

Cite this: *Green Chem.*, 2012, **14**, 2983

www.rsc.org/greenchem

Transfer hydrogenation of ketones by ceria-supported Ni catalysts†

Katsuya Shimura and Ken-ichi Shimizu*

Received 30th May 2012, Accepted 31st August 2012

DOI: 10.1039/c2gc35836k

Ni-loaded CeO₂, prepared by H₂-reduction of NiO-loaded CeO₂, was found to be an effective and recyclable catalyst for the transfer hydrogenation of aliphatic and aromatic ketones by 2-propanol to the corresponding alcohols under base free conditions with low catalyst loading (1–3 mol%).

The reduction of carbonyl compounds to the corresponding alcohols is an important transformation in organic synthesis. Among various methods such as the use of stoichiometric reducing reagents and hazardous molecular hydrogen (H₂), transfer hydrogenation¹ has attracted much attention, because the hydrogen donor (e.g. 2-propanol) is cheap and easy to handle, and no elaborate setups (e.g. high pressure reactors) are required. Homogeneous noble metal catalysts such as Ru² and Ir³ complexes are known to be effective for this reaction, but they suffer from problems such as difficulty in the recovery and reuse of expensive catalysts, and the necessity of co-catalysts (base and ligand). Recently, noble metal (Pt,⁴ Pd,⁵ Ru,⁶ and Au⁷)-based heterogeneous catalysts have been reported to act as effective and reusable catalysts for this reaction. However, these systems have problems such as necessity of basic additives (except for supported Ru(OH)_x catalysts^{6a,d}) and high cost. As cost-effective and eco-friendly alternatives, heterogeneous catalysts such as non-noble metal catalysts (Ni,^{8–10} Co¹¹ and Cu¹²), solid bases (hydratalcites^{13a} and K₃PO₄^{13b}), and Sn- or Zr-zeolite¹⁴ catalysts were developed. However, they suffer from drawbacks such as high catalyst loading (10–20 mol%),^{8–10b} high reaction temperature (150 °C),^{10g} special reaction methods (microwave heating),^{10h,12a} or excess amounts of a co-catalyst (1 equiv. KOH).^{10b–f,11} Although a few systems (Ni nanoparticles,⁹ Cu-zeolite,^{12b} solid bases¹³ and zeolites¹⁴) succeeded in the reaction of activated (aromatic and α,β-unsaturated) carbonyl compounds under co-catalyst free conditions, these systems were not generally effective for less reactive aliphatic carbonyl compounds. We report herein that Ni/CeO₂ catalyst, prepared from inexpensive commercial materials, acts as a recyclable catalyst for the transfer hydrogenation of ketones including less reactive aliphatic ketones under additive-free conditions with low catalyst loading (1–3 mol%).

First, we compared the activity of various Ni catalysts, bare CeO₂ and metal-loaded CeO₂ samples for transfer hydrogenation

of 2-octanone (Table 1). NiO-loaded precursors (Ni = 5 wt%) were prepared by evaporation to dryness of the slurry composed of an aqueous solution of Ni nitrate and support, followed by calcination in air at 350 °C for 4 h. Before the reaction the precursors were reduced in a flow of H₂ at 500 °C for 0.5 h, followed by cooling in H₂ to room temperature. Then, the reaction mixture was injected into the pre-reduced catalyst inside the glass tube through a septum inlet, and the mixture was stirred and heated at 85 °C (reflux conditions) in a N₂ atmosphere. The initial formation rate of 2-octanol (*V*₀) listed in Table 1 was measured under the condition where the conversion of 2-octanone was below 40%. Among the various Ni(5 wt%)-loaded MO_x catalysts (MO_x = CeO₂, Al₂O₃, ZrO₂, SiO₂, SiO₂-Al₂O₃ and TiO₂), Ni/CeO₂ showed a one to four orders higher activity than the other catalysts. Commercially available Ni compounds (Ni powder, RANEY® Ni and NiO) and CeO₂ showed negligible activity. The activity of the Ni/CeO₂ catalyst was higher than those of CeO₂-supported noble metal (Pd, Ru) and non-noble metal (Cu, Co) catalysts. Next, we optimized the preparation conditions of Ni/CeO₂ catalysts. First, we investigated the effect of pre-treatment conditions of Ni/CeO₂ (results not shown). Without the pre-reduction treatment, the NiO/CeO₂ catalyst showed no activity. Although the catalyst pre-reduced at

