



A Journal of the Gesellschaft Deutscher Chemiker

Angewandte Chemie

GDCh

International Edition

www.angewandte.org

Accepted Article

Title: Hydrogenation of Pyridines using a Nitrogen-Modified Titania Supported Cobalt Catalyst

Authors: Feng Chen, Wu Li, Basudev Sahoo, Carsten Kreyenschulte, Giovanni Agostini, Henrik Lund, Kathrin Junge, and Matthias Beller

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: *Angew. Chem. Int. Ed.* 10.1002/anie.201803426
Angew. Chem. 10.1002/ange.201803426

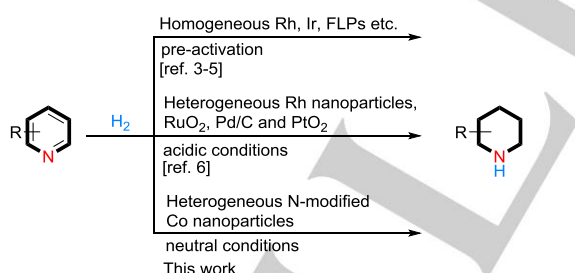
Link to VoR: <http://dx.doi.org/10.1002/anie.201803426>
<http://dx.doi.org/10.1002/ange.201803426>

Hydrogenation of Pyridines using a Nitrogen-Modified Titania Supported Cobalt Catalyst

Feng Chen,^[a] Wu Li,^[a] Basudev Sahoo,^[a] Carsten Kreyenschulte,^[a] Giovanni Agostini,^[a] Henrik Lund,^[a] Kathrin Junge,^[a] and Matthias Beller^{*[a]}

Abstract: Novel heterogeneous catalysts were prepared by impregnation of titania with a solution of cobalt acetate/melamine and subsequent pyrolysis. The resulting materials show an unusual nitrogen-modified titanium structure through partial implementation of nitrogen into the support. The optimal catalyst displayed good activity and selectivity for challenging pyridine hydrogenation under acid free conditions in water as solvent.

Piperidines constitute an important structural motif found in many natural products, synthetic drugs and biologically active compounds.^[1] Their synthesis has been extensively developed and numerous methods based on heterocycle construction, cycloaddition, ring expansions and rearrangements are known.^[2] Alternatively, direct hydrogenations of readily available substituted pyridines into the corresponding piperidines are undoubtedly attractive in terms of efficiency as well as step and atom economy. Although some protocols using homogeneous Rh,^[3] Ir^[4] and metal free^[5] systems were reported (Scheme 1), catalyst costs, limited substrate scope and required conditions restrict applications of these methods so far. In industry, heterogeneous catalysts are preferred because of their stability and easy separation from the products. Known materials for pyridine hydrogenation are based on precious metals,^[6] such as Rh nanoparticles, RuO₂, Pd/C and PtO₂. Here, in general the addition of acid is required for pre-activation of the substrate, which causes corrosion problems (Scheme 1).



Scheme 1. Known catalytic hydrogenations of pyridines.

In the past decades, catalysis using earth abundant metals became an actual and important subject in chemistry.^[7] While several non-noble based heterogeneous catalysts have been used for reduction of quinolones, isoquinolines and related heterocycles,^[8] the hydrogenation of less active pyridine is rarely

known. Herein, we report the first example of nitrogen-modified cobalt nanoparticles for efficient pyridine hydrogenations under neutral conditions in water.

In recent years, materials containing non-noble metal nanoparticles and nitrogen-modified carbon structures were developed with special electronic properties,^[9] allowing several interesting catalytic (de)hydrogenation reactions.^[10] Encouraged by all these works and our recent hydrogenation of heterocycles,^[8a,c,11] we became interested in the development of a general protocol for reduction of pyridines.

At the start of our studies, a series of materials was synthesized by pyrolysis of cobalt salts with melamine in the presence of different inorganic supports. Notably, melamine is a nitrogen-rich, inexpensive monomer,^[12] which has been also applied as a precursor for the preparation of g-C₃N₄.^[13] However, so far it has been rarely used for catalyst synthesis.^[8a]

For the preparation of the potential catalysts TiO₂, ZrO₂, Al₂O₃, CeO₂, carbon, BN and Nb₂O₅ were impregnated with an ethanolic solution of cobalt acetate and melamine and subsequently pyrolyzed at 500-1000 °C. A detailed preparation procedure and screening conditions are described in the SI. The best catalyst Co/Melamine-6@TiO₂-800-5 was selected for further exploration.

