

## *Electronic Supplementary Information (ESI)*

Catalytic activity and stability of porous Co-Cu-Mn mixed oxides modified  
microfibrinous-structured ZSM-5 membrane/PSSF catalyst for VOCs oxidation

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1 ***Supporting Information I: Characterization results of the as-synthesized and tested***  
2 ***microfibrinous-structured ZSM-5 membrane/PSSF catalyst***

3 The morphologies of the catalysts were observed by scanning electron microscopy (SEM,  
4 Hitachi S-3700N). All of the samples were coated with an ultra-thin film of gold to make them  
5 conductive before analysis. The Si/Al ratio in the zeolite membrane, Cu/Mn ratio as well as the  
6 weight loading of metal were also measured by Energy dispersive X-ray spectrometer (EDS,  
7 Quantax, Bruker Co., Germany) coupled with the microscope chamber. X-ray diffraction (XRD)  
8 patterns of catalysts were recorded on a D8 Advance (Bruker Co.) diffractometer using Cu K $\alpha$   
9 radiation (40kV, 40mA) with 2 $\theta$  range of 5~80°. The X-ray tube was operated at 40kV and 40mA.  
10 N<sub>2</sub> adsorption/desorption isotherms of catalysts were tested using an ASAP 2020 (Micromeritics  
11 Instrument Co., USA) at 77K. Before measurements, all of the samples were out-gassed at 523 K for  
12 8 h.

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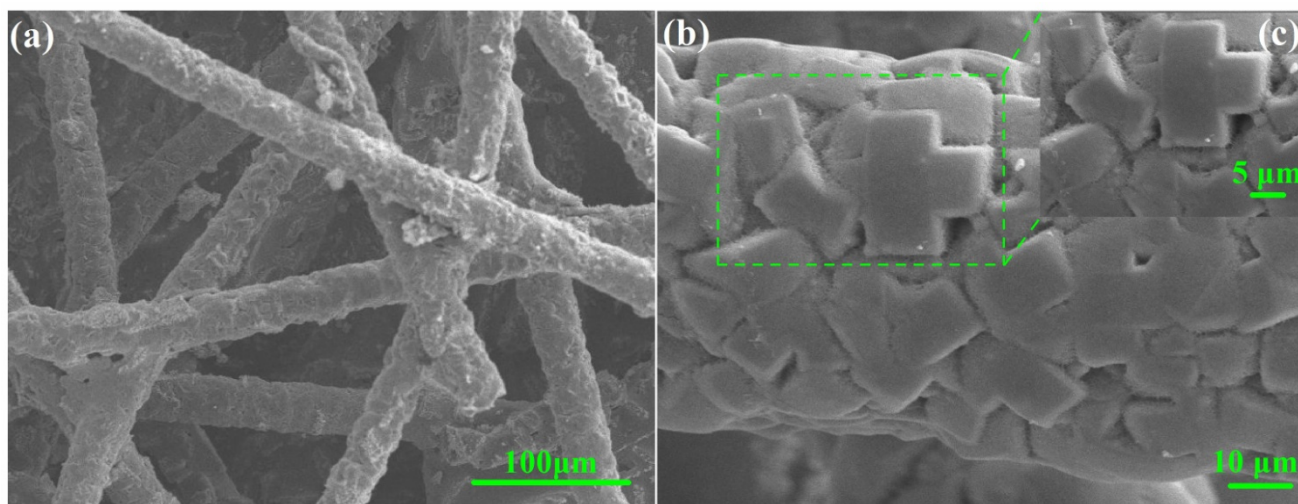
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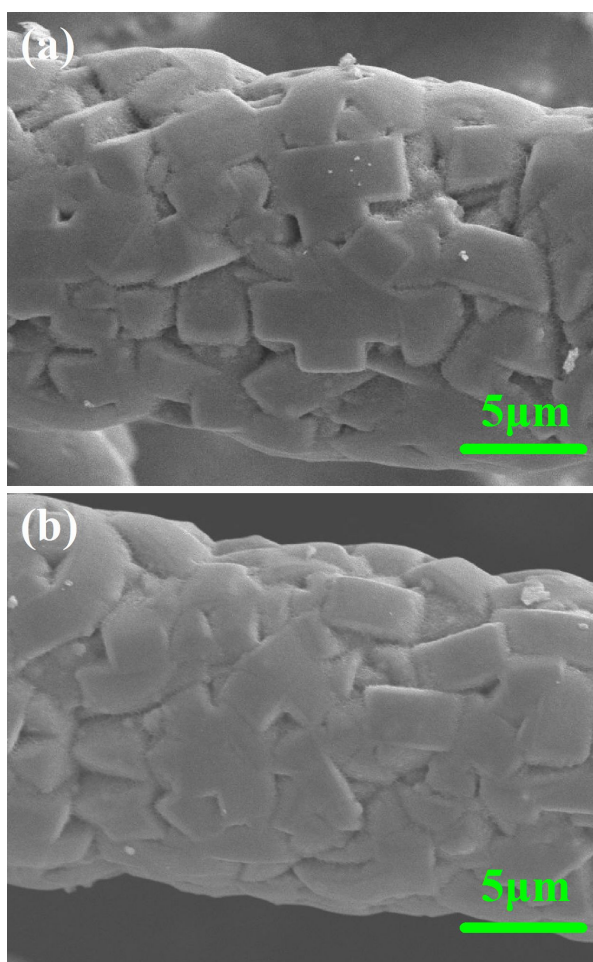
## 1 ***(1) SEM and EDS results of as-synthesized and tested catalyst***

