Journal of Catalysis 300 (2013) 242-250

Contents lists available at SciVerse ScienceDirect

Journal of Catalysis

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

Acceptor-free dehydrogenation of secondary alcohols by heterogeneous cooperative catalysis between Ni nanoparticles and acid-base sites of alumina supports

Ken-ichi Shimizu^{a,b,*}, Kenichi Kon^a, Katsuya Shimura^a, Siddiki S.M.A. Hakim^b

^a Catalysis Research Center, Hokkaido University, N-21, W-10, Sapporo 001-0021, Japan
^b Elements Strategy Initiative for Catalysts and Batteries, Kyoto University, Katsura, Kyoto 615-8520, Japan

ARTICLE INFO

Article history: Received 30 November 2012 Revised 8 January 2013 Accepted 9 January 2013

Keywords: Alcohols Alumina Cooperative catalysis Dehydrogenation Nickel

ABSTRACT

Nickel-nanoparticle-loaded θ -Al₂O₃ (Ni/ θ -Al₂O₃), prepared by H₂-reduction of NiO/ θ -Al₂O₃, acts as an effective and reusable heterogeneous catalyst for acceptor-free dehydrogenation of alcohols in a liquid phase. Among various supports, amphoteric supports (such as θ -Al₂O₃), having both acidic and basic sites, gave higher activity than acidic or basic supports. Among Ni/ θ -Al₂O₃ catalysts with different Ni particle sizes, turnover frequency (TOF) per surface Ni increases with decreasing Ni particle size. These results suggest that low-coordinated Ni⁰ sites and metal/support interfaces play important roles in the catalytic cycle. The reaction mechanism is investigated by in situ IR study combined with kinetic analysis (kinetic isotope effect), and the following mechanism is proposed: (1) reaction of an alcohol with Lewis acid (Al⁶⁺)-base (Al–O^{6–}) pair site of alumina yields an alkoxide on the Al⁸⁺ site and a proton on the Al–O^{6–} site, (2) C–H dissociation of the alkoxide by Ni⁰ site to form Ni–H and a ketone, and (3) protolysis of Ni–H by a neighboring proton to release H₂ gas. The proposed mechanism provides fundamental reasons for the higher activity of Ni on the acid–base bifunctional support (Al₂O₃) than on basic and acidic ones.

© 2013 Elsevier Inc. All rights reserved.

1. Introduction

Replacement of noble metal catalysts with cheap and abundant metals is a major goal of sustainable chemistry. Nickel (Ni), as a cheap element, is an ideal candidate if high activity and selectivity can be achieved. Despite the fact that Ni-containing solids, such as sponge Ni (Raney Ni), have been used as promoters or catalysts for hydrogenation of various compounds, advances in the field of heterogeneous non-noble metal-catalyzed organic synthesis are still in their infancy. Recently, Yus et al. [1] demonstrated that stoichiometric or substoichiometric amounts (20-100 mol%) of Ni nanoparticles (NPs) promote various types of hydrogen-transfer reactions, which are typically implemented by noble metal-based catalysts. Our ongoing interest in supported metal NP catalysis for dehydrogenation/hydrogenation reactions [2,3], combined with the pioneering studies [1], motivated us to investigate possibilities of supported Ni NPs as cheaper alternatives to the well-established noble metal catalysts in hydrogen-transfer-type reactions [4].

Oxidation of alcohols to carbonyl compounds is one of the most important topics in synthetic catalysis [5–8]. To achieve environ-

E-mail address: kshimizu@cat.hokudai.ac.jp (K.-i. Shimizu).

mental and economical acceptability, much effort has been devoted to developing heterogeneous catalysts based on noble metals (Pd [9], Ru [10,11], Pt [12], and Au [13,14]) for aerobic oxidation of alcohols. Non-noble metal-based heterogeneous catalysts also catalyze the aerobic oxidation of alcohols [5-7,15-20], but their efficiencies in terms of activity and substrate scope are generally lower than for the noble metal catalysts. For example, Nibased catalysts [15-20] reported so far are effective only for activated (aromatic) alcohols, but not for aliphatic alcohols, and their turnover numbers (TONs) are low (TON = 0.2-1.5). From the viewpoint of atom efficiency and safety of the reaction, oxidant-free catalytic dehydrogenation of alcohols to carbonyl compounds and molecular hydrogen is ideal. This process is also of current interest as a potential method for hydrogen production from biomass products [21,22]. Several systems for the dehydrogenative oxidation of alcohols using homogeneous Rh [23], Ru [24-29], and Ir [30–32] catalysts are reported, but most of them suffer from the requirement for acid or base additives, difficult catalyst synthesis and manipulation, difficulties in catalyst reuse, and high price. To overcome these problems, heterogeneous Ru [33-35], Ag [2,36], and Au [37-39] catalysts have recently been developed, but these systems require the use of noble metals. There are a few examples based on non-noble metals (Ni [40-42], Co [43], and Cu [44,45]), but they suffer from drawbacks such as high cat-





^{*} Corresponding author at: Catalysis Research Center, Hokkaido University, N-21, W-10, Sapporo 001-0021, Japan. Fax: +81 11 706 9163.

^{0021-9517/\$ -} see front matter © 2013 Elsevier Inc. All rights reserved. http://dx.doi.org/10.1016/j.jcat.2013.01.005

alyst loading, low yields of carbonyl compounds [40–42], limited scope [40–42,45], or high reaction temperature (200–350 °C) [42,43].

As for a catalyst design concept, it is notable that excellent organometallic catalysts for acceptor-free oxidation of alcohols are rationally designed by a concept of cooperative catalysis, where the metal center acts as a C-H activation site while a basic site in a ligand abstracts proton from a OH group [28-32,34]. For example, the Ru catalyst developed by Milstein possesses a cooperative basic site in the β position to the metal, which facilitates binding of the alcohol substrate to give an alkoxide intermediate [28]. Knowing that amphoteric metal oxides, such as alumina, have acid-base sites on the surface, we hypothesized that the alumina surface might show a similar cooperative effect. We report here that Niloaded alumina acts as an effective heterogeneous catalyst for the acceptor-free alcohol dehydrogenation of aliphatic secondary alcohols to ketones. Studies on structure-activity relationships will clarify that Ni⁰ species and acid-base sites on the support are indispensable for this catalytic system. Spectroscopic and kinetic studies will suggest a cooperative reaction mechanism of Ni⁰ species and the acid-base sites.

