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

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ABSTRACT

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, N₂ 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.

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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 cyclo-

hexane 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 catalysts

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

Typically, a mixture of $\text{Ni}(\text{NO})_3 \cdot 6\text{H}_2\text{O}$ (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-III A; 3 kW) using $\text{Cu K}\alpha$ radiation (40 kV, 30 mA, $\lambda = 0.1543$ 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 $\times$ 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.

mostly microporous (Fig. 1(b)). The Brunauer-Emmett-Teller (BET) surface area was calculated to be $\sim 1700 \text{ m}^2/\text{g}$.

The Ni@C-N materials were prepared by pyrolysis of Ni-MOF under a continuous flow of Ar for 8 or 15 h at varying temperatures. The Ni contents in the samples were $\sim 35\text{--}40 \text{ wt\%}$. Fig. 2 shows the PXRD patterns of the Ni@C-N materials. All the prepared materials displayed five diffraction peaks at $\sim 44.4^\circ$, 51.8° , 76.4° , 92.9° , and 98.5° , which are characteristics of metallic Ni (JCPDS No. 04-0850) [44]. The intensity of the Ni diffraction peaks increased with increasing pyrolysis temperatures employed, indicating the formation of Ni phase with a higher crystallization degree. The crystallite sizes of Ni Particles in the materials were in the range of 7–10 nm, as calculated by the Scherrer formula.

Fig. 3 shows the N_2 adsorption-desorption isotherms of the Ni@C-N materials measured at -196°C . All isotherms featured typical adsorption curves of types I and IV, with an apparent hysteresis loop in the relative pressure (P/P_0) range of 0.5–1.0, suggesting the presence of a micro-/meso-/macroporous structure in the Ni@C-N materials. The BET surface areas of the

Ni@C-N materials were calculated to be $\sim 100\text{--}200 \text{ m}^2/\text{g}$.

The surface morphology of the Ni@C-N materials was examined by SEM. The SEM images in Fig. 4(a)–(d) depict the initial shape of the Ni-MOF crystals when MOF was calcined below 700°C for 8 h. The surface of the materials became distorted and considerably rougher upon decomposition and carbonization of the MOF. When the pyrolysis temperature increased to 800°C , numerous nanotubes were obtained (Fig. 4(e)), which might be catalyzed by the generated Ni nanoparticles.

The TEM images in Fig. 5 revealed that the metallic Ni nanoparticles were highly dispersed in the carbon matrix derived from carbonization of the organic linker in Ni-MOF. At the higher MOF pyrolysis temperatures, aggregation of the Ni nanoparticles into larger particles was observed. When the thermolysis temperature increased to 900°C , most of the particles agglomerated into large particles with an average size of $\sim 18 \text{ nm}$ (Fig. 6). High-resolution TEM analysis of an individual large particle indicated that each Ni nanoparticle was tightly embedded in the graphitic carbon (Fig. 6(c)).

Fig. 2. PXRD patterns of (a) Ni@C-N-x-8h and (b) Ni@C-N-x-15h.

Fig. 3. N_2 adsorption (ads)-desorption (des) isotherms of (a) Ni@C-N-x-8h and (b) Ni@C-N-x-15h.

Fig. 4. SEM images of (a) Ni-MOF, (b) Ni@C-N-500-8h, (c) Ni@C-N-600-8h, (d) Ni@C-N-700-8h, (e) Ni@C-N-800-8h, and (f) Ni@C-N-900-8h.

Fig. 5. TEM images of (a) Ni@C-N-500-8h, (b) Ni@C-N-600-8h, (c) Ni@C-N-700-8h, and (d) Ni@C-N-800-8h.

