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Article

Mechanochemical redox-based synthesis of highly porous $\text{Co}_x\text{Mn}_{1-x}\text{O}_y$ catalysts for total oxidation

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ARTICLE INFO

Article history:

Received 21 March 2020

Accepted 23 April 2020

Published 5 December 2020

Keywords:

Mechanochemical synthesis

Solid-state synthesis

Porous metal oxide

 $\text{Co}_x\text{Mn}_{1-x}\text{O}_y$ catalyst

Hydrocarbon combustion

ABSTRACT

A mechanochemical redox reaction between KMnO_4 and CoCl_2 was developed to obtain a $\text{Co}_x\text{Mn}_{1-x}\text{O}_y$ catalyst with a specific surface area of $479 \text{ m}^2 \text{ g}^{-1}$, which was higher than that obtained using a co-precipitation (CP) method ($34 \text{ m}^2 \text{ g}^{-1}$), sol-gel (SG) method ($72 \text{ m}^2 \text{ g}^{-1}$), or solution redox process ($131 \text{ m}^2 \text{ g}^{-1}$). During catalytic combustion, this $\text{Co}_x\text{Mn}_{1-x}\text{O}_y$ catalyst exhibited better activity (T_{100} for propylene = $\sim 200^\circ\text{C}$) than the control catalysts obtained using the SG (325°C) or CP (450°C) methods. The mechanical action, mainly in the form of kinetic energy and frictional heating, may generate a high degree of interstitial porosity, while the redox reaction could contribute to good dispersion of cobalt and manganese species. Moreover, the as-prepared $\text{Co}_x\text{Mn}_{1-x}\text{O}_y$ catalyst worked well in the presence of water vapor (H_2O 4.2%, >60 h) or SO_2 (100 ppm) and at high temperature (400°C , > 60 h). The structure $\text{MnO}_2 \cdot (\text{CoOOH})_{2.93}$ was suggested for the current $\text{Co}_x\text{Mn}_{1-x}\text{O}_y$ catalyst. This catalyst could be extended to the total oxidation of other typical hydrocarbons ($T_{90} = 150^\circ\text{C}$ for ethanol, $T_{90} = 225^\circ\text{C}$ for acetone, $T_{90} = 250^\circ\text{C}$ for toluene, $T_{90} = 120^\circ\text{C}$ for CO, and $T_{90} = 540^\circ\text{C}$ for CH_4). Scale-up of the synthesis of $\text{Co}_x\text{Mn}_{1-x}\text{O}_y$ catalyst (1 kg) can be achieved via ball milling, which may provide a potential strategy for real world catalysis.

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1. Introduction

The catalytic combustion of hydrocarbons is of great importance in the control of volatile organic compounds (VOCs) and automobile exhaust gases [1–6]. At present, most commercial catalysts are noble-metal-based materials with low combustion temperatures and long catalyst lifetimes [1,7–11]. In contrast, transition metal oxide catalysts are inexpensive and based on earth-abundant elements, but their activities and stabilities are somewhat low [4,12–15], obstructing their path

toward commercialization. In particular, cobalt-manganese oxides ($\text{Co}_x\text{Mn}_{1-x}\text{O}_y$) with multi-redox cycles are promising candidates in the catalytic oxidation of hydrocarbons [16–19]. Several synthetic methods have been developed for these catalysts. Among the parameters that determine the catalytic performance of combustion catalysts, the porosity and surface active oxygen species appear to be most critical [11,20,21].

The traditional strategies for $\text{Co}_x\text{Mn}_{1-x}\text{O}_y$ synthesis are the co-precipitation (CP) method, sol-gel (SG) method [22] and redox method [23], all of which are solution-based processes

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This work was supported by the National Natural Science Foundation of China (21776174), the Open Foundation of the State Key Laboratory of Ocean Engineering (Shanghai Jiao Tong University of China) (1809), Shanghai Jiao Tong University Scientific and Technological Innovation Funds (2019QYB06), China Shipbuilding Industry Corporation (CSIC) and Zhejiang XinAn Chemical Industry Corporation.

DOI: 10.1016/S1872-2067(20)63635-X | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 41, No. 12, December 2020

(SBPs). From the viewpoint of process intensification, there is still some room to modify the SBP. For example, the scope of metal precursors in SBPs is limited to liquid or soluble solid materials. Several operation units, such as the dissolution of metal precursors and liquid-liquid mixing, are required. Meanwhile, good dispersion of cobalt and manganese species is a key factor in $\text{Co}_x\text{Mn}_{1-x}\text{O}_y$ catalysts, since active oxygen species are expected to form at the $\text{Co}_x\text{Mn}_{1-x}\text{O}_y$ interfaces. Because of the different equilibrium constants for the Co^{2+} (1.6×10^{-15}) and Mn^{2+} (1.9×10^{-13}) ions involved, local separation of cobalt and manganese oxides is often observed when the CP method is used. Thus, the development of efficient methods for the synthesis of $\text{Co}_x\text{Mn}_{1-x}\text{O}_y$ catalysts is of great interest.