2. Experimental

2.1. General

Commercially available organic compounds (from Tokyo Chemical Industry or Kishida Chemical) were used without further purification. 2-Propanol-O-*d*, $(CH_3)_2$ CHOD with 98 atom% D, and 2propanol-2-*d*₁, $(CH_3)_2$ CDOH with 99.4 atom% D, were purchased from Aldrich. The GC (Shimadzu GC-14B) and GCMS (Shimadzu GCMS-QP2010) analyses were carried out using N₂ and He as the carrier gases, respectively, with an Ultra ALLOY capillary column UA⁺-5 (Frontier Laboratories Ltd.).

2.2. Catalyst preparation

 γ -Al₂O₃ (with surface area 124 m² g⁻¹), θ -Al₂O₃ (112 m² g⁻¹), and α -Al₂O₃ (17 m² g⁻¹) were prepared by calcination of γ -AlOOH (Catapal B Alumina purchased from Sasol) for 3 h at 900, 1000, and 1200 °C, respectively. MgO (JRC-MGO-3, 19 m² g⁻¹), TiO₂ (JRC-TIO4, 50 m² g⁻¹), and CeO₂ (JRC-CEO3, 81.4 m² g⁻¹) were supplied from the Catalysis Society of Japan. Hydroxides of Zr, Sn, Y, and La were prepared by hydrolysis of zirconium oxynitrate 2-hydrate, SnCl₄·6H₂O, or metal nitrates in distilled water by gradually adding an aqueous NH₄OH solution (1.0 mol dm⁻³), followed by filtration of precipitate, washing with distilled water three times, and drying at 100 °C for 12 h. Ca(OH)2 and Nb₂O₅·nH₂O (supplied by CBMM) were commercially supplied. CaO, Y₂O₃, La₂O₃, ZrO₂, Nb₂O₅, and SnO₂ were prepared by calcination of these hydroxides at 500 °C for 3 h.

NiO/ θ -Al₂O₃ (Ni loading = 5 wt.%) was prepared by an impregnation method; a mixture of θ -Al₂O₃ (18 g) and an aqueous solution of Ni(NO₃)₂·6H₂O (0.162 M, 100 cm³) were evaporated at 50 °C, followed by drying at 90 °C for 12 h, and calcination in air at 300 °C for 1 h. Before each catalytic experiment, Ni/ θ -Al₂O₃ was prepared by in situ prereduction in NiO/ θ -Al₂O₃ in a glass (Pyrex or quartz) tube under a flow of H₂ (20 cm³ min⁻¹) at a reduction temperature (*T*_{H2}) of 500 °C for 0.5 h. Ni/ θ -Al₂O₃ with different Ni loadings (5, 10, 20, 50 wt.%) and 5 wt.% Ni loaded on various supports (α -Al₂O₃, La₂O₃, Y₂O₃, CeO₂, ZrO₂, TiO₂, Nb₂O₅, SnO₂) were prepared in the same manner as Ni/ θ -Al₂O₃. CaO-, and MgO-supported Ni (5 wt.%) were prepared by the impregnation method, followed by drying at 90 °C for 12 h, and by in situ prereduction under H₂ at 500 °C. γ -Al₂O₃-supported metal catalysts, M/ γ -Al₂O₃

(M = Ni, Co, Cu, Ru, Pd, Rh, Ag), with metal loading of 5 wt.% were prepared by an impregnation method in a manner similar to that for Ni/ θ -Al₂O₃ using an aqueous solution of metal nitrates (for Ni, Co, Cu), RuCl₃, or an aqueous HNO₃ solution of Rh(NO₃)₃, Pd(NO₃)₂, or Pt(NH₃)₂(NO₃)₂. Au/ γ -Al₂O₃ (Au = 1 wt.%) was prepared by the deposition–precipitation method with HAuCl₄. Raney Ni (B113W, Ni > 90%) was supplied by Evonik Industries.

2.3. Characterization

Transmission electron microscopy (TEM) measurements were carried out using a JEOL JEM-2100F TEM operated at 200 kV. XRD patterns of the powdered catalysts were recorded with a Rigaku MiniFlex II/AP diffractometer with Cu Kα radiation. Temperatureprogrammed reduction under H₂ (H₂ TPR) was carried out with BELCAT (BELL Japan Inc.). The sample, NiO/0-Al₂O₃ (Ni loading = 5 wt.%, 20 mg), mounted in a quartz tube, was heated with a temperature ramp-rate of 5 °C min⁻¹ in a flow of 5% H_2/Ar $(20 \text{ cm}^3 \text{ min}^{-1})$. The effluent gas was passed through a trap containing MS4A to remove water and then through the thermal conductivity detector. The amount of H₂ consumed during the experiment was detected by a thermal conductivity detector. Temperature-programmed desorption (TPD) experiments were carried out using BELCAT. Prior to each experiment, catalyst (0.1 g) was heated in a flow of He (20 cm³ min⁻¹) at 500 °C for 0.5 h, followed by cooling to 40 °C under He flow. Then, the catalyst was exposed to a flow of 100% CO₂ or 5% NH₃/He for 10 min. After being purged in He for 0.5 h, the catalyst was heated linearly at 10 °C min⁻¹ to 900 °C in a flow of He, and CO₂ (m/e = 44) and NH₃ (m/e = 16 and 17) in the outlet gas were analyzed by the mass spectrometer (BEL-MASS). The BET surface area was obtained by measuring N₂ adsorption at -196 °C by BELCAT. The results are summarized in Table 1.

2.4. Typical procedures of catalytic reactions

Typically, Ni/ θ -Al₂O₃ (Ni loading = 5 wt.%) prereduced in H₂ at 500 °C for 0.5 h was used as a standard catalyst. After the prereduction, we carried out catalytic tests using a batch-type reactor without exposing the catalyst to air. A mixture of *o*-xylene (1 g), alcohol (1 mmol), and *n*-dodecane (0.5 mmol) was injected into the prereduced catalyst inside a reactor (cylindrical glass tube) through a septum inlet, followed by filling with N₂. Then, the resulting mixture was stirred under reflux conditions; the heating temperature was 155 °C, and the reaction temperature was ca. 144 °C.

