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Effect of pore size in mesoporous MnO₂ prepared by KIT-6 aged at different temperatures on ethanol catalytic oxidation

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ABSTRACT

KIT-6 mesoporous silica aged at 40, 100, and 150 °C were used as hard templates to prepare different mesoporous MnO₂ catalysts, marked as Mn-40, Mn-100, and Mn-150, respectively. The catalytic activities of these catalysts and the effect of pore sizes on ethanol catalytic oxidation were investigated. Mn-40, Mn-100, and Mn-150 have triple, double, and single pore systems, respectively. On decreasing the aging temperature of KIT-6, the pore sizes of KIT-6 decrease and that of mesoporous MnO₂ catalysts increase. The pore sizes and catalytic activities increase in the order: Mn-40 > Mn-100 > Mn-150. Mn-40 catalyst has a higher TOF (0.11 s⁻¹ at 120 °C) and the best catalytic activity for ethanol oxidation because of a bigger pore size with three pore systems with maximum distribution at 1.9, 3.4, and 6.6 nm, decrease in symmetry and degree of order, more surface lattice oxygen species, oxygen vacancies resulting from more Mn³⁺ ions, and better low-temperature reducibility.

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1. Introduction

Ethanol, a widely used solvent, is released into the atmosphere through exhaust gases emitted from ethanol-fueled vehicles. It is a type of volatile organic compounds (VOCs), and is considered a substantial contributor to the air pollution and photochemical pollution [1–4]. Catalytic oxidation is one of the most promising technologies for the elimination of VOCs. This technology has many advantages, such as high removal efficiency, a low light-off temperature, a wide range of applications, simple operational technique of the equipment, and no secondary pollution effect. The key is to choose and prepare the catalysts properly. At present, catalysts used in ethanol catalytic

oxidation mainly contain metal oxides and noble metals, such as Pt/Al₂O₃ [1], M/TiO₂ (M = Pt, Pd, Ir, Rh, and Au) [5], Rh/Al₂O₃ [6], Ag/La_{0.6}Sr_{0.4}MnO₃ [7], MnO_x [8], MnO₂ [3], OMS-2 [4], MnCuO_x [9], MnO_x-CeO₂ [10], CuO/MnO_x [11], CuO/Al₂O₃ [12], CuO/Fe₂O₃ [13], LaCoO₃ [14], Ce_{1-x}Mn_xO₂ [15], MnCu/ZrO₂ [16], LaMnO₃ [17], Mn_{0.6}Ce_{0.4}O₂ [18], La_{0.8}Sr_{0.2}MnO_{3+x} [19], and CuMn₂O₄/Al₂O₃ [20].

Same materials with different morphologies, such as tubes, sheets, flowers, rods, spheres, and pores, exhibit different catalytic activities for VOC oxidation [21–25]. MnO₂ has different types of morphology structures such as α, β, γ, and δ types, and exhibits synthetic shapes such as tubes, wires, rods spheres, and pores. It is widely used in catalysis and exhibits excellent

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catalytic performance [22,31–33]. Mesoporous MnO_2 has been used as an effective environmentally friendly material for VOCs.

A previous literature reported that mesoporous MnO_2 , particularly 3D- MnO_2 , shows better activity for catalytic oxidation [3]. Tüysüz et al. [34] reported that increasing the aging temperature of KIT-6 could increase its pore size and decrease the single pore size of nanocast Co_3O_4 materials prepared by KIT-6 as hard templates, because of the change in the interconnectivities between two channels of KIT-6. Currently, the influence of aging temperature of KIT-6 on pore sizes in a 3D- MnO_2 material with a double pore system has not been clarified; moreover, the influence of pore size of 3D- MnO_2 on catalysis is also not well understood. If the pore size in 3D- MnO_2 is changed by adjusting the aging temperature of KIT-6, there is a possibility to improve the important factors influencing catalytic activity, such as low-temperature reducibility, oxygen species, and active sites. This would help further improve the catalytic performance for ethanol oxidation on 3D- MnO_2 .

In this work, mesoporous MnO_2 samples with different pore sizes were prepared using KIT-6 templates aged at different temperatures as the hard template. The catalytic activities of these samples on ethanol oxidation were investigated, and the effect of pore sizes on catalytic activity was addressed.

