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Synthesis of Palladium Nanoparticles Supported on Mesoporous N-doped Carbon and Their Catalytic Ability for Biofuel Upgrade

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Supporting Information Placeholder

ABSTRACT: We report here a catalyst made of Pd nanoparticles supported on a mesoporous N-doped carbon, Pd@CN_{0.132}, which was shown to be highly active and promoted the biomass refining. Using task-specific ionic liquid (3-methyl-1-butylpyridine dicyanamide) as precursor and silica nanoparticles as hard template, high nitrogen (12 wt%) content, mesoporous carbon material was yielded and this N-doped carbon showed high activity in stabilizing Pd nanoparticles. It is demonstrated that the resulting Pd@CN_{0.132} catalyst shows very high catalytic activity in hydrodeoxygenation of vanillin (a typical model compound of lignin) in low H₂ pressure under mild conditions in aqueous media. Excellent catalytic results (100% conversion of vanillin and 100% selectivity of 2-methoxy-4-methyl phenol) were achieved and no loss of catalytic activity was observed after 6 recycles.

Catalysts are the philosopher's stones of the chemical industry. In principle, one can use solids, small organic molecules, or enzymes as catalysts. However, solid catalysts, for the ease of catalysts separation after reactions, are the preferred options for most processes and dominate the chemical industry. (It is estimated that 80-85% of the processes use solid catalysts).¹ Basically, solid catalyst consists of an active phase (metal or metal oxide) and a high-surface-area porous support on which active phase is finely dispersed.^{2,3} Notably, the catalytic activity of solid catalyst could be significantly enhanced by suitably controlling and selecting the support.^{4,5} Characteristics of the support that have been proposed to play a key role in determining overall reactivity include acid-base properties, redox properties, and the strength of the metal-support interaction.⁴⁻⁶

There are a great number of kinds of materials that are suitable as supports, in which metal oxides such as Al₂O₃,⁷ ZrO₂,⁸ and TiO₂,⁹ zeolites¹⁰ and carbons^{4,5,11,12} including carbon black, activated carbon, carbon nanofibers, and carbon nanotubes are the most frequently used ones. As carbon materials are mainly composed of carbon and even can be made directly out of biomass, they are obviously the most "sustainable" host materials for metal nanoparticles. However, noble metals, like Pt, Pd and Ru deposited on carbons easily leach dur-

ing catalytic process since the interaction between metal nanoparticles and carbon surface is weak, while the chemical or catalytic properties of carbons could not always satisfy the sharply increasing demand of catalysis, so modification of carbons is necessary in most cases.^{5,13} Typically, without defects, the SWNT cannot effectively anchor the Pd nanoparticles.¹⁴ In fact, carbons are generally oxidized by using H₂O₂ or HNO₃ before used as the host materials to introduce more defects and strengthen the interaction between metal nanoparticles and the supports.¹⁵

Nitrogen-containing carbons, as a kind of fascinating materials, have attracted worldwide attention recently.^{16,17} They promise access to a wide range of applications because the incorporation of nitrogen atoms in carbon architecture can enhance chemical, electrical, and functional properties.^{18,19} Among the methods used for preparation of the nitrogen-doping carbon, in situ doping by using nitrogen-containing precursors can realize a homogeneous incorporation of nitrogen into carbons with a controlled chemistry.^{20,21} Typical examples include the employing of task-specific ionic liquids (ILs) as excellent precursors to produce functional N-doped carbons with controlled pore architectures.^{17,22-25} In this work, we synthesized a kind of N-doped mesoporous carbon by using nitrogen-containing ionic liquid as a suitable precursor, and focused on supported Pd nanoparticles as the catalytic agent and considered the use of this mesoporous N-doped carbon (CN_x) as a basic host to construct binary Pd@CN_x heterojunctions for biofuel upgrade.

Ionic liquid with dicyanamide anion (3-methyl-1-butyl pyridine dicyanamide, 3-MBP-dca, Scheme S1) was chosen as precursor, for the cross-linkable anion might form the C-N condensation scheme. N-doped carbon with both narrowly distributed mesoporosity (Figure 1, A) and local N-C-N structural motifs was obtained from precursor mixture of 3-MBP-dca and 12-nm SiO₂ nanoparticles after condensation under 900 °C for 1h (Figure S3) and removal of SiO₂ template. The as made N-doped carbon was then used as support for the loading of Pd nanoparticles (NPs) by ultrasound assistant method.