Recently, mechanochemistry has been revisited; mechanochemical methods could enable the synthesis of porous catalytic materials (e.g., zeolites, ordered mesoporous polymers and carbons, porous metal oxides, metal-organic frameworks, MgAl layered double hydroxide), and are attractive due to their solvent-free nature. Herein, we demonstrate a mechanochemical redox process (MRP) for the facile synthesis of a $\text{Co}_x\text{Mn}_{1-x}\text{O}_y$ catalyst via ball milling. The solution-based redox reaction involving the oxidation of a cobalt (II) salt with potassium permanganate (KMnO_4) is a well-known method for the synthesis of $\text{Co}_x\text{Mn}_{1-x}\text{O}_y$ catalysts [23,24]. However, in solution processes, the oxidative ability of KMnO_4 depends on its concentration, which may affect the formation of high valence species and high porosity within the $\text{Co}_x\text{Mn}_{1-x}\text{O}_y$. Unexpectedly, the $\text{Co}_x\text{Mn}_{1-x}\text{O}_y$ catalyst prepared via MRP exhibited a surface area of $479 \text{ m}^2 \text{ g}^{-1}$, which was higher than that of control samples prepared via CP ($34 \text{ m}^2 \text{ g}^{-1}$), SG ($72 \text{ m}^2 \text{ g}^{-1}$), and liquid redox ($131 \text{ m}^2 \text{ g}^{-1}$) methods. The physical effects of the mechanical action continually reduced the particle size during redox, leading to the formation of interstitial porosity.

In the aerobic combustion of propylene, propylene was completely oxidized at 200°C using the $\text{Co}_x\text{Mn}_{1-x}\text{O}_y$ prepared by MRP; this temperature was much lower than those of the control $\text{Co}_x\text{Mn}_{1-x}\text{O}_y$ catalysts fabricated via CP (450°C) and SG (400°C). In addition, the $\text{Co}_x\text{Mn}_{1-x}\text{O}_y$ obtained by MRP also showed good resistance to water vapor (4.2%, >65 h) and sulfur dioxide (20–100 ppm SO_2). At the same time, this catalyst can be extended to other substrates, such as carbon monoxide and methane, to give low combustion temperatures ($T_{90} = 120^\circ\text{C}$ for CO, $T_{90} = 150^\circ\text{C}$ for ethanol, $T_{90} = 225^\circ\text{C}$ for acetone, $T_{90} = 250^\circ\text{C}$ for toluene, $T_{90} = 540^\circ\text{C}$ for CH_4). Furthermore, this mechanochemical redox process is scalable, and the kilogram-scale preparation is already complete, making it an attentive alternative to the traditional methods.

2. Experimental

2.1. Preparation of catalysts

Typical procedure for the synthesis of $\text{Co}_x\text{Mn}_{1-x}\text{O}_y$ by MRP. $\text{Co}_x\text{Mn}_{1-x}\text{O}_y$ was synthesized by MRP based on the redox reaction of cobalt chloride, sodium hydroxide, and potassium permanganate without any templates. In a typical process, 2.8600 g of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and 0.8000 g of NaOH were added to a stain-

less-steel reactor (25 mL) along with six stainless steel balls (two with a diameter of 1.0 cm, and four with a diameter 0.6 cm). The reactor was placed in a high-speed ball milling apparatus (Focucy Planetary Ball Mill F-P50) and the reactants were ball-milled for 30 min at a frequency of 50 Hz. After the first round of ball milling, 0.6321 g of KMnO_4 was added to the reactor. The mixture was then ball-milled for a further 30 min, and the resulting solid was washed in 80 mL deionized water three times and dried in a vacuum oven at 100°C for 12 h. This method allowed the $\text{Co}_x\text{Mn}_{1-x}\text{O}_y$ -M catalyst to be obtained without thermal treatment.

Typical procedure for the synthesis of $\text{Co}_x\text{Mn}_{1-x}\text{O}_y$ by the SG method. In a typical process, 1.4940 g of cobalt acetate tetrahydrate, 0.4900 g of manganese acetate tetrahydrate, and 1.000 g of citric acid were added to 60 mL of deionized water. The mixture was stirred for 1 h at room temperature and then dried at 80°C for 12 h to obtain a sticky solid. Finally, the resulting solid was calcined at 350°C for 2 h under air.

Typical procedure for the synthesis of $\text{Co}_x\text{Mn}_{1-x}\text{O}_y$ by the CP method. In a typical process, 0.2520 g of MnCl_2 and 1.4280 g of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ were added to 60 mL of deionized water. Separately, 0.6400 g of NaOH was added to 20 mL of deionized water. The NaOH solution was then added to the 60 mL mixture. The final mixture was stirred for 1 h at room temperature and then aged for 6 h. After centrifugation, the solid was dried at 80°C for 12 h. Finally, the resulting solid was calcined at 350°C for 2 h under air.