Table 1	
List of metal oxide-supported Ni (5wt%)	catalyst

Catalysts	$\frac{S_{\text{BET}}^{a}}{(m^2 \text{g}^{-1})}$	Acid amount ^b (mmol g ⁻¹)	Base amount ^c (mmol g ⁻¹)	Acid density ^d (µmol m ⁻²)	Base density ^d (µmol m ⁻²)
Ni/CaO	8.0	<0.001	0.176	0	22
Ni/MgO	15	0.008	0.180	0.53	12
Ni/La ₂ O ₃	15	0.029	0.182	1.9	12
Ni/Y ₂ O ₃	12	0.023	0.171	1.9	14
Ni/CeO ₂	69	0.207	0.484	3.0	7.0
$Ni/\theta-Al_2O_3$	70	0.211	0.348	3.0	5.0
Ni/ZrO ₂	74	0.287	0.234	3.9	3.2
Ni/TiO ₂	45	0.083	0.022	1.8	0.49
Ni/Nb ₂ O ₅	40	0.150	0.021	3.7	0.53
Ni/SnO ₂	25	0.029	0.015	1.2	0.60
$Ni/\alpha - Al_2O_3$	4.2	0.008	0.002	1.9	0.48
Ni/γ - Al_2O_3	122	0.287	0.234	2.4	1.9

 $^a\,$ Specific surface area of the catalyst determined by N_2 adsorption at $-196\,^\circ C.$

^b Amount of surface acidic site determined by TPD of NH₃.

^c Amount of surface basic site determined by TPD of CO₂.

^d Density of surface acidic or basic site (from the surface area and TPD results).

Conversion and yields of products were determined by GC using *n*-dodecane as an internal standard. Progress of the reaction was monitored by GC analysis of aliquots (ca. 0.05 g). The initial rate of reaction was measured under the conditions where the conversion was below 40%. The products were identified by GC-MS equipped with the same column as GC and by comparison with commercially pure products. GC analysis of the gas-phase product (H₂) was carried out by the mass spectrometer (BELMASS).

2.5. In situ IR

In situ IR spectra were recorded on a JASCO FT/IR-620 equipped with a quartz IR cell connected to a conventional flow reaction system. The sample was pressed into a 50-mg self-supporting wafer and mounted into the quartz IR cell with CaF₂ windows. Spectra were measured by accumulating 10 scans at a resolution of 4 cm⁻¹. A reference spectrum of the catalyst wafer in He taken at the measurement temperature was subtracted from each spectrum. Prior to each experiment, the catalyst disk was heated in 10% H₂/He flow (100 cm³ min⁻¹) at 500 °C for 0.5 h, followed by cooling to 150 °C in H₂/He 60 °C and to 60 °C in He.

3. Results and discussion

3.1. Catalyst optimization

Table 2 shows the influence of various catalyst parameters on the catalytic activity for dehydrogenation of cyclododecanol 1a to cyclododecanone 2a under the same reaction conditions (under N_2 in reflux conditions for 1 h). First, we carried out catalytic tests

Table 2

Dehydrogenation of cyclododecanol.^a

Denyulogen	Denydrogenation of cyclododecanol.					
	1.0 mmol ^{1a}	cat.(1 mol%) <i>o</i> -xylene (1 g 144 ^o C, 1 h		+ H ₂		
Entry	Catalyst	Conv. (%)	Yield (%)	$V_0^{\rm b}$ (mol mol _{Ni} h ⁻¹)		
1 ^c	NiO/0-Al ₂ O ₃	0	0	0		
2	Ni/0-Al ₂ O ₃	45	45	64		
3	$Ni/\gamma - Al_2O_3$	43	43	61		
4	$Ni/\alpha - Al_2O_3$	7	7	7		
5 ^d	θ -Al ₂ O ₃	0	0	-		
6 ^e	Ni powder	4.3	1.7	0.33		
7 ^e	Raney Ni	35	32	6.0		
8	Ni/CaO	1.1	1.1	1.1		
9	Ni/MgO	1.6	1.6	1.6		
10	Ni/La ₂ O ₃	2.9	2.9	2.9		
11	Ni/Y ₂ O ₃	15	15	15		
12	Ni/CeO ₂	35	35	35		
13	Ni/ZrO ₂	16	16	16		
14	Ni/TiO ₂	8.0	7.0	7.0		
15	Ni/Nb ₂ O ₅	1.6	1.6	1.6		
18	Ni/SnO ₂	2.0	1.3	1.3		
17	$Co/\gamma - Al_2O_3$	30	30	30		
18	$Cu/\gamma - Al_2O_3$	39	34	45		
19	$Ru/\gamma - Al_2O_3$	4.6	4.6	4.6		
20	$Rh/\gamma - Al_2O_3$	3.1	2.8	2.7		
21	$Pd/\gamma - Al_2O_3$	2.5	2.5	2.5		
22	$Ag/\gamma - Al_2O_3$	3.0	3.0	3.0		

^a Conversion of 1a and yield of 2a were determined by GC.

12

 b Initial formation rate of cyclododecanone 2a per total Ni atoms (mol of 2a mol_{\text{Ni}}\,h^{-1}).

8.6

8.6

^c Catalysts were not prereduced.

 $Au/\gamma - Al_2O_3$

^d θ -Al₂O₃ = 50 mg.

23°

e 5 mol% of Ni.

Table 3

Preparation conditions, Ni particle size, and catalytic activity of Ni/0-Al₂O₃ catalysts.

Ni loading (wt.%)	Т _{Н2} (°С)	D ^b (nm)	Dv ^c (nm)	V_0^{d} (mol mol _{Ni} h ⁻¹)	TOF^{e} (h^{-1})
5	500	6.1	7.6	53	346
10	500	6.5	9.0	35	267
20	500	8.8	9.6	25	203
50	500	12.2	13.5	6	67
50	800	15.6	16.3	5	68

^a Temperatures of prereduction in H₂.

^b Mean diameter of Ni particles estimated by TEM.

^c Volume-area mean diameter of Ni particles estimated by TEM.

 d Initial formation rate of cyclododecanone 2a per total Ni atoms (mol of 2a mol_{Ni}\,h^{-1}).

