available at www.sciencedirect.com

journal homepage: www.elsevier.com/locate/chnjc

Article (Special Issue on the 2nd International Congress on Catalysis for Biorefineries (CatBior 2013))

Highly selective formation of imines catalyzed by silver nanoparticles supported on alumina

Jerrick Mielby, Raju Poreddy, Christian Engelbrekt, Søren Kegnæs *

DTU Chemistry, Technical University of Denmark, 2800 Kgs. Lyngby, Denmark

ARTICLE INFO

Article history:

Received 2 January 2014

Accepted 9 January 2014

Published 20 May 2014

Keywords:

Heterogeneous catalysis

Silver nanoparticle

Oxidative dehydrogenation

Alcohol

Aldehyde

Imine

ABSTRACT

The oxidative dehydrogenation of alcohols to aldehydes catalyzed by Ag nanoparticles supported on Al_2O_3 was studied. The catalyst promoted the direct formation of imines by tandem oxidative dehydrogenation and condensation of alcohols and amines. The reactions were performed under mild conditions and afforded the imines in high yield (up to 99%) without any byproducts other than H_2O . The highest activity was obtained over 5 wt% $\text{Ag}/\text{Al}_2\text{O}_3$ in toluene with air as oxidant. The reactions were also performed under oxidant-free conditions where the reaction was driven to the product side by the production of H_2 in the gas phase. The use of an efficient and selective Ag catalyst for the oxidative dehydrogenation of alcohol in the presence of amines gives a new green reaction protocol for imine synthesis.

© 2014, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

1. Introduction

In recent years there has been rising demand for efficient solid catalyzed processes for the oxidation of alcohols for the production of fine and bulk chemicals [1]. Much effort has been devoted to the development of aerobic oxidation methods using molecular oxygen or air as the oxidant. Compared to the use of high valence inorganic metal oxides, such as chromate or permanganate, these methods are very attractive because oxygen is a cheap and abundant oxidant that produces water as the only byproduct [2].

Another attractive alternative is the oxidant-free dehydrogenation of alcohols to carbonyl compounds and molecular hydrogen [3]. Although tremendous advances have been achieved in the dehydrogenation of alcohols with homogeneous platinum-group metals [4–7], only a limited number of similar solid catalysts that are effective under mild reaction

conditions, have appeared to date. Recently, Kaneda et al. [8] used Ag supported on hydrotalcite (Ag/HT) for the dehydrogenation of alcohols under oxidant-free conditions. The reaction afforded high yields of the corresponding carbonyl compounds at 130 °C with the co-production of H_2 . Shimizu et al. [9] reported that $\text{Ag}/\text{Al}_2\text{O}_3$ showed higher catalytic activity than the conventional catalysts based on platinum group metals (such as $\text{Rh}/\text{Al}_2\text{O}_3$ and $\text{Pd}/\text{Al}_2\text{O}_3$), and suggested that the high activity was due to the presence of sub-nanometer sized Ag particles and the acidic and basic surface sites on $\gamma\text{-Al}_2\text{O}_3$. Furthermore, Shimizu et al. [10,11] showed that $\text{Ag}/\text{Al}_2\text{O}_3$ could be used for amide synthesis and also for the direct synthesis of secondary amines via intermediate imine formation by the borrowing hydrogen mechanism when it is used together with a strong Lewis acid co-catalyst. Liu et al. [12] showed that with Ag nanoparticles, secondary amines could be formed from alcohols and amines via intermediate imine formation by

* Corresponding author. Tel: +45-45252402; Fax: +45-45883136; E-mail: skk@kemi.dtu.dk

This work was supported by the Danish Council for Independent Research (10-093717, 12-127580).

DOI: 10.1016/S1872-2067(14)60033-4 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 35, No. 5, May 2014

the borrowing hydrogen mechanism. Similar reactions have also been shown possible with metals other than Ag [13,14]. Although reports on Ag catalyzed reactions is increasing, the application of supported Ag catalysts is still limited in liquid phase organic chemistry. Furthermore, the addition of additives such as a base is usually required to give high yields.

In this work, we showed that Ag supported on Al_2O_3 was an active and highly selective catalyst for the formation of aldehydes from alcohols without the use of additives. Furthermore, we showed that $\text{Ag}/\text{Al}_2\text{O}_3$ catalyzed the direct formation of imines by consecutive oxidative dehydrogenation and condensation of alcohols and amines as shown in Scheme 1.

