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New insight into the enhanced activity of ordered mesoporous nickel oxide in formaldehyde catalytic oxidation reactions

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ABSTRACT

Highly ordered mesoporous materials synthesized by a nanocasting method offer vast opportunities in catalytic applications. However, considerable debates remain as to the mechanism by which the mesoporous structure results in enhanced performance. We demonstrate new insights into the role of ordered mesoporous metal oxides in the catalytic oxidation reaction by preparing nickel (II) oxide (NiO) rather than a multiple valence compound such as Co_3O_4 as model catalyst. Mesoporous NiO using KIT-6 as a template (m-NiO-k) achieved total formaldehyde (HCHO) mineralization at 90 °C using oxygen (O_2) as oxidant, while bulk NiO (b-NiO-c) oxidized HCHO completely at 170 °C. Moreover, using ozone (O_3) as oxidant, m-NiO-k attained increased HCHO conversion by ~34% with a twofold increase in CO_2 selectivity and a 100% O_3 decomposition rate. We conclude that the surface sodium functionalization of m-NiO significantly promotes the total oxidation of HCHO with O_2, likely via contribute to hydroxyl regeneration during reaction. Furthermore, the extra active oxygen species and undercoordinated NiO on the mesoporous surface owing to the properties of mesoporous structures contribute almost exclusively to the high activity and selectivity in the simultaneous catalytic removal of HCHO and O_3, which are also involved in the further enhanced activity for HCHO oxidation using m-NiO with O_2. These findings provide additional new insight into engineering efficient mesoporous metal oxides for VOCs catalysis under mild condition. Furthermore, they provide an innovative perspective on optimizing other reactions employing nanocast mesoporous catalysts.

1. Introduction

Active and selective catalysts are important for the catalytic elimination of environmental pollutants, as well as energy conversion and storage [1,2]. Nanocasting, a general and straightforward approach to synthesize ordered mesostructure metal oxides from preformed hard templates, is one possible strategy to accomplish this objective. It has already been demonstrated in a number of studies that showed that mesoporous transition metal oxide materials achieved significantly higher activity in catalytic reactions than their nonporous counterparts [3–8]. The better performance is generally ascribed to the following factors: mesoporosity, ultrahigh surface area, tunable pore sizes, and large pore volume, together with some other possible nanoscale effects, such as nanocrystallinity and nanoconfinement effect.

Recently, however, we have demonstrated new perspectives on the structure–function relationships of mesoporous catalysts [9]. We proved that the surface sodium functionalization introduced during the hard template removal step is critical for the high performance of the soot–NO_x catalytic removal reaction by mesoporous Co_3O_4 (m-Co_3O_4), while the pore structure plays a less prominent role. This result gives rise to the following three interesting questions:

(1) Is the role of surface sodium functionalization universal or is it dependent on the reaction? This question is mainly based on the following facts: The soot–NO_x catalytic reaction occurs at the solid–gas–solid triphase interface, and thus the interaction of soot and NO_x/O_2 facilitated by the enhanced adsorption and activation of the NO and O_2 species due to the surface alkali metal is rather important [10]. Then how about catalytic gas–solid reactions, such as the catalytic oxidation reaction of VOC? It is commonly known that such

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gas–solid interaction is a more general reaction than the special gas–solid–solid reaction. And elimination of VOCs under mild conditions is a vital topic of environmental catalysis research [11]. Therefore, the structure–performance relationship for such reactions will be of general interest.

(2) Can we investigate a model catalyst providing a mechanism with which to focus on the concerns of surface sodium species, active oxygen species, and metal oxide fine structure, independent of the others? The emerging mechanisms for enhanced activity of mesoporous Co_3O_4 in the HCHO catalytic oxidation reaction include but are not limited to factors such as surface Co^{3+}/Co^{2+} cationic ratio, adsorbed oxygen species, and specific surface area [3]. However, high Co^{3+}/Co^{2+}, which is generally related to the theoretical high-activity crystal planes, does not necessarily translate to improved performance in applications [8,12,13]. Considering that the above parameters may also correspond to each other, it would be better to consider decreasing the variables for mechanism investigation based on the selection of materials.

(3) How do the structure–function relationships vary with experimental parameters? Can we hope, for example, to discover a universal relationship of oxidation performance for formaldehyde (HCHO) with the structure properties, such as surface sodium functionalization, whether using oxygen or ozone as oxidant? Ozone is specially mentioned here because ozone is another dangerous air pollutant and also a by-product of emerging air quality control technologies, such as plasma, ionizers, and electrostatic precipitators (ESPs) [14–16]. Catalytic oxidation of VOCs with ozone could completely oxidize VOCs under mild conditions [17,18]. Hybrid treatments combining catalytic oxidation with ozone ideally could provide an alternative mild strategy for simultaneously removing VOCs and/or particulate matter together with O_3 in one device, which could not only address the concern for VOC destruction at ambient temperature but also help to eliminate O_3. The latter is one of the major obstacles to applying emerging air quality control technologies such as plasma and ESP [19]. It is also worth mentioning that this research focused on simultaneous removal of HCHO and ozone using ozone as oxidant. This is different from previous studies focused on total oxidation of VOCs, which generally applied a high molar ratio of ozone to VOCs (even up to 10:1) to achieve high VOC removal efficiency [17,20].

