Preparation of three-dimensionally ordered macroporous SiO_2-supported nanoparticle $KMnO_x$ catalysts for soot combustion

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Introduction

As a main source of urban atmospheric particulate matters (PM2.5, paricle size <2.5 μm), the soot particles emitted from diesel engines is directly threatening the environment and people's health[1]. Alkaline metal oxides (especially for potassium) show high catalytic activity for soot oxidation[2]. Unfortunately, their activity usually tends to degrade due to the loss of potassium. In this work, K and Mn are formed a phase of cryptomelane-M to enhance stability of catalyst. In addition, our previous work have demonstrated that three-dimensionally ordered macroporous (3DOM) materials exhibited good catalytic performance for diesel soot combustion[3]. Therefore, 3DOM SiO_2 supported $KMnO_x$ nanoparticles can be taken as cheap and efficient candidate catalysts for soot oxidation.

Materials and Methods

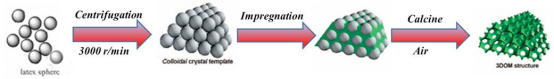

Figure 1 Schematic illustration for preparation of 3DOM SiO_2

Synthesis of 3DOM SiO_2: 3DOM SiO_2 was synthesized by colloidal crystal template (CCT) method with PMMA arrays as template and using tetraethyl orthosilicate (TEOS) as precursors. As shown in the Figure 1, the monodispersed PMMA latex spheres were assembled to form CCT by centrifugation, and then the PMMA arrays were added into the precursor solution for impregnation. After completely impregnate, the PMMA arrays were separated by vacuum filter and dried at 30 °C for 24h. The dried sample was calcined to remove the CCT in a tube furnace with an air flow (80 mL min^{-1}) at 600 °C for 4h. Then, 3DOM SiO_2 was obtained.

Synthesis of 3DOM $KMnO_x/SiO_2$: a series of 3DOM $KMnO_x/SiO_2$ catalysts with different $KMnO_x$ loading amounts were synthesized by incipient wetness impregnation method. In a typical procedure, a certain amount of KNO_3 and $Mn(NO_3)_2$ solution(50 wt%) was dissolved into deionized water, and then the mixed solution was added into 3DOM SiO_2. After that, the impregnated $KMnO_x/SiO_2$ was dealt with ultrasound for 10 min and dried at 80 °C for 24 h. Then, the sample was calcined at 550 °C for 4 h in tube furnace and 3DOM $KMnO_x/SiO_2$ catalysts were obtained.

Results and Discussion

The SEM images (Figure 2a,b) show that the materials have three-dimensionally ordered macropores with average diameter of ca. 310±20 nm. As shown in the TEM images, a great number of nanoparticles $KMnO_x$ are adhered on the surface of 3DOM SiO_2, while nothing is observed on the pure 3DOM SiO_2. HRTEM image indicates that the lattice fringes of 0.69 nm is belong to [101] planes of cryptomelane-M. From the XRD of 3DOM $KMnO_x/SiO_2$ (Figure 3), it can be seen that the intensity of diffraction peaks of amorphous SiO_2 are weaken and some feature peaks of cryptomelane-M are appeared and enhanced with increasing of $KMnO_x$.

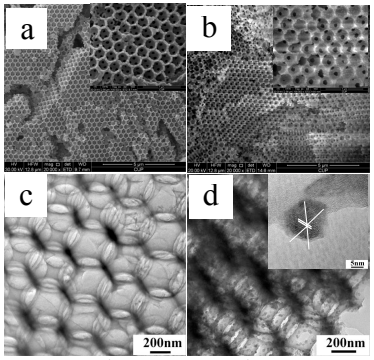

Figure 2 SEM, TEM images
(SEM: 3DOM SiO_2(a), 50%$KMnO_x/SiO_2$(b); TEM: 3DOM SiO_2(c), 50%$KMnO_x/SiO_2$(d);)

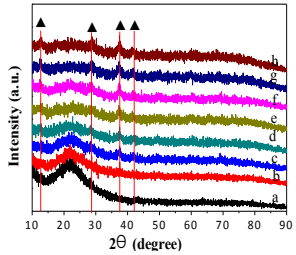

Figure 3 XRD of 3DOM $KMnO_x/SiO_2$
($KMnO_x$ loadings of 0% (a), 10% (b), 20% (c), 30% (d), 40% (e), 50% (f), 60% (g) and 70% (h))

Table 1 Catalytic activity of 3DOM $KMnO_x/SiO_2$ catalysts for soot combustion

Catalysts	T_{10} /°C	T_{50} /°C	T_{90} /°C	S_{CO2}^{m}/%
pure soot	482	564	609	71.6
3DOM SiO_2	354	503	550	78.1
10%$KMnO_x/SiO_2$	315	380	420	93.5
30%$KMnO_x/SiO_2$	296	346	382	94.7
50%$KMnO_x/SiO_2$	283	328	363	96.7
70%$KMnO_x/SiO_2$	286	330	360	96.5

The catalytic activity results of 3DOM $KMnO_x/SiO_2$ catalysts for soot oxidation are listed in Table 1. All catalysts show high catalytic activities for soot combustion. The catalytic activity enhanced with increasing of $KMnO_x$ loading amounts when loading is lower than 50%. However, the catalytic activity is steady when $KMnO_x$ loading amounts is over 50%. In this work, it can be said that 50%$KMnO_x/SiO_2$ catalyst exhibits the highest catalytic activities for soot combustion.

Significance

3DOM $KMnO_x/SiO_2$ catalysts were successfully synthesized by simple method. The as-prepared catalysts show high catalytic activities for soot combustion. 50%$KMnO_x/SiO_2$ catalyst show higher activities than noble metal supported catalysts. The 3DOM $KMnO_x/SiO_2$ catalysts are promising for practical applications in diesel soot combustion due to low cost, simple synthetic process and high catalytic activity.

Acknowledgements

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References

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