2. Experimental

2.1. Catalyst preparation

Mesoporous MnO_2 with different pore sizes was prepared. KIT-6 mesoporous silica aged at different temperatures was used as a hard template to prepare mesoporous MnO_2 catalysts with different pore sizes. Synthesis of KIT-6 templates and preparation of mesoporous 3D- MnO_2 were carried out following a method reported previously [35]. The KIT-6 templates aged at 40, 100, and 150 °C were marked as KIT-6-40, KIT-6-100, and KIT-6-150, corresponding to the preparation of Mn-40, Mn-100, and Mn-150 samples, respectively.

2.2. Catalyst characterization

X-ray diffraction (XRD) patterns were recorded on a TTR3 type X-ray diffractometer using a $0.05^\circ/\text{min}$ scanning speed of $\text{Cu K}\alpha$ radiation source (40 mA and 40 kV). N_2 adsorption-desorption (BET) were tested on an Autosorb-1MP instrument. All samples were outgassed at 300 °C for 4 h under nitrogen gas before the test. The surface areas and isotherms were calculated by the Barrett-Joyner-Halenda (BJH) method. Scanning electron microscopy (SEM) images were acquired on a Hitachi S-5500 instrument. All samples were dispersed on a carbon film supported by a copper grid, using ultrasonic waves in deionized water for 10 min. The samples were dried at 110 °C for 20 min. Hydrogen temperature programmed reduction (H_2 -TPR) was tested on a Chemisorb 2720 apparatus with a TCD detector. All samples (0.05 g, 40–60 mesh) were pretreated in flowing N_2 at 300 °C for 1 h. All samples were reduced in 50 mL/min of gas flow with 5% H_2 -95% Ar at 30–900 °C at a heating rate of 10 °C/min after the pretreatment. Hydrogen

consumptions of reduction peaks were calculated by using a standard CuO sample. X-ray photoelectron spectroscopy (XPS) patterns were tested on a PHI-5300 spectrometer, utilizing $\text{Mg K}\alpha$ X-ray source. The C 1s binding energy at 284.6 eV was referenced as binding energy (BE) calibration of all elements.

2.3. Evaluation of catalytic activity

Ethanol oxidation was studied in a fixed-bed quartz tube reactor. The gas flow rate through the reactor with 0.2 g of catalyst (60–80 mesh) was maintained at 200 mL/min, which included 500 ppm ethanol and 20% (vol) O_2 and N_2 equilibrium gas. The effluent product was analyzed by an on-line Agilent 7890A gas chromatograph (GC) equipped with a TCD detector and a flame ionization detector (FID), using Porapak-Q and HP-INNOWAX columns, respectively. Ethanol conversion was calculated based on the export and import concentrations of ethanol from the GC. The TOFs of the samples were defined as the number of ethanol molecules converted per active site per hour.

$$\text{TOF} = \frac{C_{\text{ethanol}} \times X_{\text{ethanol}} \times V_{\text{gas}}}{n} \text{ (h}^{-1}\text{)}$$

where C_{ethanol} : concentration of ethanol in gas mixture; X_{ethanol} : ethanol conversion; V_{gas} : total molar flow rate; and n : the sum of mole number of Mn^{4+} and Mn^{3+} ions calculated by H_2 -TPR.

