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Decoration of the internal structure of mesoporous chromium terephthalate MIL-101 with NiO using atomic layer deposition

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ABSTRACT

Mesoporous chromium terephthalate MIL-101 was modified with NiO via atomic layer deposition (ALD) process using bis(cyclopentadienyl)nickel (Ni(Cp)$_2$) as a metal precursor and O$_2$ as an oxidizing agent, respectively. Based on the results of transmission electron microscopy (TEM), N$_2$ and Ar isotherms, X-ray photoelectron spectroscopy (XPS), and inductively coupled plasma-atomic emission spectroscopy (ICP-AES), we show that the deposited NiO nanoparticles were distributed inside internal mesoporous cages as well as on the external surface of MIL-101(Cr). Studies using *in situ* X-ray photoelectron spectroscopy show that NiO selectively occupied ligand sites without affecting metal sites of MIL-101. The NiO deposition using ALD enhanced thermal stability of MIL-101 compared to that without NiO and provided catalytic activity for CO oxidation, i.e., ALD provided novel chemical functionality to the metal-organic frameworks (MOFs).

1. Introduction

Metal-organic frameworks (MOFs), which are hybrid functional porous materials consisting of metal clusters or ions connected by organic linkers, have been in the limelight as attractive materials for various applications including catalysis, gas storage, separation, sensing, and drug delivery [1–11]. Recently, numerous approaches for enhancing the chemical competency of MOFs and providing new functionality have been intensively studied [12,13]. In particular, post-metalation based on volatile inorganic vapor phase is a widely used method for the modification of MOFs, since contamination of the MOF by solvent molecules can be excluded and no additional purification is required using this method [14–18].

Atomic layer deposition (ALD) is one deposition technique based on vapor phase precursors. Since ALD employs the purging and pumping step between alternating exposures of substrate to chemical precursors, not only the reaction in the gas phase is prevented, but also any physisorption of the precursor is not involved for deposition. As enough time is given for the formation of the chemisorbed layer on surface, the deposition per cycle in the ALD process is "self-limiting", which allows precise and uniform control of the amount of deposited thin films and nanoparticles on complex-structured substrates [19–21]. In addition, the ALD process is effective for deposition of thin films on substrates with lower stability due to its lower working temperatures compared to chemical vapor deposition (CVD). It was anticipated that the uniqueness of ALD is suitable for functionalization of the interior surface of MOF materials, which show the porosity in the nm-size and have low thermal stability. However, despite these advantages, ALD has very rarely been utilized for the modification of MOFs [22].

The aim of this study is to deposit nickel oxide on MOFs using the ALD technique to provide novel chemical functionality. Nickel oxide, which is one of the relatively less expensive transition

metals, has been widely investigated as an alternative material for noble metal catalysts of various reactions, such as CO and volatile organic compound (VOC) oxidations and oxidative dehydrogenation of alkanes [21,23,24]. A porous chromium terephthalate MIL-101, which has been exploited in a variety of application fields because of its large surface area, hierarchical pore structure with mesoporous cages, and numerous unsaturated chromium sites [9–11], was selected as the substrate for NiO ALD.

2. Experimental details

2.1. Synthesis of MIL-101 (Cr)

166 mg of 1,4-benzendicarboxylic acid (H_2BDC) and 400 mg of $Cr(NO_3)_3 \cdot 9H_2O$ were added into teflon bottle containing a mixture of 0.05 ml of hydrofluoric acid and 4.8 ml of H_2O, and then reacted at 220 °C for 8 h. The as-synthesized MIL-101(Cr) was further purified by a three-step process: first, as-synthesized sample was filtered by glass and paper filters with a pore size between 40 and 100 μm. Second, the filtrated sample was further treated with hot ethanol/water mixture (95% ethanol with 5% water) at 80 °C for 24 h to remove the non-reacted terephthalic acid within the pores of MIL-101 (Cr). Finally, the resulting solid was soaked in 150 ml of an aqueous solution of 30 mM of NH_4F at 60 °C for 10 h and then immediately filtered and washed with hot water at 60 °C to remove traces of NH_4F. Through these procedures, the refined MIL-101(Cr) could be obtained.

2.2. NiO ALD on MIL-101 (Cr)

NiO was deposited on MIL-101(Cr) using ALD with two precursors, bis-(cyclopentadienyl)nickel ($Ni(Cp)_2$, sigma aldrich) as a metal precursor and O_2 as an oxidizing agent, respectively. Table S1 shows the detailed parameters of the ALD process. MIL-101(Cr) of 150 mg in a home-made holder for powder sample was placed in the ALD reactor, which was kept at 150 °C during NiO deposition. For each ALD cycle, $Ni(Cp)_2$ vapor, which was vaporized at 60 °C, and O_2 were sequentially introduced into the chamber for 300 and 270 s at working pressures of 150 mtorr and 1.5 torr, respectively. Between the injections of each precursor, the purging with high purity N_2 (purity: 99.999%) and pumping were employed four times to remove gaseous byproducts from the reactor. We hereafter denote x cycled-NiO deposited MIL-101(Cr) as xNiO-MIL-101.