To understand the structural features of these titanium-based cobalt catalysts, scanning transmission electron microscopy (STEM), X-ray photoelectron spectroscopy (XPS) and powder X-ray diffraction (PXRD) investigations were performed. Firstly, PXRD measurement was carried out to understand the formation of the active catalyst and the possible interaction of the deposited pre-catalyst with the support. After thermal treatment of the material at different temperatures the obtained catalysts were investigated ex-situ (Figure S4a).

Next to the titania phase mixture (anatase and rutil) of the support, metallic Co can be indexed from the powder pattern after treatment at 700 °C (see Figure S4a). If the temperature of the treatment procedure is increased to 800 °C, the relative intensity of the TiO₂-phases reflection peaks decreases and broad reflection peaks appear, which can be interpreted as the formation of titania suboxides of the general formula Ti_xO_{2x-1}.^[14] Anyway, the diffraction data does not allow the identification of a specific titania suboxide at this stage. If the temperature is further increased during catalyst preparation titania is reduced to Ti₄O₇ (900 °C) and finally to Ti₃O₅ (1000 °C),^[15] emphasizing the interpretation of Magnéli suboxide formation via carbothermic reduction. Additional reduction products such as titanium oxycarbides (TiO_{1-x}C_x) which are typically formed in an excess of carbon are not identified in the investigated temperature range. Due to the usage of melamine in the synthesis of metal nitrides, the formation of titanium oxynitrides (TiO_{1-x}N_x) or nitrides (TiN) might be possible as well.^[16] At 1000 °C the presence of rock-salt structured titanium (oxy-)nitride phase (Figure S4a, empty squares), which starts to appear at 700 °C, is also possible.

[a] Dr. F. Chen, Dr. W Li, Dr. B. Sahoo, Dr. C. Kreyenschulte, Dr. G. Agostini, Dr. H. Lund, Dr. K. Junge, and Prof. Dr. M. Beller* Leibniz-Institut für Katalyse e.V. an der Universität Rostock, Albert-Einstein-Str. 29a, Rostock, 18059, Germany. E-mail: matthias.beller@catalysis.de

Supporting information for this article is given via a link at the end of the document.

Remarkably, the diffraction peaks which were assigned to this phase do exhibit a shift to smaller angles 2θ if the pyrolysis temperature is increased to 1000 °C. This finding leads to the assumption that pure TiN is formed at 1000 °C from the titanium oxynitrides which is present after treatment at lower temperatures. Beside the reduction of titania the ongoing crystal growth of metallic cobalt can be stated (*cf.* 4.6 nm at 800 °C, 10.3 nm at 1000 °C).^[17] However, the presence of Co-O-species, specially CoO, or Co-C-phases cannot clearly ruled out from the diffraction data in general. Interestingly, the occurrence of the discussed titanium suboxides seems to be dependent on the applied heating rate (Figure S4b). If the material is heated with 5 °C/min to 800 °C the reduction of the titania support is less advanced compared to an applied rate of 25 °C/min. Consequently, the formation of titania suboxides seems to diminish the activity of this catalyst.

For the most active catalyst, Co/Melamine-6@TiO₂-800-5, the STEM images show that cobalt particles are formed, which are always connected with support TiO₂ (Figure 1 and Figures S5-7). Some Co particles seem to be metallic as shown in Figure 1, while some seem to conform to the underlying support like in the upper Co particle shown and are of undetermined type. Also, Co oxide particles and a Co containing carbon phase were found. Interestingly, nitrogen is implanted into the support and a Ti-N-O phase is formed (Figures S5-7). The energy loss near edge structure (ELNES) in the electron energy loss spectrum (EELS) reveals a difference in the electronic structure for the N containing particle compared to those without (see SI, XPS data). For the material Co/Melamine-6@TiO₂-1000-25, also a Ti-N-O structure could be found (Figures S12-14), however it might have a different crystal structure consistent to PXRD data. Nevertheless, the material pyrolyzed at 1000 °C showed lower activity for pyridine hydrogenation (15% conversion). Moreover, the material Co/Melamine-6@TiO₂-500-25 without the formation of cobalt particles and Ti-N-O or Ti-N structures also exhibited nearly no activity (Figures S15-16). Therefore, the formation of nitrogen modified TiO₂ structure in the presence of cobalt particles is crucial to realize the improved hydrogenation activity.