The reactions were performed under mild reaction conditions with a number of different alcohols and amines, which demonstrated that the method was versatile and applicable to a broad range of substrates. Although the highest catalytic activity was obtained with 5 wt% $\text{Ag}/\text{Al}_2\text{O}_3$ in toluene using air as oxidant, the reaction also occurred under oxidant-free conditions where the reaction was driven to the product side by the production of H_2 in the gas phase [9].

2. Experimental

2.1. Catalyst preparation

A series of supported Ag catalysts were prepared by incipient wetness impregnation of the solid supports with an aqueous solution of AgNO_3 to give 1, 5, and 10 wt% Ag on the support. Before each reaction, the impregnated and dried catalysts were reduced with 10% H_2/N_2 in a tube oven for 2 h at 300 °C and a heating ramp of 5 °C/min.

The support materials investigated were various combinations of magnesium and aluminum oxides, including metal oxides (Al_2O_3 and MgAl_2O_4) and layered double hydroxides ($\text{Mg}_6\text{Al}_2(\text{CO}_3)(\text{OH})_{16}$, hydrotalcite, HT). All supports were purchased from commercial sources (Saint-Gobain and Sigma Aldrich) and used without further purification or pretreatment. For comparison, 5 wt% $\text{Au}/\text{Al}_2\text{O}_3$ catalyst was prepared by the standard impregnation procedure. In addition, a HT-like catalyst was prepared by the co-precipitation of AgNO_3 , $\text{Mg}(\text{NO}_3)_2$, and $\text{Al}(\text{NO}_3)_3$ in an aqueous alkaline solution of Na_2CO_3 and NaOH using a modified literature procedure [15]. The amounts of metal nitrates used were calculated to give a final composition of 5 wt% Ag. The metal nitrates were dissolved in water and added dropwise to the alkaline solution under vigorous stirring. After ageing for 24 h, the catalyst was collected by filtration, washed in water, and dried at 90 °C overnight. Finally, the catalyst was reduced using the standard procedure.

2.2. Characterization

N_2 physisorption was performed on a Micromeritics ASAP 2020 surface area and porosimetry analyzer. The samples were outgassed in vacuum at 200 °C prior to measurement. The specific surface area (S_{BET}) was calculated by the BET method. X-ray diffraction (XRD) analysis was carried out on a Huber G670 diffractometer operated in transmission mode with Cu

Scheme 1. Formation of imines by consecutive oxidative dehydrogenation and condensation of alcohols and amines using $\text{Ag}/\text{Al}_2\text{O}_3$ as catalyst.

$K_{\alpha 1}$ irradiation from a focusing quartz monochromator. The sample was fixed on a piece of tape. Transmission electron microscopy (TEM) was performed on a FEI Tecnai T20 G2 microscope operated at 200 kV. All specimens were dispersed in ethanol and left to dry on the TEM grids at room temperature before the analysis. The diameter of the nanoparticles was estimated from the measurements of about 100 particles.

2.3. Standard oxidation procedure

In a typical experiment, alcohol (2.0 mmol), amine (2.0 mmol), anisole (internal standard, 0.2 mmol), and toluene (6.0 ml) was charged into a reaction tube and connected to the reaction station (Radley Carrousel 12 Plus). The reaction station provided stirring, heating and an atmosphere of Ar, O_2 or atmospheric air at ambient pressure. The reaction tube was flushed with gas, heated to the desired temperature and then 100 mg catalyst was added. Unless otherwise noted, the reactions were performed at 100 °C for 24 h.

During the reaction, samples of 0.1 ml were periodically collected, filtered and analyzed by GC-FID and GC-MS using a HP-5 column from Agilent Technologies Inc. The amounts of substrates and products were quantified using anisole as an internal standard. The conversions were calculated from the conversion of alcohol. The reported values were consistent with the corresponding values calculated from the conversion of amine within $\pm 5\%$. The selectivity and yield were determined from the area of the product peak relative to the total area of all product peaks.

3. Results and discussion

3.1. Characterization

Table 1 shows the overview of the prepared catalysts. As expected, S_{BET} of all the catalysts were similar to those of the parent support, that is, the Ag loading only has a relatively small effect on the surface area.