2 SEM images of the as-synthesized and tested (after being used at 260 °C for 550 h) Co-Cu-Mn  
3 (1:1:1)/ZSM-5 membrane/PSSF catalyst are clearly shown in Fig. S1 and S2. From the SEM top  
4 view in Fig. S1, after incipient wetness impregnation process, the zeolite crystals in ZSM-5  
5 membrane can be clearly observed. However, it is difficult to clearly observe the cobalt-copper-  
6 manganese mixed oxides on the surface of ZSM-5 membrane. The possible reason is that the cobalt-  
7 copper-manganese mixed oxides with relatively smaller crystal sizes are uniformly dispersed on the  
8 ZSM-5 membrane. After being used at 260 °C for 550 h, SEM image of the tested Co-Cu-Mn  
9 (1:1:1)/ZSM-5 membrane/PSSF catalyst in Fig. S2 (b) shows small difference with that of as-  
10 synthesized catalyst. EDS spectrum results of the as-synthesized and tested (after being used at 260  
11 °C for 550 h) Co-Cu-Mn (1:1:1)/ZSM-5 membrane/PSSF catalyst are presented in Fig. S3. The  
12 elements of Co, Cu and Mn present in the as-synthesized and tested catalysts, and the small intensity  
13 difference between the as-synthesized and tested catalysts can be observed from the EDS spectrum  
14 results. EDS mapping images of the as-synthesized and tested catalysts are also presented in Fig. S4.  
15 The modified ZSM-5 membrane catalyst consisting of Si, Al, Co, Cu and Mn element is revealed.  
16 The elements of Si and Al are attributed to the ZSM-5 membrane. EDS mapping images can also  
17 exhibit and confirm that the uniform dispersion of cobalt, copper and manganese on the surface of  
18 ZSM-5 membrane. The small composition difference between the as-synthesized and tested catalysts  
19 can be observed from the EDS mapping images. The EDS results also indicate that the Co-Cu-Mn  
20 mixed oxides are well dispersed in the ZSM-5 membrane, which are in well agreement with the SEM  
21 results. Therefore, it can be found that the Co-Cu-Mn (1:1:1)/ZSM-5 membrane/PSSF catalyst  
22 possesses excellent structural and textural stability.

