

Catalytic oxidation of toluene over Co-modified manganese oxide octahedral molecular sieves (OMS-2) synthesized by different methods

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Abstract. Co/OMS-2 catalysts were prepared by different preparation methods, and their catalytic performance was investigated for the oxidation of toluene. The catalytic activity was revealed as sequence: OMS-2 > Co/OMS-2(one step method) > Co/OMS-2(impregnation method) > Co/OMS-2(ion exchange method), and the over performances of the different methodologies are quite similar to each other. It was found that OMS-2 achieved 90% toluene conversion at 225 °C. The decrease of catalytic performance over Co-containing catalysts originates from lower reducibility as well as the oxygen mobility on the surface of the Co/OMS-2 catalyst.

1. Introduction

Volatile organic compounds (VOCs) produced by industrial processes and automobile are harmful to human health and atmospheric pollution [1-2]. Removal of VOCs has various methods such as adsorption, absorption, pyrolysis, catalytic oxidation and photocatalytic degradation [1, 3-6]. Among them, catalytic combustion is considered as one of the most effective and energy-saving methods due to its lower operating temperature and higher efficiency. In the last decades, complete oxidation of VOCs has been widely investigated over either noble metals or metal oxides catalysts [7, 8]. However, noble metals are prone to deactivate when treating the heteroatomic-containing VOCs or under extreme reaction temperatures. Compared with noble metal supported catalysts, metal oxides are more suitable for relatively higher operating temperature as their superior thermal stability and antipoisoning capability. Among them, the copper and manganese oxides have been reported to be the most efficient catalyst in the oxidation of aromatic and chlorinated VOCs, such as Cl-VOCs [9], toluene [10-12], CO [13].

In the last few years, octahedral molecular sieve of manganese oxide (OMS-2) has gained intensive interest as potential catalyst in dealing with VOCs removal. OMS-2 is a form of manganese dioxide with a one-dimensional tunnel structure composed of 2×2 MnO₆ octahedral chains. A mixed-valent manganese framework is formed due to the coexistence of Mn⁴⁺, Mn³⁺ and Mn²⁺. It presents a superior

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catalytic activity of formaldehyde, benzene, toluene, ethanol and o-xylene oxidation due to the porous structure, redox property, excellent hydrophobicity and surface acidity^[14-17]. To the best of our knowledge, the Co/OMS-2 catalyst for toluene oxidation is seldom reported. Especially, the effect of Co/OMS-2 catalyst with different preparation methods on the reaction mechanism and structural explanations should be further explored. In order to obtain more information about the influence of Co on the structure of OMS-2 and catalytic performance, we choose toluene oxidation as a research subject, and further explore the effect of Co/OMS-2 catalysts on redox property and catalytic performance.

2. Experimental

2.1 Catalyst preparation

OMS-2 was synthesized by a reflux method similar to that reported on the literature^[18]. In a typical synthesis, $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ (4.4 g, 26.0 mmol) and concentrated HNO_3 (1.5 ml) were dissolved in deionized water (15.0 ml). A second solution was prepared by dissolving 38 mmol KMnO_4 in 100 DDW. The latter solution was subsequently added into the former solution under vigorous stirring to form a dark brown precipitate at 100 °C for 24h. After the products were washed with deionized water and filtered, the acquired products were dried at 110 °C overnight, then were calcined at 500 °C for 4h. The resulting catalysts were named OMS (OMS-2).

3.8g of ground-up OMS-2 was impregnated by 15ml solution of $\text{Co}(\text{NO}_3)_2$ (0.35mol/L) under vigorous stirring for 24h. The acquired slurry was dried at 120 °C for 8h to remove the moisture. After that, the acquired products were calcined at 400 °C for 4h. The resulting catalysts were named CoI.

1g of OMS-2 was exchanged with 30ml solution of $\text{Co}(\text{NO}_3)_2$ (0.2 mol/L). Every four hours, the solution was substituted with a fresh $\text{Co}(\text{NO}_3)_2$ solution (0.2mol/L), and the whole process lasted 24h. After that, the acquired products were filtered, washed and dried at 80 °C for 24h. The acquired products were calcined at 400 °C for 4h. The resulting catalysts were named CoE.

To prepare CoP catalyst, 10 ml CoSO_4 solution (0.5mol/L) was added to the solution of OMS-2 synthesized before refluxing to form OMS-2 structure. After that, the acquired products were calcined at 500 °C for 4h. The resulting catalysts were named CoP.

2.2 Catalyst Characterization

X-ray diffraction (XRD) patterns were recorded on a powder diffraction system (X'Pert PRO; PANalytical, Almelo, The Netherlands) using $\text{Cu K}\alpha$ radiation ($\lambda=0.15418$ nm) in the 2θ range of 5-80 ° (scanning rate of 3 °/min).

N_2 adsorption/desorption isotherms of catalysts were collected at 77 K on a gas sorption analyzer ASAP 2020M. All samples were degassed under vacuum at 350 °C for 4 h before measurement. The total pore volume was estimated from the amount of nitrogen adsorbed at a relative pressure (P/P_0) of 0.05-0.3. The specific surface area (S_{BET}) was calculated using the Brunauer-Emmett-Teller (BET) method.

