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ARTICLE

Degradation of Low Concentration Formaldehyde by Mesoporous MnO_2 at Room Temperature

Xu Lingliang[1], Fang Jianfei[2], Tang Huijie[1], Han Zhe[1], Jin Hongxiao[1], Ge Hongliang[1], Wang Xinqing[1], Lou Hui[3], Jin Dingfeng[1,3], Peng Xiaoling[1], Li Jing[1], Yang Yanting[1], Hong Bo[1]

[1] China Jiliang University, Hangzhou 310018, China; [2] Quality and Technical Supervision Inspection Center of Yongkang, Yongkang 321300, China; [3] Zhejiang University, Hangzhou 310028, China

Abstract: Mesoporous MnO_2 was prepared by sol-gel method using $KMnO_4$ and P123 as raw materials, and the effects of reactant ratio and pH on the catalytic oxidation performance of the product were investigated. The structure and properties of the synthesized materials were characterized by XRD, N_2 adsorption and desorption, and FT-IR. Finally, the influencing factors of the catalytic oxidation of HCHO by mesoporous MnO_2 were discussed. The results show that the mesoporous MnO_2 has good catalytic oxidation performance to HCHO. The optimum conditions of the preparation are as follows: the ratio of $KMnO_4$ and P123 is 10:1 and the pH is 7, when the specific surface area of mesoporous MnO_2 (pH 7-10:1) is largest, the oxidation performance is the strongest, and the degradation rate of formaldehyde maintains at 95% within 10 h.

Key words: formaldehyde; mesoporous MnO_2; catalytic oxidation; sol-gel method; indoor air

Formaldehyde is one of the most important VOCs (volatile organic compounds) and ranks second in the list of China's toxic chemicals priority control[1-4]. It has become one of the most important indoor air pollutants, not only affecting the upper respiratory tract and lungs of the human body, stimulating allergies, causing liver function, immune function, nervous system abnormalities, but also leading to loss of central part function, and long-term exposure to high quality concentration. When the concentration of formaldehyde in the air is 0.06~0.07 mg/m^3, children will have mild asthma[5-7]. When it reaches 0.1 mg/m^3, it will feel odor and discomfort. When it is higher, it can cause nausea, vomiting, cough and chest tightness, while reaching 30 mg/m^3 can cause death. In June 2004, the International Agency for Research on Cancer raised formaldehyde from a second-class carcinogen to a class of carcinogens[8-11]. The release process of formaldehyde in indoors lasts for 3 years to 15 years. At present, the commonly used method is activated carbon adsorption, but this method only transfers the pollution source, and cannot decompose the pollutants, because the physical adsorption of the activated carbon on the pollutants is only a simple accumulation, which will lead to problems such as adsorption saturation and secondary pollution[12-15]. In order to fundamentally eliminate the harm of formaldehyde to the human body, the method of photocatalytic degradation of formaldehyde in air has become a hot spot in recent years[16]. Photocatalytic oxidation is the oxidation of formaldehyde to CO_2 and H_2O by holes (h^+) and ·OH with strong oxidizing ability generated by photocatalysts such as TiO_2, but the photocatalyst must be activated by irradiation with a light source (mainly ultraviolet light)[17-20].

In recent years, mesoporous inorganic materials have become a new research hotspot, and have been widely used in many fields such as catalysis, lithium ion batteries, and

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Corresponding author: Jin Dingfeng, Ph. D., Professor, College of Materials Science and Engineering, China Jiliang University, Hangzhou 310018, P. R. China, Tel: 0086-571-86875610, E-mail: dfjin@cjlu.edu.cn

supercapacitors[21]. Mesoporous materials generally refer to a class of porous materials with a pore diameter of 2 to 50 nm. They have extremely high specific surface area, regular ordered pore structure, narrow pore size distribution, and continuously adjustable pore size, so that they are worked in adsorbed, separation, especially in catalytic reactions[22]. Ordered mesoporous manganese oxide has become a hot spot in the synthesis of transition metal mesoporous oxides due to its valence variability and its excellent cation exchange capacity, molecular adsorption and catalytic properties, and excellent electromagnetic properties[23-25].

