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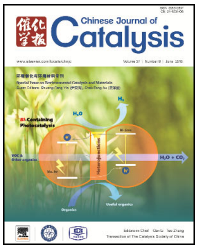

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Ni-based catalysts derived from a metal-organic framework for selective oxidation of alkanes

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Ni nanoparticles embedded in nitrogen-doped carbon (Ni@C-N) materials were prepared by thermolysis of a Ni-containing metal-organic framework (Ni-MOF) under inert atmosphere. The as-synthesized Ni@C-N materials were characterized by powder X-ray diffraction, N_2 adsorption-desorption analysis, scanning electron microscopy, transmission electron microscopy, atomic absorption spectroscopy, and X-ray photoelectron spectroscopy. The MOF-derived Ni-based materials were then examined as heterogeneous catalysts for the oxidation of alkanes under mild reaction conditions. The Ni@C-N composites displayed high activity and selectivity toward the oxidation of a variety of saturated C–H bonds, affording the corresponding oxidation products in good-to-excellent yields. Furthermore, the catalysts could be recycled and reused for at least four times without any significant loss in activity and selectivity under the investigated conditions.

1. Introduction

The selective partial oxidation of alkanes is an important transformation in the production of valuable chemicals and intermediates such as ketones and alcohols [1]. For example, cyclohexanone and cyclohexanol (also known as KA-oil), the two main products of the partial oxidation of cyclohexane, are the key intermediates in the fabrication of polyamide and plastics such as Nylon 6 and Nylon 66 [2]. However, control over the selective oxidation of saturated hydrocarbons is challenging because of the inertness of the saturated C–H bonds and subsequent oxidation issues resulting from the higher reactivity of the products when compared with that of the reactants. Accordingly, the industrial manufacture of KA-oil from cyclohexane oxidation needs careful control (at conversions of <5% with 75%–80% selectivity to KA-oil) to prevent the production of excessive amounts of byproducts owing to over-oxidation [3–5].

Over the past few decades, considerable research efforts have been devoted to exploring efficient and environmentally sound methodologies for the selective oxidation of alkanes. In this regard, heterogeneous catalysis has received the most attention, and various efficient metal catalysts have been developed [6–23]. These catalysts include metal-incorporated molecular sieves [12], metal-substituted molecular sieves [13,15], supported Au nanoparticles [6,7,10,23], metal-organic frameworks (MOFs) [22], and carbon-based materials [24,25]. However, the development of cost-effective, and highly active and

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selective heterogeneous catalysts for the oxidation of alkanes remains a great challenge to date.

Of particular interest, MOFs are a well-known, new class of porous functional materials constituting metal ions and organic ligands. Owing to their ordered structures and relatively low thermal stability, MOFs have been used for the preparation of new metal oxides or carbon nanomaterials by thermal decomposition. As reported, MOF-derived materials exhibit excellent performance in various applications including heterogeneous catalysis [26–36], electrochemistry [37,38], and gas adsorption [39–41]. To our knowledge, reports on the use of MOF-derived materials as catalysts for liquid-phase organic synthesis are rare.

Herein, we report a novel, non-noble Ni-based heterogeneous catalytic system for the selective oxidation alkanes. Various alkanes, such as cyclohexane and ethylbenzene, could be selectively transformed into the desired aldehydes or ketones in high yields under mild conditions. The catalysts were prepared by simple thermolysis of a Ni-containing MOF under inert atmosphere.

2. Experimental

2.1. Synthesis of Ni@C-N catalysis

All chemicals were purchased from commercial corporations and used without further treatment.

Typically, a mixture of $Ni(NO)_3{\cdot}6H_2O$ (0.9 mmol), 1,4-benzenedicarboxylic acid (H_2bdc; 0.72 mmol), triethylenediamine (dabco; 0.58 mmol), and dimethylformamide (DMF; 15 mL) were added to a Teflon-lined autoclave. The reactor was heated in an oven at 120 °C for 2 d. The obtained green powder was then washed with DMF and methanol, and finally dried under vacuum at 150 °C for 2 h.