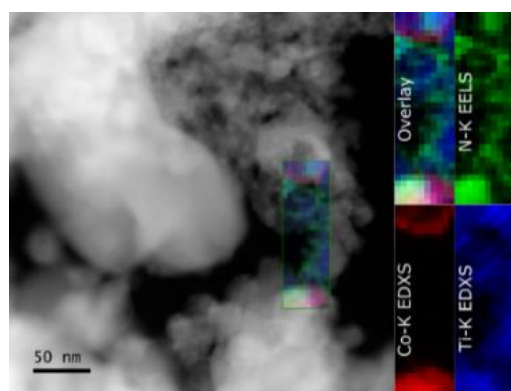


Figure 1. STEM-HAADF image and elemental maps from EELS and EDXS signals of the marked areas of the Co/Melamine-6@TiO₂-800-5 catalyst. Large amount of nitrogen modified titanium structure is observed when pyrolyzation temperature is 800 °C mostly in the surface regions of larger TiO₂ particles but also in the bulk of the small fraction of TiO₂ particles.

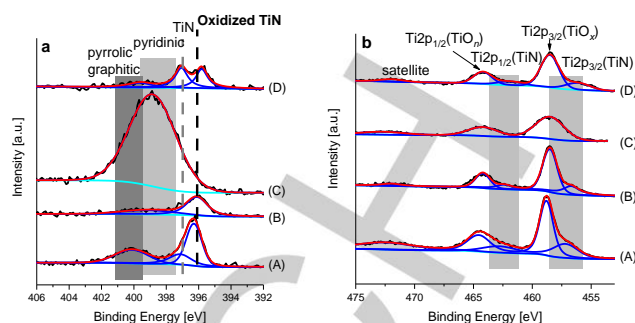
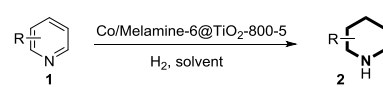


Figure 2. XPS measurements for materials prepared at different temperatures. (a) N1s spectra: (A) Co/Melamine-6@TiO₂-800-5; (B) Co/Melamine-6@TiO₂-800-25; (C) Co/Melamine-6@TiO₂-500-25; (D) Co/Melamine-6@TiO₂-1000-25. (b) Ti2p spectra: (A) Co/Melamine-6@TiO₂-800-5; (B) Co/Melamine-6@TiO₂-800-25; (C) Co/Melamine-6@TiO₂-500-25; (D) Co/Melamine-6@TiO₂-1000-25.

XPS spectra were collected to elucidate the presence of TiO_x and TiO_{1-x}N_x phases on the surface of the materials, N1s and Ti2p regions are reported in Figure 2. According to literature TiN is characterized to a contribution around 455-456 eV and 397 eV for Ti2p_{3/2} and N1s region, respectively. In presence of TiO_{1-x}N_x phase, Ti2p_{3/2} contribution is shifted at higher binding energy towards to TiO₂ peak centered at 459 eV, while N-Ti-O in N1s region is moved to lower binding energy.^[18] The sample treated at 500 °C exhibited very broad peaks in both Ti2p and N1s region in typical binding energy for TiO₂ and pyridinic and combination pyrrolic and graphitic N species.^[19] Increasing temperature treatment, in Ti2p_{3/2} of sample Co/Melamine-6@TiO₂-800-25 a contribution at 457.7 eV appeared and it is shifted to 457.4 eV and 456.7 eV for Co/Melamine-6@TiO₂-800-5 and Co/Melamine-6@TiO₂-1000-25 samples, respectively. This behavior can be explained as formation of TiO_{1-x}N_x phase that progressively enriches in N amount. This hypothesis is confirmed by the energy peaks in the N1s region. For Co/Melamine-6@TiO₂-800-25 only a peak due to Ti-N-O species was measured but Ti-N band appeared in Co/Melamine-6@TiO₂-800-5 becoming more intense in Co/Melamine-6@TiO₂-1000-25 material. The presence of TiO_x phases cannot be identified due to over imposition with a TiO_yN_z signal in Ti2p_{3/2} region.