^e TOF per surface Ni atoms calculated from V_0 and D_v .

for a series of metal oxide (MO_x)-supported Ni catalysts with the same loading (5 wt.%). Alumina with different crystal phases was tested as a support of Ni (entries 2-4). The alumina with spinel structure (θ -Al₂O₃ and γ -Al₂O₃) gave higher yields than that with corundum structure (α -Al₂O₃), and θ -Al₂O₃ gave the highest yield (45%). Among various support materials (entries 2, 8-18), Ni/ θ -Al₂O₃ showed the highest yield. Use of large amounts (5 mol%) of conventional Ni catalysts, Raney Ni, and Ni powder (entries 6, 7) resulted in a lower yield of 2a than Ni/ θ -Al₂O₃. NiO-loaded θ - Al_2O_3 (NiO/ θ - Al_2O_3) and θ - Al_2O_3 were inactive (entries 1, 5). To optimize the metal content in Ni/0-Al₂O₃, catalysts with different Ni content (5, 10, 20, 50 wt.%) were tested under the reflux condition, and the initial formation rate of 2a was measured under the condition where the conversion of 1a was below 40% (Table 3). It was found that the metal content of 5 wt.% gives the highest activity. The effect of the prereduction temperature (300-600 °C) of 5 wt.% Ni/ θ -Al₂O₃ was also tested, and the results showed that a reduction temperature of 500 or 600 °C was optimum (Table S1 in the supporting information). Among various metal (Ni, Co, Cu, Ru, Rh, Pd, Ag, Au)-loaded γ -Al₂O₃ catalysts (Table 1, entries 2, 17–23), Ni/ γ -Al₂O₃ showed the highest yield of 2a.

3.2. Catalytic performance of Ni/ θ -Al₂O₃

The catalyst optimization results show that the 5 wt.% Ni/0-Al₂O₃ catalyst prereduced at 500 °C is the best catalyst. With this catalyst, we studied reusability and the scope of the present system (Table 4). The dehydrogenation of cyclooctanol by Ni/ θ -Al₂O₃ (1 mol%) for 3 h resulted in a >99% yield of cyclooctanone (entry 1). After 0.5 h of the reaction, the yields of gas-phase H_2 (27%) and cyclooctanone (30%) were nearly identical to the alcohol conversion (30%), indicating that H₂ was generated quantitatively. The reaction was completely terminated by removal of the catalyst from the reaction mixture after 0.5 h; further heating of the filtrate for 2.5 h under reflux conditions did not increase the yield. ICP analysis of the filtrate confirmed that the content of Ni in the solution was below the detection limit. These results confirm that the reaction is attributable to the heterogeneous catalysis of Ni/0-Al₂O₃. After the reaction, the catalyst was easily separated from the reaction mixture by centrifugation. The filtered catalyst was washed with acetone, followed by drying in air at 90 °C for 1 h, and by reducing in H₂ at 500 °C for 0.5 h. As shown in Table 4 (entry 1), the recovered catalyst was reused at least four times [46]. In the low-catalyst-loading (Ni = 0.02 mol%) and solvent-free conditions at 180 °C, the catalyst showed 81% yield of the product after 47 h, corresponding to the TON of 4050 and turnover frequency (TOF) of 86 h^{-1} (Scheme 1). The TON is three orders of magnitude higher than those of previous Ni-based catalysts (TON = 0.2-1.5) [15–20] for the liquid-phase aerobic oxidation of alcohols.

Table 4

Dehydrogenation of various alcohols by Ni/0-Al2O3.

OH

$$R_1 R_2$$
 $cat.(Ni: 0.01 mmol)$
1 mmol
 o -xylene (1 g), 144 \circ C $R_1 R_2 + H_2$

Entry	Alcohol	<i>t</i> (h)	Conv. (%)	Yield (%)
1	Cyclooctaol	3	99, 99,ª, 94 ^b , 94, ^c , 95 ^d	99, 98ª, 94 ^b , 94 ^c , 92 ^d
2	Cycloheptanol	24	100	75
3	Cyclohexanol	72	94	74
4	Cyclopentadecanol	24	86	86
5	Cyclododecanol	8	91	91
6	exo-Norborneol	24	96	93
7	4-Octanol	24	96	91
8	2-Octanol	12	86	82
9	5-Nonanol	24	97	97

^a First reuse.

^b Second reuse.

^c Third reuse.

^d Fourth reuse.



Scheme 1. A gram scale dehydrogenation of cyclooctanol by Ni/θ -Al₂O₃ under neat conditions under N₂ flow.

The scope of the Ni/0-Al2O3-catalyzed dehydrogenation of various alcohols is shown in Table 4. In the presence of Ni/θ -Al₂O₃ (1 mol%), various aliphatic secondary alcohols were selectively converted to the corresponding ketones with good to high yield (74-93%). Because H₂ escapes from the reaction mixture into the gas phase, the overall endothermic dehydrogenation reaction is driven to the product side, leading to a high conversion of alcohols to ketones. For the reaction of a primary alcohol (1-octanol), yields of the corresponding aldehydes were low (2%). It should be noted that the previous examples of Ni-based heterogeneous catalysts for the aerobic alcohol oxidation were effective for activated (aromatic) alcohols but not for less activated aliphatic alcohols [15-20]. Considering that previous Ni catalysts for the acceptor-free dehydrogenation of alcohols suffer from high reaction temperature (200-350 °C) [42], low yields of ketones (<70%) [41,42], and limited scope [41,42], our result represents the first successful example of Ni-catalyzed dehydrogenation of various alcohols. The catalytic activity of Ni/0-Al₂O₃ for dehydrogenation of alcohols is higher than that of Ag/Al₂O₃, reported in our previous study [2]. For the dehydrogenation of cyclododecanol, as an example, Ni/0- Al_2O_3 shows a TOF of 11 h⁻¹, which is five times higher than that of Ag/Al_2O_3 (TOF = 2.0 h⁻¹) [2].