The catalysts were also characterized by XRD. The results were as expected, but the co-precipitated HT-like catalyst displayed poor crystallinity. The diffraction peaks assigned to Ag on both the co-precipitated and impregnated catalysts were distinct. Figures 1–4 show TEM images and the size distribution of the nanoparticles of the 5 wt% Ag catalysts together with the XRD patterns.

The TEM results showed that the nanoparticle size distribution was relatively broad. As expected, the average size of the nanoparticles increased with the Ag loading. In general, the nanoparticles were evenly dispersed over the support and

Table 1
Overview of the catalysts.

Entry	Catalyst	Ag(Au) loading (wt%)	S_{BET} (m^2/g)	Diameter (nm)
1	MgAl_2O_4	—	74	—
2	$\text{Ag}/\text{MgAl}_2\text{O}_4$	5	76	20–70
3	HT	—	135	—
4	Ag/HT	5	142	10–60
5	Ag/HT^*	5	135	10–70
6	Al_2O_3	—	219	—
7	$\text{Ag}/\text{Al}_2\text{O}_3$	1	241	10–30
8	$\text{Ag}/\text{Al}_2\text{O}_3$	5	223	20–50
9	$\text{Ag}/\text{Al}_2\text{O}_3$	10	227	20–70
10	$\text{Au}/\text{Al}_2\text{O}_3$	5	217	10–50

*Prepared by co-precipitation.

were < 30, < 50, and < 70 nm for the 1, 5, and 10 wt% $\text{Ag}/\text{Al}_2\text{O}_3$ catalyst, respectively.

3.2. Catalytic activity

First, the dehydrogenation of benzyl alcohol to benzaldehyde was used as a model reaction to study the effect of the support material and Ag loading. Table 2 shows the conversion, selectivity, and yield from the oxidative dehydrogenation of benzyl alcohol under Ar (i.e. under oxidant-free conditions) at 100 °C for 24 h. Table 2 showed that the pure support materials were inactive for the reaction and that no reaction occurred

without a catalyst (Entry 11). In contrast, the Ag impregnated catalysts afforded benzaldehyde in moderate to good yields. The activity of 5 wt% $\text{Ag}/\text{MgAl}_2\text{O}_4$ and the activity of 5 wt% Ag/HT were similar and they gave 17%–18% conversion with 70%–72% selectivity. However, the 5 wt% $\text{Ag}/\text{Al}_2\text{O}_3$ surprisingly gave 60% conversion and 96% selectivity under the same reaction conditions. The co-precipitated Ag/HT^* catalyst did not give any conversion, while the 5 wt% $\text{Au}/\text{Al}_2\text{O}_3$ only gave 8% yield. The main byproduct was benzyl benzoate.

Entries 7–9 in Table 2 shows the effect of the Ag loading. The conversion increased with the Ag loading up to 5 wt% and then decreased with further loading. Since the same amount of catalyst was used in the reactions the increase in conversion from 1 to 5 wt% was expected. However, when the Ag loading was increased to 10 wt% the conversion and selectivity decreased significantly. This may be explained by the increased size of the nanoparticles. It is noteworthy that both the conversion and the selectivity depended on the Ag loading and the nature of the support material. Recently Shimizu et al. [9] proposed a mechanism where the dehydrogenation of alcohol is favored by the special acid-base sites on Al_2O_3 . In this mechanism, the reaction proceeds in three steps: (1) the reaction of the alcohol on a basic site to give an alkoxide and an adsorbed water molecule, (2) C-H activation of the alkoxide on the Ag nanoparticle to give a silver hydride species and a carbonyl compound, and (3) H_2 desorption from an alumina acid site.

Fig. 1. TEM image (a), size distribution (b), and XRD patterns (c) of the nanoparticles on 5 wt% $\text{Ag}/\text{MgAl}_2\text{O}_4$.

Fig. 2. TEM image (a), size distribution (b), and XRD patterns (c) of the nanoparticles on 5 wt% Ag/HT .

Fig. 3. TEM image (a), size distribution (b), and XRD pattern (c) of the co-precipitated nanoparticles on 5 wt% Ag/HT*.

Fig. 4. TEM image (a), size distribution (b), and XRD patterns (c) of the nanoparticles on 5 wt% Ag/Al₂O₃.

The proposed mechanism may explain the higher activity of Ag on Al₂O₃ with respect to other supports.

