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Self-coupling of secondary alcohols by Ni/CeO_2 catalyst

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ABSTRACT

Supported nickel catalysts are studied for the liquid phase C—C self-coupling of aliphatic secondary alcohols under additive free conditions in N_2 atmosphere. Among various Ni catalysts, 1 or 3 wt% Ni/CeO_2 catalysts pre-reduced in H_2 shows highest yield (94%) of a dimer product (a higher ketone) for the self-coupling of 1-octanol at 130 °C, and the catalyst is reused. The catalysts are also effective for self-coupling of various secondary alcohols, providing the first heterogeneous catalytic system for the self-coupling of secondary alcohols under mild conditions. Effects of support material and oxidation state of Ni on the activity are studied and it is found that both CeO_2 and metallic Ni are indispensable for the reaction. A possible reaction mechanism is proposed, in which ketones, formed by dehydrogenation of alcohol, undergone Aldol condensation to give α,β-unsaturated ketone which is finally hydrogenated by in situ formed Ni—H species.

1. Introduction

The construction of C—C bonds is of fundamental importance in organic synthesis. Generally, the coupling of enolate derivatives with alkyl halides has been applied for this purpose. However, this method has some disadvantages such as the use of strong base, the large amount of weight lost with the leaving group of the alkylation agent (i.e. low atom efficiency) and the formation of undesirable waste. Recently, C—C bond formation through the coupling of alcohols as cheap and readily available alkylation agents has attracted much attention [1–4], because it can give a catalytic method to produce chemicals from bio-alcohols. The reaction proceeds through a hydrogen-borrowing (or hydrogen autotransfer) mechanism, which consists of (1) dehydrogenation of alcohols to the corresponding carbonyl compounds, (2) Aldol condensation of them to form α,β-unsaturated carbonyl compounds, and (3) hydrogenation of the C═C (and C═O) bonds using the borrowed hydrogen atoms from alcohols. Only water is produced as byproducts, and the atom efficiency of this system is high. Various homogeneous (Ru [5–13], Ir [12–21], Pd [22–24], Cu [25,26], Ni [27] and Fe [28]) and heterogeneous (Pd [23,24,29], Ir [30], Ag [31], Cu [24,32–36], Ru [37], Rh [37,38], Ni [37,38] and basic oxides [39–47]) catalysts have been developed for this reaction. However, these systems suffered from problems such as high temperature (>200 °C) [23,24,31–47], high reaction pressure (30–80 atm) [23,24,32,33,37,38], high cost of noble metals [5–24,29–31,37,38] or needs of additives [5–33,37,48] such as hydrogen donor or acceptor, or base. Generally, the reported catalysts for the coupling of alcohols were not effective under additive free condition at low temperature. Importantly, previous reports on the self-coupling of secondary alcohols are limited [22,34–36]. Cu-based heterogeneous catalysts for self-coupling of 2-propanol to give methyl isobutyl ketone [34–36] are known, but these examples suffer from high temperature (>200 °C) and low selectivity. A homogeneous Pd catalyst for self-coupling of 1-phenyethanol at low temperatures [22] was reported, but this system suffers from high catalyst cost and difficulties in catalyst reuse. From the environmental and economical point, it is desirable to develop cheap and recyclable heterogeneous catalysts for the coupling of secondary alcohols under mild and additive-free conditions. In the course of our recent findings [49] on the CeO_2-supported Ni (Ni/CeO_2) catalyzed transfer hydrogenation of ketones by 2-propanol we have discovered that that Ni/CeO_2 acts as a recyclable heterogeneous catalyst for self-coupling of aliphatic secondary alcohols without any additives under relatively mild conditions. The structure-activity relationship and mechanistic aspects are also discussed to clarify the factors affecting the activity of this catalytic system.