3.3. Structure-activity relationship

Adopting the dehydrogenation of cyclododecanol 1a to cyclododecanone 2a by Ni/ θ -Al₂O₃ as a model reaction, we studied the structure–activity relationship. First, we studied the effect of Ni oxidation states on the activity. NiO/ θ -Al₂O₃, as an inactive precursor, was reduced in a flow of H₂ at various reduction temperatures $(T_{H2} = 300, 400, 500, 600 \,^{\circ}C)$, and the fraction of metallic Ni⁰ in each catalyst (Table S1 in the supporting information) was estimated by H₂ TPR (Fig. S1). Fig. 1 shows the formation rate of cyclododecanone 2a per total moles of Ni as a function of the fraction of metallic Ni⁰. It is clear that the activity increases with the fraction of metallic Ni⁰, which indicates that the metallic Ni⁰ is the active species.

Next, we discuss the effect of Ni metal particle size. As shown in Table 2, a series of Ni/ θ -Al₂O₃ catalysts with different particle sizes were prepared by changing the Ni loading and reduction temperature, and the initial rate for the formation rate of 2a was determined. The XRD patterns of these Ni/ θ -Al₂O₃ catalysts are shown in Fig. S2. A sharp line at 51.9° due to Ni metal was observed in the patterns of the high-Ni-loading (20, 50 wt.%) catalysts. A significantly broad and weak line due to Ni metal was observed in the patterns of the 5 and 10 wt.% Ni catalysts. When this is combined with the H₂ TPR result, it can be concluded that dominant Ni species in these catalysts are Ni metal particles. TEM analysis of Ni/ θ -Al₂O₃ catalysts (Ni = 5, 10, 20, 50 wt.%) showed spherical or semispherical Ni particles. The particle size distributions and the mean diameter of Ni particles (*D*) are shown in Fig. S3 and Table 3,



Fig. 1. Formation rate of cyclododecanone per total mole of Ni versus the fraction of metallic Ni⁰ (from H₂ TPR) for 5 wt.% Ni/ θ -Al₂O₃ catalysts reduced under H₂ at various temperatures.

respectively. It is known that the mean particle diameter estimated from the number of surface atoms on the assumption of spherical particles agrees with a volume–area mean diameter (D_V) measured by TEM [47]. Adopting this model, the number of the surface Ni atoms was estimated using volume–area mean diameter. Using the number of surface Ni atoms and the initial rates, the TOF per surface Ni atom was estimated (Table 3). As shown in Fig. 2, the TOF per surface Ni atom decreases with the mean diameter of Ni particles. Considering that the fraction of Ni atoms at coordinatively unsaturated sites and metal/support perimeter sites decreases with the particle size, the results suggest that the present catalytic system requires Ni⁰ species located at coordinatively unsaturated sites and metal/support perimeter sites.

If the metal/support perimeter sites play an important role, the activity should depend strongly on the type of support material. Here, we discuss the effect of the support. As listed in Table 1. we prepared a series of metal oxide-supported Ni catalysts with the same Ni content (5 wt.%) and the same reduction temperature (500 °C). Basic (MgO, CaO), amphoteric (θ-Al₂O₃, Y₂O₃, La₂O₃, CeO₂, ZrO₂), and relatively acidic (TiO₂, Nb₂O₅, SnO₂) supports were selected according to well-known classifications of the acid-base character of metal oxides [48]. The initial rate of the reaction is plotted in Fig. 3 as a function of the electronegativity of the support metal oxide, which is generally used as a parameter of acidity of metal oxides [49]. The rate of dehydrogenation of 2-octanol 1b to 2-octanone 2b by Ni/0-Al₂O₃ (Table S2) was also determined and shown in Fig. 3. Clearly, volcano-type relationships between the catalytic activity of the support and the electronegativity of the support are obtained. Among the supports with basic to amphoteric nature (CaO $-\theta$ -Al₂O₃), the activity increases with the electronegativity (acidity) of the support oxide, while acidic support result in lower activity than amphoteric supports. As listed in Table 1, densities of surface acidic and basic site on Ni-loaded catalvst were estimated based on the surface area of the catalyst and the number of desorbed NH₃ and CO₂ during NH₃ TPD and CO₂ TPD experiments. In Fig. 3, the densities of acidic and basic site as experimental indexes of the acid-base character of the catalyst are plotted versus the support electronegativity. For the supports with basic to amphoteric nature (CaO $\sim \theta$ -Al₂O₃), the increase in electronegativity generally results in a decrease in the density of the basic sites and an increase in the acid site density. The supports with electronegativity higher than 2.5 (TiO₂ \sim SnO₂) show negligible value of basic site density. Comparison of the trends observed



Fig. 2. Formation rate of cyclododecanone per total mole of Ni as a function of average Ni particle size in Ni/θ -Al₂O₃ (from Table 3).



Fig. 3. Reaction rates per total mole of Ni for the dehydrogenation reactions of (\bigcirc) cyclododecanol and (\diamondsuit) 2-octanol and the surface densities of basic (\blacktriangle) and acidic (∇) sites as a function of the electronegativity of the support metal oxide.

in acid–base character with those found in the catalytic activity allows us to conclude that the co-presence of acidic and basic sites on the surface of support oxides is indispensable for the Nicatalyzed dehydrogenation of alcohols.

To verify this hypothesis, we studied the poisoning effects of acidic or basic additives in the reaction mixture on the activity of Ni/ θ -Al₂O₃ for the dehydrogenation of 1a. As shown in Fig. 4, the presence of catalytic amounts of acidic (acetic acid) and basic (pyridine) additives decreased the reaction rate. It is established that adsorption of acetic acid on Al₂O₃ results in the formation of the acetate ion at the acid–base pair site (Al⁸⁺ $-O^{8-}$ site) [50], while pyridine adsorbs on the surface Lewis acid site (exposed Al cation) of Al₂O₃ [51]. Therefore, the result of the poisoning experiment indicates that the acid–base pair site and the surface Lewis acid site are necessary for this reaction.