Based on the reasoning that the oxidative dehydrogenation is dependent on the abstraction of hydrogen by the Ag atoms and that a fast removal of this hydrogen is important for a high reaction rate, the reactions were also tested using atmospheric air and pure molecular oxygen. Under these reaction conditions, water was formed as the byproduct rather than molecular hydrogen.

Figure 5 show the yield of benzaldehyde as a function of reaction time over 5 wt% Ag/Al₂O₃. While the initial reaction rate

was the same, after 24 h, the reaction performed under air resulted in almost 50% higher yield than that under the inert Ar atmosphere and also higher than that under pure O₂. These result suggested that only a small amount of oxygen was needed to efficiently remove the hydrogen from the Ag atoms to increase the catalytic activity. On the other hand, too high partial pressure of O₂ may decrease the catalytic activity, possibly by the oxidation of the active Ag atoms into inactive Ag₂O [16]. The formation of Ag₂O has been previously studied using a variety of different techniques [16,17].

Table 2

Effect of support material and Ag loading.

Entry	Catalyst	Conversion (%)	Selectivity (%)	Yield (%)
1	MgAl ₂ O ₄	1	30	<1
2	5% Ag/MgAl ₂ O ₄	17	70	12
3	HT	0	0	0
4	5% Ag/HT	18	72	13
5	5% Ag/HT*	0	0	0
6	Al ₂ O ₃	5	20	1
7	1% Ag/Al ₂ O ₃	28	3	1
8	5% Ag/Al ₂ O ₃	60	96	57
9	10% Ag/Al ₂ O ₃	15	60	9
10	5% Au/Al ₂ O ₃	10	82	8
11	—	0	0	0

Reaction conditions: benzyl alcohol 2 mmol, anisole 0.2 mmol, toluene 6 ml, catalyst 100 mg, 24 h, 100 °C, under Ar.

Fig. 5. Yield of benzaldehyde as a function of reaction time using 5 wt% Ag/Al₂O₃ at 100 °C under atmospheric air, O₂, and Ar.

Table 3

Effect of reaction temperature on the oxidation of benzyl alcohol to benzaldehyde.

Entry	Temperature (°C)	Conversion (%)	Selectivity (%)	Yield (%)
1	60	19	75	14
2	80	45	70	32
3	100	95	97	92

Reaction conditions: benzyl alcohol 2 mmol, anisole 0.2 mmol, toluene 6 ml, 5 wt% Ag/Al₂O₃ 100 mg, 24 h, atmospheric air.

In order to investigate the effect of the temperature, the 5 wt% Ag/Al₂O₃ catalyst was tested under atmospheric air for 24 h at different temperatures. As expected, the conversion decreased significantly as the temperature was decreased from 100 to 60 °C (Table 3). Furthermore, the formation of benzylbenzoate was suppressed at higher temperatures, which resulted in 95 % conversion with 97% selectivity at 100 °C.

A number of different alcohols were oxidized under the optimized reaction conditions in order to investigate the range of substrates that can be used (Table 4). All reactions were carried out over 5 wt% Ag/Al₂O₃ for 24 h under atmospheric air at 100 °C. All the alcohols were converted into the corresponding carbonyl compounds. However, while the oxidation of benzyl alcohol reached almost full conversion in 24 h, the aliphatic 1-hexanol only reached 27% conversion (Table 4, Entry 1). This result suggested that the conversion of aliphatic alcohols required longer reaction time or higher temperatures than benzylic alcohols. The secondary alcohol 1-phenylethanol reached full conversion within 24 h and afforded the corresponding ketone acetophenone in 94% yield (Table 4, Entry 3). Entries 4–6 show the effect of different substituents at the *para* position of the benzyl alcohol. The decrease in conversion on going from *p*-OCH₃ to *p*-CH₃ to *p*-Cl suggested a linear free en-

Table 4

Oxidation of different alcohols over 5 wt% Ag/Al₂O₃ under atmospheric air.