2. Experimental

2.1. Catalyst preparation

CeO_2 (JRC-CEO-2) and TiO_2 (JRC-TIO-4) were supplied from Catalysis Society of Japan. γ-Al_2O_3 was prepared by calcination of γ-AlOOH (Catapal B Alumina purchased from Sasol) at 900 °C for

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3 h. ZrO_2 was prepared by hydrolysis of zirconium oxynitrate 2-hydrate in distilled water by gradually adding an aqueous NH_4OH solution (1.0 mol dm^{-3}), filtration of precipitate, washing with distilled water three times, drying at 100 °C, and calcining at 500 °C. SiO_2 (Q-10) was supplied from Fuji Silysia Chemical Ltd. C (active carbon) was purchased from Kishida Chemical Co., Ltd. Ni metal, NiO and Ni_2O_3 were purchased from Mitsuwa Chemical. Raney Ni (B113W, Ni >90%) was supplied from Evonik Industries.

The catalyst precursor (named NiO/CeO_2) was prepared by an impregnation method. A mixture of the support and an aqueous solution of Ni nitrates were evaporated at 50 °C, followed by drying at 90 °C for 12 h, calcination in air at 350 °C for 4 h. Before catalytic experiments, the precursor (NiO/CeO_2) was pre-reduced in a pyrex tube under a flow of H_2 (20 cm^3 min^{-1}) at a reduction temperature (T_{H2}) for 0.5 h. The specific surface area of 5 wt% Ni/CeO_2 was 69 m^2 g^{-1}.

2.2. Characterization

XRD patterns of the powdered catalysts were recorded with a Rigaku MiniFlex II/AP diffractometer with Cu Kα radiation. Specific surface area was obtained by measuring N_2 adsorption at −196 °C by BELCAT.

Ni K-edge XAFS measurements were performed in a transmission mode at the BL01B1 in SPring-8 operated at 8 GeV. A Si(1 1 1) single crystal was used to obtain a monochromatic X-ray beam. A pressed pellet of the pre-reduced Ni/CeO_2 sample (Ni = 5 wt%) was placed in a quartz in situ cell in a flow of 100% H_2 (100 cm^3 min^{-1}) for 0.5 h at each temperature under atmospheric pressure, then the sample was cooled to 40 °C under a flow of He, and then a XAFS spectrum was obtained. The analysis of EXAFS was performed using the REX version 2.5 program (RIGAKU). The Fourier transformation of the k^3-weighted EXAFS oscillation from k space to r space was performed over the range 22–126 nm^{-1} to obtain a radial distribution function. The inversely Fourier filtered data were analyzed with a usual curve fitting method in the k range of 22–126 nm^{-1}. The parameters for the Ni—O and Ni—Ni shells have been provided by the FEFF6.

2.3. Typical procedures of catalytic reactions

Commercially available organic compounds were used without further purification. Typically, 3 or 5 wt% Ni/CeO_2 (3 mol% of Ni with respect to alcohol) was used in catalytic experiments. After the pre-reduction, we carried out catalytic tests without exposing the catalyst to air as follows. The mixture of *o*-xylene (1.5 mL), alcohol (1 mmol), and *n*-dodecane (0.5 mmol) was injected to the pre-reduced catalyst inside a reactor (cylindrical glass tube) through a septum inlet. Then, the reactor was purged by N_2 and set in a reaction vessel equipped with a condenser. The resulting mixture was stirred at 80–144 °C. Conversion and yields of products were determined by GC using *n*-dodecane as an internal standard. The GC-FID (Shimadzu GC-14B) and GC–MS (Shimadzu GCMS-QP5000) analyses were carried out with a Rtx-65 capillary column (Shimadzu) using nitrogen or helium as the carrier gas. The products were identified by GC–MS and by comparison with commercially pure products.