The elemental compositions of the samples were analyzed by X-ray fluorescence (XRF) in a ZSX-Primus II spectrometer with Rh tube as excitation source.

Thermal gravimetric analysis (TGA) experiments were carried out on a PerkinElmer TGA 4000 instrument, where *ca.* 20 mg of finely ground sample was heated from 35 to 900 °C at a heating rate of 10 °C/min with nitrogen flowing at 30ml/min.

The temperature programmed reduction of H_2 (H_2 -TPR) were performed on a Finetec Finesorb-3010. TPR profiles were obtained by passing 10 % H_2/He flow (15 ml/min) through the catalysts (about 20 mg) which had been dried in a helium flow (15 ml/min) at 300 °C for 1 h.

2.3 Catalytic activity evaluation

All evaluation experiments were performed on a continuous flow fixed-bed reactor of steel tube (6 mm, i.d.) at atmospheric pressure. In each test, 0.1 g of the catalyst (40-60 mesh) was placed into the

tube reactor. The VOC-containing gas was generated by bubbling air through the VOC saturator, which was further diluted with another air stream before reaching the reaction bed. The total flow rate was kept at 150 ml/min, i.e, gas hourly space velocity (GHSV) of 30, 000 h⁻¹ with toluene concentration of 1000 ppm. The reaction temperature (RT) was first raised to 130 °C with the feed stream passing and stabilized for 30 min. Then the reaction bed temperature was increased to the following setting one and stabilized about 20 min for the online detection prior to the next point. Online analysis was carried out on a GC (Trustworthy Instrument GC- 7806) instrument, which equipped with FID detector was employed for the quantitative analysis.

3. Results and discussion

3.1 Catalyst characterization

3.1.1. A XRD, XRF and BET analysis

The XRD patterns of OMS, CoI, CoE, and CoP are presented in Fig. 1. In all materials, the reflections expected for the cryptomelane structure were clearly visible [17], which indicated that the Co doped samples didn't change the crystalline structure of the OMS-2 support. No obvious diffraction peak ascribable to Co metal or oxides was observed for the Co-containing catalysts. It seemed that the doped metals were well-dispersed in the OMS-2 structure.

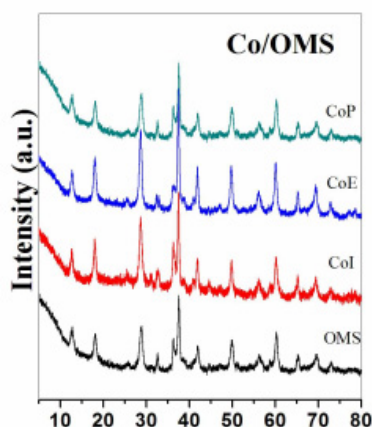


Fig.1 XRD profiles of catalysts: OMS, CoI, CoE, CoP.

The specific surface area (S_{BET}) and total pore volume (D_v) of the prepared samples are summarized in Table 1. The order of S_{BET} was as follows: OMS (67.0 m²/g) > CoP (60.9 m²/g) > CoE (47.6 m²/g) > CoI (40.4 m²/g). CoE and CoI possessed a relatively high D_v (1.2 cm³/g), which was smaller than CoP (1.4 cm³/g), but slightly larger than OMS (0.82 cm³/g). An XRF technique was used to analyze the Co and Mn contents. The Co contents of the prepared by different methods were 0.2 wt% for CoE, 0.8 wt% for CoP, and 1.8 wt% for CoI, respectively.

Table.1 Physicochemical properties of the synthesized catalysts: OMS, CoI, CoE, CoP.

Catalyst	$S_{\text{BET}}^{\text{a}}$ (m ² /g)	D_v^{b} (cm ³ /g)	Co ^c (wt%)	Mn ^c (wt%)
OMS	67.0	0.82	-	-
CoI	40.4	1.2	1.8	63.7
CoE	47.6	1.2	0.2	70.5
CoP	60.9	1.4	0.8	67.8

^a BET specific surface area.

^b Total pore volume estimated at $P/P_0=0.05-0.3$.

^c Co and Mn contents by XRF analysis.

3.1.2. B Thermogravimetric analysis

The profiles of TGA of the samples are shown in Fig. 3. TGA profiles exhibited the different thermal stability, and the total weight losses were 8.8 % for CoP, 7.8 % for CoE, 7.2 % for CoI, 6.8 % for OMS, respectively. This indicated that CoP catalyst was more thermally stable than the other catalysts. The losses below 300 °C were attributed to adsorbed water, carbon dioxide, as well as some physically absorbed oxygen^[19]. There were slight weight losses of the sample in 300-450 °C, which were considered as the effects of chemisorbed oxygen. A significant weight loss occurred between 450 °C and 650 °C (4.1 % for OMS, 3.4 % for CoI, 4.2 % for CoE, 4.1 % for CoP), which could be attributed to the evolution of lattice oxygen species of OMS-2 catalyst^[20]. As a result, the lattice oxygen species of CoI was less than the other catalysts, while the other catalysts were almost the same. It has been reported the weight losses above 650 °C were due to the collapse of OMS-2 and the decomposition of manganese oxide to lower oxidation state with the second lattice oxygen release^[19, 21].

