for the oxidation of HMF by molecular oxygen under mild conditions, achieving >99% conversion and >99% yield of FDCA. The HY supercage plays an important role in restricting the gold nanoclusters to grow in physical dimensions and thus retain them in uniform and small size. Moreover, the acidic -OH groups inside the supercage can stabilize the Au nanoclusters and promote the reaction activity by strong interaction between gold and the hydroxyl groups. This study opens new opportunities in the development of high-performance heterogeneous catalysts by using cage-typed zeolite as hosts for metal nanoclusters, thereby providing an efficient catalyst for the oxidation of various biomass-derived hydroxyl compounds.

Experimental Section

Material: All reagents and chemicals were analytical reagents, obtained from commercial sources, and used as received unless otherwise stated. Tetrachloroauric acid tetrahydrate (HAuCl₄·4H₂O) was purchased from Shenyang Research Institute of Nonferrous Metals, China. Zeolite HY (Si/A1=4) and NaY (Si/A1=4) were purchased from Nankai University Catalyst Co., Ltd., China. Pyridine was purchased from Tianjin Kemiou Chemical Reagent Co., Ltd. Malonic acid (>99%) and 2,6-di-*tert*-butyl-pyridine (>96%) were obtained from Sigma–Aldrich. 5-Hydroxymethyl-furfural (98%), 5-hydroxymethyl-2-furancarboxylic acid (98%), and 2,5-furandicarboxylic acid (98%) were purchased from a local manufactory and further purified before use. The purified water was obtained by passing commercial deionized water through a Millipore water purification system.

Characterization: X-ray diffraction (XRD) patterns of the Au-based catalysts were collected by using a D-2500 power diffractometer equipped with a Cu_{Ka} radiation source ($\lambda = 0.15418$ nm) operating at 45 mA and 40 kV. Surface areas and the micropore-size distribution of the catalysts were determined by nitrogen adsorption and desorption measurements at liquid nitrogen temperature (-196°C) on Autosorb-1 (Quantachrome). All Au catalyst samples were out-gassed in vacuum at 150°C for 6-8 h prior to measurement. The total surface areas were calculated according to the HK method. X-ray photoelectron spectroscopy (XPS) was conducted on a VG ESCALAB MkII Spectrometer by using $Al_{K\alpha}$ radiation. The binding energies were calibrated with the C 1s level (284.6 eV) as the internal standard reference. High-resolution TEM studies were performed in a FEI Tecnai G2 F30 S-Twin electron microscope. Samples were ultrasonically dispersed in alcohol before deposition on carboncoated copper grids. Particle size distributions were taken from a count of 200 particles. The FTIR spectra for pyridine adsorption of the catalysts were conducted on a Bruker Tensor27 FTIR spectrometer in the absorbance mode with a resolution of 2 cm⁻¹. Prior to pyridine adsorption, all catalyst samples (18 mg) were evacuated at 150 °C for 1 h, then the samples were cooled down to room temperature. After that, an IR spectrum of the sample was collected and used as background reference. Subsequently, pulses of pyridine were introduced in an in situ cell for 3 min for adsorption. Then the catalysts were heated to 200 °C and evacuated for 30 min. After the reaction cell was cooled to room temperature, the spectra of the catalysts were collected and subtracted with the background reference. H2-TPR was performed in an AutoChem II 2920 (Micromeritics), and a sample of 50 mg was used in each measurement. The samples were first pretreated under an Ar flow at 150°C for 1 h, followed by cooling down to room temperature. The flow of 10 vol % H2-Ar mixture gas

 (30 mLmin^{-1}) was then switched into the system, and the sample was heated to 700 °C from room temperature at a rate of 10 °Cmin⁻¹. The amount of H₂ consumption during the reduction was measured by a thermal conductivity detector, which was calibrated by the quantitative reduction of AgO to metallic Ag.

Catalyst preparation: HY or NaY zeolite support was added into an aqueous solution of HAuCl₄ (50 mL, 0.1 mM). After stirring at 60 °C for 2 h, an aqueous solution of sodium citrate (2 mL) was added to this solution. The obtained mixture was stirred at 60 °C for another 2 h. Then the as-prepared samples were centrifuged and washed with distilled water for seven times until the supernatant was neutral. The catalyst was treated at 100 °C under an H₂ atmosphere (1 atm) for 6 h. The Au loading for these catalysts was 1.5 wt %. Other materials-supported catalysts were synthesized following the same procedure.