In this work, highly ordered mesoporous nickel (II) oxide (NiO) was chemically prepared by nanocasting and used as a model catalyst in the HCHO oxidation reaction with the goal of achieving more insight into the above three questions. The selection of NiO, instead of other transition metal oxides such as Co_3O_4 with multiple valence states, not only could help explore the above-mentioned second question but also has the additional benefit of providing an opportunity to investigate nickel (II) oxide, an oxide previously believed to be inactive for the heterogeneous catalytic oxidation of organic compounds [21]. Ordered mesoporous nickel oxides (m-NiO) synthesized by the nanocasting method significantly improved the activity and selectivity for HCHO oxidation with/without ozone. Mesoporous NiO using KIT-6 as a hard template (m-NiO-k) achieved total formaldehyde (HCHO) mineralization at 90 °C using oxygen as an oxidant, while bulk NiO (b-NiO-c) oxidized completely at 170 °C. However, surface-sodium-functionalized bulk NiO synthesized by the citric acid method (b-NiO-c) also exhibited unexpectedly high activity towards HCHO oxidation. Moreover, using ozone as oxidant, m-NiO-k attained an HCHO conversion ratio increased by ~34% with a twofold increase in CO_2 selectivity. A systematic investigation reveals that, using oxygen as oxidant, the surface sodium, present in the form of carbonate, contributes to regeneration of hydroxyls and favors the further oxidation of intermediate species, hence increasing the activity dramatically. Thus, the surface alkali metal residues on the mesoporous NiO (m-NiO) due to etching of silica in alkaline solutions could partially explain the activity gap between m-NiO and b-NiO using oxygen as oxidant. Moreover, the extra adsorbed active oxygen species and undercoordinated NiO on the surface of m-NiO contribute almost exclusively to the high activity and CO_2 selectivity in the simultaneous catalytic removal of HCHO and ozone at room temperature. The m-NiO catalysts also benefit from these unique structure properties for further improved catalytic oxidation activity using oxygen as oxidant. These findings hence enable us to unravel the mechanism to overcome one of the challenges in environmental catalysis, oxidation of VOCs under mild conditions using mesoporous materials. More importantly, this study provides an additional new perspective on optimizing the performance of other catalytic reactions employing nanocast catalysts.

2. Experimental

2.1. Chemicals and synthesis

TEOS ($Si(OC_2H_5)_4$), concentrated hydrochloric acid (35%), nickel nitrate ($Ni(NO_3)_2 \cdot 6H_2O$), N-butyl alcohol ($CH_3(CH_2)_3OH$), methanol, and citric acid ($C_6H_8O_7$) (analytical grade) were obtained from Sino Reagent. P123 ($M_w = 5800$) and nickel oxides, NiO and Ni_2O_3 (used as reference samples during X-ray absorption spectroscopy characterization), were obtained from Sigma-Aldrich. All the chemical reagents were used as received.

Hard templates, SBA-15 and KIT-6, were synthesized by a hydrothermal method described in the supporting information (SI). Mesoporous NiO was synthesized by nanocasting method using $Ni(NO_3)_2 \cdot 6H_2O$ as the nickel precursor. Portions of 1.16 g $Ni(NO_3)_2 \cdot 6H_2O$ precursor and 0.50 g silica template were mixed in 20 mL methanol, stirred under 40 °C to evaporate and dry thoroughly, and then calcined in air at 450 °C for 4 h. The silica templates were washed using a 2 mol L^{-1} NaOH solution (60 °C) for 2 h and the removing process was repeated twice. Centrifugal separation and washing using deionized water were repeated three times to eliminate sodium residues. The powder was dried at 60 °C to obtain the final product. The mesoporous NiO replicated from SBA-15 and KIT-6 was denoted as m-NiO-s and m-NiO-k, respectively. Unless indicated otherwise, the reactions were carried out under a dry atmosphere. For the m-NiO-k catalyst, the catalytic activity was additionally tested with humid air (RH = 50%), denoted as m-NiO-k/H. In the XPS analysis section, m-NiO-k/r is the m-NiO-k catalyst after the HCHO oxidation reaction using ozone as oxidant.

As a comparison, b-NiO-c was bulk NiO prepared by a citric acid method. Typically, 0.92 g citric acid was dispersed in 40 mL deionized water to form a clear solution, and then 1.16 g of nickel nitrate was added into the citric acid solution. The mixture was stirred in an 80 °C water bath to produce a gel and then dried at 130 °C to form foamy gel. After the dry gel was ground, the resulting powder was calcined at 450 °C for 4 h to obtain b-NiO-c. Additional post-treated b-NiO-c using the same exact NaOH solution washing process in nanocasting were denoted as b-NiO-c-Na-w1 and b-NiO-c-Na-w3, respectively, with the number 1 or 3 denoting once or threes deionized water washing processes during the last step in the nanocasting, centrifugal separation and washing using deionized water to get the final NiO powder. Additional b-NiO-c soaking with KOH was denoted as b-NiO-c-K-w1.