



Toluene combustion over NiO nanoparticles on mesoporous SiO₂ prepared by atomic layer deposition



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HIGHLIGHTS

- The catalytic activity of NiO/SiO₂ catalysts for toluene combustion was measured.
- NiO catalysts can be efficient for toluene combustion below as well as above 200 °C.
- High activity of NiO/SiO₂ catalysts is related to large surface area of mesoporous SiO₂ substrates.

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ABSTRACT

NiO nanoparticles were deposited on mesoporous SiO₂ by atomic layer deposition (ALD) consisting of sequential exposures to Ni(Cp)₂ and H₂O. NiO/SiO₂ catalysts were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), inductively coupled plasma-optical emission spectroscopy (ICP-OES) and X-ray photoelectron spectroscopy (XPS). The catalytic activity of NiO/SiO₂ catalysts for toluene combustion was measured in terms of toluene removal efficiency and conversion to CO₂ and compared with that of commercial NiO nanoparticle catalysts. In order to investigate dependence of reaction temperature on toluene combustion, the toluene combustion experiments over NiO catalysts were carried out at various temperatures. We show that NiO catalysts can be efficient catalysts for toluene combustion below as well as above 200 °C. The catalytic activity per Ni atom of NiO/SiO₂ catalyst was higher than that of unsupported NiO nanoparticles. This high activity of NiO/SiO₂ catalysts is attributed to large surface area of mesoporous SiO₂ substrates, which is able to adsorb a large amount of toluene molecules and expedite oxidation of toluene by spill-over.

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1. Introduction

Volatile organic compounds (VOCs), which have high vapor pressure at room temperature, can be easily released into atmosphere. Since the harmfulness of VOCs to human body has been widely known, much effort has been devoted to abate them in recent years [1–18]. There are diverse strategies for abatement of VOCs; e.g. adsorption using porous adsorbents [1–6], and (photo)-catalytic oxidation, etc. [7–13]. Among them, catalytic combustion is one of the most widely used methods for removing VOCs: VOCs are commonly oxidized at harsh temperature conditions. However, the oxidation temperature can be significantly lowered using proper oxidative catalysts. Noble metal catalysts (e.g. Pt, Au and Pd) have been extensively used as heterogeneous catalysts for removal of VOCs owing to their high activity [14,17,19–25]. However, the utilization of noble metal is limited in actual applications for catalytic combustion due to their high

cost. Therefore, development of catalysts based on cheaper materials (such as Ni, Mn, W, Cr, Cu, and Ce.) for catalytic combustion of VOCs has been briskly progressed [26–35].

Nickel oxide has been used as catalysts in various oxidative reactions including CO oxidation, VOCs oxidation and oxidative dehydrogenation of alkane molecules [26,27,36–39]. Even if nickel oxide catalysts have less activity than noble metal catalysts, they have potential to be exploited in actual application due to its lower cost. Several methods for synthesis of nickel oxide catalysts have been reported, such as precipitation, impregnation and sol-gel [38,40–43].

Atomic layer deposition (ALD) process for deposition of metal oxide is composed of sequential and individual injection of two different precursors, which allows homogeneous deposition of nanoparticles and thin films on porous substrates [44–49]. In the present work, NiO nanoparticles supported by mesoporous SiO₂ (NiO/SiO₂) were prepared using ALD. We studied VOCs combustion over NiO catalysts, and toluene was employed as a model compound of VOCs. The catalytic activity of NiO/SiO₂ was compared with those of unsupported NiO nanoparticles.

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Table 1
Detailed parameters of the NiO ALD processes used in present work.

	NiO ALD process	
Precursors	Ni(Cp) ₂ at 200 mtorr	H ₂ O at 300 mtorr
Precursors exposure time	250 s	15 s
N ₂ purging time	30 s	
Pumping time	60 s	
Substrate temperature	260 °C	
Reactor base pressure	<10 mtorr	

2. Experiment

2.1. Preparation of NiO/SiO₂

NiO nanoparticles were deposited on mesoporous SiO₂ (average pore size = 13.8 nm, Aldrich) using ALD process. Table 1 shows the detailed parameters of ALD process used in this study. Bis(cyclopentadienyl) nickel (Ni(Cp)₂, Aldrich) was used as metal precursor. Unlike the previous ALD process with Ni(Cp)₂, which employed O₃ as oxidizing reactant of Ni precursor [50–52], only H₂O was utilized as co-reactant here. Mesoporous SiO₂ of 0.6 g was placed in ALD reactor with a home-made sample holder for powder ALD process. The temperature of Ni(Cp)₂ and H₂O bottles were maintained at 60 °C and room temperature, respectively, during deposition. The vapor of Ni(Cp)₂ was injected for 250 s with working pressure of 200 mtorr. The H₂O vapor with pressure of 300 mtorr was infused into the reactor for 15 s. The base pressure between injections of each reactant was kept below 10 mtorr by N₂ purging and pumping. During ALD process, temperature of mesoporous SiO₂ substrates was kept at 260 °C.

