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Article (Special Issue on Environmental and Energy Catalysis)

Preparation of MnCo/MCM-41 catalysts with high performance for chlorobenzene combustion

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ARTICLE INFO

Article history:

Received 18 November 2017

Accepted 25 December 2017

Published 5 April 2018

Keywords:

MCM-41

Mn/Co

Catalytic combustion

Chlorobenzene

Characterization

ABSTRACT

MCM-41 was synthesized by a soft template technique. The specific surface area and pore volume of the MCM-41 were 805.9 m²/g and 0.795 cm³/g, respectively. MCM-41-supported manganese and cobalt oxide catalysts were prepared by an impregnation method. The energy dispersive X-ray spectroscopy clearly confirmed the existence of Mn, Co, and O, which indicated the successful loading of the active components on the surface of MCM-41. The structure and function of the catalysts were changed by modulating the molar ratio of manganese to cobalt. The 10%MnCo(6:1)/MCM-41 (Mn/Co molar ratio is 6:1) catalyst displayed the best catalytic activity according to the activity evaluation experiments, and chlorobenzene (1000 ppm) was totally decomposed at 270 °C. The high activity correlated with a high dispersion of the oxides and was attributed to the exposure of more active sites, which was demonstrated by X-ray diffraction and high-resolution transmission electron microscopy. The strong interactions between MnO₂, Co₃O₄, MnCoO_x, and MCM-41 indicated that cobalt promoted the redox cycles of the manganese system. The bimetal-oxide-based catalyst showed better catalytic activity than that of the single metal oxide catalysts, which was further confirmed by H₂ temperature-programmed reduction. Chlorobenzene temperature-programmed desorption results showed that 10%MnCo(6:1)/MCM-41 had higher adsorption strength for chlorobenzene than that of single metal catalysts. And stronger adsorption was beneficial for combustion of chlorobenzene. Furthermore, 10%MnCo(6:1)/MCM-41 was not deactivated during a continuous reaction for 1000 h at 260 °C and displayed good resistance to water and benzene, which indicated that the catalyst could be used in a wide range of applications.

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1. Introduction

Volatile organic compounds (VOCs) are chemicals that are defined by a saturated vapor pressure that exceeds 70 Pa at room temperature or a boiling point that is lower than 260 °C at standard pressure. They are present in haze, photochemical smog, and contribute to the greenhouse effect. They are also involved in the depletion of atmospheric ozone and the production of ground-level ozone [1,2]. In particular, chlorinated volatile organic compounds (CVOCs), which are highly toxic, are difficult to decompose in air because of the occurrence of

polychlorinated byproducts, being increasingly one of the VOCs which handle hardly [3]. The CVOCs, as semi-finished chemical products, are widely used as solvents for dry cleaning and degreasing processes in industrial manufacturing [4,5].

Generally, the techniques for the destructive removal of CVOCs include high-temperature direct combustion, catalytic hydrodechlorination, catalytic steam reforming, photocatalytic oxidation, and catalytic combustion. Compared with other techniques, catalytic combustion is applied in a wide range of applications because of its lower energy consumption, lower handling temperature, and higher purification efficiency.

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This work was supported by the National Natural Science Foundation of China (21577094).

DOI: 10.1016/S1872-2067(17)62950-4 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 39, No. 4, April 2018

For the catalytic combustion of CVOCs, catalyst support materials with a large specific surface area and pore volume, which are beneficial for the dispersion of the active substances, are always prevalent. They usually consist of molecular sieves (such as γ - Al_2O_3 , HFAU, HZSM-5, MCM-41), metal oxides, and honeycomb ceramics [3]. Compared with other two supports, molecular sieves not only have better thermal stability, but also possess higher specific surface areas and more acidic sites [6]. However, the problem of carbon deposition is yet to be solved. As a nanostructured material, MCM-41 with a hexagonal ordered pore arrangement and large adsorption quantity was first discovered in 1992 [7]. It has been widely applied in resid catalytic cracking, heavy oil catalytic hydrogenation, alkyl isomerization, and macromolecular fine chemicals. Furthermore, it is completely composed of silica and has no acidity, effectively avoiding the issue of carbon deposition.