Entry	Product	Conversion (%)	Selectivity (%)	Yield (%)
1		27	74	20
2		95	97	92
3		100	99	99
4		100	98	98
5		96	98	94
6		46	97	45
7		100	99	99
8		23	73	17

Reaction conditions: alcohol 2 mmol, anisole 0.2 mmol, toluene 6 ml, 5 wt% Ag/Al₂O₃ 100 mg, 24 h, 100 °C, atmospheric air.

ergy relationship where substrates with electron donating substituents (*p*-OCH₃ and *p*-CH₃) are more reactive than substrates with electron withdrawing substituents (*p*-Cl). These results indicated a positive charge build-up in the benzylic position during the rate determining step, which was in good agreement with the hydride abstraction step proposed by Shimizu et al. [9]. Furthermore, furan-2,5-dicarbaldehyde was obtained in 17% yield from the oxidation of 5-hydroxymethylfurfural (Table 4, Entry 8).

The optimized reaction conditions were used to study the direct formation of imines by the tandem oxidative dehydrogenation and condensation of alcohols and amines. The results of adding one equivalent of aniline to the reaction solution is shown in Table 5. All reactions were performed under the same reaction conditions and no further optimization was attempted for the individual substrates.

The results in Table 5 show that all the substrates reacted to give the corresponding imines with the exception of 1-hexanol and aniline, which did not react. Although the conversion of benzyl alcohol was decreased from 95% to 82% by the addition of amine, the selectivity to the desired product increased as less benzyl benzoate was formed. The formation of benzyl benzoate was due to the condensation of benzyl alcohol with benzoic acid (formed by over-oxidation or aldehyde disproportionation) or by the oxidation of a hemiacetal (formed by the reac-

Table 5

Oxidation of different alcohols in the presence of aniline over 5 wt% Ag/Al₂O₃ under atmospheric air.

Entry	Product	Conversion (%)	Selectivity (%)	Yield (%)
1		0	—	—
2		82	98	81
3		71	95	68
4		95	98	94
5		100	99	99
6		65	98	64
7		100	68	68
8		20	80	16

Reaction conditions: alcohol 2 mmol, aniline 2 mmol, anisole 0.2 mmol, toluene 6 ml, 5 wt% Ag/Al₂O₃ 100 mg, 24 h, 100 °C, atmospheric air.

tion of benzyl alcohol and benzaldehyde). In either case, the amine increased the selectivity by removing the benzaldehyde intermediate in a fast condensation step. For this reason, it is expected that even higher selectivity would be achieved by increasing the ratio of amine to alcohol. As expected, a similar trend in yield was observed for the three *para*-substituted alcohols, which indicated that the oxidation of the alcohol is the rate determining step of the overall reaction. 2-((phenylimino)-methyl)phenol was obtained in 68% yield due to the low selectivity, while the diphenylimine of HMF was obtained in 16% yield due to the low conversion.

The effect of different amines was also studied. Table 6 shows the conversion, selectivity, and yield from the reaction of benzyl alcohol with different amines, including benzyl amine, cyclohexylmethanamine, hexan-1-amine, and pentan-3-amine. All amine substrates reacted with benzyl alcohols to afford the desired products with high selectivity (> 94%). While the reaction with benzyl amine and cyclohexylmethanamine only gave 10% and 17% conversion, respectively, and pentan-3-amine gave 32% conversion. The highest conversion of 82% was obtained with aniline, followed by hexan-1-amine with 66% conversion.

Compared to the previously reported results with Au-catalyzed imine synthesis [18–21], the supported Ag catalysts used here were different in several aspects. First, the Ag catalysts required higher temperatures than the Au catalysts that were active even at room temperature. Furthermore, the Au catalysts were not deactivated by high partial pressures of oxygen. On the other hand, Au catalysts required a strongly alkaline solution. In some systems this would be detrimental as various base-catalyzed side reactions can decrease the selectivity [2]. It is noteworthy that the supported Ag catalysts need no additives or co-catalysts and were even active under oxidant-free conditions with only one equivalent of amine.

4. Conclusions

The Ag nanoparticles supported on Al_2O_3 ($\text{Ag}/\text{Al}_2\text{O}_3$) is an efficient catalyst for the oxidative dehydrogenation of alcohols to aldehydes without any additives. This catalytic system can

Table 6

Oxidation of benzyl alcohol in the presence of different amines over 5 wt% $\text{Ag}/\text{Al}_2\text{O}_3$ under atmospheric air.