3. Results and discussion

3.1. Structure of Ni/CeO_2

The XRD spectrum of 5 wt% Ni/CeO_2 showed no peaks due to metallic Ni and NiO possibly due to high dispersion of Ni species. Thus, the structure of Ni species on the Ni/CeO_2 catalysts was studied by Ni K-edge X-ray absorption near-edge structures (XANES) and extended X-ray absorption fine structure (EXAFS) shown in Fig. 1. Table 1 shows the results of curve-fitting analyses of the EXAFS. The curve-fitting of the EXAFS of unreduced precursor, named NiO/CeO_2, gave a Ni—O shell at 1.99 Å with Ni—Ni coordination number (N) of 6.9 and a Ni—Ni shell at 2.95 Å of N = 7.8 (Table 1). By comparison with the crystallographic data of NiO, the EXAFS feature of NiO/CeO_2 was assigned to NiO species. On the other hand, the EXAFS of the Ni/CeO_2 catalyst reduced at 400 °C consists of a Ni—Ni shell at 2.44 Å (N = 5.9) with a weak Ni—O shell at 1.84 Å (N = 0.4). By comparison with the crystallographic data of Ni metal, the Ni—Ni shell was assigned to metallic Ni. The Ni—Ni coordination number (5.9) was smaller than that of Ni foil (12), indicating a small size of Ni metal nanoparticles on Ni/CeO_2. The weak contribution of the Ni—O shell indicates the presence of NiO species as minor species. The EXAFS of the Ni/CeO_2 catalyst reduced at a medium temperature (250 °C) consists of characteristic features due to NiO (a Ni—O shell at 2.02 Å with N = 2.4 and a Ni—Ni shell at 2.94 Å with N = 1.8) and a feature due to Ni metal (a Ni—Ni shell at 2.49 Å with N = 2.0), which indicates the co-presence of NiO and Ni metal species. To estimate the fraction of Ni metal and NiO species in the catalysts, we carried out pattern fitting analysis of Ni K-edge XANES. We obtained the fractions of the Ni metal and NiO by the least-squares fitting of the XANES spectrum of the Ni/CeO_2 sample with a linear combination of XANES spectra of Ni foil and NiO. The fraction of Ni metal and NiO species in each catalyst was plotted in Fig. 2A as a function of the reduction temperature. The fraction of metallic Ni increased with increase in the reduction temperature.

Table 1
Ni K-edge EXAFS analysis of CeO_2-supported Ni (5 wt%) samples.

T_{H2}[a]/°C	Shell	N[b]	R[c]/Å	σ[d]/Å	R_f[e]/%
–	O	6.9	1.99	0.145	1.4
	Ni	7.8	2.95	0.106	
200	O	5.8	2.08	0.129	6.6
	Ni	6.4	2.95	0.100	
250	O	2.4	2.02	0.100	4.2
	Ni	2.0	2.49	0.085	
	Ni	1.8	2.94	0.080	
300	O	0.8	1.88	0.040	1.46
	Ni	5.3	2.45	0.103	
350	O	0.5	1.86	0.00	0.86
	Ni	5.6	2.44	0.107	
400	O	0.4	1.84	0.03	1.1
	Ni	5.9	2.44	0.109	
NiO[f]	O	6	2.02	–	–
	Ni	12	2.94	–	–
Ni[f]	Ni	12	2.49	–	–

[a] Temperature of H_2 reduction.
[b] Coordination number.
[c] Bond distance.
[d] Debye-Waller factor.
[e] Residual factor.
[f] Crystallographic data of NiO and Ni metal.

3.2. Catalytic performance and structure-activity relationship

First, we compared the activity of various Ni(5 wt%)-loaded catalysts pre-reduced at 500 °C and Ni compounds for self-coupling of 2-octanol (Table 2). Among various Ni catalysts, Ni/CeO_2 showed highest yield of dimer products (ketone **1a** and alcohol **2a**). In contrast, Ni-loaded ZrO_2, γ-Al_2O_3, TiO_2, SiO_2 and active carbon catalyzed the dehydrogenation of 2-octanol to give 2-octanone as the main products (entries 3–7). Yield of the dimer products for Ni/CeO_2 was much higher than those on other Ni-loaded catalysts even under a similar conversion level (38–74%, entries 2–7). Ni-loaded ZrO_2, γ-Al_2O_3 or TiO_2 catalysts pre-reduced at lower temperature (250 °C) were also tested (not shown), but the yields of the dimers were below 8%. Cu/CeO_2 and Co/CeO_2 catalysts (entries