Typical procedure for the synthesis of $\text{Co}_x\text{Mn}_{1-x}\text{O}_y$ by the solution redox process. In a typical process, 0.6321 g of KMnO_4 and 2.8600 g of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 200 mL of deionized water under vigorous stirring. After being stirred at 80°C for 30 min, the catalyst was obtained by filtration and dried at 80°C for 12 h.

2.2. Catalyst characterization

X-ray diffraction (XRD) patterns of the catalyst were obtained using a D8 Advance Diffractometer with $\text{Cu } K_\alpha$ (-10° – 168°) radiation. Each sample was scanned at a rate of 6° min^{-1} over the 2θ range 10° – 70° .

The specific surface areas and pore structure of the catalysts were determined using N_2 adsorption-desorption isotherms measured at -196°C using a Micromeritics TriStar II 3020 Version 3.02 analyzer. The catalysts were degassed under vacuum at 180°C for 12 h prior to testing. The specific surface areas were calculated from the isotherms using the Brunauer-Emmett-Teller (BET) method. The pore size distribution was obtained using the Barrett-Joyner-Halenda (BJH) method.

The thermal behavior of the catalysts was analyzed using a thermogravimetry analyzer (TGA) at a heating rate of $10^\circ\text{C min}^{-1}$ from 50 to 800°C in air.

2.3. Catalytic performance test

The performance of the catalysts was evaluated in a fixed-bed reactor at atmospheric pressure. A detailed experimental flow chart is shown in Fig. S1. A 30 mg of the catalyst

Scheme 1. Schematic of the formation of porous $\text{Co}_x\text{Mn}_{1-x}\text{O}_y\text{-M}$ by the mechanochemical redox process.

mixed with 10 mg of quartz sand was used for each measurement; the flow rate was 10 mL min^{-1} , which corresponds to a gas hourly space velocity (GHSV) of $20000 \text{ mL h}^{-1} \text{ g}^{-1}$. The feed gas was composed of 1 vol% C_3H_6 , 19.9 vol% O_2 , and 79.1 vol% N_2 . The effluent gas was analyzed using an online gas chromatograph (GC2060). The feed gas C_3H_6 and product CO_2 could be detected in real time.

In the catalyst water resistance experiment, the feed gas was passed through a constant temperature (30°C) bubbling device before being introduced into the reactor; the space velocity was kept unchanged.

In the catalyst sulfur resistance experiment, the feed gas was first mixed with 1000 ppm of SO_2 in different volume ratios and then introduced into the reactor; the space velocity was kept unchanged.

In the extended experiment, the feed gas was changed to CO (1 vol% CO, 20 vol% O_2 , and 79 vol% N_2) or CH_4 (1 vol% CH_4 , 20 vol% O_2 , and 79 vol% N_2), or bubbling by air; the space velocity was kept unchanged.

The C_3H_6 conversion was calculated using the following expression:

$$\text{C}_3\text{H}_6 \text{ conversion}(\%) = \frac{[\text{C}_3\text{H}_6]_{\text{in}} - [\text{C}_3\text{H}_6]_{\text{out}}}{[\text{C}_3\text{H}_6]_{\text{in}}} \times 100$$

$[\text{C}_3\text{H}_6]_{\text{in}}$ and $[\text{C}_3\text{H}_6]_{\text{out}}$ represent the concentrations of C_3H_6 in the inlet and outlet gases.

3. Results and discussion

3.1. Catalyst synthesis and characterization

The chemistry in the MRP mainly followed the redox equation below:

The synthesis of $\text{Co}_x\text{Mn}_{1-x}\text{O}_y$ by the mechanochemical redox process was conducted in two steps, as shown in Scheme 1. First, cobalt chloride and sodium hydroxide were added to the ball-milling apparatus, and the solid mixture was ball-milled for 30 min, resulting in the formation of cobalt ions in a basic environment. Next, the oxidant KMnO_4 was added to the reactor, and the mixture was ball-milled for a further 30 min; it was expected that the redox process would take place in the solid state. The primary catalyst was obtained after the removal of alkali metal salts by washing the product in water ($\text{Co}_x\text{Mn}_{1-x}\text{O}_y\text{-M}$). At the same time, control $\text{Co}_x\text{Mn}_{1-x}\text{O}_y$ catalysts were synthesized by the co-precipitation method, sol-gel method, and solution redox method; these catalysts are referred to $\text{Co}_x\text{Mn}_{1-x}\text{O}_y\text{-P}$, $\text{Co}_x\text{Mn}_{1-x}\text{O}_y\text{-SG}$, and $\text{Co}_x\text{Mn}_{1-x}\text{O}_y\text{-SR}$. All samples were ground to a powder between 80 and 100 mesh for catalytic performance tests.