To explore the scope of the optimal catalyst, hydrogenation of pyridine derivatives with diverse substitution patterns under acid free reaction conditions was tested (Table 1). Pyridine is successfully hydrogenated to piperidine in 99% yield in methanol using a reduced amount of catalyst (Table 1, entry 1). Interestingly, when ethanol was selected as solvent, 1-ethylpiperidine was obtained in 94% yield (Table 1, entry 2). Apparently, in this case after hydrogenation of the heterocyclic ring reductive alkylation occurred due to the higher activity of this alcohol in such reactions. A similar transformation occurred with *n*-pentanol leading the corresponding product in 93% yield. Thus, depending on the alcoholic solvent our catalyst allows preparing both alkylated as well as N-H piperidines.

Table 1. Substrates scope for cobalt catalyzed pyridine hydrogenations.


| entry | substrate | Cat. [mg] | Solvent | product | Yield [%] ^[a] |
|-------|-----------|-----------|------------------|-----------|--------------------------|
| 1 | | 20 | MeOH | | 99 |
| 2 | 1b | 20 | EtOH | | 94 |
| 3 | 1b | 20 | 1-Pentanol | | 93 |
| 4 | 1b | 20 | iPrOH | | 29 ^[b] |
| 5 | | 80 | iPrOH | | 98 ^[c,d] |
| 6 | 1c | 40 | iPrOH | 2c | 96 ^[d] |
| 7 | | 80 | iPrOH | | 95 ^[c] |
| 8 | | 40 | iPrOH | | 91 |
| 9 | 1b | 20 | H ₂ O | 2b | 85 |
| 10 | 1b | 80 | H ₂ O | 2b | 96 |
| 11 | | 100 | H ₂ O | | 71 |
| 12 | | 120 | H ₂ O | | 57 |
| 13 | | 80 | H ₂ O | | 94 |
| 14 | | 80 | H ₂ O | | 98 ^[e] |
| 15 | | 40 | H ₂ O | | 97 |
| 16 | | 100 | H ₂ O | | 71 ^[f] |
| 17 | | 80 | H ₂ O | | 95 |
| 18 | | 80 | H ₂ O | | 98 |

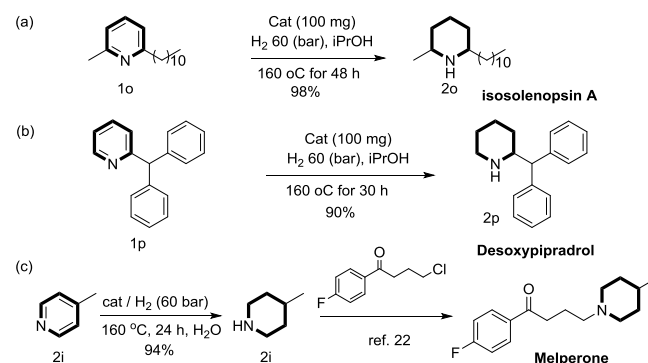
[a] Reaction conditions: 0.25 mmol scale with 60 bar hydrogen at 160 °C for 24 hours with isolated yield. [b] 4% GC yield of 1-isopropylpiperidine is detected. [c] 40 bar hydrogen at 140 °C. [d] GC yield determined using dodecane as a standard. [e] 140 °C [f] 36 hours.

Applying the less reactive solvent *iso*-propanol a mixture of piperidine (29%) and 1-isopropylpiperidine (4%) was obtained (Table 1, entry 4; see also Table S2).). Notably, in case of 2-substituted pyridines such as 2-ethylpyridine, 2-pentylpyridine or 2,6-dimethyl pyridine the corresponding 2-substituted piperidines were produced in excellent yields (Table 1, entries 5-8). In order to circumvent potential alkylation side reactions water was used

as solvent. Gratifyingly, the hydrogenation of pyridine proceeded with improved yields even at low catalyst loading (Table 1, entries 9-10). Other substrates, for instance 3-ethylpiperidine (**2f**), 4-ethylpiperidine (**2g**), 4-propylpiperidine (**2h**), and 4-methylpiperidine (**2i**) were also obtained in good to excellent yields (Table 1, entries 11-13). Furthermore, to investigate the chemoselectivity for this hydrogenation process, pyridines bearing phenyl, benzyl, amide or acid groups were tested. Here, 3-, and 4-phenylpyridine as well as 2-benzylpyridine were hydrogenated to the corresponding piperidines without hydrogenation of the phenyl ring (Table 1, entries 14-16). Additionally, isonicotinamide and isonicotinic acid were successfully converted to piperidine-4-carboxamide (**2m**) and piperidine-4-carboxylic acid (**2n**) simply using water as solvent (Table 1, entries 17-18).