Table 1 Transfer hydrogenation of 2-octanone

Catalyst	<i>V</i> ₀ ^a /mmol h ⁻¹ g ⁻¹
Ni/CeO ₂	20.8
Ni/Al ₂ O ₃	1.7
Ni/ZrO ₂	1.5
Ni/SiO ₂	0.020
Ni/SiO ₂ -Al ₂ O ₃	0.015
Ni/TiO ₂	0.009
Ni powder	0
RANEY® Ni	0.10
NiO	0
CeO ₂	0.070
Pd/CeO ₂	5.1
Ru/CeO ₂	3.8
Cu/CeO ₂	0.80
Co/CeO ₂	0.70

^a Initial formation rate of 2-octanol per weight of the catalyst.

Catalysis Research Center, Hokkaido University, N-21, W-10, Sapporo 001-0021, Japan. E-mail: kshimizu@cat.hokudai.ac.jp; Fax: +81-11-706-9163

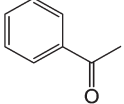
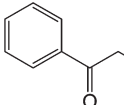
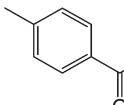
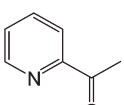
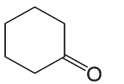
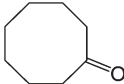
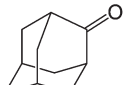
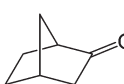
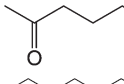
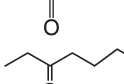
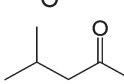
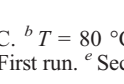
† Electronic supplementary information (ESI) available. See DOI: 10.1039/c2gc35836k

500 °C (Ni/CeO₂) showed high activity, the catalyst was completely deactivated when it was exposed to air at room temperature. From the optimization tests of H₂-reduction temperature (400–600 °C), the reduction temperature of 500 °C was found to be the best (not shown). The effect of the Ni loading (3–10 wt%) showed that the activity monotonically decreased with the loading (Fig. S1†). From these results, the Ni/CeO₂ (Ni = 3 wt%) catalyst pre-reduced at 500 °C was the best catalyst.

Using the optimized catalyst, we examined the scope and limitation for transfer hydrogenation of ketones by 2-propanol (Table 2). Aromatic (entries 1–4) and aliphatic (entries 5–12) ketones were reduced to the corresponding alcohols in good to excellent yields (70–98%). The present system is especially effective for the reaction of aliphatic ketones. For example, the reaction of 2-adamantanone at 80 °C for 24 h resulted in a 98% yield of *exo*-norbornanol. The turnover number (TON) of 65 is more than four times higher than those of the recently reported heterogeneous non-noble metal catalysts: Cu-zeolite (16)^{12b} and Ni nanoparticles (4).^{9a} We performed catalyst recycle tests for the reaction of 2-octanone (entry 9). After the reaction, the catalyst separated from the reaction mixture by centrifugation was washed with acetone, followed by calcination in air at 300 °C for 1 h, and by reducing in H₂ at 500 °C for 0.5 h.¹⁵ The recovered catalyst was reused at least four times without any indication of catalyst deactivation. The total TON for the five successive reactions is 464, which is more than 5 times higher than those of the previously reported heterogeneous catalysts: Ru(OH)_x/TiO₂ (95),^{6a} Ni nanoparticles (9),^{10a} Zr_{0.8}Ni_{0.2}O₂ (7),^{10c} and RANEY® Ni (0.2).^{8c} ICP analysis of the solution after the reaction showed that the amount of Ni species dissolved in the solution was below the detection limit. These results show that Ni/CeO₂ is a highly effective and recyclable catalyst for transfer hydrogenation of ketones. To the best of our knowledge, this is the first successful example of the heterogeneous non-noble metal catalyst for the transfer hydrogenation of aliphatic ketones under base free conditions with low catalyst loading (1–3 mol%).