Currently, the catalysts used for the destruction of CVOCs can be classified into two types according to their active components, including noble metals catalysts [8–10] and non-noble metal catalysts. In practice, noble-metal-based catalysts show higher activity. However, they are more expensive and undergo deactivation because of chlorine poisoning and the formation of polychlorinated compounds. Therefore, many efforts have been devoted to the synthesis of transition-metal oxide catalysts [11–16] because they resist deactivation to a larger extent and are cheaper. Usually, metal oxides (such as V_2O_5 , Cr_2O_3 , MnO_2 , Co_3O_4 and NiO) or composite metal oxides are used as active components of transition metal oxide catalysts. In particular, manganese and cobalt oxides possess better activity, lower cost, and create little or no environmental pollution. Therefore, they have been widely used both domestically and internationally [17,18]. However, when use only one component, the loss of active sites (which could adsorb HCl and/or Cl_2) or the formation of volatile species (metal chloride or metal chloride oxide) at lower temperature may cause partial deactivation of these transition metal oxides catalysts, which may restrict the applications of transition metal oxides catalysts [19]. Thus, composite metal oxides catalysts have been reported, which improve the mobility of the surface-active oxygen and increase the surface acidic sites through the synergistic effect of the metal-metal and metal-support interactions.

There have been numerous reports of molecular-sieves-supported transition-metal oxides as catalysts that have been used to eliminate CVOCs [20–27]; for example, Cu-ZSM-5 [26] and $\text{Cr}_2\text{O}_3\text{-CuO/HZSM-5}$ [27]. Furthermore, the MCM-41 as a catalyst support, its applications for the destruction of CVOCs have also been reported, including Pt/P-MCM-41 , La/MCM-41 , Ce/MCM-41 , and Pt/MCM-41 , which showed a high catalytic performance [28–30]. In the catalytic combustion field of CVOCs, there are rarely reports about MCM-41 supported MnCo catalysts for destruction of chlorobenzene (CB). Therefore, we synthesized MCM-41-supported MnCo catalysts for CB combustion.

In this paper, we prepared MCM-41-supported MnCo catalysts, and explored their catalytic performance for combustion of CB in air. Furthermore, the synergistic effect between Mn (the main active phase), Co (the second active phase) and

MCM-41 was studied. The catalysts were analyzed by X-ray diffraction (XRD), high-resolution transmission electron microscopy (HRTEM), and energy dispersive X-ray spectroscopy (EDS), nitrogen (N_2) adsorption-desorption, temperature-programmed reduction of hydrogen (H_2 -TPR), and temperature-programmed desorption of CB (CB-TPD). Furthermore, the activity and durability of the materials was evaluated to further investigate the performance of the catalysts.

2. Experimental

2.1. Synthesis

The MCM-41 was prepared according to the following procedure. Tetrabutylammonium silicate (TBAS) was obtained from tetrabutylammonium hydroxide (TEAOH, 40 wt%, Aldrich) and fumed silica (Sigma) in a 10:1 ratio. Then, 12.21 g of TBAS was combined with 20.3 g of cetyltrimethylammonium chloride (CTAC, 25 wt%, Aldrich) and 5.94 g of H_2O under stirring, followed by the addition of 5.91 g of fumed silica. The resulting gel was placed in a Teflon bottle and heated for 120 h at 100 °C to perform the crystallization. After cooling to room temperature, the solid product was recovered by filtration, washed thoroughly with deionized water, and dried in an oven at 80 °C overnight. Finally, the template CTAC was removed by calcination in a stream of air at 550 °C for 5 h [31]. A series of MnCo/MCM-41 catalysts with different molar ratios of Mn/Co (3:1, 6:1, and 9:1) were prepared by co-impregnation of MCM-41 with an aqueous solution of $\text{Mn}(\text{NO}_3)_2$ (50%) and $\text{Co}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ overnight. Then, the samples were stirred in the electrothermal setup until desiccation. Later, calcination was performed at 500 °C for 2 h. The particles with a 40–60 mesh size were sieved to obtain the products. The total content of the single metal (Mn or Co) and mixed MnCo (the sum of both Mn and Co) for all the catalysts was 10 wt%.

2.2. Catalytic activity test

The activity evaluation of the catalysts (350 mg) was performed in a WFS-3010 microreactor (Xianquan, Tianjin, China), in which the space velocity was 20000 h^{-1} and the concentration of CB was 1000 ppm. The concentration of O_2 in the gas flow stream was 21%. The on-line measurements were conducted using a Shimadzu GC-14 (Japan), which had a flame ionization detector (FID). The temperatures of the vaporizer and column were both 120 °C. The data were obtained and analyzed using a N2000 chromatography data workstation. The degradation products were detected by mass spectrometry (MS, QGA, Hiden, UK). No byproducts other than H_2O , CO_2 , and HCl were detected. Thus, the conversion was calculated based on CB consumption. The durability of the catalysts for CB combustion was also investigated under the same conditions.