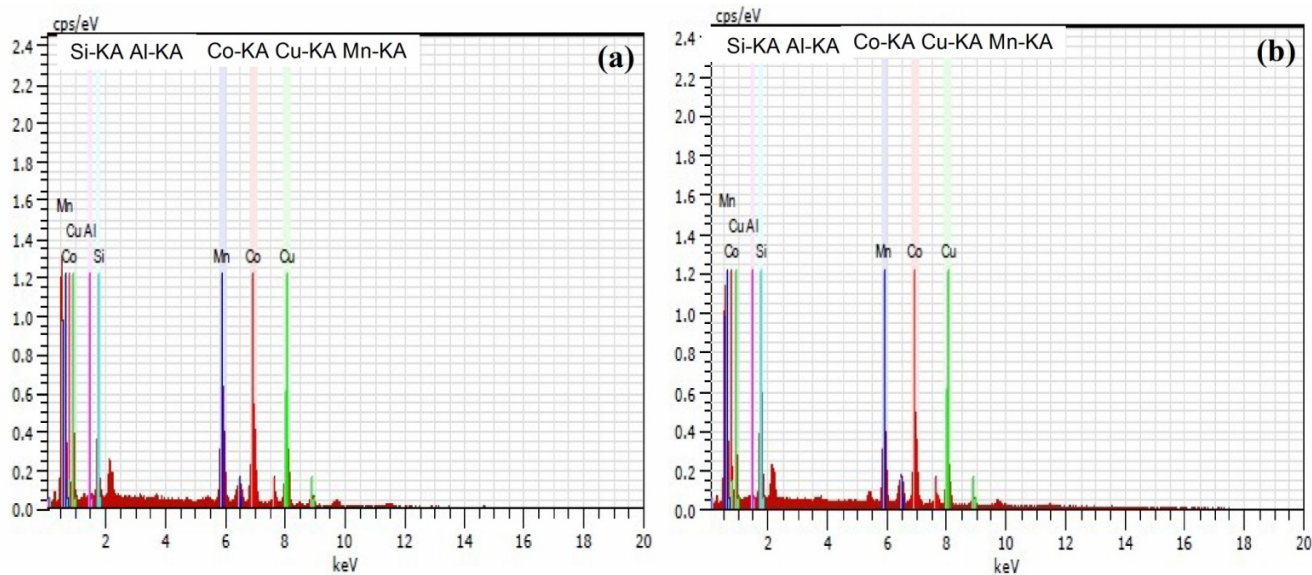


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2 **Fig. S1** (a) SEM surface images and (b-c) top views of the as-synthesized Co-Cu-Mn (1:1:1)/ZSM-5  
3 membrane/PSSF catalyst