Finally, we studied the structure–activity relationship. The structure of Ni species on Ni/CeO₂ was studied by Ni K-edge X-ray absorption near-edge structures (XANES) and extended X-ray absorption fine structures (EXAFS) shown in Fig. S2.† Fitting analysis of XANES showed that more than 90% of Ni species on the catalyst are metallic Ni. The EXAFS of Ni/CeO₂ consisted of one Ni–Ni shell at a bond distance of 2.47 Å due to metallic Ni (Table S1†). The Ni–Ni coordination number (7.5) was smaller than that of Ni foil (12). These results suggest that small Ni metal particles are the dominant Ni species on Ni/CeO₂. Exposure of Ni/CeO₂ to air at room temperature resulted in the appearance of the EXAFS feature due to the Ni–O bond and an increase in the fraction of NiO species from 0.07 to 0.40. Combined with the catalytic result that air-exposure of Ni/CeO₂ leads to catalyst deactivation, these results indicate that the surface metallic Ni species, as catalytically active species, are re-oxidized by O₂ to form inactive NiO species. The Ni–Ni coordination number increases from 7.5 to 8.9 with an increase in the Ni loading from 5 wt% to 10 wt%, indicating that the size of Ni metal particles increases with the loading. Considering the result that the catalytic activity decreased with Ni loading (Fig. S1†), it

Table 2 Transfer hydrogenation of ketones by Ni/CeO₂

Entry	Substrate	Conv./%	Yield/%
1		85	85
2		97	97
3		96	94
4		96	96
5 ^a		100	98
6 ^a		72	70
7 ^b		98	98
8 ^a		86	85
9 ^c		92, ^d 93, ^e 93, ^f 93, ^g 93, ^h	92, ^d 93, ^e 93, ^f 93, ^g 93, ^h
10 ^a		86	85
11 ^a		90	90
12		91	90

^a T = 80 °C. ^b T = 80 °C, catalyst = 1.5 mol%. ^c T = 80 °C, catalyst = 1 mol%. ^d First run. ^e Second run. ^f Third run. ^g Fourth run. ^h Fifth run.

is shown that Ni metal with smaller particle size shows higher activity. From these results, it is concluded that metallic Ni species on small Ni particles is the active species. In Fig. 1 the catalytic activity is plotted as a function of the number of surface basic sites of Ni/MO_x catalysts estimated by CO₂-TPD (Fig. S3†). There is a tendency that the activity increases with the number of desorbed CO₂ (number of surface basic sites), and Ni/CeO₂ as the most basic catalyst showed the highest activity. The *in situ* IR spectrum of the adsorption complexes formed by

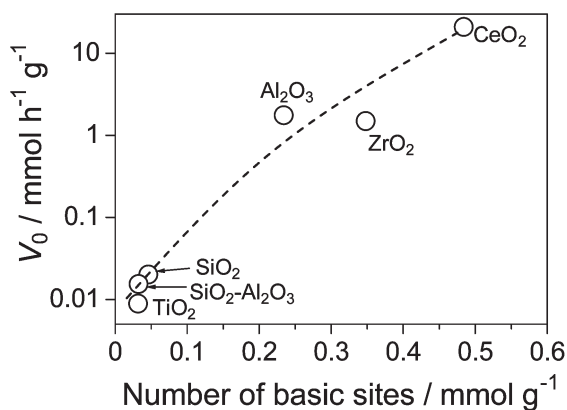
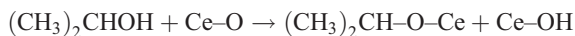