Typical experiments for the aerobic oxidation of HMF: All oxidation reactions were carried out in a 20 mL stainless steel autoclaves equipped with an internal thermocontrollor (Teflon beaker insert). A typical reaction procedure was as follows: the autoclave was charged with HMF (2.5 mmol), water (3.0 g), and aqueous NaOH solution (20 vt%, 2.0 g). The initial HMF concentration (0.48 mol g⁻¹) was chosen based on experimental data of FDCA solubility in water and extrapolation of this data to 60 °C. Subsequently, the supported gold catalyst (0.3 g, 0.023 mmol Au) was added into the solution. The autoclave was charged with dioxygen (0.3 MPa), and the pressure was kept constant throughout the reaction. The reaction was finished, the autoclave was rapidly cooled down to room temperature with water.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (20803074, 21233008, and 21203180) and the Main Direction Program of Knowledge Innovation of Chinese Academy of Science, Grant. No. KSCX2-EW-G-5. We also thank Dr. J. D.. Huang for his help with the theoretical studies.

- [1] A. J. Ragauskas, C. K. Williams, B. H. Davison, G. Britovsek, J. Cairney, C. A. Eckert, W. J. Frederick, J. P. Hallett, D. J. Leak, C. L. Liotta, J. R. Mielenz, R. Murphy, R. Templer, T. Tschaplinski, *Science* 2006, *311*, 484–489.
- [2] J. J. Bozell, Clean Soil Air Water 2008, 36, 633–633.
- [3] J. J. Bozell, G. R. Petersen, Green Chem. 2010, 12, 539-554.
- [4] D. L. An, A. H. Ye, W. P. Deng, Q. H. Zhang, Y. Wang, *Chem. Eur. J.* 2012, 18, 2938–2947.
- [5] A. Corma, S. Iborra, A. Velty, Chem. Rev. 2007, 107, 2411-2502.
- [6] J. N. Chheda, G. W. Huber, J. A. Dumesic, Angew. Chem. 2007, 119, 7298–7318; Angew. Chem. Int. Ed. 2007, 46, 7164–7183.
- [7] T. Werpy, G. Petersen, Top Value-Added Chemicals from Biomass, Volume I: Results of Screening for Potential Candidates from Sugars and Synthesis Gas, PNNL-14808, Pacific Northwest National Laboratory, Richland, 2004.
- [8] A. Gandini, A. J. D. Silvestre, C. P. Neto, A. F. Sousa, M. Gomes, J. Polym. Sci. Pol. Chem. 2009, 47, 295–298.
- [9] C. Carlini, P. Patrono, A. M. R. Galletti, G. Sbrana, V. Zima, *Appl. Catal. A* 2005, 289, 197–204.
- [10] S. Dutta, S. De, B. Saha, ChemPlusChem 2012, 77, 259-272.
- [11] S. E. Davis, B. N. Zope, R. J. Davis, Green Chem. 2012, 14, 143-147.
- [12] S. E. Davis, L. R. Houk, E. C. Tamargo, A. K. Datye, R. J. Davis, *Catal. Today* **2011**, *160*, 55–60.
- [13] B. Saha, S. Dutta, M. M. Abu-Omar, Catal. Sci. Technol. 2012, 2, 79-81.
- [14] O. Casanova, S. Iborra, A. Corma, ChemSusChem 2009, 2, 1138– 1144.
- [15] Y. Y. Gorbanev, S. K. Klitgaard, J. M. Woodley, C. H. Christensen, A. Riisager, *ChemSusChem* 2009, 2, 672–675.