The XRD patterns of the as-synthesized catalysts are shown in Fig. 1. As shown in Fig. 1(a), the $\text{Co}_x\text{Mn}_{1-x}\text{O}_y\text{-M}$ catalyst obtained via MRP had an amorphous structure and presented two broad peaks. No obvious peaks were detected for the $\text{Co}_x\text{Mn}_{1-x}\text{O}_y\text{-SR}$ sample. The lack of sharp features indicates that both catalysts obtained via redox reactions were poorly crystallized. The $\text{Co}_x\text{Mn}_{1-x}\text{O}_y$ catalysts obtained by the other two methods were then compared; the results are shown in Fig. 1(b). Both $\text{Co}_x\text{Mn}_{1-x}\text{O}_y\text{-P}$ and $\text{Co}_x\text{Mn}_{1-x}\text{O}_y\text{-SG}$ exhibited peaks at 31° , 36° , 45° , 60° , and 65° . The crystal structure of these two catalysts was similar to that of $\text{Co}_2\text{MnO}_{4.5}$.

The N_2 adsorption-desorption isotherms of $\text{Co}_x\text{Mn}_{1-x}\text{O}_y\text{-M}$ and the corresponding pore size distribution are shown in Fig. 2(a) and (b). Significant N_2 adsorption was observed at low relative pressure (e.g., <0.05), which was attributed to the presence of abundant micropores. The N_2 uptake continued to increase from $P/P_0 > 0.05$, and a clear hysteresis loop was observed, indicating its mesoporous structure. Its BET specific surface area was $479 \text{ m}^2 \text{ g}^{-1}$, which was a higher value compared to those of other reported cobalt manganese oxides (e.g., $227 \text{ m}^2 \text{ g}^{-1}$ for $\text{Mn}_x\text{Co}_{3-x}\text{O}_4$ [24], $59 \text{ m}^2 \text{ g}^{-1}$ for CoOOH [25], $205 \text{ m}^2 \text{ g}^{-1}$ for Mn_2O_3 [26], $150 \text{ m}^2 \text{ g}^{-1}$ for MnO_2 [27], and $55 \text{ m}^2 \text{ g}^{-1}$ for Co_3O_4 [25]). The pore size distribution (PSD) calculated using the BJH model was quite narrow and centered around 3.6 nm, as shown in Fig. 2(b). Figure 2(c) compares the N_2 adsorp-

Fig. 1. XRD patterns of $\text{Co}_x\text{Mn}_{1-x}\text{O}_y\text{-M}$ and $\text{Co}_x\text{Mn}_{1-x}\text{O}_y\text{-SR}$ (a), and $\text{Co}_x\text{Mn}_{1-x}\text{O}_y\text{-P}$ and $\text{Co}_x\text{Mn}_{1-x}\text{O}_y\text{-SG}$ (b).

Fig. 2. (a) N₂ adsorption-desorption isotherms of Co_xMn_{1-x}O_y-M; (b) the corresponding pore size distribution obtained from the adsorption branch; (c) N₂ adsorption-desorption isotherms of Co_xMn_{1-x}O_y-M, Co_xMn_{1-x}O_y-P, Co_xMn_{1-x}O_y-SG, and Co_xMn_{1-x}O_y-SR.

tion-desorption curves of the three control samples. The results demonstrate that the mechanochemical method (479 m² g⁻¹) significantly promoted the formation of a porous structure (131 m² g⁻¹ by solution redox, 72 m² g⁻¹ by sol-gel, and 34 m² g⁻¹ by co-precipitation). The mechanical action, mainly in the form of kinetic energy and frictional heating, may generate a high degree of interstitial porosity during the solid-state redox reaction, which encouraged us to carry out further characterization.

The morphology of the Co_xMn_{1-x}O_y-M was directly observed using scanning TEM-high angle angular dark field (STEM-HAADF) images (Figs. 3 and S2). As shown in Fig. 3, the Co_xMn_{1-x}O_y-M sample exhibited a honeycomb-like structure with irregular porous aggregates. Abundant pores with sizes of ~2–12 nm from the surface to the bulk were observed, in agreement with the pore size distribution determined from the N₂ sorption isotherm. The interstitial porosity side by side was the main factor contributing to its high specific surface area.

The electron energy loss spectroscopy (EELS) images obtained using Co-K_α and Mn-K_α are shown in Fig. S3, and demonstrated the presence of cobalt and manganese in the Co_xMn_{1-x}O_y-M sample. The STEM-EDX mapping images were collected in Fig. 4. The Co and Mn species were uniformly dispersed throughout the porous structure. (Figs. 4(b–d)). This result demonstrated that the Co_xMn_{1-x}O_y catalyst synthesized by the mechanochemical redox method showed good dispersion of its constituent elements.

In the HR-TEM images, the visible interlayer spacings of 0.35 and 0.32 nm were attributed to the (220) plane of MnO₂ and the (120) plane of CoOOH, respectively (Figs. 5(a) and (b)).

Fig. 3. STEM-HAADF images of Co_xMn_{1-x}O_y-M.

These results further suggested that the Co_xMn_{1-x}O_y-M sample might exist in the form MnO₂-CoOOH. Interestingly, most of the MnO₂ or CoOOH NPs were smaller than 5 nm and poorly crystallized, which was consistent with the broad reflections in the XRD patterns.