Fig. 1 Rate for transfer hydrogenation of 2-octanone by Ni/MO_x vs. number of surface basic sites estimated by CO₂-TPD.

the adsorption of 2-propanol on CeO₂ (Fig. S4†) showed the bands at 1166 and 1130 cm⁻¹ (C–O/C–C coupled stretching) due to 2-propoxide groups.¹⁶ The absence of the OH deformation band (1280 cm⁻¹) of the 2-propanol molecule indicates the absence of non-dissociatively adsorbed 2-propanol on the catalyst. These results indicate that deprotonation of 2-propanol to the 2-propoxide species occurs according to the following scheme, where the surface oxygen on CeO₂ as a basic site abstracts a proton from 2-propanol.



In conclusion, we have developed Ni/CeO₂-catalyzed heterogeneous transfer hydrogenation of aliphatic and aromatic ketones under base free conditions as a clean, versatile, and economic method for the reduction of ketones. The metallic Ni species on the surface of small Ni particles is the active species and the reaction was promoted by basic sites on the CeO₂ support.

This work was supported by a “Grant for Advanced Industrial Technology Development” in 2011 from the New Energy and Industrial Technology Development Organization (NEDO) of Japan. The X-ray absorption experiment was performed with the approval of the Japan Synchrotron Radiation Research Institute (Proposal No. 2010B1447).

Notes and references

- (a) R. A. W. Johnstone, A. H. Wilby and I. D. Entwistle, *Chem. Rev.*, 1985, **85**, 129–170; (b) G. Zassinovich, G. Mestroni and S. Gladioli, *Chem. Rev.*, 1992, **92**, 1051–1069; (c) J. S. Cha, *Org. Process Res. Dev.*, 2006, **10**, 1032–1053.
- (a) R. Noyori and S. Hashiguchi, *Acc. Chem. Res.*, 1997, **30**, 97–102; (b) M. J. Palmer and M. Wills, *Tetrahedron: Asymmetry*, 1999, **10**, 2045–