3.4. Reaction mechanism

To study the reaction mechanism, we studied in situ IR experiments at 60 °C (Fig. 5). Fig. 5 shows the spectra of adsorbed species



Fig. 4. Formation rate of cyclododecanone over Ni/0-Al₂O₃ per total moles of Ni as a function of the concentration of pyridine and acetic acid.

formed from the adsorption of 2-propanol-O-d, (CH₃)₂CHOD, on θ-Al₂O₃ preheated in He at 500 °C for 0.5 h. In the initial spectrum (t = 60 s), bands due to 2-propoxide groups [2,52] are predominant: 2970 cm^{-1} (methyl asymmetric C–H stretching), 2940 cm⁻¹ (methyl asymmetric C–H stretching), 2874 cm⁻¹ (coupling of α -C—H stretching and methyl symmetric C—H stretching), 2722 cm⁻¹ (α -C–H stretching), 1465 cm⁻¹ (methyl asymmetric deformation), 1376 cm⁻¹ (methyl symmetric deformation), 1328 cm⁻¹ (α -C–H deformation), and 1166 and 1130 cm⁻¹ (C-O/C-C coupled stretching). Broad and multiple bands in the range 2300–2750 cm⁻¹ due to Al–OD groups are also observed. The broad feature due to the OD stretching vibration indicates the acidic (protonic) nature of the Al-OD groups. The band due to OH deformation of undissociated 2-propanol (1280 cm⁻¹) is hardly observed. These results indicate the presence of aluminum alkoxide, (CH₃)₂CH–OAl, and acidic Al–OD groups on the alumina surface and the absence of non-dissociatively adsorbed 2-propanol. Intensities of the bands due to (CH₃)₂CH-OAl and Al-OD species gradually decreased with time in a flow of He, but these bands still remained after 600 s, which indicates that these species were relatively stable. The following surface reaction,

$$(CH_3)_2CH - OD + Al^{\delta+} + Al - O^{\delta-} \rightarrow (CH_3)_2CH - OAl + Al - OD$$
(1)



Fig. 5. IR spectra of adsorbed species on θ -Al₂O₃ as a function of time in a flow of He at 60 °C. At *t* = 0 s, (CH₃)₂CHOD (0.5 mmol g⁻¹) was introduced into the sample.

should account for the experimental result: the reaction of 2-propanol with Al–O^{δ –} group (basic site on alumina) results in the formation of 2-propoxide coordinated to the unsaturated Al^{δ +} site (Lewis acid site) and an Al–OD group.

The same IR experiment was conducted using Ni/0-Al₂O₃ prereduced in H₂ at 500 °C for 0.5 h (Fig. 6A). The bands due to (CH₃)₂CH-OAl and Al-OD species were also observed for Ni/0-Al₂O₃. It is noteworthy that band positions for θ -Al₂O₃ and Ni/ θ -Al₂O₃ are exactly the same, indicating that 2-proposide is not adsorbed on the Ni site but on the support surface. Fig. 6B shows the height of the bands due to 2-propoxide, adsorbed acetone, and Al-OD species as a function of time in a flow of He. After fast formation of 2-propoxide species (t = 60 s), intensity of the bands due to the 2-propoxide species gradually decreased, and a new band at 1700 cm^{-1} due to C=O stretching of adsorbed acetone appeared and its intensity increased with time. The same IR results were observed for the reaction of 2-propanol. $(CH_3)_2$ CHOH, on Ni/ θ -Al₂O₃ (Fig. 7A). These results suggest that 2-propoxide undergoes C–H cleavage, resulting in the formation of acetone:

$$R_2CH - OAl + Ni^0 \rightarrow (CH_3)_2C = O + Ni - H + Al$$
(2)

Note that 2-propoxide species on Ni-free alumina did not convert to acetone (Fig. 5). Thus, metallic Ni is necessary in the C—H dissociation step. The kinetic curve in Fig. 6B clearly shows that the formation rate of 2-propoxide is higher than its consumption rate, which indicates that step (1) is faster than step (2).

The intensity of the band due to Al–OD groups (2300–2750 cm⁻¹) decreased with time, indicating the consumption of the acidic Al–OD groups. The following pathway should account for this result: protolysis of Ni–H^{δ -} species with the protonic D^{δ +} species in an adjacent Al–OD group would release dihydrogen (HD) accompanied by the regeneration of the Ni⁰ site and the basic Al–O^{δ -} site of alumina:

$$Ni - H + Al - OD \rightarrow HD + Ni^{0} + Al - O^{\delta^{-}}$$
(3)

Fig. 7B shows IR spectra of adsorbed species formed by the reaction of Ni/ θ -Al₂O₃ with 2-propanol-2- d_1 (α -deuterized 2-propanol, (CH₃)₂CDOH). Bands at 2970 cm⁻¹(methyl asymmetric C—H stretching), 2940 cm⁻¹ (methyl asymmetric C—H stretching), 2870 cm⁻¹ (methyl symmetric C—H stretching), 2104 cm⁻¹ (α -C—D stretching), 1465 cm⁻¹ (methyl asymmetric deformation), 1376 cm⁻¹ (methyl symmetric deformation), and 1190 cm⁻¹ (C—O/C—C coupled stretching) were assigned to α -deuterized 2-



Fig. 6. (A) IR spectra of adsorbed species on Ni/ θ -Al₂O₃ and (B) height of the bands due to (\bigcirc) 2-propoxide on the support (1130 cm⁻¹), (\bullet) adsorbed acetone (1700 cm⁻¹), and (\triangle) Al–OD group (2570 cm⁻¹) as a function of time in a flow of He at 60 °C. At *t* = 0 s, (CH₃)₂CHOD (0.5 mmol g⁻¹) was introduced into the sample.



Fig. 7. IR spectra of adsorbed species on Ni/0-Al₂O₃ under He flowing at 60 °C. At t = 0 s, 0.5 mmol g⁻¹ of (A) (CH₃)₂CHOH or (B) (CH₃)₂CDOH was introduced into the sample.



Fig. 8. First-order plots for the decomposition of the surface 2-propoxide species on Ni/ θ -Al₂O₃ at 60 °C. Rate constants estimated from the changes in the area of the IR band in the range 1080–1210 cm⁻¹ for (CH₃)₂CHOH (\bigcirc) and 1100–1250 cm⁻¹ for (CH₃)₂CDOH (\blacktriangle) were 3.4 × 10⁻³ s⁻¹ and 1.7 × 10⁻³ s⁻¹, respectively.



Fig. 9. A possible mechanism for the dehydrogenation of alcohols by Ni/0-Al₂O₃.

propoxide groups on alumina, $(CH_3)_2CD$ —OAI [2]. A weak band at 2174 cm⁻¹ may be assigned to α -C—D stretching of a different type of 2-propoxide. The band at 2104 cm⁻¹ due to the C—D bond of $(CH_3)_2CD$ —OAI species decreased with time, and a new band due to adsorbed acetone (1700 cm⁻¹) increased. This is direct evidence of Ni-catalyzed C—D bond dissociation of the $(CH_3)_2CD$ —OAI species (Eq. (2)).