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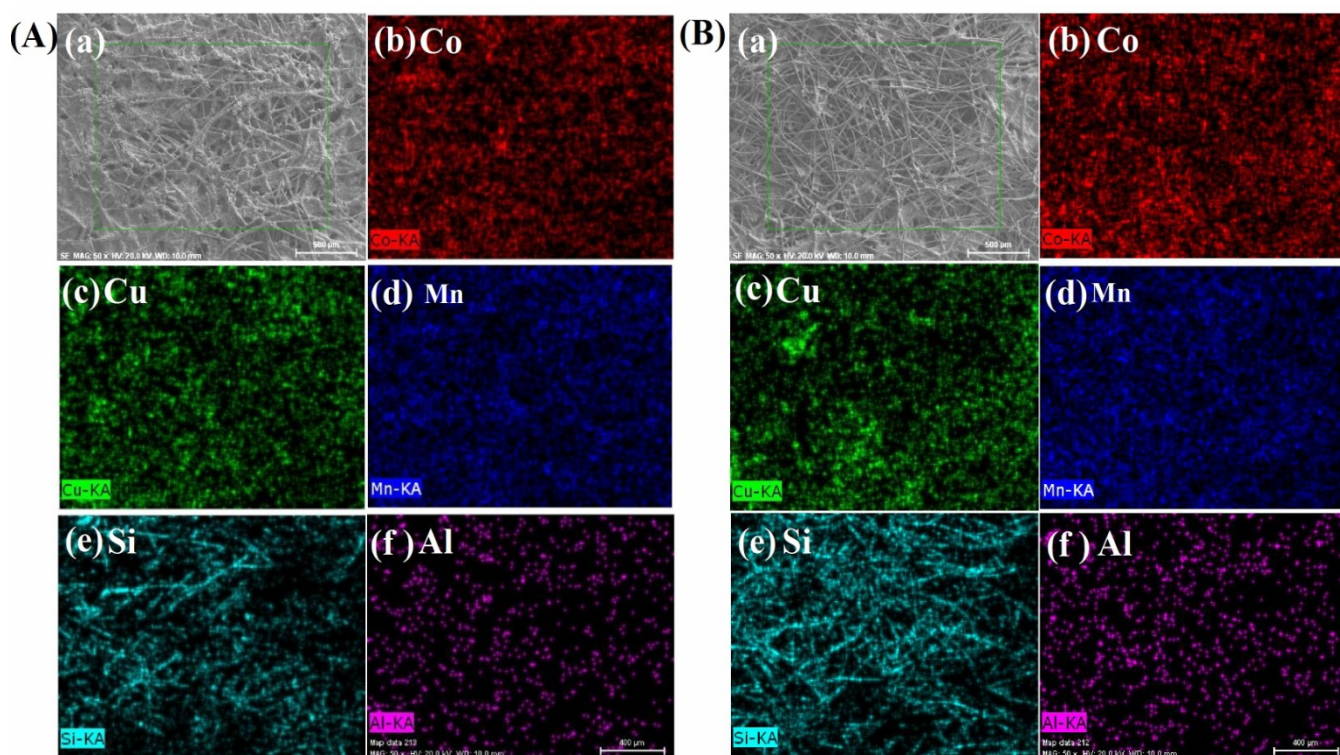


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6 **Fig. S2** SEM surface micrographs of the Co-Cu-Mn (1:1:1)/ZSM-5 membrane/PSSF catalyst: as-  
7 synthesized (a) and tested (after being used at 260 °C for 550 h) (b)



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 2 **Fig. S3** EDS elemental analysis spectrum of the Co-Cu-Mn (1:1:1)/ZSM-5 membrane/PSSF catalyst:  
 3 as-synthesized (a) and tested (after being used at 260 °C for 550 h) (b)

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 6 **Fig. S4** EDS elemental mapping images of the Co-Cu-Mn (1:1:1)/ZSM-5 membrane/PSSF catalyst:  
 7 as-synthesized (A) and tested (after being used at 260 °C for 550 h) (B)