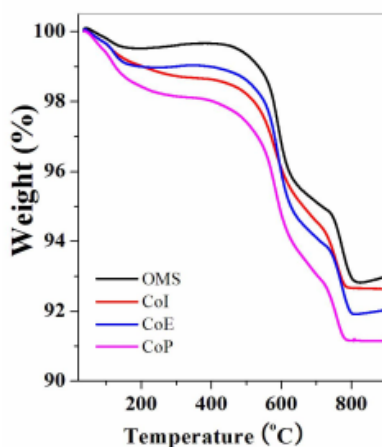


Fig.2 TGA of OMS-2, CoI, CoE, CoP.

3.1.3. C Hydrogen temperature-programmed reduction

Fig.3 presents the H₂-TPR profiles of OMS, CoI, CoE and CoP catalysts. The peaks between 200 °C and 350 °C were originated from the hydrogen consumption during the formation of Mn₂O₃, the reduction of Mn₂O₃ to Mn₃O₄, and Mn₃O₄ to MnO^[22]. After loading of Co, the reduction peak didn't show a clear change. Nevertheless, the hydrogen consumption can be calculated by the area of the reduction peaks. Compared with the other catalysts, OMS catalyst had the largest area of reduction peaks, while the area of CoI was the smallest. As a result, the reducibility of OMS was the strongest, while the reducibility of CoI was the weakest in these catalysts.

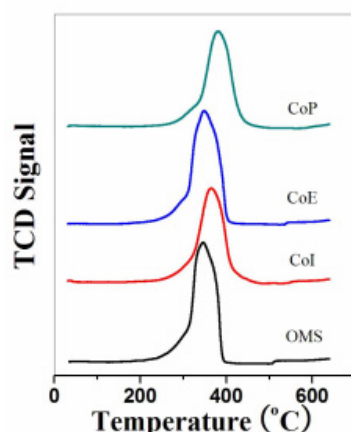


Fig.3 H₂-TPR profiles of OMS, CoI, CoE and CoP.

3.2 Toluene oxidation

The toluene conversion of the OMS, CoI, CoE and CoP catalysts during toluene oxidation is presented in Fig.4. OMS catalyst exhibited the highest catalytic activity of toluene oxidation and achieved 90 % toluene conversion at 225 °C. The complete oxidation temperature of toluene over OMS-2 series catalysts decreased as follows: OMS > CoP > CoE > CoI, based on the T₉₀ values (the temperature required to achieve 90 % toluene conversion). It was well known that toluene diameter was 5.8 Å, while OMS-2 had the dimensions of tunnels of 4.6 Å×4.6 Å. It was reasonable to conclude that the catalytic reaction occurred on the external surface of OMS-2. The catalytic activity was thought to benefit from the Mn-O lattice in the cryptomelane structure. The catalytic oxidation of VOCs over different manganese oxides were reported to proceed by a MvK mechanism^[22]. This effect operated when the catalyst was reduced by VOCs and was then recovered by oxidation. The available oxygen originated from chemisorbed oxygen or lattice oxygen. The addition of Co didn't increase the lattice oxygen species, which was consistent with the result of TGA. Hence, the higher mobility of the oxygen species on the external surface of OMS-2 series catalysts indicated better catalytic activity. It has been considered that the higher reducibility indicated the higher mobility of the oxygen species in catalysts. And the reducibility of Co-containing catalysts was weaker than OMS, this was well coincided with the results obtained by H₂-TPR. Therefore, the OMS-2 catalyst had better catalytic activity compared with the Co-containing catalysts.

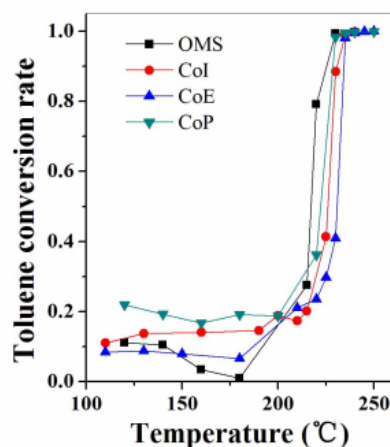


Fig.4. Toluene conversion of OMS, CoI, CoE and CoP.

4. Conclusions

In summary, a series of OMS-2-based Co catalysts were prepared by ion exchange method, impregnation method and one-step reflux method. The catalytic processes of toluene oxidation over the OMS-2, CoI, CoE, and CoP catalysts were studied by GC, and OMS-2 showed the highest catalytic activity. The catalytic activity of Co-containing materials decreased. It can be attributed to a lower reducibility as well as the oxygen mobility on the surface of the Co/OMS-2 catalyst.

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