Kinetic analysis of the conversion of the 2-propoxide groups was undertaken using time-resolved IR data (Fig. 7). The relative amounts of (CH₃)₂CH–OAl and (CH₃)₂CD–OAl species were estimated from the changes in the area of the IR band in the ranges $1080-1210 \text{ cm}^{-1}$ and $1100-1250 \text{ cm}^{-1}$, respectively, because these bands had the least overlap with other bands. As shown in Fig. 8, the first-order plots of the 2-proposide group during its conversion to acetone gave fairly good straight lines. The first-order rate constants of 2-propoxide consumption were estimated to be 3.4×10^{-3} and $1.7 \times 10^{-3} \text{ s}^{-1}$ for $(CH_3)_2$ CH–OAl and (CH₃)₂CD–OAl species, respectively. The kinetic isotope effect $(k_{\rm H}/k_{\rm D})$ at 60 °C was estimated to be 2.0, corresponding to the difference in the activation energies of $1.9 \text{ kJ} \text{ mol}^{-1}$. This value is lower than the zero-point energy difference $(3.7 \text{ kJ mol}^{-1})$ in α -C-H (2722 cm⁻¹) and α -C-D (2104 cm⁻¹) in the IR spectra. This indicates that the rate-determining step of 2-propoxide conversion to acetone is the cleavage of the α -C–H bond, but other kinetically relevant steps may also exist.

Based on the mechanistic experiments on the dehydrogenation of alcohols by Ni/θ -Al₂O₃, a reaction mechanism is presented in Fig. 9. Initially, a basic Al– $O^{\delta-}$ group of alumina abstracts a proton from alcohol to afford an alkoxide group on an adjacent Al^{δ^+} site (Lewis acid site) and a proton on the Al– $O^{\delta-}$ site (Al– $OH^{\delta+}$). An alkoxide at the interface between the Ni NP and alumina undergoes hydride abstraction to yield hydride species on Ni (Ni-H) and acetone as the rate-determining step. Then, the Ni-H species undergoes protolysis by a neighboring Al–OH^{δ^+} site to release H₂ gas, accompanied by the regeneration of the Ni⁰ site and the basic Al– $O^{\delta-}$ site of alumina. On the basis of the proposed mechanism, the strong effect of support acid-base nature on the Ni-catalyzed alcohol dehydrogenation (Fig. 3) can be explained as follows. The abstraction of protons in alcohol by the metal oxide surface requires basic sites. Thus, on the Ni-loaded acidic oxides (Nb₂O₅, SnO₂), dissociative adsorption of 2-propanol is limited by the weak nucleophilic character of the metal oxide surface. On the other hand, the protonic (electrophilic) nature of the OH groups on the basic oxides (CaO, MgO) is weaker than that on the amphoteric oxide (alumina), and the protolysis of Ni– $H^{\delta-}$ species with an adjacent OH group is slow.

4. Conclusions

Alumina-supported Ni metal NP was found to act as a heterogeneous and reusable catalyst for the acceptor-free oxidation of secondary alcohols. Among various supports, amphoteric supports (such as alumina) having both acidic and basic sites gave higher activity than acidic and basic supports. The TOF per surface Ni increases with decreasing Ni particle size. These results suggest that low-coordinated Ni⁰ sites and the metal/support interface play important roles in the catalytic cycle. On the basis of in situ IR and kinetic experiments, the following mechanism is proposed: (1) reaction of an alcohol with the Lewis acid (Al^{δ^+}) -base $(Al-O^{\delta^-})$ pair site of alumina yields an alkoxide on the AI^{δ^+} site and a proton on the Al– $O^{\delta-}$ site, (2) C–H dissociation of the alkoxide by Ni⁰ site to form Ni-H and ketone, (3) protolysis of Ni-H by a neighboring proton to release H₂ gas, accompanied by the regenerations of the Ni^0 site and the basic Al– $O^{\delta-}$ site of alumina. Fundamental information in this study will be useful as a design concept for noble metal-free and ligand-free catalysts for hydrogen-transfer-type reactions.

Acknowledgments

This work was supported by a "Grant for Advanced Industrial Technology Development" in 2011 from the New Energy and Industrial Technology Development Organization (NEDO) and a MEXT program "Elements Strategy Initiative to Form Core Research Center" (since 2012), Japan. The authors thank Naomichi Imaiida (Nagoya University) for his contributions in the preliminary experiments.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcat.2013.01.005.