2.3. Characterization

The composition of the catalyst phase was determined by XRD, which was performed with a PANalytical EMPYREAN

powder diffractometer operated with a Cu $K\alpha$ source ($\lambda = 0.15406$ nm). The experimental conditions were as follows: tube current of 40 mA, tube voltage of 40 kV, scanning rate of $0.02^\circ/\text{s}$ and scanning limitation of $10^\circ\text{--}80^\circ$.

HRTEM was carried out using a JEOL-2010 to investigate the morphologies of MCM-41 and 10% MnCo (6:1)/MCM-41. The working voltage was 200 kV. The elements present in the catalyst were determined by EDS using an OXFORD INCA instrument (Oxford Instruments, UK).

The specific surface area and pore volume of the catalysts were measured by a Tristar II 3020 apparatus (Micromeritics Company, USA), by using the N_2 adsorption-desorption technique (-195.8°C). The sample was pretreated at 200°C for 4 h. The specific total surface area (A_{BET}) was calculated using the Brunauer-Emmett-Teller (BET) equation, whereas the total pore volume (V_p) was evaluated from the nitrogen uptake at a relative N_2 pressure of $p/p_0 = 0.99$. The Barrett-Joyner-Halenda method was used to calculate the average pore size.

The oxidation properties of the catalysts were determined by H_2 -TPR experiments. 50 mg of the catalyst was pretreated at 450°C in argon for 1 h, after which the temperature was decreased to 50°C . When the adsorption of the organic compounds was at a state of dynamic balance, in other words, the base line was stable, and then the temperature was programmed to rise at a constant rate of $7.5^\circ\text{C}/\text{min}$ up to 450°C . Hydrogen uptake was measured with a thermal conductivity detector, and the compounds were detected by gas chromatography-mass spectrometry (GC-MS) (QGA, Hiden, UK) on-line.

The CB-TPD experiments were performed in a quartz tube. Before the adsorption of CB, 350 mg of catalyst was pretreated in dry air at 300°C for 0.5 h. After it was cooled down to 50°C , the adsorption of CB was carried out under a flow of CB/N_2 until adsorption saturation, which was symbolized by a stable CB signal in the mass spectrometer. Then, pure N_2 was blown for 1 h to clean the CB of the tubing in the system. Finally, desorption of CB was implemented by flowing pure N_2 at a temperature step of $7.5^\circ\text{C}/\text{min}$ from 50 to 500°C . The concentration of CB was detected on-line by GC-MS [32].

3. Results and discussion

3.1. Catalytic activity evaluation

Fig. 1 shows the catalytic oxidation activity of different catalysts. The activity of the catalysts for CB combustion with 1000 ppm decreased in the order: MnCo (6:1)/MCM-41 > MnCo (9:1)/MCM-41 > MnCo (3:1)/MCM-41 > Mn/MCM-41 > Co/MCM-41. The 10% MnCo (6:1)/MCM-41 catalyst exhibited the highest activity, and the temperature for complete CB degradation was 270°C . The 10% MnCo (9:1)/MCM-41 catalyst exhibited a relatively low activity; this was attributed to the higher amount of Co. Too much Co loading could override the MnO_x sites (main active sites). The catalyst activity was also lower when the Mn/Co molar ratio was 3, as a consequence of the lack of oxygen vacancies. Thus, the appropriate loading of Mn and Co played an important role in improving the

Fig. 1. The conversion curves of the catalytic combustion for CB over MnCo/MCM-41 catalysts with various Mn/Co molar ratios.

MnCo/MCM-41 activity. The catalytic activity of similar catalysts reported in the literature for the catalytic combustion of CB are listed in Table S1 [33–37], which shows that 10% MnCo (6:1)/MCM-41 had higher activity.

3.2. Durability test

Apart from catalytic activity, the durability of a catalyst is also very important in determining the performance of catalysts. The MnCo (6:1)/MCM-41 catalyst showed good durability in a continuous 1000 h reaction under dry air at 260°C (Fig. 2). However, the conversion of CB dropped in the presence of benzene because of competitive adsorption. Notably, the conversion of CB decreased more when the water was also added, indicating that water also inhibited CB oxidation, because some active sites were overlapped. Nonetheless, the conversion of CB recovered without the presence of benzene and water.