14222 -

© 2013 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Chem. Eur. J. 2013, 19, 14215-14223

- [16] N. K. Gupta, S. Nishimura, A. Takagaki, K. Ebitani, Green Chem. 2011, 13, 824–827.
- [17] M. Kröger, U. Prüe, K. D. Vorlop, Top. Catal. 2000, 13, 237-242.
- [18] M. Lilga, R. Hallen, M. Gray, Top. Catal. 2010, 53, 1264–1269.
- [19] W. Partenheimer, V. V. Grushin, Adv. Synth. Catal. 2001, 343, 102– 111.
- [20] E. Taarning, I. S. Nielsen, K. Egeblad, R. Madsen, C. H. Christensen, *ChemSusChem* 2008, 1, 75–78.
- [21] P. Verdeguer, N. Merat, A. Gaset, J. Mol. Catal. 1993, 85, 327-344.
- [22] P. Vinke, H. E. van Dam, H. van Bekkum, Stud. Surf. Sci. Catal. 1990, 55, 147–158.
- [23] H. Ma, X. Nie, J. Y. Cai, C. Chen, J. Gao, H. Miao, J. Xu, Sci. China Chem. 2010, 53, 1497–1501.
- [24] B. N. Zope, S. E. Davis, R. J. Davis, Top. Catal. 2012, 55, 24-32.
- [25] Y. Z. Lu, W. Chen, Chem. Soc. Rev. 2012, 41, 3594-3623.
- [26] R. Jin, Nanoscale 2010, 2, 343-362.
- [27] S. I. Tanaka, J. Miyazaki, D. K. Tiwari, T. Jin, Y. Inouye, Angew. Chem. 2011, 123, 451–455; Angew. Chem. Int. Ed. 2011, 50, 431– 435.
- [28] K. Yamamoto, T. Imaoka, W. J. Chun, O. Enoki, H. Katoh, M. Takenaga, A. Sonoi, *Nat. Chem.* 2009, 1, 397–402.
- [29] L. Shang, S. J. Dong, Chem. Commun. 2008, 1088–1090.
- [30] C. I. Richards, S. Choi, J. C. Hsiang, Y. Antoku, T. Vosch, A. Bongiorno, Y. L. Tzeng, R. M. Dickson, J. Am. Chem. Soc. 2008, 130, 5038–5039.
- [31] Y. Shichibu, Y. Negishi, T. Tsukuda, T. Teranishi, J. Am. Chem. Soc. 2005, 127, 13464–13465.
- [32] Z. K. Wu, E. Lanni, W. Q. Chen, M. E. Bier, D. Ly, R. C. Jin, J. Am. Chem. Soc. 2009, 131, 16672–16674.
- [33] P. D. Jadzinsky, G. Calero, C. J. Ackerson, D. A. Bushnell, R. D. Kornberg, *Science* 2007, 318, 430–433.
- [34] Z. T. Du, J. P. Ma, F. Wang, J. X. Liu, J. Xu, Green Chem. 2011, 13, 554–557.
- [35] J. P. Ma, Z. T. Du, J. Xu, Q. H. Chu, Y. Pang, ChemSusChem 2011, 4, 51–54.
- [36] Theoretical calculations demonstrated that the molecular sizes of HMF, FDCA, and disodium furane dicarboxylate are small enough to penetrate in or out of HY (see the Supporting Information, Figures S1, S2 a, and S2 b), thus the pore of HY does not retard the HMF oxidation.
- [37] H. Tsunoyama, H. Sakurai, Y. Negishi, T. Tsukuda, J. Am. Chem. Soc. 2005, 127, 9374–9375.
- [38] M. Haruta, M. Daté, Appl. Catal. A 2001, 222, 427-437.
- [39] M. Haruta, Catal. Today 1997, 36, 153-166.
- [40] Y. M. Kang, B. Z. Wan, Appl. Catal. A 1995, 128, 53-60.
- [41] J. N. Lin, B. Z. Wan, Appl. Catal. B 2003, 41, 83-95.
- [42] R. M. West, M. S. Holm, S. Saravanamurugan, J. Xiong, Z. Beversdorf, E. Taarning, C. H. Christensen, J. Catal. 2010, 269, 122–130.
- [43] U. Navarro, C. A. Trujillo, A. Oviedo, R. Lobo, J. Catal. 2002, 211, 64–74.
- [44] J. N. Kondo, R. Nishitani, E. Yoda, T. Yokoi, T. Tatsumi, K. Domen, *Phys. Chem. Chem. Phys.* **2010**, *12*, 11576–11586.
- [45] M. A. Makarova, A. E. Wilson, B. J. van Liemt, C. de Winter, A. W. Mesters, C. Williams, J. Catal. 1997, 172, 170–177.