Entry	Product	Conversion (%)	Selectivity (%)	Yield (%)
1		82	99	81
2		10	99	10
3		17	94	16
4		66	99	66
5		32	97	31

Reaction conditions: benzyl alcohol 2 mmol, amine 2 mmol, anisole 0.2 mmol, toluene 6 ml, 5 wt% $\text{Ag}/\text{Al}_2\text{O}_3$ 100 mg, 24 h, 100 °C, atmospheric air.

also be used for the oxidative coupling of alcohols and amines to form the corresponding imines. The highest catalytic activity was obtained with 5 wt% $\text{Ag}/\text{Al}_2\text{O}_3$ in toluene using atmospheric air as oxidant. Performing the reaction with pure oxygen resulted in decreased conversion, which suggested that active Ag atoms were oxidized to Ag_2O . The reaction can also be performed under oxidant-free conditions, where the reaction was driven to the product side by the production of H_2 in the gas phase. The reactions were performed at relatively mild conditions (100 °C and atmospheric pressure) without any additives or co-catalysts and afforded the desired imines with high selectivity (up to 99%) from equivalent amounts of alcohols and amines. The reaction was performed with a number of different alcohols and amines to demonstrate the range and versatility of the reaction. The use of an efficient and selective Ag catalyst for the oxidative dehydrogenation of alcohols in the presence of amines is a new green reaction protocol for imine synthesis.

Graphical Abstract

Chin. J. Catal., 2014, 35: 670–676 doi: 10.1016/S1872-2067(14)60033-4

Highly selective formation of imines catalyzed by silver nanoparticles supported on alumina

Jerrik Mielby, Raju Poreddy, Christian Engelbrekt, Søren Kegnaes*
Technical University of Denmark, Denmark

A green method to synthesis imines by aerobic oxidative coupling of amines and alcohols under mild reaction conditions with $\text{Ag}/\text{Al}_2\text{O}_3$ as catalyst was shown.

References

- [1] Franz G, Sheldon R A. 'Oxidation', Ullmann's Encyclopedia of Industrial Chemistry. 6th Ed. Weinheim: Wiley-VCH, 2000
- [2] Mallat T, Baiker A. *Chem Rev*, 2004, 104: 3037
- [3] Friedrich A, Schneider S. *ChemCatChem*, 2009, 1: 72
- [4] Maggi A and Madsen R. *Organometallics*, 2012, 31: 451
- [5] Rigoli J W, Moyer S A, Pearce S D, Schomaker J M. *Org Biomol Chem*, 2012, 10: 1746
- [6] Esteruelas M A, Honczek N, Oliván M, Oñate E, Valencia M. *Organometallics*, 2011, 30: 2468
- [7] Boopathy G, Jing Z, David M. *Angew Chem Int Ed*, 2010, 49: 1468
- [8] Mitsudome T, Mikami Y, Funai H, Mizugaki T, Jitsukawa K, Kaneda K. *Angew Chem Int Ed*, 2008, 47: 138
- [9] Shimizu K-i, Sugino K, Sawabe K, Satsuma A. *Chem Eur J*, 2009, 15: 2341
- [10] Shimizu K-i, Ohshima K, Satsuma A. *Chem Eur J*, 2009, 15: 9977
- [11] Shimizu K-i, Nishimura M, Satsuma A. *ChemCatChem*, 2009, 1: 497
- [12] Liu H H, Chuah G-K, Jaenicke S. *J Catal*, 2012, 292: 130
- [13] Patil R D, Adimurthy S. *Asian J Org Chem*, 2013, 2: 726
- [14] Mielby J, Kegnaes S, Fristrup P. *ChemCatChem*, 2012, 4: 1037
- [15] Kirm I, Medina F, Rodríguez X, Cesteros Y, Salagre P, Sueiras J. *Appl Catal A*, 2004, 272: 175
- [16] Li W X, Stampfl C, Scheffler M. *Phys Rev Lett*, 2003, 90: 256102
- [17] Yamamoto R, Sawayama Y, Shibahara H, Ichihashi Y, Nishiyama S, Tsuruya S. *J Catal*, 2005, 234: 308
- [18] Kegnaes S, Mielby J, Mentzel U V, Christensen C H, Riisager A. *Green Chem*, 2010, 12: 1437
- [19] Soulé J-F, Miyamura H, Kobayshi S. *Chem Commun*, 2013, 49: 355
- [20] Grirrane A, Corma A, Garcia H. *J Catal*, 2009, 264: 138
- [21] Sun H, Su F Z, Ni J, Cao Y, He H Y, Fan K N. *Angew Chem Int Ed*, 2009, 48: 4390