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Bridging the reaction route of toluene total oxidation and the structure of ordered mesoporous Co_3O_4: The roles of surface sodium and adsorbed oxygen

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ABSTRACT

Catalysts with ordered mesoporous structure usually behave superior in total oxidation of toluene. However, the link between reaction route and ordered mesoporous structure is still not fully founded currently. In this work, Co_3O_4 is selected as a model catalyst to illustrate the reaction route. The intermediates in the oxidation of toluene were analyzed via *in situ* Fourier transform infrared spectroscopy (*in situ* FTIR), high performance liquid chromatography (HPLC) and temperature programmed oxidation (TPO) experiment. Here we prove benzoquinone route as a special reaction route only observed in ordered mesoporous Co_3O_4, coexisting with the commonly reported benzoate route. Benzoquinone route is favored especially at lower temperature, accelerating the reaction rate, and acts as a crucial intrinsic reason for the better performance of ordered mesoporous Co_3O_4. The results also indicate that the activity of Co_3O_4 for oxidation of toluene depends on the quantity and nucleophilicity of surface oxygen species, which could be increased by the irregular surface morphology and the introduction of sodium.

1. Introduction

Volatile organic compounds (VOCs) are a group of chemicals released from solvent utilization, industrial processes, road vehicle emissions and other activities related to humankind, as well as from natural resources, which raise concerns for its environmental damages [1]. Among them, toluene is a typical aromatic VOCs widely used in solvent and gasoline [2,3], which will participate in atmospheric chemical reaction to cause air pollution [4] and to risk human health. Catalytic total oxidation is considered to be one of the most excellent ways to reduce toluene emission. Among available catalytic formulations, noble metals exhibit excellent performance in eliminating toluene [5], however, the application of noble metals based catalysts has some disadvantages, such as high price and the potential to aggregate.

Metal oxides are promising to replace noble metals as catalysts for VOCs oxidation. Recently, transition metal oxides including Co_3O_4, MnO_x, CuO and CeO_2 are being investigated as the prominent candidates for further application [6–14]. Among them, cobalt oxide exhibits encouraging performance for the total oxidation of VOCs [9,15], as well as the oxidation of CO [16,17]. To enhance the performance of catalysts, modification of metal oxides is widely researched.

Chemical composition and physical morphology are among the key factors to optimize the performance of the catalysts. The significant promotion effect of alkali metal cations has attracted much attention. Jirátová et al. [9] reported that 90% of toluene can be oxidized at a temperature as low as around 165 °C with the adding of 1% K. Similarly, this promotion effect was also reported on other research [18,19] as well as in our group's previous research [20]. The promotion effect was accounted by the generation of oxygen defect [18], while others suggested it stemmed from the nucleophilicity of surface oxygen [19,21]. In addition, ordered mesoporous structured catalysts were reported to possess better performance due to its special pore morphology [10,15,22,23]. The ordered mesoporous morphology usually contributes to higher surface area, and smaller restricted crystal size, which will benefit the catalysis. However, rarely reported is the fact that previous treatment in NaOH has left a small dose of alkali metal cations in the ordered mesoporous catalysts, which is one of the focuses in this work.

The knowledge of the mechanism of the catalytic total oxidation of toluene is the foundation for the catalyst optimization. Two possible reaction routes were suggested by Andersson [24]. In one

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mechanism, methyl group was first oxidized to benzaldehyde or benzoate and detached to generate benzene, which was later oxidized to benzoquinone; while in another mechanism, aromatic ring was attacked by the catalysts to produce methyl benzoquinone, regardless of the methyl group. All the molecules were oxidized to maleic anhydride before further oxidized to CO_2 and H_2O. Busca [25] suggested the oxidation of methyl group to be the initial step and the intermediates were later oxidized to maleic anhydride via benzoate salt reaction route. Further research including our group's previous work [11,26] confirmed the benzoate salt as intermediate. When focused on the role of catalysts, generally, a larger amount of adsorbed surface oxygen benefited the total oxidation of organic compounds, and denser electrons surrounding oxygen favored the cracking of C—H bond [27]. However, a detailed reaction route concerning about both the reaction routes and the structure of the catalysts is yet to be established. The understanding of a catalyst structure-based reaction route and the relationship between catalysts and reactants is essential to further designing of new catalysts. Especially, ordered mesoporous Co_3O_4 (OM-Co_3O_4) has been of much research interests for its excellent catalytic performance and specific structure. In this research, a detailed investigation was carried out to take OM-Co_3O_4 as representative to analyze the mechanism of the total oxidation of toluene, and to illustrate the performance of OM-Co_3O_4 in molecule scale. *In situ* Fourier transform infrared spectroscopy (*in situ* FTIR) was applied to observe the possible intermediates during the reaction to establish the reaction mechanism concerning the adsorbed toluene and the structure of Co_3O_4. The relationship among sodium, surface oxygen species and reaction routes were investigated to shed light on the intrinsic factors that influence the total oxidation of toluene. Co_3O_4 nanoparticles (NP-Co_3O_4) were specifically controlled within similar crystal size to investigate the influence of morphology. And comparable dose of sodium was added to NP-Co_3O_4 (Na + NP-Co_3O_4) to investigate the effect of sodium for the reaction.