Surfactant intermediate phases have been widely used as templating agents for nanostructured materials[26]. Among them, P123 (average Mn~5800) can be used as a structure-directing agent as a nonionic amphiphilic triblock copolymer[27]. In the present study, mesoporous MnO_2 was synthesized by sol-gel method using potassium permanganate and P123 in different ratios of materials. It was characterized by X-ray diffraction (XRD), specific surface area (BET) and Fourier transform infrared spectroscopy (FTIR). Catalytic oxidation of formaldehyde in air was carried out at room temperature, atmospheric pressure and no light by using MnO_2 as catalyst.

1 Experiment

Mesoporous MnO_2 was synthesized as follows: $KMnO_4$ and P123 were dissolved in water and the pH value was adjusted with HCOOH. The solution was heated in a water bath, and stirred at 25 °C for 24 h. After completion of the reaction, the mixture was aged for 24 h, filtered, washed several times with distilled water, and then dried at 80 °C. The dried products were placed in a wire extractor and extracted with absolute ethanol for 24 h to remove remaining organic matter. After extraction, it was dried in a drying oven at 80 °C to obtain mesoporous MnO_2. All chemicals used for sample preparation are analytical grade.

The crystal structure of samples was collected by Powder X-ray diffraction (XRD, Smart Lab SE, Japan) with Cu Kα radiation at 40 kV and 40 mA. A scanning step of 0.02° and scanning speed of 0.2°/s were applied in the 2θ range of 0.5°~90°. The large angle XRD scan has an angle range of 10°~90°. The physical adsorption isotherm for the sample was tested by the ASAP 2020 specific surface and porosity analyzer produced by Micromeritics Instruments, Inc., and the adsorption gas is nitrogen. The specific surface area of the material was tested by BET (Brunauer-Emmett-Teller) method, and the pore size distribution and total pore volume of the material were characterized by BJH (Barrett-Joiner-Halenda) model. The total pore volume was calculated at a relative pressure of 0.99. Fourier transform infrared (FT-IR) spectra were obtained from 2000 cm^{-1} to 500 cm^{-1} on a SHIMADZU FTIR-8400S using KBr pellets.

The 0.1 mol/L formaldehyde solution vessel was maintained in a water bath at 0 °C, and a mixture of 40 mL/min of O_2 and 160 mL/min of N_2 was passed through it to produce gaseous HCHO. The gas was passed through a quartz tube reactor filled with 500 mg of MnO_2 (150~180 μm), and both ends were wrapped with quartz wool. The weight hourly space velocity (WHSV) was fixed at 24000 mL/g/h. The reaction temperature was maintained at 25 °C. Quartz tube reactor inlet and outlet gases were monitored by a PPM-400 ST HCHO detector (detection range and limits were 0~20 μL/L and 20 μL/L, respectively). The initial concentration of HCHO was fixed at about 4 μL/L and monitored by the HCHO detector.

The degradation of HCHO was calculated according to Eq.(1).

$$\text{HCHO degradation }(\%)=\frac{\text{HCHO}_1-\text{HCHO}_2}{\text{HCHO}_1}\times100\% \qquad (1)$$

where, $HCHO_1$ is the initial HCHO concentration and $HCHO_2$ is the HCHO concentration at different time after passing through catalyst.

2 Results and Discussion

2.1 Structure characterization of catalysts

The XRD patterns of mesoporous MnO_2 samples prepared under different conditions and commercial MnO_2 are shown in Fig.1. It shows that commercial MnO_2 belongs to γ-MnO_2, which is composed of ramsdellite and akhtenskite. The characteristic peak at 21° is the (101) crystal plane of ramsdellite. The four characteristic peaks in the 2θ of 37°, 42°, 56°, 66° are the (100), (101), (102), and (110) crystal faces of akhtenskite, respectively. The mesoporous MnO_2 prepared under different conditions show (100) and (110) crystal faces, indicating that the crystal structure of mesoporous MnO_2 is amorphous.