To showcase the applicability of this novel catalyst, the hydrogenation protocol was utilized as a key step in the syntheses of bioactive compounds (Scheme 2). Firstly, isosolenopsin A (**2o**),^[20] a fire ant venom alkaloid and potent and selective inhibitor of neuronal nitric oxide synthase, was synthesized in 98% yield from 2-methyl-6-undecylpyridine (**1o**). Furthermore, 2-benzhydrylpyridine (**1s**) was successfully converted to Desoxypipradrol^[21] (**2p**, 90%), which is a norepinephrine-dopamine reuptake inhibitor (NDRI). Finally, 4-methylpiperidine (**2i**) which was obtained in 94% yield is known to react with 4-chloro-1-(4-fluorophenyl)butan-1-one to give Melperone in a straightforward manner.^[22]

Stability and recyclability represent important aspects of heterogeneous catalysis. Considering that, the Co/Melamine-6@TiO₂-800-5 material was recycled 5 times for the hydrogenation of pyridine on 1 mmol scale (Figure S3). No significant drop of the activity of the catalyst was noticed as the piperidine was obtained in 92% yield even after the 5th run. TEM investigation of the recycled catalyst shows the formation of an extended carbon phase containing N and Co as well as a change of the small Ti-O-N particles (Figures S8-10). This indicates that the Ti-O-N takes part in the reaction and undergoes a slight deactivation process. Nevertheless, these recycling experiments signify that the catalyst is quite stable under the acid free hydrogenation conditions.

**Scheme 2.** Co-catalyzed hydrogenation of pyridines as a key step for the syntheses of bioactive compounds.

In conclusion, novel heterogeneous cobalt catalysts were prepared by impregnation of titania with an ethanolic solution of cobalt acetate and melamine and subsequent pyrolysis. The

resulting material shows a distinctive nitrogen-modified titanium structure through partial implementation of nitrogen into the TiO₂ support. The optimal catalyst system displays good activity and selectivity for pyridine hydrogenation under acid free conditions, which is a highly demanding transformation. Several substituted pyridines were successfully hydrogenated into the corresponding functionalized piperidines in water as solvent. The reusability of the catalyst and its application for the synthesis of bioactive compounds were demonstrated, too.

Acknowledgements

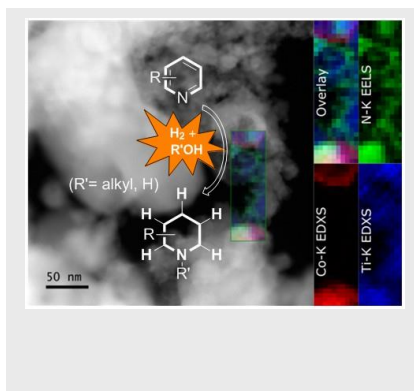
The Federal Ministry of Education and Research (BMBF) and the State of Mecklenburg-Vorpommern are gratefully acknowledged for their generous support. We thank the analytical department of the Leibniz-Institute for Catalysis, Rostock for their excellent analytical service.

Keywords: Hydrogenation • Pyridine • Cobalt • Heterogeneous catalysis • Titanium oxide