The XPS spectra of Ni-MOF and Ni@C-N-900-8h are shown in Fig. 7. The Ni 2*p* peaks at 856.0 and 873.6 eV could be assigned to Ni²⁺ in Ni-MOF (Fig. 7(a)). After thermolysis, the two Ni 2*p* peaks of Ni@C-N-900-8h respectively shifted to lower binding energies by ~3.2 and ~3.3 eV relative to those of Ni-MOF, indicating that most of the Ni(II) ions in MOF were reduced to Ni(0) [45]. This result agreed with common experimental observations, whereby central metal ions of MOF with reduction potentials higher than 0.27 V are typically reduced to

Fig. 6. (a, b) TEM images of Ni@C-N-900-8h. (c) High-resolution TEM image of a Ni particle and (d) corresponding size distribution of the Ni nanoparticles.

their metallic states upon calcination in an inert atmosphere [46–48]. The N 1*s* peak of Ni-MOF appeared at 399.8 eV and could be assigned to the N of triethylenediamine coordinated with a metal ion [49]. Interestingly, this bonding energy was slightly higher than that of amino nitrogen (399.6 eV) owing to the influence of the magnetic metal center (i.e., Ni) [50,51]. After thermolysis, the N 1*s* spectra of Ni@C-N-900-8h showed two new peaks at 398.9 and 401.0 eV, which could be assigned to pyridinic N and graphitic N, respectively [52]. This phenomenon was consistent with the TEM result (Fig. 6(c)) with respect to the formation of a graphitic structure.

3.2. Catalytic oxidation of ethylbenzene over Ni@C-N

First, ethylbenzene oxidation was employed as a model reaction to evaluate the catalytic activities of the as-synthesized Ni@C-N materials. The catalytic reaction was conducted at 80 °C using TBHP as oxidant, and the results are summarized in Table 1. The blank reaction, without any catalyst, achieved minimal conversion performance only (Table 1, entry 1). In contrast, in the presence of the Ni@C-N materials, the oxidation transformation was efficiently promoted. The activity of the catalysts was strongly dependent on the pyrolysis temperature and time. Generally, the Ni@C-N materials prepared under higher MOF thermolysis temperatures showed higher activities (Table 1, entries 2–11), possibly because of the higher carbonization degree of the organic linkers in the MOF. In contrast, a longer pyrolysis time reduced the catalytic activity of the obtained Ni@C-N materials. Among the examined catalysts, Ni@C-N-900-8h displayed the best ethylbenzene oxidation performance (Table 1, entry 6), achieving an ethylbenzene-to-acetophenone conversion of 77% within 48 h of reaction at 80 °C. Moreover, a higher yield of acetophenone could be achieved by simply increasing the amount of TBHP, while

Fig. 7. (a) Ni 2p and (b) N 1s XPS spectra of Ni-MOF and Ni@C-N-900-8h.

maintaining other conditions constant (Table 1, entry 12).

Subsequently, the recyclability of Ni@C-N-900-8h catalyst toward ethylbenzene oxidation was examined. The results are presented in Table 1 (entries 6, 13–15); no significant decline in the conversion and selectivity performance was observed during repeated catalytic runs (up to four runs). These results demonstrate the high stability of the Ni@C-N catalyst under the investigated conditions.

3.3. Oxidation of different alkanes over Ni@C-N

To demonstrate the general applicability of the Ni@C-N catalysts, we extended the use of the present catalytic system (specifically, Ni@C-N-900-8h) to the oxidation transformations

Table 1

Results of the oxidation of ethylbenzene catalyzed by different Ni@C-N catalysts.

Entry	Catalyst	Conversion (%)	Yield ^a (%)
1	Blank	7	7
2	Ni@C-N-500-8h	47	47
3	Ni@C-N-600-8h	47	47
4	Ni@C-N-700-8h	48	48
5	Ni@C-N-800-8h	65	65
6	Ni@C-N-900-8h	77	77
7	Ni@C-N-500-15h	37	37
8	Ni@C-N-600-15h	45	45
9	Ni@C-N-700-15h	50	50
10	Ni@C-N-800-15h	47	47
11	Ni@C-N-900-15h	40	40
12 ^b	Ni@C-N-900-8h	>99	>99
13 ^c	Ni@C-N-900-8h	78	78
14 ^d	Ni@C-N-900-8h	75	75
15 ^e	Ni@C-N-900-8h	76	76

^a Reaction conditions: ethylbenzene (0.5 mmol), catalyst (Ni 10 mol% relative to ethylbenzene), DMF (2 mL), TBHP (1.5 mmol), 80 °C, 48 h.