To investigate the change of the internal structure of corresponding samples, the FTIR was explored to determinate characteristic functional groups. Fig.2 shows the FTIR spectra of samples prepared under different conditions. It can be seen from the figure that the samples prepared under different conditions have similar absorption spectra. Fig.3 shows the

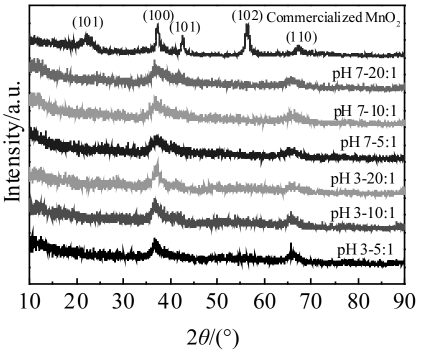

Fig.1 XRD patterns of different samples and commercialized MnO_2

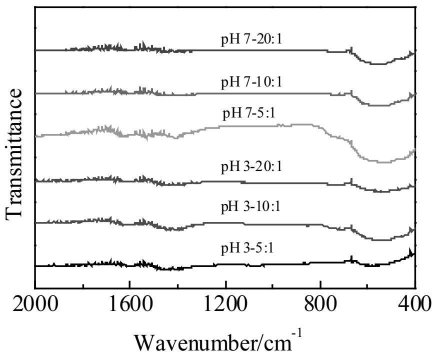

Fig.2 FTIR spectra of samples prepared under different conditions

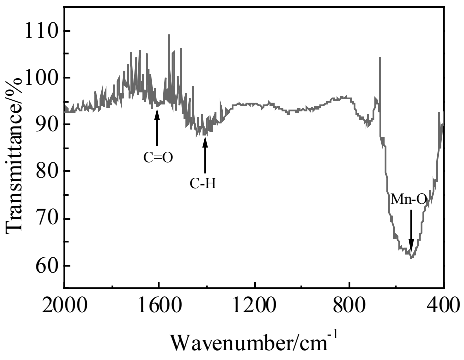

Fig.3 FTIR spectrum of samples prepared under pH 7-10:1

FTIR spectra of samples prepared under pH 7-10:1. The infrared absorption peak at about 585 cm^{-1} is the absorption peak of MnO_2. The peak near the wave number of 1400 cm^{-1} is the absorption peak of C-H, and the weak peak of C=O is at near 1580 cm^{-1}, indicating that P123 and other organic residue have been nearly removed.

To further investigate the pore structure of samples, N_2 adsorption-desorption measurement was conducted and the results are shown in Fig.4. According to IUPAC's classification, the isotherm of MnO_2 samples by the sol-gel method exhibits a type IV isotherm, indicating the existence of a small amount of mesopore structure. The N_2 adsorption-desorption measurement of commercial MnO_2 is shown in Fig.5.

The primary textural properties of the commercial MnO_2, MnO_2 samples by the sol-gel method calculated according to the corresponding N_2 isotherms are listed in Table 1. Samples prepared under different conditions have S_{BET} greater than commercial S_{BET}. At the same pH, a specific surface area with pore ratio of 10:1 is greater than 5:1 and 20:1, which can be derived from Table 1. When the raw material ratio is the same, the specific surface area of the sample prepared under pH 3 is larger than that of MnO_2 prepared under the condition of pH 7, both between 2 and 50 nm, indicating that it belongs to the mesoporous materials.