3. Results and discussion

3.1. Catalytic activity of ethanol oxidation

The catalytic activities for ethanol oxidation using the catalysts are shown in Fig. 1. Ethanol conversions at 60 °C were 22% on Mn-40, 20% on Mn-100, and 8.3% on Mn-150, and complete conversion was observed at 150 °C on Mn-40, at 160 °C on Mn-100, and at 170 °C on Mn-150, under the following conditions: 500 ppm ethanol, 20 vol % O_2 , and GHSV = 60000 mL/(g·h) (Fig. 1(a)). The maximum acetaldehyde yields were observed at 130 °C on Mn-40, at 140 °C on Mn-100, and at 140 °C on Mn-150 (Fig. 1(b)). In this catalyst system, acetaldehyde is an important intermediate species of ethanol oxidation. On increasing the reaction temperature, the acetaldehyde species are further oxidized to CO_2 and H_2O . Complete oxidation of ethanol to CO_2 was achieved at 160 °C on Mn-40, at 170 °C on Mn-100, and at 180 °C on Mn-150 (Fig. 1(c)). These results show that Mn-40 has a better catalytic activity for ethanol oxidation, because of the changes in pore sizes caused by templates with different aging temperatures. Mn^{4+} and Mn^{3+} ions provided efficient active sites for ethanol oxidation reaction, because the oxidation reaction often occurs through redox recycles of high- and low-valence state cations, like $\text{Co}^{3+}/\text{Co}^{2+}$ [23] and $\text{Ce}^{4+}/\text{Ce}^{3+}$ [36]. For comparison, TOFs of the samples were estimated based on Mn^{4+} and Mn^{3+} ions as active sites (Fig. 2). The TOF of Mn-40 is 0.033 h^{-1} at 60 °C. With increasing reaction temperature, the TOF rapidly soars to 0.11 h^{-1} at 120 °C. The TOF of Mn-100 is 0.03 h^{-1} at 60 °C, and promptly increases up to 0.097 h^{-1} at 120 °C. The TOFs for Mn-150 are 0.017 h^{-1} at 60 °C and 0.007 h^{-1} at 120 °C. This result further

Fig. 1. Ethanol catalytic performance of the catalysts. (a) Ethanol conversion, (b) acetaldehyde yield during ethanol oxidation and (c) CO₂ yield during ethanol oxidation. Reaction conditions: 500 ppm ethanol, 20 vol % O₂, N₂ as balance gas, GHSV = 60000 mL/(g·h).

confirms that Mn-40 has the best catalytic activity. Although Mn-40 and Mn-100 have an approximate quantity of active sites from Table 2, the catalytic activity of Mn-40 is still superior to that of Mn-100 because of the change in the pore channel structure and pore size.

3.2. Textural characterization

The wide-angle XRD patterns of samples are shown in Fig. 3. All samples exhibit diffraction peaks at $2\theta = 28.7^\circ, 37.3^\circ, 42.8^\circ$,

Fig. 2. TOFs for ethanol oxidation of the catalysts. Reaction conditions: 600 ppm ethanol, 20 vol% O₂, N₂ as balance gas, GHSV = 60000 mL/(g·h).

Fig. 3. Large-angle XRD patterns of the samples.

$56.7^\circ, 59.4^\circ, 64.8^\circ$, and 72.3° , which correspond to the (110), (101), (111), (211), (220), (002), and (301) planes, respectively. The diffraction peaks indicate that the materials consist of a β -MnO₂ crystalline phase, which corresponds to pyrolusite with a rutile structure [37]. The Mn-40 catalyst also exhibits diffraction peaks at 33.0° and 55.2° (2θ), which correspond to the (222) and (440) planes, respectively. It indicates that the Mn-40 catalyst has a small amount of Mn₂O₃ crystalline phase (PDF#65-1798), except a MnO₂ crystalline phase, probably because of the stable pore structure. After a repeated preparation, Mn-40 calcined at 400 °C still contains a little of Mn₂O₃ crystalline phase under the same preparation conditions, but Mn-100 and Mn-150 do not, because of the change in the pore channels.

Fig. 4 shows a low-angle XRD patterns of the samples and templates. Different low angles and peak intensity of the samples can lead to different pore sizes and mesoporous characteristics. All samples have low-angle diffraction peaks, indicating that they contain ordered mesoporous characteristics. Apart from the (211) peak at 1.24° , Mn-40 possesses one (110) diffraction peak at 0.62° because of the low interconnectivity of KIT-6 aged at 40 °C to reduce the symmetry of the sample [34]. In a nanocasting process of Mn-40, it is impossible to completely fill two relatively independent pore systems by the manganese oxide phase. The manganese material is only collected in some regions of the two pore systems of the template to form a metal oxide phase. If the internetwork between double channel systems of the KIT-6-40 template is plugged up, the

Fig. 4. Low-angle XRD patterns of the samples and templates.

Table 1
Physical parameters of the samples and templates.