^b TBHP 2.5 mmol. ^c Second run. ^d Third run. ^e Fourth run.

of various saturated alkanes under similar reaction conditions. The results are summarized in Table 2. As observed, the various secondary C–H bonds were oxidized smoothly with excel-

Table 2

Oxidation of various alkanes catalyzed by Ni@C-N-900-8h.

Entry	Substrate	T/°C	t/h	Conversion (%)	Selectivity (%)
1		80	18	>99	100
2		80	22	>99	40, 60
3		80	18	>99	38, 62
4		100	20	>99	100
5		100	48	58	100
6		80	50	>99	95
7		80	50	>99	96
8		80	20	>99	99
9		80	36	>99	95

Reaction conditions: substrate (0.5 mmol), catalyst (Ni 10 mol%), DMF (2 mL), TBHP (2.5 mmol).

lent selectivities to their corresponding partial oxidation products (Table 2, entries 1–5). For the oxidation of cyclohexane, a moderate conversion with 100% selectivity to cyclohexanone was achieved at 100 °C (Table 2, entry 5). Substituted ethylbenzene containing either electron-withdrawing or electron-donating functional groups also displayed excellent conversions and selectivities to the corresponding ketones (Table 2, entries 6–8). It was interesting to note that Ni@C-N was also highly active and selective toward the oxidation of 1,4-diethylbenzene, achieving >95% selectivity to the diketone product (Table 3, entry 9). These results demonstrate the high versatility of the MOF-derived Ni@C-N catalysts prepared herein for the selective oxidation of alkanes.

4. Conclusions

We have developed novel, efficient, and cost-effective Ni-based catalysts for application in the selective oxidation of alkanes. The Ni@C-N materials were prepared by direct thermolysis of a Ni-containing MOF under inert atmosphere. The as-prepared Ni nanoparticles embedded in the C-N composites displayed high activity and selectivity in the oxidation of alkanes to their corresponding partial oxidation products under mild reaction conditions, thus showing a broad substrate scope for diverse saturated C–H bonds. Moreover, the catalysts are highly stable and maintain high activity and selectivity during numerous repeated catalytic cycles under the investigated conditions. The present strategy may be extended to the development of other novel metal–carbon composite catalysts for selective catalytic oxidation applications.

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Graphical Abstract

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

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We developed a series of novel Ni-based catalysts by pyrolysis a Ni-containing metal-organic frameworks in an inert atmosphere at different temperatures. These Ni-based catalysts are highly active and selective in the oxidation of a variety of alkanes.

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金属有机骨架衍生 Ni 基材料催化烷烃选择氧化

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摘要: N 掺杂碳基纳米材料由于具有高稳定性、良好的导电性、较大的孔体积和比表面积等特点而受到了国内外广泛的关注, 在气体吸附、催化、电化学以及燃料电池等许多领域表现出潜在应用价值。N 掺杂碳材料的制备主要采用两种方法, 即后合成法和原位合成法。后合成法是指采用含 N 化合物 (如尿素等) 对已合成的碳材料进行处理, 但所制材料中 N 含量往往偏低, 且 N 活性位不够稳定。要得到 N 含量较高且稳定的 N 掺杂碳材料常常采用原位合成法, 即以富氮前体作为模板, 在热解过程中 N 原位嵌入碳纳米材料中, 因而具有结构稳定, N 含量丰富等优点。