Elemental analysis indicates the resulting mesoporous N-doped carbon with an atom ratio of N to C 0.132 (Table S2). For simplicity, it is denoted CN_{0.132}. X-ray diffraction mea-

surement (XRD) reveals a graphitic stacking peak at 26.0° , and the more pronounced peak at 43.5° , points to the formation of intralayer condensation for the material (Figure 1, B). The formation of graphitic order was further proved by the Raman spectrum with a G band, at $\sim 1590\text{ cm}^{-1}$, which indicates the in-plane vibration of sp^2 carbon atoms. While the D band, at $\sim 1350\text{ cm}^{-1}$, is defect induced Raman features, represents the non-perfect crystalline structure of the material (Figure 1, C). The D band appears to be stronger than the G band indicating the amorphization of the graphitic network due to much higher nitrogen percentage in the resulting mesoporous carbon. Another evidence of nitrogen doping came from X-ray photoelectron spectroscopy (XPS) measurements. Figure S4 shows two peaks of N1s corresponding to different binding energies, reveals that in this case, nitrogen is embedded into the graphitic structure mainly in two forms. The N1s peaks at 398.8 eV and 401.0 eV are attributed to pyridinic nitrogen and quaternary nitrogen in carbon texture, respectively.

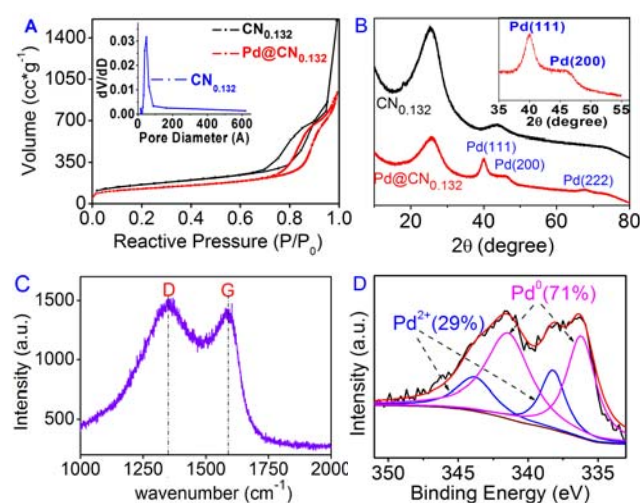


Figure 1. A: The adsorption/desorption isotherms of $\text{CN}_{0.132}$ (Black curve) and $\text{Pd@CN}_{0.132}$ (red curve) and pore size distribution of $\text{CN}_{0.132}$; B: XRD patterns of $\text{CN}_{0.132}$ (black curve) and $\text{Pd@CN}_{0.132}$ (red curve); C: Raman spectrum of $\text{CN}_{0.132}$; D: XPS curve of $\text{Pd@CN}_{0.132}$.

The $\text{CN}_{0.132}$ has a large nitrogen percentage of 12%; nitrogen in carbon texture is suitable for stabilizing highly dispersed Pd NPs and preventing the re-oxidation of Pd^0 . As expected, the $\text{Pd@CN}_{0.132}$ resulted a 71% Pd^0 as revealed by XPS Pd $3d_{5/2}$ peaks at 336.2 eV and 341.4 eV (Figure 1, D). The formation of highly dispersed Pd NPs was proven by XRD (Figure 1, B) and high resolution transmission electron microscopy (HRTEM) (Figure 2). The diffraction peaks of XRD pattern at 40.0° and 46.6° show the characteristic (111) and (200) planes of Pd NPs, respectively. The average size of the crystallites was calculated to be 4.9 nm from the diffraction peak (111) using Scherrer's formula, which is in good agreement with the value predicted by HRTEM (4.1 nm). The HRTEM images revealed well-dispersed Pd NPs on the surface of $\text{CN}_{0.132}$. Figure 2C showed two kinds of crystal planes of Pd and the crystal plane spacing were measured as 0.223 nm and 0.190 nm, corresponding to plane (111) and (200), with a plane angle of 55° .