- [1] S. Källström, R. Leino, *Bioorg. Med. Chem.* **2008**, *16*, 601-635.
- [2] a) V. Baliah, R. Jeyaraman, L. Chandrasekaran, *Chem. Rev.* **1983**, *83*, 379-423; b) M. G. P. Buffat, *Tetrahedron* **2004**, *60*, 1701-1729; c) P. Merino, T. Tejero, G. Greco, E. Marca, I. Delso, A. Gómez-SanJuan, R. Matute, *Heterocycles* **2012**, *84*, 75
- [3] a) E. Baralt, S. J. Smith, J. Hurwitz, I. T. Horvath, R. H. Fish, *J. Am. Chem. Soc.* **1992**, *114*, 5187-5196; b) M. Studer, C. Wedemeyer-Exl, F. Spindler, H.-U. Blaser, *Monatsh. Chem.* **2000**, *131*, 1335-1343.
- [4] a) X.-B. Wang, W. Zeng, Y.-G. Zhou, *Tetrahedron Lett.* **2008**, *49*, 4922-4924; b) W.-J. Tang, J. Tan, L.-J. Xu, K.-H. Lam, Q.-H. Fan, A. S. C. Chan, *Adv. Synth. Catal.* **2010**, *352*, 1055-1062.
- [5] a) Y. Liu, H. Du, *J. Am. Chem. Soc.* **2013**, *135*, 12968-12971; b) T. Mahdi, J. N. del Castillo, D. W. Stephan, *Organometallics* **2013**, *32*, 1971-1978; c) Z.-Y. Liu, Z.-H. Wen, X.-C. Wang, *Angew. Chem. Int. Ed.* **2017**, *56*, 5817-5820; *Angew. Chem.* **2017**, *129*, 5911-5914.
- [6] a) M. Freifelder, G. R. Stone, *J. Org. Chem.* **1961**, *26*, 3805-3808; b) G. N. Walker, *J. Org. Chem.* **1962**, *27*, 2966-2967; c) M. Freifelder, *J. Org. Chem.* **1964**, *29*, 2895-2898; d) H. U. Blaser, H. Hönig, M. Studer, C. Wedemeyer-Exl, *J. Mol. Catal. A: Chem.* **1999**, *139*, 253-257; e) S. A. Raynor, J. M. Thomas, R. Raja, B. F. G. Johnson, R. G. Bell, M. D. Mantle, *Chem. Commun.* **2000**, 1925-1926; f) B. Zacharie, N. Moreau, C. Dockendorff, *J. Org. Chem.* **2001**, *66*, 5264-5265; g) F. Glorius, N. Spielkamp, S. Holle, R. Goddard, C. W. Lehmann, *Angew. Chem. Int. Ed.* **2004**, *43*, 2850-2852; *Angew. Chem.* **2004**, *116*, 2910-2913; h) A. Lei, M. Chen, M. He, X. Zhang, *Eur. J. Org. Chem.* **2006**, *2006*, 4343-4347; i) L. Piras, E. Genesio, C. Ghiron, M. Taddei, *Synlett* **2008**, 1125-1128; j) M. Irfan, E. Petricci, T. N. Glasnov, M. Taddei, C. O. Kappe, *Eur. J. Org. Chem.* **2009**, *2009*, 1327-1334; k) A. Karakulina, A. Gopakumar, I. Akçok, B. L. Roullet, T. La Grange, S. A. Katsyuba, S. Das, P. J. Dyson, *Angew. Chem. Int. Ed.* **2016**, *55*, 292-296; *Angew. Chem.* **2016**, *128*, 300-304.
- [7] a) D. Wang, D. Astruc, *Chem. Soc. Rev.* **2017**, *46*, 816-854; b) B. Su, Z.-C. Cao, Z.-J. Shi, *Acc. Chem. Res.*, **2015**, *48*, 886-896; c) V. S. Thoi, Y. Sun, J. R. Long, C. J. Chang, *Chem. Soc. Rev.* **2013**, *42*, 2388-2400.
- [8] a) F. Chen, B. Sahoo, C. Kreyenschulte, H. Lund, M. Zeng, L. He, K. Junge, M. Beller, *Chem. Sci.* **2017**, *8*, 6239-6246; b) Z. Wei, Y. Chen, J. Wang, D. Su, M. Tang, S. Mao, Y. Wang, *ACS Catal.* **2016**, *6*, 5816-5822; c) F. Chen, A.-E. Surkus, L. He, M.-M. Pohl, J. Radnik, C. Topf, K. Junge and M. Beller, *J. Am. Chem. Soc.*, **2015**, *137*, 11718-11724.