The elemental composition of the Co_xMn_{1-x}O_y-M sample was then studied using inductively coupled plasma-atomic emission spectroscopy (ICP-AES). In the mechanochemical redox process, the theoretical molar ratio of Co to Mn in Co_xMn_{1-x}O_y-M should be 3:1. Interestingly, the weight contents of Co and Mn as determined by ICP-AES were 44.5 and 14.0 wt%, respectively. The corresponding molar ratio of Co to Mn is 2.93:1, which is close to the theoretical molar ratio. Additionally, the ICP analysis of the catalyst confirmed the removal of most of the alkali metal salts by the washing procedure (0.40 wt% Na and 0.47 wt% K in the Co_xMn_{1-x}O_y-M sample). Therefore, the

Fig. 4. STEM-HAADF images of Co_xMn_{1-x}O_y-M obtained using EELS.

Fig. 5. HR-TEM images of Co_xMn_{1-x}O_y-M.

Fig. 6. XPS spectra of Co 2p (a) and Mn 2p (b) of the $\text{Co}_x\text{Mn}_{1-x}\text{O}_y\text{-M}$ catalyst.

specific molecular formula of the $\text{Co}_x\text{Mn}_{1-x}\text{O}_y\text{-M}$ sample was $\text{MnO}_2 \cdot (\text{CoOOH})_{2.93}$. This result proved that the mechanochemical redox reaction between KMnO_4 , NaOH and CoCl_2 took place with the formation of MnO_2 and CoOOH .

TG analysis of the $\text{Co}_x\text{Mn}_{1-x}\text{O}_y\text{-M}$ catalyst was then carried out to further explore the elemental formula of $\text{MnO}_2 \cdot (\text{CoOOH})_{2.93}$. As shown in Fig. S4, the mass loss in the TG profile below 100 °C was about 4%, which was attributed to the evaporation of the moisture adsorbed due to its high specific surface area. Between 200 and 350 °C, the actual weight loss was about 12.0%, which was close to the theoretical mass loss (~12.7%) estimated for the pyrolysis of CoOOH to Co_3O_4 . Above 350 °C, there was no obvious mass loss. These results further demonstrated that the Co species existed as CoOOH in the $\text{Co}_x\text{Mn}_{1-x}\text{O}_y\text{-M}$ catalyst.

Subsequently, we studied the chemical states of Co and Mn using XPS. The XPS spectrum of Co 2p for the $\text{Co}_x\text{Mn}_{1-x}\text{O}_y\text{-M}$ catalyst is shown in Fig. 6(a). The Co 2p spectrum of the $\text{Co}_x\text{Mn}_{1-x}\text{O}_y\text{-M}$ catalyst contained two peaks at 795.5 and 780.4 eV, corresponding to the $\text{Co } 2p_{1/2}$ and $\text{Co } 2p_{3/2}$ spin orbits, respectively. The spin-orbit splitting value was 15.1 eV. The spin-orbit splitting value of Co^{3+} compounds is known to be ~15.0 eV [28]. Hence, the presence of trivalent Co on the $\text{Co}_x\text{Mn}_{1-x}\text{O}_y\text{-M}$ surface was suggested. By performing peak fitting, the Mn 2p band could be reasonably divided into two characteristic peaks, which were assigned as Mn^{3+} and Mn^{4+} . The fitting results are shown in Fig. 6(b) and indicated that the proportion of tetravalent manganese was 53% in the $\text{Co}_x\text{Mn}_{1-x}\text{O}_y\text{-M}$ catalyst. The XPS spectra thus revealed that the redox reaction did occur during the ball-milling process.

3.2. Catalytic application for propylene oxidation

The catalytic oxidation of hydrocarbons is attracting increasing attention because of the severe pollution caused by volatile organic compounds (VOCs) and vehicle exhaust [29–33]. Initially, catalytic combustion of the model molecule propylene was investigated using the different catalysts [34–37].

The light-off curves of the oxidation of propylene by the catalysts obtained using the three different synthetic processes