To illustrate the usefulness of this nano-hybrid catalyst, the activity of $\text{Pd@CN}_{0.132}$ for biofuel upgrade was investi-

gated. In the past decades, interest in the production of fuels or commodity chemicals from renewable biomass instead of fossil resources continues to grow.^{26,27} Compared to cellulose and hemicellulose, lignin, which constitutes about 30 wt% of woody biomass, is challenging to convert, partly because of its highly complex structure, which consists of subunits derived from phenol, p-coumaryl, coniferyl, and sinapyl alcohols connected typically with ether linkages.^{28,29} Accordingly, the deoxygenation of lignin-derived pyrolysis oil is more challenging than cellulose-derived pyrolysis oil.^{12,30-32} Here, we took vanillin (4-hydroxy-3-methoxy benzaldehyde), a common component of pyrolysis oil derived from the lignin fraction, as substrate to explore the principal hydrogenation and deoxygenation routes (Scheme S2).

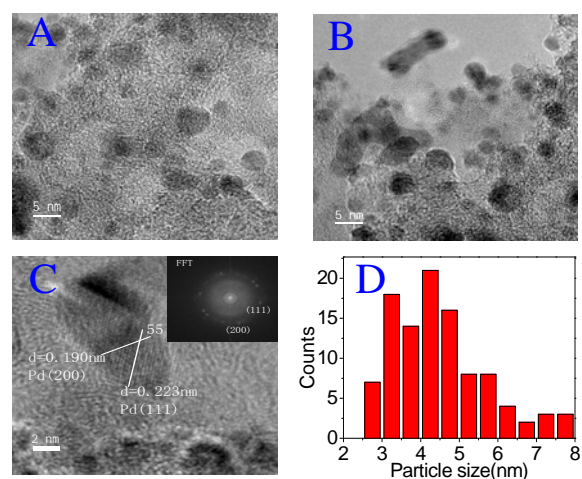


Figure 2. HRTEM images and particle size distribution of $\text{Pd@CN}_{0.132}$.

Transformation of carbonyl group to methyl group theoretically proceeds via three ways: i) hydrogenation-dehydration mechanism, ii) hydrogenation-hydrogenolytic mechanism and iii) direct hydrogenolysis of C=O bond.³³ In our case, there is no hydrogen atom at the adjacent position of hydroxy in vanillin alcohol, meaning the dehydration of vanillin alcohol would not happen, so transformation of vanillin to 2-methoxy-4-methylphenol may undergo via ii) hydrogenation-hydrogenolytic mechanism and/or iii) direct hydrogenolysis of C=O bond. Figure 3 shows evolution of reactant and products concentration with reaction time in the experiment performed with vanillin over $\text{Pd@CN}_{0.132}$ at 90°C under 1 bar of hydrogen in water. The reaction was accompanied by a rapidly increase in vanillin alcohol and a decrease in vanillin in the first 2 h. It illustrates that vanillin is mainly hydrogenated to vanillin alcohol in the first step, but it is also noticed that even in the first 20 minutes, 2-methoxy-4-methylphenol was observed, which suggested that hydrogenolysis of vanillin alcohol happened or vanillin underwent via direct hydrogenolysis of C=O as well. Later, hydrogenolysis of vanillin alcohol underwent rapidly. After 15 h, almost all vanillin alcohol had been converted to 2-methoxy-4-methylphenol via hydrogenolysis.

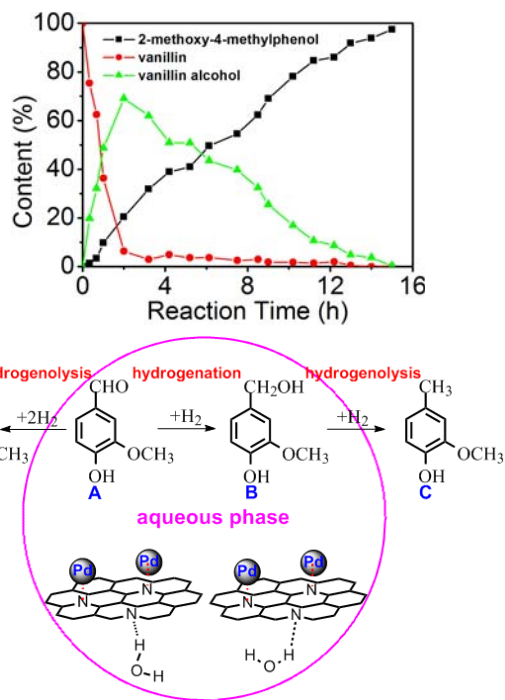


Figure 3. Evolution of reactant and products concentration with the reaction time (upper) and possible reaction pathway (bottom).