- [9] a) Y. Shao, J. Sui, G. Yin, Y. Gao, *Appl. Catal. B: Environ.* **2008**, *79*, 89-99; b) P. Ayala, R. Arenal, M. Rümmele, A. Rubio, T. Pichler, *Carbon* **2010**, *48*, 575-586; c) X.-H. Li, M. Antonietti, *Chem. Soc. Rev.* **2013**, *42*, 6593-6604; d) D. S. Su, S. Perathoner, G. Centi, *Chem. Rev.* **2013**, *113*, 5782-5816; e) W. Shen, W. Fan, *J. Mater. Chem. A* **2013**, *1*, 999-1013; f) K. N. Wood, R. O'Hayre, S. Pylypenko, *Energy Environ. Sci.* **2014**, *7*, 1212-1249; g) X.-K. Kong, C.-L. Chen, Q.-W. Chen, *Chem. Soc. Rev.* **2014**, *43*, 2841-2857; h) O. Y. Podyacheva, Z. R. Ismagilov, *Catal. Today* **2015**, *249*, 12-22; i) L. He, F. Weniger, H. Neumann, M. Beller, *Angew. Chem. Int. Ed.* **2016**, *55*, 12582-12594; *Angew. Chem.* **2016**, *128*, 12770-12783.
- [10] M. Li, F. Xu, H. Li, Y. Wang, *Catal. Sci. Technol.* **2016**, *6*, 3670-3693.
- [11] R. Adam, J. R. Cabrero-Antonino, A. Spannenberg, K. Junge, R. Jackstell, M. Beller, *Angew. Chem. Int. Ed.* **2017**, *56*, 3216-3220; *Angew. Chem.* **2017**, *129*, 3264-3268.
- [12] a) Y. Zheng, L. Lin, B. Wang, X. Wang, *Angew. Chem. Int. Ed.* **2015**, *54*, 12868-12884; *Angew. Chem.* **2015**, *127*, 13060-13077; b) W.-J. Ong, L.-L. Tan, Y. H. Ng, S.-T. Yong, S.-P. Chai, *Chem. Rev.* **2016**, *116*, 7159-7329; c) K. S. Lakhi, D.-H. Park, K. Al-Bahily, W. Cha, B. Viswanathan, J.-H. Choy, A. Vinu, *Chem. Soc. Rev.* **2017**, *46*, 72-101.
- [13] A. Thomas, A. Fischer, F. Goettmann, M. Antonietti, J.-O. Müller, R. Schlogl, J. M. Carlsson, *J. Mater. Chem.* **2008**, *18*, 4893-4908.
- [14] B. Xu, H. Y. Sohn, Y. Mohassab, Y. Lan, *RSC Adv.* **2016**, *6*, 79706-79722.
- [15] Ti₃O₅ phase seems to be the "best match". Intensity does not match at several positions. Some peaks remain unexplained.
- [16] a) H. Zhao, M. Lei, X. Chen, W. Tang, *J. Mater. Chem.* **2006**, *16*, 4407-4412; b) F.-S. Jung, *J. Ceramic Soc. Jap.* **2011**, *119*, 968-971; c) Y. Jia, Y. Wang, L. Dong, J. Huang, Y. Zhang, J. Su, J. Zang, *Chem. Commun.* **2015**, *51*, 2625-2628.
- [17] Crystallite size was calculated by applying the Scherrer equation using the integral breadth under the assumption of spherically shaped crystallites. K is set to 1.0747. The crystallite size value was calculated from the (111) reflection peak.
- [18] N. C. Saha, H. C. Tompkins, *J. Appl. Phys.* **1992**, *72*, 3072-3079.
- [19] R. Arrigo, M. Hävecker, R. Schlögl, D. S. Su, *Chem. Commun.* **2008**, 4891-4893.
- [20] G. B. Yi, D. McClendon, D. Desai, J. Goddard, A. Lister, J. Moffitt, R. K. Meer, R. de Shazo, K. S. Lee, R. W. Rockhold, *Int. J. Toxicol.* **2003**, *22*, 81-86.
- [21] J. M. Corkery, S. Elliott, F. Schifano, O. Corazza, A. H. Ghodse, *Prog. Neuropsychopharmacol Biol. Psych.* **2012**, *39*, 253-258.
- [22] A. Leyva-Pérez, J. R. Cabrero-Antonino, P. Rubio-Marqués, S. I. Al-Resayes, A. Corma, *ACS Catal.* **2014**, *4*, 722-731.

COMMUNICATION

Novel cobalt catalysts were prepared by impregnation of titania with an ethanolic solution of cobalt acetate and melamine. The resulting material shows a distinctive nitrogen-modified titanium structure and displays good activity and selectivity for pyridine hydrogenation in water.



Feng Chen, Wu Li, Basudev Sahoo, Carsten Kreyenschulte, Giovanni Agostini, Henrik Lund, Kathrin Junge, and Matthias Beller*

Page No. – Page No.

Hydrogenation of Pyridines using a Nitrogen-Modified Titania Supported Cobalt Catalyst