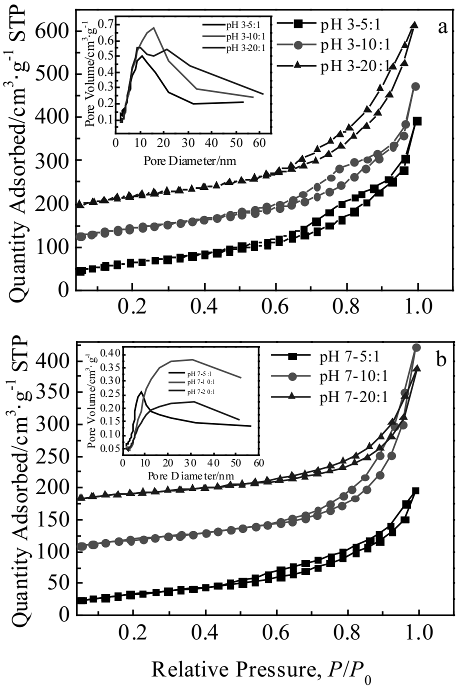

Fig.4 N_2 adsorption-desorption measurement of different raw materials ratios under pH 3 (a) and pH 7 (b) conditions

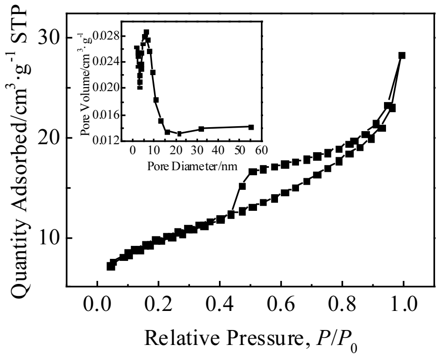

Fig.5 N_2 adsorption-desorption measurement of commercial-MnO_2

Table 1 Textural parameters of different MnO_2 catalysts

Sample	Specific surface area, S_{BET}/m^2·g^{-1}	Pore volume/ cm^3·g^{-1}	Pore size/ nm
C-MnO_2	35.40	0.04	4.96
pH 3-5:1	228.45	0.60	10.66
pH 3-10:1	232.09	0.66	11.49
pH 3-20:1	219.63	0.70	12.80
pH 7-5:1	123.55	0.30	9.82
pH 7-10:1	143.34	0.52	14.77
pH 7-20:1	114.51	0.35	12.31

2.2 Catalytic activity

The removal efficiency of commercialized MnO_2 for degradation of HCHO at room temperature is shown in Fig.6.

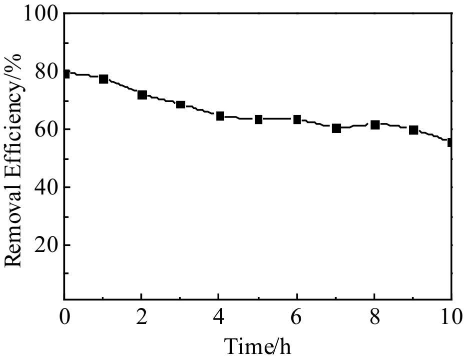

Fig.6 Removing rate for formaldehyde of commercialized MnO_2

When the initial concentration is 4 μL/L, the degradation efficiency is 60%~80%.

The removal efficiency of MnO_2 prepared under different conditions for low concentration of HCHO at room temperature is shown in Fig.7. The degradation efficiency is lower because the catalyst is in an activated state during this time, and the degradation efficiency begins to stabilize after 60 min. The MnO_2 prepared under different conditions have different catalytic properties.

In the case where the $KMnO_4$ is not excessive, as the ratio of the reactants increases, the performance of the synthesized mesoporous MnO_2 is improved. On the one hand, $KMnO_4$ provide the Mn source in the catalyst, while it cannot be completely converted into usable catalyst when the ratio of $KMnO_4$ and P123 is 20:1. On the other hand, when the content of $KMnO_4$ is low (5:1), the source of manganese is insufficient, and the content of MnO_2 in the product decreases. When the ratio is 10:1, the maximum amount of reaction can be converted into MnO_2 and carbon dioxide, and because of the presence of carbon dioxide, the specific surface area and the pore volume of MnO_2 is larger. At the same pH, larger specific surface area and pore size help release lattice oxygen, adsorb water molecules and formaldehyde to participate in the reaction, which is helpful for improving the catalytic activity of MnO_2.

