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A study of FeN_x/C catalysts for the selective oxidation of unsaturated alcohols by molecular oxygen

Jinping Zhang [a], Shinichi Nagamatsu [b], Junmou Du [a], Chaoli Tong [a], Huihuang Fang [a], Dehui Deng [a,c], Xi Liu [d], Kiyotaka Asakura [b,*], Youzhu Yuan [a,*]

[a] State Key Laboratory of Physical Chemistry of Solid Surfaces, National Engineering Laboratory for Green Chemical Productions of Alcohols–Ethers–Esters, iChEM, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China
[b] Institute for Catalysis, Hokkaido University, Kita 21, Nishi 10, Kita-ku, Sapporo, Hokkaido 001-0021, Japan
[c] State Key Laboratory of Catalysis, iChEM, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China
[d] Synfuels China Technology Co., Ltd., Beijing 101407, China

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ABSTRACT

Transition-metal nitrides can exhibit catalytic performance comparable to that of noble metal catalysts in many reactions. However, investigations on the correlation of catalyst structure, performance, and stability are still highly demanded. Here, a series of metal nitrides were prepared and evaluated for the selective oxidation of alcohols by molecular oxygen. Among them, FeN_x/C-*T* catalysts (*T* represents the pyrolysis temperature) display above 95% selectivity to the corresponding aldehydes in the selective oxidation of unsaturated alcohols. The optimized FeN_x/C-900 catalyst gives the highest TOF of 7.0 h^{-1} for the conversion of 5-hydroxymethylfurfural to 2,5-diformylfuran. A combination of characterizations and experiments suggests that Fe—N_4 species are the main active sites. In addition, we investigate the reasons for the catalyst deactivation and provide an effective approach to regenerating the catalysts. The results indicate that the deactivated catalysts can be regenerated by heat treatment under NH_3/N_2 after each run. Based on these studies, a plausible reaction mechanism over the FeN_x/C catalysts is proposed.

1. Introduction

In recent years, metal nitride catalysts have been developed rapidly in the fields of electrochemistry [1–3], catalytic oxidation [4–6], and organic synthesis [7] because of their unique structure properties. Metal nitride catalysts are often prepared by calcining different precursors obtained from template methods [6,8], ball milling [1,4], and oxidative polymerization [2,9]. Deng et al. reported a graphene-supported FeN_4 (an iron moiety coordinated with four nitrogen groups) catalyst synthesized by ball milling and calcination. It achieved the oxidation of benzene using H_2O_2 as oxidant with 23.4% conversion and 18.7% yield of phenol at room temperature over 24 h [4]. Li and co-workers demonstrated that a N-doped graphene-supported cobalt catalyst could convert benzyl alcohol to benzaldehyde under O_2 with a yield of 92.4% after 5 h at 130 °C [5]. Xie et al. proposed an Fe—N—C catalyst using a template method, which was active for the oxidative dehydrogenation of 5-hydroxymethylfurfural (HMF) in aerobic solution with only a 40% yield of 2,5-diformylfuran (DFF) over 8 h at 80 °C under 1.0 MPa O_2 [8]. Quite recently, Liu et al. prepared atomically dispersed Fe—N—C catalysts at high temperature using MgO nanoparticles as the template. The Fe—N—C-700 catalyst exhibited high activity for the selective oxidation of C—H bonds using *tert*-butyl hydroperoxide (TBHP) as an oxidant [6].

Despite considerable studies of metal nitrides, the structure of active sites and stability still deserve further investigation. The difficulties in investigating the active phases mainly lie in the complexities of structure and uncertainties of catalyst composition. To date, no consensus on the correlation of catalyst structure, performance, and stability has been achieved in the literature. Much researches has been conducted on active sites of iron-based nitrides for the oxygen reduction reaction (ORR) [1,10,11]. Artyushkova et al. proposed that a pyrrolic N species acted as the active site for O_2 reduction to H_2O_2 and that Fe—N_x species and pyridinic N atoms were the active sites for H_2O_2 reduction to H_2O [10]. Choi and co-workers reported that FeN_xC_y moieties were the main active sites for H_2O_2 reduction [11]. Further, recent work by Liu et al. discriminated the form of active sites in the Fe—N—C catalysts. They verified that the Fe^{III}—N_5 entity is the main active site for the selective oxidation of C—H bonds with TBHP [6].