Sample	Interplanar spacing d_{211}^a (nm)	Surface area A_{BET} (m ² /g)	Pore volume V_p (cm ³ /g)	Pore diameter D_p^b (nm)
KIT-6-150	8.7	375	1.045	6.2
KIT-6-100	8.5	694	0.638	3.8/5.9
KIT-6-40	7.1	568	0.425	2.0/2.5
Mn-150	9.6	39	0.108	1.9/2.3
Mn-100	9.2	70	0.177	1.9/6.5
Mn-40	8.3	47	0.107	1.9/3.4/6.6

^a Interplanar spacing of the samples calculated through Bragg equation from the (211) diffraction peak in low-angle XRD patterns. ^b Pore sizes obtained from the N₂ adsorption isotherms by the BJH method.

manganese material will be aggregated in both relatively independent channel systems. Then, the original symmetry of the double pore systems will change after removing the template by using NaOH solution. Mn-100 shows stronger (211) and (332) diffraction peaks at $2\theta = 1.0^\circ$ and 1.85° , respectively, which are the same as those of the corresponding template KIT-6-100, indicating that this sample is a perfect replica of the used KIT-6-100 template with cubic symmetry (ia3d) [3]. The Mn-150 sample has a very weak (211) diffraction peak at 1.0° , indicating a worse mesoporous regulation exists in this sample. This may be attributed to a dense particle structure or collapse of the partial mesoporous structure when removing the KIT-6 template aged at 150 °C.

Fig. 5 shows the N₂ adsorption-desorption isotherms and pore size distributions of the samples. The physical parameters are displayed in Table 1. With increasing aging temperature, d_{211} interplanar spacing of KIT-6 decreases gradually, and the amount of MnO₂ materials prepared by KIT-6 at different aging temperatures also decreases (Table 1). It further indicates that mesoporous MnO₂ is a replica of the KIT-6 templates. With increasing aging temperature, the pore size of KIT-6 gradually increases. N₂ adsorption-desorption isotherms of the samples have hysteresis rings and display type IV isotherms, confirming that the samples have mesoporous characteristics (Fig. 5(a)) [38]. Mn-100 has the largest surface area and hysteresis ring (Table 1) because of the most perfect replica of KIT-6-100. Mn-150 has the smallest surface area and hysteresis ring, indi-

cating a weak mesoporous property because of the collapse of the partial pore channels, in agreement with the low-angle XRD results. Mn-40 lies somewhere in between the two. The inset of the top left corner in Fig. 5(a) shows the pore size distribution using the Barrett-Joyner-Halenda method. All the samples have a pore size at 1.9 nm of maximum distributions, which is related to the density of the metal oxide phase in two channels or one of the double channels of KIT-6 [27,28,34]. The pore size at 1.9 nm of mesoporous MnO₂ cannot be affected by the change in the pore size of KIT-6. Except for the pore size at 1.9 nm, the other pore size of mesoporous MnO₂ increases with decreasing aging temperature of the templates.

Mn-100 shows two pore sizes with maximum distributions at 1.9 and 6.5 nm, because it perfectly replicated the double pore channels of the KIT-6 template (Table 1). Interestingly, the Mn-40 catalyst has three pore sizes of maximum distribution at 1.9, 3.4, and 6.6 nm (Table 1), different from those of the KIT-6-40 template with double pore systems (Fig. 5(b)). This result is a reflection on the pore size of the symmetry and degree of order. In the nanocasting process of KIT-6-40, the manganese material will be aggregated in both relatively independent channel systems to form a manganese oxide phase. The pore walls composed of bulk silica will form a bigger pore channel after the template removal. KIT-6-40 has smaller pore sizes (2.0/2.5 nm) (Table 1). Pores of size 1.9 and 6.6 nm form because of the complete filling of the manganese oxide phase in one relatively independent and bigger pore size (2.5 nm) of the double channel systems of KIT-6-40. The formation of pores of size at 1.9 and 3.4 nm results from the incomplete filling of manganese oxide phase in one relatively independent and smaller pore size (2.0 nm) of the double channel systems of KIT-6-40 [27,34]. Therefore, Mn-40 shows three pore systems after the removal of the template. Mn-150 almost shows smaller pore sizes of maximum distributions at around 1.9 nm related to KIT-6-150. KIT-6-150 only has a single pore system of maximum distributions at around 6.2 nm (Fig. 5(b)). A single pore channel was formed after the template removal.