The Ni@C-N catalysts were prepared by pyrolysis of Ni-MOF in an inert atmosphere. Ni-MOF was heated at a heating rate of 1 °C/min from room temperature to 200 °C and maintained at this temperature for 2 h in Ar. Then, the temperature was increased to the target temperature (i.e., 500, 600, 700, 800, or 900 °C) at the same heating rate and subsequently maintained for 8 or 15 h. The resulting samples were denoted as Ni@C-N-*x*-8h or Ni@C-N-*x*-15h, where *x* indicates the target thermolysis temperature (°C).

2.2. Characterization

Powder X-ray diffraction (PXRD) patterns of the prepared materials were recorded on a Rigaku diffractometer (D/MAX-IIIA; 3 kW) using Cu K_α radiation (40 kV, 30 mA, λ = 0.1543 nm). N_2 adsorption-desorption isotherms were measured on a Micromeritics ASAP 2020M instrument at –196 °C . The Ni content of the samples was determined quantitatively by atomic absorption spectroscopy (AAS) on a HITACHI Z-2300. The surface topography of Ni-MOF and the Ni@C-N materials was investigated by scanning electron microscopy (SEM; MERLIN of ZEISS). Transmission electron microscopy (TEM) images of the samples were recorded on a JEM-2010HR (JEOL) microscope. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Kratos Axis Ultra DLD system with a base pressure of 1.33×10^{-7} Pa.

2.3. Oxidation of alkanes over Ni@C-N

The oxidation of alkanes (e.g., ethylbenzene) was conducted in a 25-mL Schlenk tube. Typically, ethylbenzene (0.5 mmol), catalyst (10 mol% based on Ni), *tert*-butyl hydroperoxide (TBHP; 1.5 mmol), and DMF (2 mL) were added to the tube and heated at 80 °C. After reaction, the catalyst was isolated from the mixture solution by centrifugation, then washed with DMF and methanol. The liquid mixtures were then analyzed by gas chromatography mass spectrometry (Agilent Technologies 7890B-5977A) on a chromatograph equipped with a 0.25 mm × 30 m HP-5MS capillary column.

For the recyclability tests, the catalyst was separated from the reaction mixture and washed with DMF and methanol for several times. The solid was then dried at 80 °C in an oven and reduced by H_2 at 200 °C for 2 h before use for the next run.

3. Results and discussion

3.1. Characterization of the materials

Ni-MOF was prepared according to the procedures described in previous reports [42,43]. The PXRD pattern of the as-synthesized Ni-MOF (Fig. 1(a)) matched well with the published XRD patterns [42,43]. The N_2 adsorption-desorption isotherm measured at –196 °C indicated that Ni-MOF was

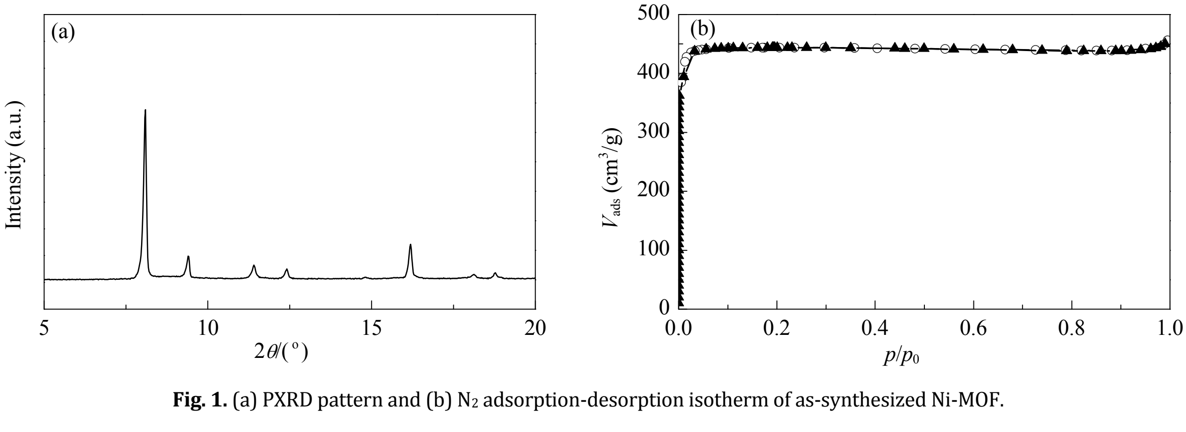

Fig. 1. (a) PXRD pattern and (b) N_2 adsorption-desorption isotherm of as-synthesized Ni-MOF.