- 2061; (c) S. Gladioli and E. Albericob, *Chem. Soc. Rev.*, 2006, **35**, 226–236; (d) T. Ikariya and A. J. Blacker, *Acc. Chem. Res.*, 2007, **40**, 1300–1308; (e) M. Zhao, Z. Yu, S. Yan and Y. Li, *Tetrahedron Lett.*, 2009, **50**, 4624–4628.
- 3 R. Malacea, R. Poli and E. Manoury, *Coord. Chem. Rev.*, 2010, **254**, 729–752.
- (a) F. Alonso, P. Riente, F. R. Reinoso, J. R. Martínez, A. S. Escibano and M. Yus, *J. Catal.*, 2008, **260**, 113–118; (b) F. Alonso, P. Riente, F. R. Reinoso, J. R. Martínez, A. S. Escibano and M. Yus, *ChemCatChem*, 2009, **1**, 75–77; (c) M. J. Gracia, J. M. Campelo, E. Losada, R. Luque, J. M. Marinas and A. A. Romero, *Org. Biomol. Chem.*, 2009, **7**, 4821–4824.
- 5 J. Q. Yu, H. C. Wu, C. Ramarao, J. B. Spencer and S. V. Ley, *Chem. Commun.*, 2003, 678–679.
- (a) K. Yamaguchi, T. Koike, M. Kotani, M. Matsushita, S. Shinachi and N. Mizuno, *Chem.–Eur. J.*, 2005, **11**, 6574–6582; (b) M. L. Kantam, B. P. C. Rao, B. M. Choudary and B. Sreedhar, *Adv. Synth. Catal.*, 2006, **348**, 1970–1976; (c) M. L. Kantam, R. S. Reddy, U. Pal, B. Sreedhar and S. Bhargava, *Adv. Synth. Catal.*, 2008, **350**, 2231–2235; (d) K. Yamaguchi, T. Koike, J. W. Kim, Y. Ogasawara and N. Mizuno, *Chem.–Eur. J.*, 2008, **14**, 11480–11487; (e) B. Baruwati, V. Polshettiwar and R. S. Varma, *Tetrahedron Lett.*, 2009, **50**, 1215–1218.
- (a) F. Z. Su, L. He, J. Ni, Y. Cao, H. Y. He and K. N. Fan, *Chem. Commun.*, 2008, 3531–3533; (b) L. He, J. Ni, L. C. Wang, F. J. Yu, Y. Cao, H. Y. He and K. N. Fan, *Chem.–Eur. J.*, 2009, **15**, 11833–11836.
- (a) M. J. Andrews and C. N. Pillai, *Indian J. Chem., Sect. B: Org. Chem. Incl. Med. Chem.*, 1978, **16**, 465–468; (b) R. C. Mebane and A. J. Mansfield, *Synth. Commun.*, 2005, **35**, 3083–3086; (c) R. C. Mebane, K. L. Holte and B. H. Gross, *Synth. Commun.*, 2007, **37**, 2787–2791.
- (a) F. Alonso, P. Riente and M. Yus, *Acc. Chem. Res.*, 2011, **44**, 379–391; (b) F. Alonso, P. Riente and M. Yus, *Tetrahedron*, 2008, **6**, 1847–1852.
- (a) G. P. Boldrini, D. Savoia, E. Tagliavini, C. Trombini and A. U. Ronchi, *J. Org. Chem.*, 1985, **50**, 3082–3086; (b) M. Kidwai, V. Bansal, A. Saxena, R. Shankar and S. Mozumdar, *Tetrahedron Lett.*, 2006, **47**, 4161–4165; (c) T. T. Upadhyay, S. P. Katdare, D. P. Sabde, V. Ramaswamy and A. Sudalai, *Chem. Commun.*, 1997, 1119–1120; (d) S. K. Mohapatra, S. U. Sonavane, R. V. Jayaram and P. Selvam, *Org. Lett.*, 2002, **4**, 4297–4300; (e) P. Selvam, S. K. Mohapatra, S. U. Sonavane and R. V. Jayaram, *Tetrahedron Lett.*, 2004, **45**, 2003–2007; (f) N. Neelakandeswari, G. Sangami, P. Emayavaramban, S. G. Babu, R. Karvembu and N. Dharmaraj, *J. Mol. Catal. A*, 2012, **356**, 90–99; (g) J. C. Park, H. J. Lee, J. Y. Kim, K. H. Park and H. Song, *J. Phys. Chem. C*, 2010, **114**, 6381–6388; (h) V. Polshettiwar, B. Baruwati and R. S. Varma, *Green Chem.*, 2009, **11**, 127–131.
- (a) P. Selvam, S. U. Sonavane, S. K. Mohapatra and R. V. Jayaram, *Adv. Synth. Catal.*, 2004, **346**, 542–544.
- (a) K. Yoshida, C. G. Arellano, R. Luque and P. L. Gai, *Appl. Catal., A*, 2010, **379**, 38–44; (b) T. Subramanian and K. Pitchumani, *Catal. Sci. Technol.*, 2012, **2**, 296–300.
- (a) J. R. Ruiz, C. Jiménez-Sanchidrián and J. M. Hidalgo, *Catal. Commun.*, 2007, **8**, 1036–1040; (b) R. Radhakrishnan, D. M. Do, S. Jaenicke, Y. Sasson and G. Chuah, *ACS Catal.*, 2011, **1**, 1631–1636.
- (a) Y. Zhu, S. Jaenicke and G. K. J. Chuah, *J. Catal.*, 2004, **227**, 1–10; (b) A. Corma, M. E. Domine and S. Valencia, *J. Catal.*, 2003, **215**, 294–304.
- 15 When the recovered catalyst was used in the second run without any pre-treatment, 8% yield of the corresponding alcohol was obtained.
- 16 P. F. Rossi, G. Busca, V. Lorenzelli, O. Saur and J. C. Lavalley, *Langmuir*, 1987, **3**, 52–58.