2.3. Characterization

The structures of MIL-101(Cr) before and after NiO ALD were characterized by transmission electron microscopy (TEM, JEM ARM 200F). For TEM analysis, MIL-101 (Cr) particles (~700 nm) were dispersed in ethanol by sonication and then distributed on a carbon-coated copper TEM grid. Also, energy dispersive spectroscopy (EDS) was used to obtain elemental mapping images of 5NiO-MIL-101. The chemical states and compositions of surfaces of NiO-MIL-101 samples with various numbers of ALD cycle were analyzed by X-ray photoelectron spectroscopy (XPS). XPS analyses were carried out under ultra-high vacuum conditions with a base pressure of 5×10^{-10} torr. XPS spectra were collected in the pass energy of 10 eV using a concentric hemispherical analyzer (CHA, PHOIBOS-HSA3500, SPECS) and Mg Kα X-ray source with 1253.6 eV. Furthermore, to shed light on the surface change of MIL-101 during 1 cycle of NiO ALD, in-situ XPS analysis was performed. For this in-situ analysis, load-lock and analysis chambers were connected via a gate valve allowing samples to be transferred without exposure to the air. MIL-101(Cr) were exposed with $Ni(Cp)_2$ and O_2 in the load-lock chamber with a base pressure of ~5.0×10^{-8} torr and then XPS

spectra for sample undergone each precursor exposure were repeatedly obtained after back-and-forth transfer between the loadlock and analysis chamber (Fig. S1).

Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) was used to measure the content of nickel and chrome in NiO-MIL-101. Powder X-ray diffraction patterns (XRD) of the as-prepared and NiO-modified samples were obtained by an X-ray diffractormeter (Miniflex, Rigaku) using Cu Ka-radiation ($\lambda = 1.5418$ Å) at a scanning range from 0.5 to 15° for the identification of crystallinity. The surface area and pore size distribution of NiO-MIL-101 (Cr) with the various ALD cycles were determined by N_2 and Ar adsorption−desorption isotherms using commercial sorption analyzers. The samples were degassed in a vacuum system at 150 °C for 12 h before each isotherm measurement. The specific surface areas were evaluated using the Brunauer−Emmett−Teller (BET) method in a P/P_0 range of 0.08−0.2. The thermal stability of NiO-MIL-101 was assessed by thermal gravimetric analysis (TGA) in the range from 30 to 550 °C with a heating rate of 10 °C/min. Before TGA, each sample was saturated by water vapors.

2.4. CO oxidation

CO oxidation experiments catalyzed by the bare and NiO-modified MIL-101(Cr) were carried out in the continuous-flow quartz fixed-bed reactor (internal diameter = 21 mm, length = 300 mm) under atmospheric pressure. 0.14 g of the NiO-MIL-101(Cr) catalyst loaded in the quartz wool was located in the center of the quartz reactor. Before each CO oxidation experiment, each catalyst was annealed at 250 °C for 6 h under dry Ar condition. After the annealing process, the quartz reactor was cooled down to the reaction temperature of 200 °C, which was maintained constantly by the temperature controller during the reaction experiments. Dry air containing 0.1% of CO with the total flow rate of 30 ml/min was injected constantly into the reactor during the reaction. Amounts of the CO and CO_2 were detected at 10 min intervals by the gas chromatography (HP6890, HEWLETT PACKARD) equipped with a capillary column (HP-PLOT Q, 30 m × 0.53 mm, AGILENT), methanizer and flame ionization detector (FID). CO conversion was calculated using the following equation (Eq. (1)):

$$CO\ conversion(\%) = \frac{[CO]_{in} - [CO]_{out}}{[CO]_{in}} \times 100 \qquad (1)$$

3. Result and discussion

In order to verify the self-limiting behavior and determine the optimum exposing time of the Ni-precursor in the NiO ALD, N_2 isotherms of MIL-101 samples of 5 cycled-NiO deposition with various $Ni(Cp)_2$ exposure times were obtained (Fig. 1). The adsorption volume of N_2 decreased with increasing exposing time of $Ni(Cp)_2$ from 50 to 300 s, while samples with the exposing times of 300 and 600 s had almost identical N_2 isotherm results. Furthermore, for exposure times larger than 300 s, the BET surface area and the Ni/Cr ratio determined by ICP-AES (Table S2) were observed to level off at ~3130 m^2/g and 0.22, respectively. These results indicate that the $Ni(Cp)_2$ adsorption reached the self-limiting state after exposing time of 300 s and no further deposition of the Ni-precursor took place after 300 s. Therefore, $Ni(Cp)_2$ exposure time was fixed to 300 s in the NiO ALD of this work.

The structures of MIL-101(Cr) before and after deposition of NiO using ALD were studied using TEM method combined with EDS analysis and X-ray diffraction (XRD). The image in Fig. 2 (a) shows a particle of MIL-101 with an octahedral shape along the [111]