金属有机骨架 (MOFs) 材料是一种新型的类沸石类多孔材料, 是由金属离子和有机配体通过配位键键合而成的拓扑结构。该类材料具有较高的孔隙率和比表面积以及结构可调控性等特点。通过调节金属中心和配体种类, 引入含 N 配体, 可以得到不同类型的含 N 的 MOFs。此外, 含 N 的 MOFs 在一定温度下热解能有效减少 N 元素的流失, 因此, MOFs 是一类优秀的用于制备 N 掺杂碳基纳米材料的模板材料。近年来, 以含 N 的金属有机骨架材料为模板, 通过简单热解一步合成 N 掺杂碳基纳米催化剂, 已成为国内外研究的热点之一。

本文在惰性气氛中采用直接热解 Ni 基 MOF 方法制备了 N 掺杂 C 包裹的 Ni 纳米颗粒, 并利用 X 射线粉末衍射 (PXRD)、N₂ 吸附脱附、扫描电子显微镜 (SEM)、透射电子显微镜 (TEM)、原子吸收光谱 (AAS)、X 射线光电子能谱 (XPS) 等对该复合材料的组成和结构进行了表征。

PXRD 测试结果表明, 经过热解, 催化剂中出现了大量的金属 Ni 粒子, 说明 Ni-MOF 中的 Ni²⁺ 离子在热解过程中被原位还原成了 Ni 纳米颗粒。N₂ 吸附脱附结果表明, 热解前的 Ni-MOF 结构中只存在微孔结构, 但是热解 Ni@C-N 材料中生成了大量的介孔或大孔结构, 从而有利于反应底物与催化剂活性位点的接触。SEM 结果表明, 在较低的温度下热解, 催化

剂可以保持 MOFs 原来的构型, 且结构疏松多孔; 而在较高的温度下热解, 如 800 °C, 将有大量的碳纳米管生成. TEM 结果表明, 随着热解温度升高, 催化剂中 Ni 纳米颗粒逐渐增大. 从 HRTEM 测试结果可以清晰看出, 高温热解时有石墨烯结构生成, 并且生成的 Ni 纳米颗粒原位嵌入了石墨烯结构中, 因而有利于 Ni 纳米颗粒的分散, 从而提高催化剂的活性. XPS 结果进一步证明, 热解过程中, Ni^{2+} 被原位还原成了零价的 Ni 纳米粒子, 此外, N 1s 谱图也进一步证明 N 在热解过程中原位嵌入了生成的石墨烯结构中.

随后, 以乙基苯选择性氧化为模型反应, 测试了 Ni@C-N 材料的催化活性. 结果表明, 该材料在烷烃选择氧化反应中表现出很高的催化活性和选择性, 尤其是 Ni@C-N-900-8h, 在温和的反应条件下, 可有效催化一系列饱和烷烃的选择氧化, 获得很高的氧化产物收率, 且重复利用多次后其活性和选择性没有明显的下降.

关键词: 镍; 纳米粒子; 金属有机骨架; 烷烃; 氧化; 多相催化

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Chinese Journal of Catalysis (《催化学报》) 文种变更为英文的通知

经国家新闻出版广电总局批准, 《催化学报》于 2016 年开始业务范围中的文种变更为英文, 变更后的期刊基本信息如下: 期刊名称 *Chinese Journal of Catalysis* (《催化学报》), 中国标准连续出版物号 ISSN 0253-9837, 国内统一连续出版物号 CN 21-1601/O6, 月刊.

今后, 本刊录用稿件全部以英文全文形式发表, 英文全文电子版在 Elsevier 出版社 ScienceDirect 网络平台上出版. 为兼顾国内读者并保持期刊的中国特色, 《催化学报》印刷版将同时刊登英文文章的扩展版中文摘要.

我们相信, 期刊文种变更为英文后将为国内外催化研究工作者提供一个更好的交流和展示平台. 《催化学报》编委会及编辑部全体成员将通过不懈努力将该刊推向一个新的高度, 使其以更好的质量、更高的学术水平面向世界, 跻身于国际优秀学术期刊行列.

(《催化学报》编辑部)