References

- [1] F. Alonso, P. Riente, M. Yus, Acc. Chem. Res. 44 (2011) 379-391.
- [2] K. Shimizu, K. Sugino, K. Sawabe, A. Satsuma, Chem. Eur. J. 15 (2009) 2341– 2351.
- [3] K. Shimizu, K. Sawabe, A. Satsuma, Catal. Sci. Technol. 1 (2011) 331-341.
- [4] K. Shimura, K. Shimizu, Green Chem. 14 (2012) 2983–2985.
- [5] C. Parmeggiani, F. Cardona, Green Chem. 14 (2012) 547-564
- [6] T. Mallat, A. Baiker, Chem. Rev. 104 (2004) 3037-3058.
- [7] T. Matsumoto, M. Ueno, N. Wang, S. Kobayashi, Chem. Asian J. 3 (2008) 196– 214.
- [8] N. Dimitratos, J.A. Lopez-Sanchez, G.J. Hutchings, Chem. Sci. 3 (2012) 20-44.
- [9] K. Mori, K. Yamaguchi, T. Hara, T. Mizugaki, K. Ebitani, K. Kaneda, J. Am. Chem. Soc. 124 (2002) 11572–11573.
- [10] K. Yamaguchi, N. Mizuno, Angew. Chem. Int. Ed. 41 (2002) 4538–4542.
- [11] S. Mori, M. Takubo, K. Makida, T. Yanase, S. Aoyagi, T. Maegawa, Y. Monguchi, H. Sajiki, Chem. Commun. 45 (2009) 5159–5161.
- [12] Y.M.A. Yamada, T. Arakawa, H. Hocke, Y. Uozumi, Angew. Chem. Int. Ed. 46 (2007) 704–706.
- [13] A. Abad, A. Corma, H. Garcia, Chem. Eur. J. 14 (2008) 212-222.
- [14] H. Tsunoyama, N. Ichikuni, H. Sakurai, T. Tsukuda, J. Am. Chem. Soc. 131 (2009) 7086–7093.
- [15] B.M. Choudary, M.L. Kantam, A. Rahman, C.V. Reddy, K.K. Rao, Angew. Chem. Int. Ed. 40 (2001) 763–766.
- [16] C. Li, H. Kawada, X. Sun, H. Xu, Y. Yoneyama, N. Tsubaki, ChemCatChem 3 (2011) 684–689.
- [17] V.R. Choudhary, P.A. Chaudhari, V.S. Narkhede, Catal. Commun. 4 (2003) 171– 175.
- [18] H. Ji, T. Wang, M. Zhang, Q. Chen, X. Gao, React. Kinet. Catal. Lett. 90 (2007) 251–257.
- [19] T. Kawabata, Y. Shinozuka, Y. Ohishi, T. Shishido, K. Takaki, K. Takehira, J. Mol. Catal. A 236 (2005) 206–215.
- [20] H. Ji, T. Wang, M. Zhang, Y. She, L. Wang, Appl. Catal. A 282 (2005) 25-30.
- [21] R.J. Angelici, ACS Catal. 1 (2011) 772-776.
- [22] T.C. Johnson, D.J. Morris, M. Wills, Chem. Soc. Rev. 39 (2010) 81-88.
- [23] S. Shinoda, T. Kojima, Y. Saito, J. Mol. Catal. 18 (1983) 99–104.
- [24] G.B.W.L. Ligthart, R.H. Meijer, M.P.J. Donners, J. Meuldijk, J.A.J.M. Vekemans, L.A. Hulshof, Tetrahedron Lett. 44 (2003) 1507–1509.
- [25] G.R.A. Adair, J.M.J. Williams, Tetrahedron Lett. 46 (2005) 8233-8235.
- [26] H. Junge, M. Beller, Tetrahedron Lett. 46 (2005) 1031-1034.
- [27] S. Shahane, C. Fischmeister, C. Bruneau, Catal. Sci. Technol. 2 (2012) 1425–1428.
- [28] J. Zhang, M. Gandelman, L.J.W. Shimon, H. Rozenberg, D. Milstein, Organometallics 23 (2004) 4026–4033.
- [29] M. Nielsen, A. Kammer, D. Cozzula, H. Junge, S. Gladiali, M. Beller, Angew. Chem. Int. Ed. 50 (2011) 9593–9597.
- [30] K.-I. Fujita, N. Tanino, R. Yamaguchi, Org. Lett. 9 (2007) 109-111.
- [31] K.-I. Fujita, T. Yoshida, Y. Imori, R. Yamaguchi, Org. Lett. 13 (2011) 2278-2281.
- [32] S. Musa, I. Shaposhnikov, S. Cohen, D. Gelman, Angew. Chem. Int. Ed. 50 (2011) 3533–3537.
- [33] M. Yamashita, K. Kawamura, M. Suzuki, Y. Saito, Bull. Chem. Soc. Jpn. 64 (1991) 272–278.
- [34] J.H. Choi, N. Kim, Y.J. Shin, J.H. Park, J. Park, Tetrahedron Lett. 45 (2004) 4607– 4610.
- [35] W.H. Kim, I.S. Park, J. Park, Org. Lett. 8 (2006) 2543-2545.
- [36] T. Mitsudome, Y. Mikami, H. Funai, T. Mizugaki, K. Jitsukawa, K. Kaneda,
- Angew. Chem. Int. Ed. 47 (2008) 138–141. [37] W. Fang, Q. Zhang, J. Chen, W. Deng, Y. Wang, Chem. Commun. 46 (2010) 1547–1549.
- [38] Q. Zhang, W. Deng, Y. Wang, Chem. Commun. 47 (2011) 9275-9292.
- [39] W. Fang, J. Chen, Q. Zhang, W. Deng, Y. Wang, Chem. Eur. J. 17 (2011) 1247– 1256.

- [40] M. Noda, S. Shinoda, Y. Saito, Bull. Chem. Soc. Jpn. 61 (1988) 961–965.
- [41] M. Yamashita, F. Dai, M. Suzuki, Y. Saito, Bull. Chem. Soc. Jpn. 64 (1991) 628-634.
- [42] Y. Uemichi, T. Sakai, T. Kanazuka, Chem. Lett. 18 (1989) 777-780.
- [43] Y. Uemichi, K. Shouji, M. Sugioka, T. Kanazuka, Bull. Chem. Soc. Jpn. 98 (1995) 385–387.
- [44] T. Mitsudome, Y. Mikami, K. Ebata, T. Mizugaki, K. Jitsukawa, K. Kaneda, Chem. Commun. 44 (2008) 4804–4806.
- [45] R.K. Marella, C.K.P. Neeli, S.R.R. Kamaraju, D.R. Burri, Catal. Sci. Technol. 2 (2012) 1833–1838.
- [46] Catalyst recycle experiment without reactivation treatment was also carried out for the reaction of cyclooctanol (t = 6 h) under the conditions of Table 3.

Yields of cyclooctanone for the first and second reuse experiments were 95% and 5%, respectively. It is found that the reactivation treatment is necessary.

- [47] K. Kunimori, T. Uchijima, M. Yamada, H. Matsumoto, T. Hattori, Y. Murakami, Appl. Catal. 4 (1982) 67–81.
- [48] G. Busca, Phys. Chem. Chem. Phys. 1 (1999) 723–736.
- [49] N.C. Jeong, J.-S. Lee, E.L. Tae, Y.J. Lee, K.B. Yoon, Angew. Chem. Int. Ed. 120 (2008) 10282–10286.
- [50] K. Shimizu, H. Kawabata, A. Satsuma, T. Hattori, J. Phys. Chem. B 103 (1999) 5240–5245.
- [51] C. Morterra, G. Magnacca, Catal. Today 27 (1996) 497–532.
- [52] Z. Martinez-Ramirez, J.A. Gonzalez-Calderon, A. Almendarez-Camarillo, J.C. Fierro-Gonzalez, Surf. Sci. 606 (2012) 1167–1172.