3.3. XRD analysis

The XRD patterns are shown in Fig. 3. A big diffraction peak attributed to silica was observed at approximately $2\theta = 22.8^\circ$.

Fig. 2. Catalyst durability test profile for 10% MnCo (6:1)/MCM-41.

Fig. 3. XRD patterns of the samples. (1) MCM-41; (2) 10% Mn/MCM-41; (3) 10% Co/MCM-41; (4) 10% MnCo (6:1)/MCM-41.

Meanwhile, the characteristic peaks of MnO_2 and Co_3O_4 were detected in 10% Mn/MCM-41 and 10% Co/MCM-41. The peak of MnCoO_x was observed in 10% MnCo (6:1)/MCM-41. In the 10% MnCo (6:1)/MCM-41 catalyst, two weakly intense peaks appeared at a diffraction angle 2θ of 36.0° and 54.2° , which corresponded to the XRD patterns of MnCo_2O_4 and CoMn_2O_4 , respectively [38]. Accordingly, we deduced the presence of

MnCo_2O_4 and CoMn_2O_4 . The presence of Co_3O_4 , CoO , MnO , Mn_3O_4 , Mn_2O_3 , and MnO_2 , or other species was not detected in the XRD pattern of 10% MnCo (6:1)/MCM-41, indicating that no Co_3O_4 , CoO , MnO , Mn_3O_4 , Mn_2O_3 , and MnO_2 crystal phases existed in the MnCo/MCM-41 composite oxide system, or that they existed in highly dispersed or amorphous forms. Thus, Mn^{4+} and Mn^{3+} were the main crystallite phase species that existed in the prepared MnCo/MCM-41 oxide catalysts.

3.4. HRTEM and EDS analysis

Fig. 4 shows the HRTEM images and the EDS spectra of the samples. Fig. 4(a) shows that MCM-41 had a well-ordered hexagonal array structure. Fig. 4(b) shows that the particles of MnO_2 and Co_3O_4 dispersed uniformly. The EDS spectrum clearly confirmed the existence of Mn, Co, and O, which indicated the successful loading of the active components on the surface of MCM-41.

3.5. N_2 adsorption-desorption analysis

Fig. 5 shows the N_2 adsorption-desorption isotherms of the samples. The A_{BET} , V_p , and average pore size of the samples are summarized in Table 1. From the figure and table, a distinct capillary condensation phenomenon could be observed at relative pressures between 0.45 and 0.85, indicating the

Fig. 4. HRTEM images of (a) MCM-41; (b) 10% MnCo (6:1)/MCM-41; (c) EDS spectrum of 10% MnCo (6:1)/MCM-41.

Fig. 5. N_2 adsorption-desorption isotherms for MCM-41 and different supported catalysts.

presence of uniform mesopores. The existence of micropores was also confirmed by the N_2 adsorption-desorption isotherms rising sharply giving 0~0.3 (p/p_0). And it could be found, for those supported active components materials, all their A_{BET} , V_p , pore size and adsorption quantity reduced compared with MCM-41. It was probably attributed to that the oxides of Mn and Co blocked the pores of MCM-41. With the addition of Mn and Co, the relative content of MCM-41 decreased, this also makes the A_{BET} , V_p , pore size and adsorption quantity of the samples smaller.

3.6. H_2 -TPR analysis

Fig. 6 shows the H_2 -TPR profile of the MnCo/MCM-41 catalysts which supported different molar ratios of Mn and Co. The reduction of the 10% Mn/MCM-41 catalyst occurred at 267, 288, and 510 °C. The 10% Co/MCM-41 was reduced in two steps [39]: the first peak centered at 270 °C was attributed to the reduction of Co^{3+} to Co^{2+} , whereas the second step reduction proceeded at 341 °C and was attributed to the subsequent reduction of Co^{2+} to Co. Compared with above two catalysts, the reduction peaks of 10% MnCo (6:1)/MCM-41 catalyst were shifted to a lower temperature. This shift indicated that the oxidation property of catalyst was improved because of the interaction between MnO_x , CoO_x , and MCM-41. The Mn–O chemical bonds that existed in the $MnCoO_x$ composite compounds could be weakened by the strong interaction; the weakened Mn–O chemical bonds could react with hydrogen molecules to achieve reduction at a low temperature. There-

Fig. 6. Catalysts H_2 -TPR profile for (1) 10% Mn/MCM-41; (2) 10% Co/MCM-41; (3) 10% MnCo (6:1)/MCM-41.

fore, the supported MnCo composite compounds showed high oxidability at a low reduction temperature. The high low-temperature oxidability could produce reactive oxygen species at a low reaction temperature. Thus, the supported MnCo composite compound catalysts provided high catalytic combustion activity for organic compounds [40]. The catalytic activity of the mixed-oxides-based catalysts depended on the redox properties of the Mn^{4+}/Mn^{3+} system that were present on the surface of the oxides. That was probably modulated by the quantity of the manganese employed in the synthesis, as well as the use of cobalt with the activity to promote redox cycles [41]. These were maybe the synergistic effect.