Fig. 6(a)–(c) clearly shows that Mn-40 has a 3D mesoporous property, but the degree of order and symmetry of pore channels decrease. These observations are consistent with the XRD and N₂ adsorption analysis results. The channels seem to be

Fig. 5. N₂ adsorption-desorption isotherms and pore size distributions of samples (a) and corresponding KIT-6 templates (b).

Fig. 6. SEM/STEM images of Mn-40 (a–d), Mn-100 (e, f) and Mn-150 (g–j).

disorganized and ruleless. Fig. 6(d) also clearly displays relatively free pore channels with reduced symmetry and degree of order. Fig. 6(e) and (f) wonderfully shows that Mn-100 pos-

sesses a 3D ordered mesoporous channel structure with excellent symmetry and regulation. In comparison with Mn-40 and Mn-100, Mn-150 has a rather dense pore structure (Fig. 6(g)–(j)). In the nanocast process, manganese oxide can be easily interpenetrated in the bigger channel system of KIT-6-150 to form a dense composite containing MnO_2 and silica phase. Mn-150 with a dense structure and smaller pore size will be formed after template removal. SEM images showed that some bulk MnO_2 nanoparticles coexist with mesoporous MnO_2 on Mn-150 because of the collapse of the partial pore structure after removing the template.

3.3. Thermal reduction behavior of catalysts

The H_2 -TPR patterns of the catalysts are shown in Fig. 7(a). Mn-40 exhibits four reduction peaks located at 242, 310, 323, and 422 °C because of the reduction of Mn_2O_3 to MnO (peak 1), MnO_2 to Mn_2O_3 (peak 2), Mn_2O_3 to Mn_3O_4 (peak 3), and Mn_3O_4 to MnO (peak 4) [3], and correspond to H_2 consumption amounts of 1.62, 3.59, 1.97, and 3.25 mmol/g, respectively (Table 2). The reduction peaks of Mn-100 were located at 310, 350, and 432 °C, and correspond to H_2 consumptions of 3.24, 3.43, and 3.66 mmol/g, respectively (Table 2). Mn-100 exhibits three reduction peaks due to the reduction of MnO_2 to Mn_2O_3 (peak 1), Mn_2O_3 to Mn_3O_4 (peak 2), and Mn_3O_4 to MnO (peak 3), respectively. The reduction peaks of Mn-150 were located at 341, and 422 °C because of the reduction of MnO_2 to Mn_2O_3 (peak 1) and Mn_2O_3 to MnO (peak 2), and correspond to H_2 consumptions of 4.99 and 2.78 mmol/g, respectively (Table 2). Mn-40 has peak 1 at a lower reduction temperature (242 °C), attributing to the reduction of a little small amount of Mn_2O_3 crystalline phase in Mn-40, as can be seen from large-angle XRD results. Peak 3 at 323 °C of Mn-40 and peak 2 at 350 °C of Mn-100 occur because of a special disproportionation reaction of Mn_2O_3 (III) to Mn_3O_4 (IV and II). The dismutation is related to more abundant surface oxygen species. In this study, the total H_2 consumption of Mn-40 and Mn-100 is quite close to their theoretical H_2 consumption (11.5 mmol/g), indicating that a substantial fraction of Mn^{4+} and Mn^{3+} ions in the catalysts have been reduced. The total H_2 consumption (7.8 mmol/g) of Mn-150 is the lowest, perhaps because Mn-150 contains Si impurity that decreases the reduction of mass because of the

Fig. 7. H_2 -TPR patterns (a) and initial H_2 consumption rates (b) of the samples.

Table 2Reduction temperatures, H₂ consumptions and surface element composition of the catalysts.

Sample	Reduction temperature ^a (°C)				H ₂ consumption ^b (mmol/g)					Active site number ^c <i>N</i> (mmol)	Surface element molar ratio ^d	
	peak 1	peak 2	peak 3	peak 4	peak1	peak 2	peak 3	peak 4	total		Mn ³⁺ /Mn ⁴⁺	O _{latt} /O _{ads}
Mn-40	242	310	323	422	1.62	3.59	1.97	3.25	10.4	2.08	1.8	1.3
Mn-100	310	350	432	–	3.24	3.43	3.66	–	10.3	2.06	0.7	1.0
Mn-150	341	422	–	–	4.99	2.78	–	–	7.8	1.56	0.4	1.2