Most recently, Resasco and coworkers achieved both good conversion and selectivity in the hydrodeoxygenation of vanillin by depositing palladium onto carbon nanotube-inorganic oxide hybrid nanoparticles (Pd@SWNT-SiO₂) in water/oil emulsion. For example, when Pd@SWNT-SiO₂ was used as a catalyst in a biphasic system, 85% of vanillin was consumed in half an hour with a 47% selectivity of 2-methoxy-4-methyl phenol (Table 1, entry 1). For comparison, we tested the activity of Pd@CN_{0.132} under the same conditions. As demonstrated in Table 1, Pd@CN_{0.132} showed remarkably high catalytic activity to give a 100% conversion of vanillin and 93% selectivity of 2-methoxy-4-methyl phenol (Table 1, entry 2). Water is a desirable solvent for chemical reactions for reasons of cost, safety, and environmental concerns. We subsequently conducted the reaction in water and found that even better selective hydrodeoxygenation could be achieved, 100% of 2-methoxy-4-methyl phenol was yield in half an hour (Table 1, entry 3). Moreover, the Pd@CN_{0.132} catalyst was compared with the commercially available Pd@C under the same conditions as well as other oxide-supported Pd NPs including Pd@TiO₂, Pd@MgO, Pd@CeO₂, and Pd@γ-Al₂O₃. The textural properties of the catalyst supports were shown in Figure S4. Results from Table 1 (entry 3 and 4) clearly show that the catalyst synthesized here gives better activity and selectivity to 2-methoxy-4-methylphenol than commercially prepared Pd@C. Oxide-supported Pd NPs showed moderately effective for this reaction, affording 2-methoxy-4-methyl phenol in lower yields than Pd@CN_{0.132}. From these results, and in first approximation, one could conclude that the nature of the support plays an important role in activity and selectivity of Pd catalysts for the hydrodeoxygenation of vanillin. We deduced that hydrophilic property of Pd@CN_{0.132} affects its catalytic performance greatly. It was found that after reaction, the catalyst Pd@CN_{0.132} dispersed well in water (Figure S5). As compared with the

highly aggregated state of the traditional solid catalysts, doping with nitrogen atoms increased the hydrophilic property of Pd@CN_{0.132} which might enhance the catalyst dispersion in water and improve the exposure of the catalyst toward the substrates (like vanillin), and finally improve the catalytic performance significantly.

Table 1. Catalytic results of different catalyst.

Entry	Catalyst	Solvent	Conv. (%)	Sel. (%)	
				B	C
1 ^a	Pd@SWNT-SiO ₂	water & decalin	85	53	47
2 ^b	Pd@CN _{0.132}	water & decalin	100	-	93
3	Pd@CN _{0.132}	water	100	-	100
4	Pd@C	water	98	26	74
5	Pd@TiO ₂	water	98	79	21
6 ^c	Pd@MgO	water	28	32	-
7	Pd@CeO ₂	water	88	86	14
8	Pd@γ-Al ₂ O ₃	water	95	31	69
9 ^d	Pd@CN _{0.132}	water	98	-	100

^a volume ratio of water to decalin is 1:1; data from literature¹⁴; ^b volume ratio of water to decalin is 1:1; ^c other byproducts are unidentified; ^d S/C=1000, H₂ pressure 1.0 MPa, 150 °C, 6 h.

For practical applications, both high yield and low cost are required. We then increased the molar ratio of vanillin to Pd (S/C) to 350 and conducted the reactions under this condition. As demonstrated in Figure 4, vanillin conversion of 65% was achieved with a 2-methoxy-4-methylphenol selectivity of 69% within 1 h at 90 °C. The reaction was accelerated at higher temperature, for example, full conversion in 1 h was obtained at 150 °C with a high 2-methoxy-4-methylphenol selectivity exceeding 99%. For comparison, using Pd@SWNT-SiO₂ as catalyst and the water/oil emulsion as solvent, high 2-methoxy-4-methyl phenol (about 95%) yield was only obtained under a higher temperature of 200 °C, however, with an S/C of 100.¹⁴ Notably, we found that the 2-methoxy-4-methylphenol is very stable in our reaction systems, with a further temperature increase to 200 °C, no deeper hydrogenolysis product was yielded. We attributed the high 2-methoxy-4-methylphenol yield to its poor solubility in water. When 2-methoxy-4-methyl phenol was formed under the reaction condition, it separated from the water phase and avoided the further hydrogenolysis to 2-methoxyphenol. An S/C ratio of 1000 was then tested for the Pd@CN_{0.132} catalyst, even under this high substrate concentration condition, the reaction went smoothly and a 98% conversion of vanillin and 100% selectivity of 2-methoxy-4-methyl phenol were yielded (Table 1, entry 9).