- [46] A. Corma, V. Fornes, L. Forni, F. Marquez, J. Martinez-Triguero, D. Moscotti, J. Catal. 1998, 179, 451–458.
- [47] K. F. Liu, S. J. Xie, S. L. Liu, G. L. Xu, N. N. Gao, L. Y. Xu, J. Catal. 2011, 283, 68–74.
- [48] S. C. L. Dias, J. L. de Macedo, J. A. Dias, Phys. Chem. Chem. Phys. 2003, 5, 5574–5579.
- [49] T. M. Davis, C. Y. Chen, N. Žilková, D. Vitvarová-Procházková, J. Čejka, S. I. Zones, J. Catal. 2013, 298, 84–93.
- [50] A. Ungureanu, T. V. Hoang, D. T. On, E. Dumitriu, S. Kaliaguine, *Appl. Catal. A* 2005, 294, 92–105.
- [51] G. Busca, Chem. Rev. 2007, 107, 5366-5410.
- [52] S. R. Zheng, H. R. Heydenrych, A. Jentys, J. A. Lercher, J. Phys. Chem. B 2002, 106, 9552–9558.
- [53] D. P. Serrano, R. A. Garcia, G. Vicente, M. Linares, D. Prochazkova, J. Cejka, *J. Catal.* **2011**, 279, 366–380.
- [54] S. H. Park, H. K. Rhee, Appl. Catal. A 2001, 219, 99-105.
- [55] We investigated the effect of pyridine on the performance of Au/ HY. When pyridine was added to the reaction mixture containing HMF and Au/HY, the catalyst achieved 61% yield of FDCA at 60°C under 0.3 MPa O_2 for 6 h, whereas over Au/HY-pyridine, the yield of FDCA was only 14%. Although pyridine has a negative effect on the performance of Au, these two results clearly show that the hydroxyl groups inside the supercage were responsible for an increase of FDCA production.
- [56] M. A. Brown, Y. Fujimori, F. Ringleb, X. Shao, F. Stavale, N. Nilius, M. Sterrer, H. J. Freund, J. Am. Chem. Soc. 2011, 133, 10668–10676.
- [57] G. M. Veith, A. R. Lupini, N. J. Dudney, J. Phys. Chem. C 2009, 113, 269–280.
- [58] D. E. Jiang, S. H. Overbury, S. Dai, J. Phys. Chem. Lett. 2011, 2, 1211-1215.
- [59] D. P. Anderson, J. F. Alvino, A. Gentleman, H. A. Qahtani, L. Thomsen, M. I. J. Polson, G. F. Metha, V. B. Golovko, G. G. Andersson, *Phys. Chem. Chem. Phys.* **2013**, *15*, 3917–3929.
- [60] Y. Kitsudo, A. Iwamoto, H. Matsumoto, K. Mitsuhara, T. Nishimura, M. Takizawa, T. Akita, Y. Maeda, Y. Kido, *Surf. Sci.* 2009, 603, 2108–2114.
- [61] C. N. R. Rao, V. Vijayakrishnan, H. N. Aiyer, G. U. Kulkarni, G. N. Subbanna, J. Phys. Chem. 1993, 97, 11157–11160.
- [62] H. G. Boyen, A. Ethirajan, G. Kästle, F. Weigl, P. Ziemann, G. Schmid, M. G. Garnier, M. Büttner, P. Oelhafen, *Phys. Rev. Lett.* 2005, 94, 016804–016807.
- [63] A. K. Santra, D. W. Goodman, J. Phys. Condens. Matter 2003, 15, R31-R62.
- [64] F. Wang, W. Ueda, J. Xu, Angew. Chem. 2012, 124, 3949–3953; Angew. Chem. Int. Ed. 2012, 51, 3883–3887.
- [65] Y. Zhu, H. F. Qian, B. A. Drake, R. C. Jin, Angew. Chem. 2010, 122, 1317–1320; Angew. Chem. Int. Ed. 2010, 49, 1295–1298.
- [66] S. Nishimura, Y. Yakita, M. Katayama, K. Higashimine, K. Ebitani, *Catal. Sci. Technol.* 2013, 3, 351–359.
- [67] P. Ganesh, P. R. C. Kent, G. M. Veith, J. Phys. Chem. Lett. 2011, 2, 2918–2924.

Received: May 5, 2013 Published online: September 2, 2013