^aReduction temperatures corresponding to the maximum values of reduction peaks in the H₂-TPR result. ^bH₂ consumptions calculated by reduction peak areas. ^cMole number of Mn⁴⁺ and Mn³⁺ ions as active sites were calculated by the H₂-TPR result. ^dSurface element molar ratio calculated by peak areas of XPS.

collapse of the pore structure, as can be seen from SEM results. H₂ consumption of peak 1 from Mn⁴⁺ to Mn³⁺ for Mn-150 can indicate the number of Mn⁴⁺ ions. If the dismutation of Mn-40 and Mn-100 is taken into consideration, the sum of H₂ consumptions from MnO₂ to Mn₂O₃ and Mn₃O₄ to MnO can confirm the number of Mn⁴⁺ ions. Mn-40 has the lowest reduction temperature, followed by Mn-100, indicating that Mn-40 possesses better low-temperature reducibility (Table 2). From Fig. 7(b), it can be deduced that Mn-40 has the highest initial H₂ consumption rate and exhibits a stronger reducibility. This indicates that oxygen species adsorbed on the surface of Mn-40 are more easily desorbed and can combine with hydrogen.

3.4. Thermal desorption behavior of catalysts

Fig. 8 shows the O₂-TPD patterns of the catalysts. The desorption peaks below 600 °C, between 600 and 700 °C, and above 700 °C are attributed to the surface-adsorbed oxygen (O₂[–] and O[–]), surface lattice oxygen (O₂[–]), and bulk phase lattice oxygen (O₂[–]), respectively [39,40]. The surface-active oxygen species are easy to desorb from the metal oxide at low temperatures. Mn-100 has three desorption peaks at 483, 538, and 813 °C, which correspond to O₂[–], O[–], and O₂[–], respectively. Mn-150 also has three desorption peaks at 562, 625, and 830 °C, belonging to O[–], surface O₂[–], and bulk phase O₂[–], respectively. The occurrence of a desorption peak at 625 °C for Mn-150 indicates that the amount of surface O₂[–] species increase with a decrease in the pore size. Mn-40 has two desorption peaks at 510 and 810 °C. The peak at 510 °C belongs to the mixture of surface O₂[–], O[–], and O₂[–] species, probably because of the lattice

defects and oxygen vacancies resulting from three pore systems and Mn₂O₃ phase. Surface O₂[–] and O[–] species of Mn-40 are directly involved in the reaction. Meanwhile, surface O₂[–] species play a role in oxygen supply. The desorption peaks of Mn-40 appear at a lower temperature than those of Mn-100 and Mn-150. This indicates that the oxygen species of Mn-40 are much easier to desorb at low temperatures and participate in the oxidation reaction, owing to three pore channels and more surface lattice oxygen vacancies resulting from lattice distortion in channels. Lower beginning desorption temperatures can lead to better catalytic ability. Therefore, Mn-40 has the best catalytic activity.

3.5. Surface composition of the catalysts

Mn 2p_{2/3} of Mn-100 and Mn-150 shows two components, indicating binding energies (BE) of 641.6 and 642.9 eV, because of the surface Mn³⁺ and Mn⁴⁺ ions, respectively (Fig. 9(a)) [41]. Mn 2p_{2/3} of Mn-40 has three components located at 641.6, 642.7, and 644.6 eV because of the presence of a small amount of Mn₂O₃ crystalline phase, corresponding to the surface Mn²⁺, Mn³⁺, and Mn⁴⁺ ions, respectively [42]. The surface Mn³⁺/Mn⁴⁺ molar ratios of Mn-40, Mn-100, and Mn-150 are 1.8, 0.7, and 0.4, respectively (Table 2). This indicates that the surface of Mn-40 possesses more abundant surface Mn³⁺ species, owing to the existence of a Mn₂O₃ crystalline phase. Fig. 9(b) shows that the O 1s signals were observed at 529.3 and 531.3 eV, corresponding to surface lattice oxygen (O_{latt}) and surface adsorbed oxygen (O_{ads}), respectively [39]. The surface O_{latt}/O_{ads} molar ratios of Mn-40, Mn-100, and Mn-150 are 1.3, 1.0, and 1.2, respectively (Table 2). These results indicate that the surface of Mn-40 has the most abundant surface lattice oxygen species because of some Mn³⁺ ions provided by the Mn₂O₃ phase, followed by Mn-150, owing to a dense structure and partial bulk MnO₂ particles. Surface active oxygen species play an important role in oxidation reactions [43]. Mn-100 has more surface adsorbed oxygen species than Mn-150. This implies that the catalytic performance of Mn-100 is very probably better than that of Mn-150. The surface lattice oxygen of Mn-40 obviously increases, which most likely results in the formation of oxygen vacancies, which are related to the coexistence of Mn³⁺ and Mn⁴⁺ ions [22].