* Corresponding authors.
E-mail addresses: askr@cat.hokudai.ac.jp (K. Asakura), yzyuan@xmu.edu.cn (Y. Yuan).

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On the other hand, the stability of metal nitride catalysts has faced great challenges. Previous work proved that Fe—N_4 and Fe—N—C catalysts were deactivated in the oxidation reaction even at room temperature [4,8]. Deactivation phenomena also occurred in the ORR system [1,4,8,12,13]. Thus, it is very important to probe the essence of catalyst deactivation. A detailed study of deactivated catalysts will promote the development of methods to regenerate their performance.

It is well known that the selective oxidation of alcohols is an important organic reaction that plays a huge role in industrial applications, such as energy conversion and storage [14–18], the production of fine chemicals [15,17], and biomedical manufacturing [16,18]. Many catalysts have been reported for such reactions, such as supported Au [19–22] and Pt-group (Pt, Pd, and Ru) [23–27] catalysts, and other non-precious-metal catalysts [28–37]. In this work, we have prepared a series of metal nitrides (MN_x/C-*T*, M = Fe, Co, Cu, Cr, and Ni; *T* represents the different pyrolysis temperatures) by two-step pyrolysis treatment and employed them for the selective oxidation of several alcohols by O_2, aiming to investigate the active phase, stability, and regeneration of metal nitrides in the process of selective oxidation of alcohols. The results indicate that the FeN_x/C-*T* catalysts exhibit superior activity and selectivity for the conversion of unsaturated alcohols to the corresponding aldehydes with O_2 as an oxidant. A Fe—N_4 entity is identified as the main active phase for the FeN_x/C-*T* catalysts though a combination of X-ray photoelectron spectroscopy (XPS), electron spin resonance (ESR), extended X-ray absorption fine structure (EXAFS), control experiments, and poisoning experiments with potassium thiocyanate (KSCN). In addition, efforts have been made to explore the reason for deactivation and the regeneration of metal nitride catalysts.

2. Experimental

2.1. Chemicals and reagents

Multiwalled carbon nanotubes (CNTs) and carbon black (XC-72 and Ketjen black EC-600JD) were purchased from Shenzhen Nanotech Port Co. Ferric trichloride ($FeCl_3{\cdot}6H_2O$), cobalt nitrate ($Co(NO_3)_2{\cdot}6H_2O$), cupric nitrate ($Cu(NO_3)_2{\cdot}3H_2O$), chromic nitrate ($Cr(NO_3)_3{\cdot}9H_2O$), and nickel nitrate ($Ni(NO_3)_2{\cdot}6H_2O$) were obtained from Sinopharm Chemical Reagent Co. 5-Hydroxymethylfurfural (HMF), 2,5-diformylfuran (DFF), and 2,5-furandicarboxylic acid (FDCA) were purchased from Aladdin Industrial Corporation (Shanghai, China).