3.7. CB-TPD analysis

Fig. 7 shows the CB adsorption-desorption profiles of the support and the catalysts in the TPD test. For supported catalysts, some Mn or Co particles entered into the pores of the supports, which caused the adsorption capacity of CB reducing than MCM-41. However, bimetal-oxide-based catalyst had larger adsorption capacity of CB than that of single metal oxide catalysts. The order of CB adsorption capacity was as follows: 10% Co/MCM-41 < 10% Mn/MCM-41 < 10% MnCo (6:1)/MCM-41 < MCM-41. The desorption temperatures of the supported catalysts increased, which indicated the increased adsorption ability of CB. Higher desorption temperature implied higher adsorption strength for CB. The order of CB desorption temperatures was as follows: MCM-41 < 10% Co/MCM-41 < 10% Mn/MCM-41 < 10% MnCo (6:1)/MCM-41. Surely, larger adsorption capacity and stronger adsorption ability of the catalysts are both beneficial for combustion of CB. In other words, 10% MnCo (6:1)/MCM-41 catalyst had the best combustion activity for CB. This conclusion was consistent with the result of the activity evaluation experiments.

Table 1

Specific surface area, pore volume and pore size for MCM-41 and supported catalysts.

Sample	$A_{BET}^a/(m^2/g)$	$V_p^b/(cm^3/g)$	d^c/nm
MCM-41	805.9	0.795	7.45
10% Mn/MCM-41	561.8	0.436	3.21
10% Co/MCM-41	536.7	0.403	3.23
10% MnCo (6:1)/MCM-41	545.4	0.502	3.43

^a BET specific surface area. ^b Total pore volume estimated at $p/p_0 = 0.99$.

^c Average pore size.

4. Conclusions

In this paper, mixed oxides with active binary phases based

Fig. 7. The CB-TPD patterns of the catalysts. (a) CB adsorption; (b) CB desorption.

on MCM-41 catalysts were prepared. The performance of CB combustion over MnCo/MCM-41 catalysts was studied. The activity tests showed that the 10% MnCo (6:1)/MCM-41 catalyst had the highest catalytic activity. The complete conversion of CB was achieved at 270 °C. The texture, structure, morphology, dispersion of the active components, and the oxidation properties of catalysts were characterized by a series of techniques. The catalytic behavior of the catalysts was significantly affected by the molar ratios of the metal oxides and the interaction between the supported components. The XRD indicated the formation of MnCoO_x compounds for 10% MnCo (6:1)/MCM-41 catalyst. The HRTEM-EDS indicated a better dispersion of Mn or Co oxides on MCM-41 for 10% MnCo (6:1)/MCM-41 catalyst. The N_2 adsorption-desorption and CB-TPD results showed that some particles of the supported components could enter into the pores, resulting in a smaller specific surface area, pore volume, pore size, and lower adsorption quantity of CB. Furthermore, the durability test demonstrated that there was no deactivation for 10% MnCo (6:1)/MCM-41 catalyst during a 1000 h continuous reaction. This research provides valuable information for the development of better catalysts with wide-spread applications.

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Graphical Abstract

Chin. J. Catal., 2018, 39: 849–856 doi: 10.1016/S1872-2067(17)62950-4

Preparation of MnCo/MCM-41 catalysts with high performance for chlorobenzene combustion

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MCM-41 supported mixed oxides catalysts were synthesized by an impregnation method. The 10% MnCo (6:1)/MCM-41 catalyst showed the highest activity for chlorobenzene combustion.