KIT-6 aged at different temperatures was used as the hard template to prepare mesoporous MnO₂ catalysts. The pore sizes of MnO₂ samples correspond to the pore walls of KIT-6 templates. With decreasing aging temperature of KIT-6, the pore

Fig. 8. O₂-TPD patterns of the samples.

Fig. 9. XPS patterns (a, b) of the samples.

sizes of KIT-6 decrease, increasing the pore sizes of mesoporous MnO₂. Mn-40, Mn-100, and Mn-150 have triple, double, and single pore systems, respectively. The increase in the pore sizes and pore channels affect the catalytic activity for ethanol oxidation. The increase in the pore size is beneficial to the adsorption and diffusion of reactants and products. Three pore systems with reduced degree of order and symmetry are favorable to form oxygen vacancies or lattice defects. In this study, active sites for mesoporous MnO₂ catalysts were defined as the combination of Mn³⁺ and Mn⁴⁺. The XPS results showed that Mn-40 had abundant surface Mn³⁺ ions because of the existence of a little Mn₂O₃ crystalline phase, which can improve the number of oxygen vacancies. The increase in the oxygen vacancies of an oxide material is beneficial to the adsorption, activation, and migration of oxygen species for the activation of the ethanol molecule, which can enhance the catalytic activity. Oxygen species of Mn-40 are much easier to desorb at low temperatures, as can be seen from the O₂-TPD results. Surface O₂⁻, O⁻ species of Mn-40 can participate in the oxidation reaction of ethanol at lower temperatures. When surface O₂⁻, O⁻ species are quickly consumed, surface O²⁻ species will provide oxygen supply for the reaction through complex oxygen migration. XPS results confirm that more surface O²⁻ species exist in the Mn-40 sample, which are beneficial to the activation and migration of oxygen species. In the entire reaction process, Mn³⁺ ions and surface O²⁻ species can mutually increase because of the gain and loss of electrons. The H₂-TPR results show that Mn-40 exhibits the best low-temperature reducibility, which is favorable to enhance the catalytic oxidation reaction. Some papers have reported that surface oxygen species, active sites, low-temperature reducibility, and oxygen vacancies are directly connected to the catalytic ability [8,9,21–23,44]. The order of pore sizes, pore systems, and catalytic activities is: Mn-40 > Mn-100 > Mn-150. The Mn-40 catalyst, prepared by KIT-6 aged at 40 °C, has the best catalytic activity for ethanol oxidation because of a bigger pore size with three pore systems owing to a decrease in the symmetry and degree of order, more surface lattice oxygen species, formation of oxygen vacancies resulting from more Mn³⁺ ions, and better low-temperature reducibility.

4. Conclusions

KIT-6 mesoporous silica aged at different temperatures was used as a hard template to prepare mesoporous MnO₂ catalysts. All catalysts belong to mesoporous materials. With decreasing aging temperature of KIT-6, the pore sizes of KIT-6 decrease and that of mesoporous MnO₂ catalysts increase. Mn-40, Mn-100, and Mn-150 have triple, double, and single pore systems, respectively. The Mn-40 catalyst has a decreased symmetry and degree of order owing to lower interconnections between the pore channels of KIT-6 aged at 40 °C. With the increase in the pore sizes and pore system numbers, the decreased order of catalytic activities for ethanol oxidation is Mn-40 > Mn-100 > Mn-150. The Mn-40 catalyst shows a higher TOF (0.11 s⁻¹ at 120 °C) and the best catalytic activity for ethanol oxidation because of a bigger pore size with three pore systems owing to a decrease in the symmetry and degree of order, more surface lattice oxygen species, formation of oxygen vacancies resulting from more Mn³⁺ ions, and better low-temperature reducibility.