are shown in Fig. 7. In the presence of the $\text{Co}_x\text{Mn}_{1-x}\text{O}_y\text{-P}$, $\text{Co}_x\text{Mn}_{1-x}\text{O}_y\text{-SR}$, and $\text{Co}_x\text{Mn}_{1-x}\text{O}_y\text{-SG}$ catalysts, which were prepared by co-precipitation, solution redox, and sol-gel methods, respectively, propylene was oxidized over a relatively high and wide temperature range (200–450 °C). Compared with these three catalysts, the $\text{Co}_x\text{Mn}_{1-x}\text{O}_y\text{-M}$ catalyst, which was obtained by MRP, afforded better activity. Propylene was completely converted over a low and narrow temperature range (150–200 °C), with oxidation beginning at 150 °C (T_{10} , temperature at which propylene reaches 10% conversion). Using $\text{Co}_x\text{Mn}_{1-x}\text{O}_y\text{-M}$, $\text{Co}_x\text{Mn}_{1-x}\text{O}_y\text{-SR}$, $\text{Co}_x\text{Mn}_{1-x}\text{O}_y\text{-SG}$, and $\text{Co}_x\text{Mn}_{1-x}\text{O}_y\text{-P}$, the T_{100} values (temperature at which propylene was completely converted) were 200, 300, 325, and 450 °C, respectively. Therefore, in the presence of $\text{Co}_x\text{Mn}_{1-x}\text{O}_y\text{-M}$, both the initial combustion temperature and the total oxidation temperature were lower. Additionally, $\text{Co}_x\text{Mn}_{1-x}\text{O}_y\text{-M}$ showed comparable activity to state-of-art catalysts (e.g., $T_{90} = 360$ °C over $\text{Pt}/\text{Al}_2\text{O}_3$, $T_{50} = 325$ °C over CeO_2 , $T_{50} = 261$ °C over 10% $\text{Ag}/\text{CeO}_2\text{-DP}$, $T_{90} = 200$ °C over 10% $\text{Ag}/\text{CeO}_2\text{-Imp}$) [10,38].

Since the reaction temperature generally fluctuates in practical conditions such as vehicle exhaust [39], we then moved to investigate the catalytic response of $\text{Co}_x\text{Mn}_{1-x}\text{O}_y\text{-M}$ during temperature change (Fig. 8). During four cycles in which the tem-

Fig. 7. Catalytic performance of the $\text{Co}_x\text{Mn}_{1-x}\text{O}_y\text{-M}$, $\text{Co}_x\text{Mn}_{1-x}\text{O}_y\text{-SG}$, $\text{Co}_x\text{Mn}_{1-x}\text{O}_y\text{-P}$, and $\text{Co}_x\text{Mn}_{1-x}\text{O}_y\text{-SR}$ catalysts during propylene combustion. (Reaction conditions: 1% C_3H_6 , 20% O_2 , 79% N_2 , GHSV = 20000 $\text{mL h}^{-1} \text{g}^{-1}$).

Fig. 8. C_3H_6 oxidation over $Co_xMn_{1-x}O_y-M$ during four heating-cooling cycles.

perature was varied between 25 and 250 °C, the C_3H_6 conversion was closely related to the temperature. After reusing the catalyst four times, only a small decrease in the activity in the low temperature region (25–150 °C) was observed. The T_{50} and T_{90} values of these four light-off curves did not exhibit obvious differences. Overall, there was almost no loss of the initial activity of the $Co_xMn_{1-x}O_y-M$ catalyst, revealing its reversible activity in the presence of changing temperature.

Encouraged by the good activity of $Co_xMn_{1-x}O_y-M$ at varied temperatures, water- and sulfur-resistance and thermal stability tests were carried out, as shown in Fig. 9. The light-off curve of C_3H_6 in the presence of water vapor (4.2%) is shown in Fig. 9(a), C_3H_6 was completely converted at ~200 °C, with activity

similar to that of $Co_xMn_{1-x}O_y-M$ in dry conditions. We then studied the hydrothermal stability of $Co_xMn_{1-x}O_y-M$ at T_{90} during long-term combustion. The results are shown in Fig. 9(b). After 65 h of continuous oxidation, the catalyst still showed good activity without any clear loss of catalytic performance. Hence, the current $Co_xMn_{1-x}O_y-M$ catalyst works well in the presence of water vapor.

In addition to water vapor, vehicle exhaust and industrial VOCs usually contain SO_2 [40]. Thus, the light-off curves for the $Co_xMn_{1-x}O_y-M$ catalyst in the presence of different SO_2 concentrations were investigated (Fig. 9(c)). Surprisingly, no significant decrease in catalyst activity was observed at SO_2 concentrations of 20 and 100 ppm. When the SO_2 concentration was further increased to 500 ppm, clear stagnation occurred when the conversion rate reached 60%. In this situation, some of the active sites might be occupied by SO_2 , causing the oxidation rate of C_3H_6 to decrease. It can be seen that $Co_xMn_{1-x}O_y-M$ catalyst exhibits competitive performance at lower concentrations of SO_2 (e.g., <100 ppm).

As the combustion temperature varies widely under practical conditions [39], we tested the thermal stability of $Co_xMn_{1-x}O_y-M$ at 400 °C. The results are shown in Fig. 9(d). During the 60 h test, the conversion of C_3H_6 was maintained at 100%. All these results demonstrated the good performance of the $Co_xMn_{1-x}O_y-M$ catalyst obtained via the mechanochemical redox process.

In view of its good stability, we further tested the catalytic performance of $Co_xMn_{1-x}O_y-M$ under different space velocity conditions (Fig. 10). At a space velocity of 10000 $mL\ h^{-1}\ g^{-1}$, the

Fig. 9. Catalytic stability of $Co_xMn_{1-x}O_y-M$ during C_3H_6 combustion under various conditions. (a) C_3H_6 light-off curve in the presence of water vapor, (b) stability test in the presence of water vapor (4.2%), (c) light-off curves in the presence of SO_2 , and (d) thermal stability test at 400 °C.