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MnCo改性的MCM-41催化剂用于氯苯催化燃烧的研究

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摘要: 含氯挥发性有机化合物(CVOCs)是对人体健康和环境危害极大的有机化合物。常见的有二氯乙烷、三氯乙烯、三氯甲烷、四氯化碳和氯苯等。有些CVOCs是“三致”(致畸、致癌、致突变)物质,有些少量进入大气就能破坏臭氧层,亦或与臭氧等形成光化学烟雾,引起全球变暖。因此,对于其消除迫在眉睫。CVOCs通常采用高温直接燃烧、吸附、光催化氧化和催化燃烧等方法降解。其中,催化燃烧是非常有效的。我们选择氯苯作为CVOCs探针分子是因为其不仅存在于农药和化工产品中,在室内环境中也大量存在,而负载贵金属和非贵金属型催化剂可用于其催化降解。贵金属催化剂价格高而且易氯中毒,但过渡金属催化剂价格低且抗失活,因而是不错的选择。通常过渡金属催化剂使用 V_2O_5 , Cr_2O_3 , MnO_2 , Co_3O_4 及 NiO 等活性组分,而Mn和Co氧化物有较好活性且没有环境污染,常用作活性组分。另外,MCM-41是有序介孔硅酸盐和硅铝酸盐家族中M41S的一员,具有高的比表面积和较窄的孔径分布,常用作催化剂的载体。我们利用具有大比表面积、大孔径的MCM-41作为载体,采用浸渍法负载 MnO_x , CoO_x , $\text{MnO}_x\text{-CoO}_x$ 等活性组分,制备系列的催化剂用于低浓度氯苯的催化燃烧,研究催化剂的催化活性、选择性及稳定性。并利用XRD、 N_2 吸脱附、高分辨电镜-能谱分析、 H_2 -TPR和CB-TPD等手段对MCM-41及催化剂的织构-结构、表面形貌、活性组分分散状态、氧化还原性能及吸附性能等做了系统的研究。

采用表面活性剂软模板技术合成了具有大比表面积、大孔径、耐热稳定性高的MCM-41介孔分子筛,负载不同比例的

Mn/Co (摩尔比是3:1、6:1及9:1, 其中总负载量为10%), 以氯苯催化燃烧为探针反应, 筛选出活性最佳时的Mn/Co比例. 活性评价实验结果表明, 各催化剂的活性以下列顺序依次降低: MnCo(6:1)/MCM-41 > MnCo (9:1)/MCM-41 > MnCo (3:1)/MCM-41 > Mn/MCM-41 > Co/MCM-41, 其中MnCo(6:1)/MCM-41活性最佳, 在270 °C即可完全催化燃烧氯苯. 耐久性实验结果显示, MnCo (6:1)/MCM-41在连续反应1000 h后, 其活性没有降低, 表明其具有非常良好的稳定性. XRD实验结果表明, 在Mn/MCM-41及Co/MCM-41催化剂上分别检测到MnO₂及Co₃O₄的特征衍射峰. 在MnCo (6:1)/MCM-41催化剂上, MnO₂及Co₃O₄的特征衍射峰消失, 同时出现了MnCoO_x的特征衍射峰, 这是由于MnO₂及Co₃O₄的强相互作用经过焙烧后形成的, 且MnCoO_x的特征衍射峰较小, 表明双金属活性组分的分散比单金属催化剂好. N₂吸脱附结果显示, MCM-41的比表面积达到805.9 m²/g, 孔体积达到0.795 cm³/g. 负载活性组分后其比表面积及孔体积均有不同程度的减小, 这是由于活性组分进入了MCM-41的孔隙. 高分辨电镜结果表明, MCM-41具有均匀的介孔孔道结构, MnCoO_x在MCM-41表面的颗粒小, 分散好. 能谱扫描出Mn, Co, O等元素, 表明活性组分成功地负载在MCM-41载体上. H₂-TPR表明, 双金属催化剂的还原峰温较单金属催化剂低, 表明其具有更好的氧化性能. CB-TPD结果表明, MnCo双金属催化剂脱附氯苯的温度高于单金属催化剂, 说明氯苯与催化剂之间的相互作用更强, 即双金属催化剂对氯苯的吸附能力更强, 使得氯苯催化燃烧更加充分, 因此其催化性能更好. 同时, 深入探讨了MnO_x, CoO_x, MnCoO_x和MCM-41之间的相互作用及对催化燃烧性能的影响.

关键词: MCM-41分子筛; Mn/Co; 催化燃烧; 氯苯; 表征

收稿日期: 2017-11-18. 接受日期: 2017-12-25. 出版日期: 2018-04-05.

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基金来源: 国家自然科学基金(21577094).

本文的全文电子版由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).