2.2. Catalyst preparation

Commercial carbon materials, including CNTs, XC-72, and Ketjen black EC-600JD, were treated in HNO_3 solution at 100 °C for 16 h. The MN_x/C-*T* catalysts were prepared in a two-step pyrolysis process using *m*-phenylenediamine as the nitrogen source according to the previous literature [2,9]. Briefly, *m*-phenylenediamine (3.0 g, 27.7 mmol) and the carbon support (Ketjen black EC-600JD, 0.4 g) were dispersed into a beaker containing a concentrated HCl aqueous solution. The suspension was stirred in an ice water bath, while the precooled oxidant $(NH_4)_2S_2O_8$ (2.0 M, 28 mL) was added slowly to oxidize *m*-phenylenediamine to cover the carbon support. After being stirred for 24 h, the suspension solution was filtered, washed, and dried to obtain the N-doped carbon support. A series of metal salts ($FeCl_3{\cdot}6H_2O$, $Co(NO_3)_2{\cdot}6H_2O$, $Cu(NO_3)_2{\cdot}3H_2O$, $Cr(NO_3)_3{\cdot}9H_2O$, and $Ni(NO_3)_2{\cdot}6H_2O$) were used as precursors. The metal salt solution (0.3 M, 10 mL) was added dropwise into the dry N-doped carbon support (1.2 g) dispersed in 20 mL of water. Then the suspension was filtered and dried in an oven overnight at 100 °C before heat treatment. The obtained precursors were calcined at different temperatures from 600 to 1000 °C for 1 h under nitrogen. Subsequently, the pyrolyzed samples were leached in HCl solution (1 M, 100 mL) at 80 °C for 8 h to remove impurities, such as MC_x, MO_x, and MS_x, from the sample and washed to neutralize the samples using deionized water. Finally, the samples were calcined again in the same atmosphere and temperature for 3 h to form the corresponding FeN_x/C-*T*, CoN_x/C-*T*, CuN_x/C-*T*, CrN_x/C-*T*, and NiN_x/C-*T* catalysts. Similarly, FeN_x/CNT-*T* and FeN_x/XC72-*T* were synthesized by changing the carbon supports. FeN_x/C-700* and FeN_x/C-600* with the same N amount as FeN_x/C-900 were also obtained by controlling the amount of the nitrogen source. Briefly, other conditions remain unchanged, only decreasing the amount of *m*-phenylenediamine to 0.2 and 0.15 g for FeN_x/C-700* and FeN_x/C-600*, respectively. M/C-*T* and CN_x-*T* were prepared using a similar method without the addition of the nitrogen source and metal salt precursor, respectively.

2.3. Catalyst characterization

The porous properties of the catalysts were analyzed by N_2 adsorption–desorption measurements at −196 °C using a Micromeritics Tristar II 3020 apparatus. The catalysts were degassed at 100 °C for 4 h under vacuum before the measurements. The specific surface area was calculated through the Brunauer–Emmett–Teller (BET) method. The average pore diameter of the catalysts was determined by the Barrett–Joyner–Halenda (BJH) desorption isotherm. Powder X-ray diffraction (XRD) analysis was carried out on a PANalytical X'pert Pro diffractometer using CuK_α radiation (λ = 1.5418 Å) at a scanning rate of 20°/min from 10° to 90°.

Raman spectra were collected on a Renishaw Invia Raman microscope with a CCD detector. The Raman data were recorded using 532 nm excitation by a He–Cd laser source with a 10 s exposure. The output power of the laser was 13 mW.

Transmission electron microscopy (TEM) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images were taken on a transmission electron microscope (TECNAI F30). The acceleration voltage was 300 kV. The catalysts were ground and ultrasonically dispersed in ethanol before observation. The suspension was dropped onto a copper grid supported by superthin carbon films.

The metal content of the catalysts was obtained by an X-ray fluorescence (XRF) spectrometer (Bruker) at 60 kV and 50 mA. Before the measurements, the catalysts were mixed with boric acid (H_3BO_3) and then pressed into 2 mm pellets. The content of C, N, and H was measured by elemental analysis on an Elementar Vario EL III instrument.

XPS measurement was performed on a Qtac-100 LEISS spectrometer with an AlK_α incident radiation source. The C1*s* peak (284.6 eV) was referenced to calibrate the binding energies of the catalysts.

ESR spectra were recorded on an X-band Bruker EMX-10/12 apparatus at −173 °C. The samples (20 mg) were poured into quartz tubes and cooled to −173 °C in liquid nitrogen. The experimental frequency was 9.45 GHz, and the operating power was 19.94 mW.

EXAFS measurement was carried out at BL9C of the Photon Factory, Institute for Materials Structure Science, High Energy Accelerator Research Organization (KEK-IMSS-PF), Japan (Proposal 2016G546). The X-rays were monochromatized by a Si(1 1 1) double crystal. The XAFS spectra were collected at room temperature. Higher harmonics were rejected by a total-reflection focusing mirror. The ionization chambers for the incident X-rays (I_0) and the transmitted X-rays (I) were both filled with N_2. The REX program was used to analyze the EXAFS spectra ($\mu(E)$) [38–40]. The