2. Materials and methods

2.1. Catalyst preparation

The ordered mesoporous structured Co_3O_4 (denoted as OM-Co_3O_4) is synthesized by nano-casting method based on previously published works [28–31]. Ordered mesoporous silica KIT-6 was used as the nano-template for OM-Co_3O_4, which was synthesized as below. A mixture of 6.0 g triblock copolymer poly(ethylene glycol)-poly(propylene glycol)-poly(ethylene glycol), (named P123, Sigma–Aldrich, average M_n ca. 5800), 11.8 g 36 wt.% HCl solution, 6 g n-butanol, and 217.0 mL deionized water was kept agitatedly stirring for 1 h in water bath at 35 °C. 13.8 mL tetraethyl orthosilicate (TEOS) was added by drop to the mixture solution. After 24 h of stirring, the mixture was transferred to a Teflon container to be hold at 100 °C for 24 h. The precipitation was washed by HCl-ethanol solution and ethanol in sequence, and then dried in ambient temperature overnight. The calcination procedure was executed as Poyraz et al. [31] reported to get KIT-6. Then 1 g KIT-6 and 1.5 g $Co(NO_3)_2{\cdot}6H_2O$ were mixed with 40 mL toluene at 70 °C for 4 h. The suspended matters were extracted by filtration and washed by hot toluene (70 °C). After that, the retaining matters were dried at ambient temperature overnight and calcined at 450 °C for 6 h. The calcined powders were mixed with 200 mL 2 M NaOH solution with stirring for 4 h. After washing by centrifuge to pH ≈ 7 and drying at 110 °C, the OM-Co_3O_4 sample was obtained.

The nanoparticle samples (denoted as NP-Co_3O_4) was synthesized by solvothermal method. 1 g $Co(CH_3COO)_2{\cdot}4H_2O$, 0.15 g Polyvinylpyrrolidone (PVP, M_n ca. 58,000), and 5 mL 25 wt.% ammonia solution were dissolved by 50 mL ethanol. After 10 min stirring, the mixture was transferred into a Teflon container, and kept at 200 °C for 3 h. The precipitates were washed and dried at 60 °C overnight, and calcined at 350 °C for 2 h (10 °C min^{-1} as ramp rate). The sample synthesized was denoted as NP-Co_3O_4. As in Table 1, 580 mg/kg sodium can be detected in OM-Co_3O_4. Sodium is introduced when dissolving KIT-6 by NaOH solution, which is hard to be removed completely. For the reason of comparison, NP-Co_3O_4 was post-treated in NaOH solution in an exact procedure to introduce sodium. NP-Co_3O_4 was post-treated by being stirred in a 2 M NaOH solution for 4 h. After washing, the sample was dried at 110 °C overnight, and calcined at 550 °C for 4 h in O_2 flow. The sample calcined was denoted as Na-NP-Co_3O_4. As in Table 1, comparable dose of sodium around 790 mg/kg has been detected in Na + NP-Co_3O_4.

Table 1
Physical and chemical parameters of different samples.

Samples	d_c[a] (nm)	C_{Na}[b] (mg/kg)	S_{BET}[c] ($m^2 g^{-1}$)
OM-Co_3O_4	14.7	580	101
NP-Co_3O_4	15.2	<10	57
Na + NP-Co_3O_4	29.0	790	39

[a] Crystal size calculated by Sherrer's equation from XRD.
[b] Sodium concentration obtained by ICP-AES.
[c] Surface area calculated by BET equation.

2.2. Catalysts characterization

Composition of catalysts was analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) using a Thermo IRIS spectrometer. Morphology was analyzed by transmission electron microscopy (TEM). The experiment was conducted on HT7700, Hitachi with an electron beam of 100 kV. X-ray diffraction (XRD) and small angle X-ray scattering (SAXS) were conducted by an X-ray diffractometer (RINT2000, Rigaku). A Cu target was applied as the X-ray source, exposed by a 40 kV, 200 mA electron beam. The continuous 2θ-θ scanning was conducted with a step width of 0.02° for XRD; and 0.01° for SAXS. Pore structure and Brunauer–Emmett–Teller (BET) specific surface area were analyzed by a Micromeritics ASAP 2020 HD system. BET equation was applied for the specific surface area calculation. Barrett-Joyner-Halenda (BJH) method was applied on the desorption branch to analyze mesoporous pore size distribution.

Reaction mechanism was analyzed by *in situ* Fourier transform infrared spectroscopy (*in situ* FTIR) on a Thermo Fisher Nicolet 6700 system, with scanning step of 4 cm^{-1}. In a typical experiment, the catalysts were firstly exposed to an air flow of 100 mL min^{-1} at 350 °C for 1 h. After cooled to 40 °C and maintained for 1 h, the catalysts were exposed in a mixture of 500 ppm toluene with N_2 as carrier, and spectra recording was conducted at the same time. Then the gas was shifted to air flow while maintaining the temperature, and the spectra were recorded. The intermediates were also analyzed by high performance liquid chromatography (HPLC) (e2695-2489, Waters). After saturation in toluene gas, the samples were immediately extracted by acetonitrile. The extraction was separated through a C18 column and analyzed using a UV-Vis detector continuously scanning from 200 to 400 nm.

Temperature-programmed oxidation (TPO) was conducted in the fixed-bed reactor followed by a gas chromatography-mass spectroscope (GC–MS) (7890A-5975C, Agilent). 50 mg catalysts were loaded and saturated by a flow gas of 1400 ppm toluene in 20 vol.% O_2 and N_2 with a flow rate of 50 mL min^{-1}. After saturation, an air flow with a rate of 50 mL min^{-1} was applied to catalysts to flush the physically weakly adsorbed toluene. Then the temperature was elevated with a rate of 2 °C min^{-1} to 400 °C. The concentration of toluene and CO_2 was recorded simultaneously. The surface elements chemical environment was analyzed by X-ray

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