Fig. 10. Catalytic performance of $\text{Co}_x\text{Mn}_{1-x}\text{O}_y\text{-M}$ under different space velocities.

conversion rate reached 10% below 130 °C. As the space velocity was further increased to 50000 $\text{mL h}^{-1} \text{g}^{-1}$, the activity of the catalyst did not decrease significantly, and the conversion rate was $\sim 100\%$ at 200 °C. A delay in the propylene conversion was observed at a space velocity at 75000 $\text{mL h}^{-1} \text{g}^{-1}$, with the $\text{Co}_x\text{Mn}_{1-x}\text{O}_y\text{-M}$ catalyst affording 100% C_3H_6 conversion at 280 °C. In theory, the space velocity affects the external diffusion process. At the same time, the higher the space velocity, the shorter the residence time of the reactants, resulting in a lower conversion rate. However, the $\text{Co}_x\text{Mn}_{1-x}\text{O}_y\text{-M}$ catalyst obtained via the mechanochemical redox process had a high surface area with abundant surface oxygen species, possibly allowing the reactants to react within a short residence time. Therefore, the $\text{Co}_x\text{Mn}_{1-x}\text{O}_y\text{-M}$ catalyst still performed well over a wide range of space velocities.

Since the $\text{Co}_x\text{Mn}_{1-x}\text{O}_y\text{-M}$ catalyst offered significant activity

and stability in propylene combustion, the scope of this material was then studied. A variety of gaseous pollutants, such as carbon monoxide and low concentrations of methane, are also found under various conditions [41,42]. Therefore, we conducted a series of tests on the activity of the $\text{Co}_x\text{Mn}_{1-x}\text{O}_y\text{-M}$ catalyst toward two different substrates, carbon monoxide and methane. As shown in Fig. 11(a) and (b), when the temperature reached 150 °C, CO was completely oxidized. At 200 °C, $\text{Co}_x\text{Mn}_{1-x}\text{O}_y$ still had a strong catalytic activity toward CO, and the conversion rate of CO remained around 100% after 100 h, demonstrating its good stability. In addition, several typical VOCs were selected as combustion substrates, and $\text{Co}_x\text{Mn}_{1-x}\text{O}_y\text{-M}$ was found to show competitive activity ($T_{90} = 150, 225, 250$ °C for ethanol, for acetone, and for toluene, respectively); the results are shown in Figs. 11(c)–(e).

Even in the case of methane, an inert molecule that is difficult to oxidize, when $\text{Co}_x\text{Mn}_{1-x}\text{O}_y\text{-M}$ was used as a catalyst, the reaction started at 300 °C and the methane was completely oxidized at 600 °C, as shown in Fig. 11(f). These results demonstrate that the $\text{Co}_x\text{Mn}_{1-x}\text{O}_y\text{-M}$ catalyst synthesized via the mechanochemical redox process exhibited good activity and stability with a variety of substrates.

4. Conclusions

In summary, we used a mechanochemical redox process to prepare the catalyst $\text{Co}_x\text{Mn}_{1-x}\text{O}_y$. XRD, XPS, HRTEM, ICP-AES, and TGA results proved that $\text{Co}_x\text{Mn}_{1-x}\text{O}_y$ existed as MnO_2 and CoOOH with a Co:Mn molar ratio of 2.97:1, which was close to the theoretical value (3:1). The obtained $\text{Co}_x\text{Mn}_{1-x}\text{O}_y$ catalyst had a specific surface area of 479 $\text{m}^2 \text{g}^{-1}$, which was higher than that of the control catalysts prepared by the co-precipitation method (34 $\text{m}^2 \text{g}^{-1}$), sol-gel method (72 $\text{m}^2 \text{g}^{-1}$), and solution

Fig. 11. (a) Catalytic performance of $\text{Co}_x\text{Mn}_{1-x}\text{O}_y\text{-M}$ towards CO; (b) stability test of $\text{Co}_x\text{Mn}_{1-x}\text{O}_y\text{-M}$ in the presence of CO; Catalytic performance of $\text{Co}_x\text{Mn}_{1-x}\text{O}_y\text{-M}$ towards ethanol (c), acetone (d), toluene (e), and CH_4 (f).

redox process ($131 \text{ m}^2 \text{ g}^{-1}$). Moreover, $\text{Co}_x\text{Mn}_{1-x}\text{O}_y\text{-M}$ showed good activity in the complete oxidation of propylene; its T_{100} value (200°C) was lower than that of $\text{Co}_x\text{Mn}_{1-x}\text{O}_y\text{-SG}$ (325°C) and $\text{Co}_x\text{Mn}_{1-x}\text{O}_y\text{-P}$ (450°C). A series of stability tests also proved that $\text{Co}_x\text{Mn}_{1-x}\text{O}_y\text{-M}$ had good hydrothermal stability and sulfur resistance. The mechanochemical action may contribute to the formation of a porous structure, while the redox reaction between Co^{2+} and MnO_4^- promotes good dispersion of the cobalt and manganese species at the atomic scale. This mechanochemical redox process for $\text{Co}_x\text{Mn}_{1-x}\text{O}_y\text{-M}$ synthesis in kilogram scale is already complete, which may provide a potential strategy for processing porous transition metal oxide catalysts.