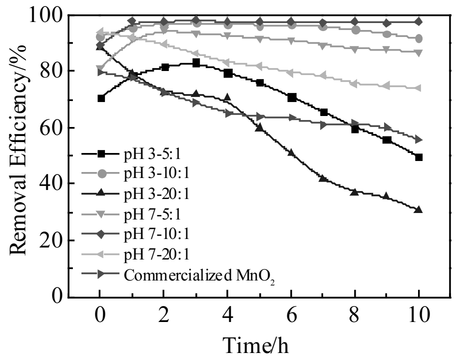

Fig.7 Removing rate for formaldehyde of different samples

Through the structural analysis of MnO_2, in the case of the same pH, when the ratio is 10:1, the specific surface area is the largest and the catalytic efficiency is the highest. Comprehensive studies have shown that the optimal reactivity ratio of synthetic mesoporous MnO_2 is 10:1. The pH value is an important factor affecting the catalytic oxidation of HCHO by mesoporous MnO_2. Mn as a transition metal element, in the process of preparing MnO_2, the enhancement of acidity easily leads to the loss of the raw material $KMnO_4$ to Mn^{2+} and reduces the content of MnO_2 in the product. When the acidity is high (pH=3), the precipitate is easily decomposed, resulting in a decrease in the content of MnO_2 in the product. The specific surface area of pH 3 is larger than that of pH 7, but the catalyst under pH 3 is easily deactivated compared with the activity of pH 7.

In summary, the optimal condition is that the ratio of $KMnO_4$ to P123 is 10:1, the reaction time is 24 h, the reaction temperature is 25 °C, the pH is 7, and the extraction time with C_2H_6O is 24 h. This sample is stable to 95% or more for HCHO degradation within 10 h.

3 Conclusions

1) Mesoporous MnO_2 was prepared by sol-gel method under different pH and raw material ratios.

2) The existence of mesoporous MnO_2 are confirmed by XRD, N_2 adsorption-desorption and FT-IR. The prepared mesoporous MnO_2 has a high specific surface area and a large pore diameter.

3) Mesoporous MnO_2 has excellent catalytic performance in catalytic oxidation of low concentration HCHO at room temperature. The mesoporous MnO_2 (pH 7-10:1) is stable to 95% within 10 h, which is greatly improved compared with commercial MnO_2.

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室温下介孔 MnO_2 降解低浓度甲醛的研究

许凌亮[1]，方建飞[2]，汤惠睫[1]，韩　哲[1]，金红晓[1]，葛洪良[1]，王新庆[1]，
楼　辉[3]，金顶峰[1,3]，彭晓领[1]，李　静[1]，杨艳婷[1]，洪　波[1]
(1. 中国计量大学，浙江 杭州 310018)
(2. 永康市质量技术监督检测中心，浙江 永康 321300)
(3. 浙江大学，浙江 杭州 310028)

摘　要：以 $KMnO_4$ 和 P123 为原料采用溶胶-凝胶法在不同条件下制备了介孔 MnO_2，研究了反应物比和 pH 对催化剂结构和催化降解性能的影响。合成材料的结构和性能采用 XRD、N_2 吸脱附、FT-IR 的测试方法表征。最后讨论了介孔 MnO_2 催化氧化 HCHO 的影响因素。结果表明，溶胶-凝胶法制备介孔 MnO_2 的最佳条件为：原料配比为 10:1，pH 值为 7。P123 和 $KMnO_4$ 合成的介孔 MnO_2 具有较大的比表面积和孔径，且有良好的 HCHO 催化降解性能。在 pH=7 的情况下最有利于介孔 MnO_2 的活性稳定；在原料比为 10:1 情况下生成的介孔 MnO_2 比表面积较大，催化降解性能较强，在 10 h 内保持在对甲醛的降解率为 95%以上。

关键词：甲醛；介孔 MnO_2；催化氧化；溶胶凝胶法；室内空气

作者简介：许凌亮，男，1995 年生，硕士生，中国计量大学材料科学与工程学院，浙江 杭州 310018，电话：0571-86875610，E-mail: 1004484341@qq.com