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Graphical Abstract

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Effect of pore size in mesoporous MnO₂ prepared by KIT-6 aged at different temperatures on ethanol catalytic oxidation

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KIT-6 mesoporous silica aged at different temperatures was used as a hard template to prepare different mesoporous MnO₂ catalysts. The catalytic activities for ethanol oxidation of the catalysts were investigated, and the effect of pore size on the ethanol catalytic activity has been discussed.

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不同KIT-6老化温度制备的介孔MnO₂孔径对其催化氧化乙醇的影响

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摘要: 乙醇既是一种被广泛使用的溶剂, 也大量存在于乙醇燃料车尾气中。它是一种挥发性有机化合物(VOCs), 能直接参与光化学反应影响空气质量, 因此去除乙醇很有必要。催化氧化法消除VOCs是很有前景的技术, 其关键是催化剂的制备和筛选。目前, 用于乙醇催化氧化的催化剂主要是贵金属催化剂(Pt, Pd, Rh, Au, Ag)和金属氧化物催化剂(Cu, Mn, Co, Fe), 此外, 还有一些钙钛矿型催化剂。MnO₂具有多种结构(α , β , γ 和 δ)和形貌(管状, 棒状, 球状和孔状等)。不同形貌和结构的MnO₂具有不同的VOCs催化氧化性能。我们已经报道了介孔MnO₂, 特别是三维有序介孔MnO₂, 具有良好的乙醇催化氧化活性, 有一定的应用前景。然而, KIT-6老化温度对介孔MnO₂孔径的影响, 以及MnO₂孔径对催化氧化乙醇活性的影响尚不清楚。如果通过调整KIT-6老化温度改变介孔MnO₂的孔径, 很有可能改善催化剂低温还原性, 氧物种和活性位等, 进而提高其催化性能。本文以40, 100和150 °C老化合成的KIT-6介孔硅为硬模板, 制备出不同的介孔MnO₂催化剂, 分别记作Mn-40, Mn-100和Mn-150, 用于乙醇氧化反应中, 讨论了催化剂孔径对其活性的影响。采用X射线粉末衍射(XRD), 氮气吸附-脱附(BET), 扫描电子显微镜(SEM), 氢气程序升温还原(H₂-TPR), 氧气程序升温脱附(O₂-TPD), X射线光电子能谱(XPS)等技术对催化剂进行了表征。

XRD广角结果表明, 各催化剂均具有软锰矿型MnO₂晶相, 其中Mn-40催化剂存在少量Mn₂O₃晶相。XRD小角和SEM结果表明, 各催化剂均为介孔材料, Mn-100催化剂的有序度和对称性最好, KIT-6老化温度的改变使Mn-40和Mn-150的有序度和对称性降低。BET结果表明, Mn-40, Mn-100和Mn-150分别具有三孔, 双孔和单孔体系。随着KIT-6老化温度的降低, KIT-6的孔径降低, 而介孔MnO₂催化剂的孔径增加。XPS结果表明, Mn-40因少量Mn₂O₃晶相的存在而具有较多的Mn³⁺阳离子和表面晶格氧物种, 能增加催化剂氧空位的数量, 有利于氧物种的吸附, 活化和迁移, 从而增强催化活性。TPR和TPD表明, Mn-40催化剂具有良好的低温还原性, 它的氧物种容易在低温下脱附并参与氧化反应。催化剂活性测试结果表明, 随着介孔MnO₂催化剂的孔径增加, 其活性增加。催化剂孔径和活性从大到小的顺序为Mn-40 > Mn-100 > Mn-150。以老化温度为40 °C的KIT-6模板制备的Mn-40催化剂, 具有较高的乙醇转化频率(TOF), 120 °C的TOF为0.11 s⁻¹。Mn-40催化剂具有良好的乙醇氧化催化活性归因于较大孔径, 其孔径呈三孔体系分布, 最大孔径分布在1.9, 3.4和6.6 nm处, 三孔体系的形成是因为催化剂孔道的对称性和有序度降低。此外, Mn-40催化剂具有良好的乙醇氧化催化活性也归因于由较多Mn³⁺阳离子引起的较多表面晶格氧物种和氧空位以及较好的低温还原性。

关键词: 介孔MnO₂; 孔通道; KIT-6介孔硅; 催化性能; 乙醇氧化

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