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Graphical Abstract

Chin. J. Catal., 2020, 41: 1846–1854 doi: 10.1016/S1872-2067(20)63635-X

Mechanochemical redox-based synthesis of highly porous $\text{Co}_x\text{Mn}_{1-x}\text{O}_y$ catalysts for total oxidation

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A mechanochemical redox reaction ($\text{MnO}_4^- + 3\text{Co}^{2+} + 5\text{OH}^- = \text{MnO}_2 + 3\text{CoOOH} + \text{H}_2\text{O}$) was introduced to obtain a $\text{Co}_x\text{Mn}_{1-x}\text{O}_y$ catalyst with a high specific surface area. The synthesized $\text{Co}_x\text{Mn}_{1-x}\text{O}_y$ catalyst exhibited good performance in the catalytic combustion reaction of VOCs.

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基于机械化学的高比表面积 $\text{Co}_x\text{Mn}_{1-x}\text{O}_y$ 催化剂合成及其VOCs燃烧研究

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摘要: 碳氢化合物的催化燃烧在控制挥发性有机化合物(VOCs)和汽车尾气方面非常重要。目前, 商用催化剂通常是燃烧温度低且催化剂寿命长的贵金属基材料。相反, 过渡金属氧化物催化剂价格便宜, 而它们的活性和稳定性却较低, 阻碍了它们的商业化。实际上, 具有多重氧化还原循环的钴锰氧化物(CoMnO_x)在烃类的催化氧化中有不错的性能。在影响燃烧催化剂性能参数中, 孔隙率和表面活性物种是关键, 目前已经有多种钴锰氧化物的合成方法。

$\text{Co}_x\text{Mn}_{1-x}\text{O}_y$ 传统的合成方法是共沉淀法, 溶胶-凝胶法和溶液氧化还原法等湿化学的工艺。从合成的角度来看, 仍存在一些改善的空间。例如, 溶液法合成过程中, 金属前驱体必须是液体或可溶性固体原料; 而且需要几个操作单元, 包括金属前体的溶解和液-液混合。同时, 钴锰物种的良好分散是合成高效催化剂的关键。由于液体环境下 Co^{2+} 和 Mn^{2+} 离子具有不同的平衡常数, 利用共沉淀方法合成时, 经常观察到钴和锰氧化物的局部分离。因此, 开发一种有效的合成 $\text{Co}_x\text{Mn}_{1-x}\text{O}_y$ 催化剂的方法非常重要。

最近, 机械化学重新引起了人们的兴趣, 已有大量文献报道用来合成多孔材料。本文提出了一种通过球磨法简单合成 $\text{Co}_x\text{Mn}_{1-x}\text{O}_y$ 催化剂的机械化学氧化还原工艺。众所周知, 在溶液中钴(II)盐与 KMnO_4 进行氧化还原反应可以合成 $\text{Co}_x\text{Mn}_{1-x}\text{O}_y$ 催化剂, 但反应的进行程度取决于 KMnO_4 浓度, 这可能会影响 $\text{Co}_x\text{Mn}_{1-x}\text{O}_y$ 内高价物种和孔道的形成。出乎意料的是, 采用机械化学氧化还原法合成的 $\text{Co}_x\text{Mn}_{1-x}\text{O}_y$ 催化剂的表面积高达 $479 \text{ m}^2 \text{ g}^{-1}$ 。

在丙烯的催化燃烧反应中, 使用机械化学氧化还原法合成的 $\text{Co}_x\text{Mn}_{1-x}\text{O}_y$ 时, 丙烯在 200°C 时被完全氧化, 远低于共沉淀法(450°C)和溶胶-凝胶法(400°C)合成的。此外, 该催化剂还具有良好的抗水性($4.2\% \text{ H}_2\text{O}$, $> 65 \text{ h}$)和抗硫性($20\text{--}100 \text{ ppm SO}_2$)。同时, 该催化剂可以扩展到其他VOCs底物的低温催化燃烧, 如一氧化碳、甲烷、乙醇、丙酮、甲苯。此外, 机械化学氧化还原法可放大制备催化剂。目前, 实验室已经完成公斤级制备, 有望替代传统方法。

关键词: 机械化学; 固相合成; 多孔金属氧化物; $\text{Co}_x\text{Mn}_{1-x}\text{O}_y$ 催化剂; 烃类燃烧

收稿日期: 2020-03-21. 接受日期: 2020-04-23. 出版日期: 2020-12-05.

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基金来源: 国家自然科学基金(21776174); 海洋工程国家重点实验室开放基金(1809); 上海交通大学重点前瞻布局基金(2019QYB06); 中船重工集团委托项目; 浙江新安化工集团委托项目。

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