In order to characterize NiO/SiO₂ catalysts prepared by ALD process, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), and inductively coupled plasma-optical emission spectroscopy (ICP-OES) were employed. To identify ordering of mesostructure in SiO₂, XRD pattern was obtained in low angle with 2θ range of 0.5–5° using X-ray diffractometer (RIGAKU, UltimaIV) with Cu Kα radiation (λ = 0.15406 nm) source. The operating condition of XRD was 30 kV and 40 mA, and the scanning rate was 0.5°/min. XPS spectra were obtained to investigate the chemical composition of NiO/SiO₂ catalysts surface. The ultrahigh vacuum chamber for XPS analysis was equipped with concentric hemispherical analyzer (CHA; PHOIBOS-Has 2500, SPECS) and monochromatic X-ray source (Mg Kα, 1253.6 eV). The operating pressure was kept below 5.0 × 10⁻¹⁰ torr during each XPS measurement. In order to obtain information about structure and crystallinity of NiO/SiO₂ catalysts, TEM images of the samples before and after ALD process were acquired (JEOL, JEM-3010). For TEM analysis, shaved samples with mean particle size of ~300 nm were dispersed in ethanol by sonication. Then, the solution was distributed on carbon-coated copper TEM grid. Also, energy dispersive spectroscopy (EDS) analysis was carried out for elemental analysis in narrow local spots of samples. ICP-OES was used to determine the overall atomic ratio of nickel and silicon contained in the sample.

2.2. Catalytic activity evaluation

In order to evaluate the catalytic activity of NiO/SiO₂ catalysts for toluene combustion, we used the flow type reactor, which consists of mass flow controller (MFC) for dry air, a bottle with toluene liquid, quartz tube, furnace and gas chromatography (GC). The schematic figure of experimental set up can be found in Ref. [26]. Each sample was put into the quartz boat (70 × 20 × 8 mm³), and then the quartz boat was placed in the quartz tube (20 mm diameter, 250 mm length). Before injection of toluene vapor with dry air into quartz

tube, NiO/SiO₂ catalysts were annealed at 450 °C for 3 h to remove impurities. During toluene combustion, the flow of dry air (N₂ 80% and O₂ 20%) including toluene vapor of 80 ppm was maintained at 5 sccm by MFC. The catalytic activity for toluene combustion was estimated in terms of toluene removal efficiency and selectivity to CO₂ by GC (agilent-6890 N GC), which was equipped with capillary column (HP-5, 30 m × 0.32 mm × 0.25 μm), methanizer and flame ionization detector (FID). Temperature programmed oxidation (TPO) analysis was conducted after toluene combustion to identify amount of carbon species remaining on catalyst surface after reaction. Each TPO experiment started at 120 °C. During TPO, air flow of 5 sccm without any toluene vapor was passed through the quartz tube, and the temperature of the reactor was increased with a ramping rate of 1 °C/min from 120 °C to 450 °C. Also, we carried out temperature programmed desorption (TPD) experiments to investigate the toluene uptake of each sample. Before TPD experiments, each sample was treated thermally at 450 °C for 3 h, and then the samples were exposed to toluene vapor-containing air (toluene concentration = 80 ppm) at room temperature until the breakthrough curve of toluene was saturated. During TPD experiments, the flow of N₂ gas (99.999%) with the rate of 5 sccm passed via quartz tube and the reactor temperature was elevated from 30 °C to 210 °C with the heating rate of 1 °C/min.

2. Results and discussion

3.1. Characterization of NiO/SiO₂ catalysts

Fig. 1(a) shows low angle XRD patterns of mesoporous SiO₂ before and after NiO deposition using 40 cycles of ALD. The XRD pattern of NiO/SiO₂, in which a broader peak related to disordered mesostructure could be seen, was similar to that of bare SiO₂. In Fig. 1, TEM image provides structural information of NiO/SiO₂, which was prepared by deposition of 40 ALD cycles at 260 °C and a subsequent annealing at 450 °C for 3 h. We can identify that NiO nanoparticles with an average size of ~1.8 ± 0.4 nm were distributed randomly on mesoporous SiO₂. A close inspection of magnified TEM image revealed crystallinity of NiO nanoparticle, and the observed lattice spacing of 0.21 nm corresponds to (200) plane in cubic phase of NiO [53,54]. The atomic composition of sample prepared by ALD was determined using EDS and ICP-OES analysis (Table 2). In our EDS analysis, atomic composition of Ni at NiO island spots was about 10.3%, whereas that of non-island region was only ~1.7%. This result verifies that islands generated on surface of mesoporous SiO₂ after ALD process are really NiO nanoparticles. The overall atomic ratio of Ni in NiO/SiO₂ was determined to be 2.3% by ICP-OES.

Table 3 compares characteristics of commercial NiO nanoparticle (C-NiO) and NiO/SiO₂ catalysts determined by N₂ sorption isotherms and H₂ uptake (temperature programmed reduction, TPR). After NiO had been deposited on SiO₂ by 40 ALD cycles, BET surface area was slightly changed from 297.66 m²/g (bare SiO₂) to 302.59 m²/g. In the case of average pore diameter, significant difference could not be observed between bare SiO₂ (13.84 nm) and NiO/SiO₂ (13.40 nm). Also, H₂ uptake per 1 g NiO of NiO/SiO₂ was higher than that of C-NiO. The dispersion of NiO nanoparticles on SiO₂, defined as the ratio of NiO exposed at the surface to total NiO, calculated by TPR result was 56.57%, indicating that NiO nanoparticles were well dispersed on surface of mesoporous SiO₂.

XPS spectra of bare and NiO deposited mesoporous SiO₂ with 40 ALD cycles are shown Fig. 2. XPS intensity of each element in bare SiO₂ and NiO/SiO₂ was normalized by the intensity of the respective Si 2p peak and the binding energy of each spectrum was calibrated using Si(IV) 2p binding energy at 103.3 eV as reference [55]. In Fig. 2(a), the Si 2p peak of NiO/SiO₂ shows a broad shoulder at

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