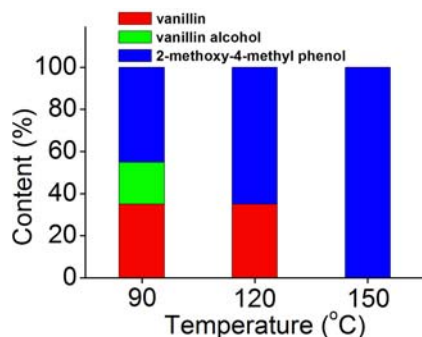


Figure 4. Products distribution at different temperatures. Reaction condition: vanillin 1000 mg, S/C=350, water 80 mL, H₂ pressure 1.0 MPa, 1h.

Furthermore, the catalyst can easily be separated from the reaction solution by simple filtration. The catalyst is highly stable and can be reused for several cycles without losing activity, which is a prerequisite for practical applications. (Table S3). The concentration of Pd in reaction solution was determined by ICP-AES, and it was below 0.1 ppm, meaning the leaching of the Pd in solvent is neglectable. Since nitrogen is strong electronegative and usually has a lone pair of electrons, the nitrogen functionalities on the surface might act as Lewis base sites and are expected to be more effective in retaining metal nanoparticles.

In conclusion, Pd nanoparticles have been heterogeneously supported on mesoporous N-doped carbon with its special base properties and electronic behavior. The novel Pd catalyst exhibits a high activity for the hydrodeoxygenation of vanillin, a common component in lignin-derived bio-oil, under mild reaction conditions and using water as a clean solvent. The high catalytic performance has been attributed to the special structure of the catalytic N-doped carbon-metal heterojunction, which leads not only to a very stable and uniform dispersion of Pd nanoparticles but also to additional electronic activation of the metal nanoparticles and well dispersion of catalyst in water. This Pd@CN_{0.132} catalyst hold promising potential for the biofuel upgrade and further work will be directed toward the applications to natural lignin and other model systems.

ASSOCIATED CONTENT

Supporting Information

Experimental and characterization sections, Scheme S1 and S2, Figures S1-6, Tables S1-4. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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REFERENCES

- (1) Rinaldi, R.; Schuth, F. *Energy Environ. Sci.* **2009**, *2*, 610.
- (2) Beaumont, S. K. *J. Chem. Technol. Biotechnol.* **2012**, *87*, 595.
- (3) Thomas, J. M.; Johnson, B. F. G.; Raja, R.; Sankar, G.; Midgley, P. A. *Acc. Chem. Res.* **2003**, *36*, 20.
- (4) Wang, Y.; Yao, J.; Li, H.; Su, D.; Antonietti, M. *J. Am. Chem. Soc.* **2011**, *133*, 2362.
- (5) Robin J. White; Rafael Luque; Vitaliy L. Budarin; Clark, J. H.; Macquarrie, D. J. *Chem. Soc. Rev.* **2009**, *38*, 481.
- (6) Martono, E.; Vohs, J. M. *J. Catal.* **2012**, *291*, 79.
- (7) Bond, J. Q.; Alonso, D. M.; Wang, D.; West, R. M.; Dumesic, J. A. *Science* **2010**, *327*, 1110.
- (8) Peng, B. X.; Yuan, X. G.; Zhao, C.; Lercher, J. A. *J. Am. Chem. Soc.* **2012**, *134*, 9400.
- (9) Enache, D. I.; Edwards, J. K.; Landon, P.; Solsona-Espriu, B.; Carley, A. F.; Herzing, A. A.; Watanabe, M.; Ckiely, C. J.; Knight, D. W.; Hutchings, G. J. *Science* **2006**, *311*, 362.
- (10) Zhang, C.; Lercher, J. A. *Angew. Chem., Int. Ed.* **2012**, *51*, 5935.
- (11) Deng, W. P.; Liu, M.; Tan, X. S.; Zhang, Q. H.; Wang, Y. *J. Catal.* **2010**, *271*, 22.
- (12) Zhao, C.; Kou, Y.; Lemonidou, A. A.; Li, X. B.; Lercher, J. A. *Angew. Chem., Int. Ed.* **2009**, *48*, 3987.
- (13) Clippel, F.; Dusselier, M.; Van Rompaey, R.; Vanelderden, P.; Dijkmans, J.; Makshina, E.; Giebler, L.; Oswald, S.; Baron, G. V.; Denayer, J. F. M.; Pescarmona, P. P.; Jacobs, P. A.; Sels, B. F. *J. Am. Chem. Soc.* **2012**, *134*, 10089.
- (14) Crossley, S.; Faria, J.; Shen, M.; Resasco, D. E. *Science* **2010**, *327*, 68.
- (15) Radkevich, V. Z.; Senko, T. L.; Wilson, K.; Grishenko, L. M.; Zaderko, A. N.; Diyuk, V. Y. *Appl. Catal., A* **2008**, *335*, 241.
- (16) Yang, S. B.; Feng, X. L.; Wang, X. C.; Mullen, K. *Angew. Chem., Int. Ed.* **2011**, *50*, 5339.
- (17) Lee, J. S.; Wang, X. Q.; Luo, H. M.; Baker, G. A.; Dai, S. *J. Am. Chem. Soc.* **2009**, *131*, 4596.
- (18) Yang, W.; Fellingner, T. P.; Antonietti, M. *J. Am. Chem. Soc.* **2011**, *133*, 206.
- (19) Fulvio, P. F.; Lee, J. S.; Mayes, R. T.; Wang, X. Q.; Mahurin, S. M.; Dai, S. *Phys. Chem. Chem. Phys.* **2011**, *13*, 13486.
- (20) Liu, R.; Mahurin, S. M.; Li, C.; Unocic, R. R.; Idrobo, J. C.; Gao, H. J.; Pennycook, S. J.; Dai, S. *Angew. Chem., Int. Ed.* **2011**, *50*, 6799.
- (21) Zhao, L.; Fan, L. Z.; Zhou, M. Q.; Guan, H.; Qiao, S. Y.; Antonietti, M.; Titirici, M. *Adv. Mater.* **2010**, *22*, 5202.
- (22) Paraknowitsch, J. P.; Zhang, J.; Su, D. S.; Thomas, A.; Antonietti, M. *Adv. Mater.* **2010**, *22*, 87.
- (23) Wang, X. Q.; Dai, S. *Angew. Chem., Int. Ed.* **2010**, *49*, 6664.
- (24) Lee, J. S.; Wang, X. Q.; Luo, H. M.; Dai, S. *Adv. Mater.* **2010**, *22*, 1004.
- (25) Yuan, J. Y.; Giordano, C.; Antonietti, M. *Chem. Mater.* **2010**, *22*, 5003.
- (26) Vispute, T. P.; Zhang, H. Y.; Sanna, A.; Xiao, R.; Huber, G. W. *Science* **2010**, *330*, 1222.
- (27) Huber, G. W.; Iborra, S.; Corma, A. *Chem. Rev.* **2006**, *106*, 4044.
- (28) Zakzeski, J.; Bruijninx, P. C. A.; Jongerius, A. L.; Weckhuysen, B. M. *Chem. Rev.* **2010**, *110*, 3552.
- (29) Mohan, D.; Pittman, C. U., Jr.; Steele, P. H. *Energy Fuels* **2006**, *20*, 848.
- (30) Nimmanwudipong, T.; Runnebaum, R. C.; Block, D. E.; Gates, B. C. *Energy Fuels* **2011**, *25*, 3417.
- (31) Nimmanwudipong, T.; Runnebaum, R. C.; Ebeler, S. E.; Block, D. E.; Gates, B. C. *Catal. Lett.* **2012**, *142*, 151.
- (32) Yan, N.; Yuan, Y.; Dykeman, R.; Kou, Y.; Dyson, P. J. *Angew. Chem., Int. Ed.* **2010**, *49*, 5549.
- (33) Prochazkova, D.; Zamostny, P.; Bejblova, M.; Cerveny, L.; Cejka, J. *Appl. Catal., A* **2007**, *332*, 56.