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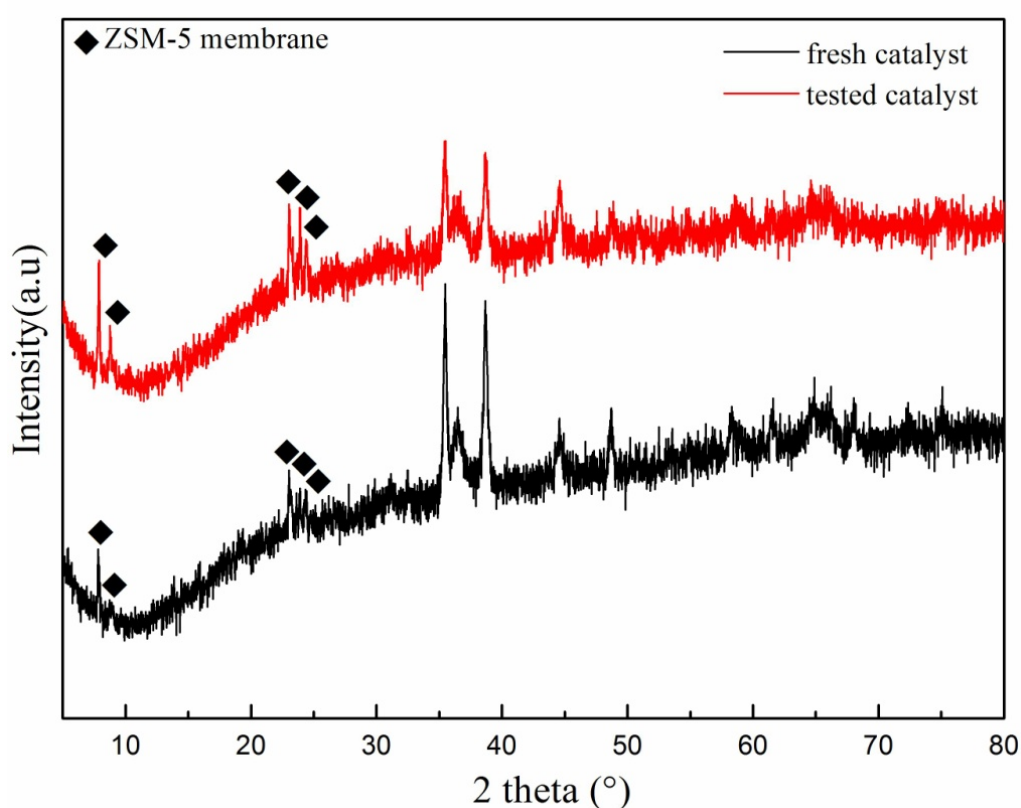
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## 2 (2) *Structural and textural properties of the as-synthesized and tested catalysts*

3 The XRD patterns of as-synthesized and tested (after being used at 260 °C for 550 h) Co-Cu-Mn  
4 (1:1:1)/ZSM-5 membrane/PSSF catalyst are shown in Fig. S5. As can be seen in Fig. S5, all the  
5 XRD patterns clearly present the diffraction peaks related to the ZSM-5 membrane at the ranges of  
6  $2\theta=7-9^\circ$  and  $2\theta=23-25^\circ$ , matching well with the standard pattern of ZSM-5 zeolite.<sup>1</sup> It can be  
7 observed in Fig. S5 that the diffraction peaks at  $2\theta=35-40^\circ$  of catalysts could be attributed to the  
8 cobalt-copper-manganese mixed oxides. However, after being used at 260 °C for 550 h, the  
9 diffraction peaks at  $2\theta=35-40^\circ$  of tested catalyst are relatively smaller, indicating that some crystal  
10 sizes of mixed oxides decreased during the long-term catalytic oxidation reaction process. Fig. S6  
11 shows the N<sub>2</sub> adsorption-desorption isotherms of as-synthesized and tested (after being used at 260  
12 °C for 550 h) Co-Cu-Mn (1:1:1)/ZSM-5 membrane/PSSF catalyst, and their BET surface area as well  
13 as pore properties are also presented in Table S1. As can be seen in Fig. S6, the volume adsorbed  
14 increases obviously with increasing relative pressures ( $P/P_0$ ) for all isotherms, which could be  
15 attributed to the volume filling of micro-pores in ZSM-5 zeolite membrane. Then the relative  
16 pressure close to 1, Fig. S6 clearly show that the isotherms of the as-synthesized and tested (after  
17 being used at 260 °C for 550 h) Co-Cu-Mn (1:1:1)/ZSM-5 membrane/PSSF catalyst all exhibit a  
18 large hysteresis loop, which could be attributed to the existence of meso-pores between very small  
19 particles of mixed Co-Cu-Mn oxides. The micro-pore volume was calculated by using t-Plot method,  
20 the meso-pore volume was calculated by using BJH (Barrett-Joyner-Halenda) method, and the total  
21 pore volume was calculated by using data at relative pressure  $P/P_0=0.97$ . As listed in Table S1, the  
22 fresh catalyst exhibits a BET specific surface area (109 m<sup>2</sup>/g) and total pore volume (0.133 cm<sup>3</sup>/g),

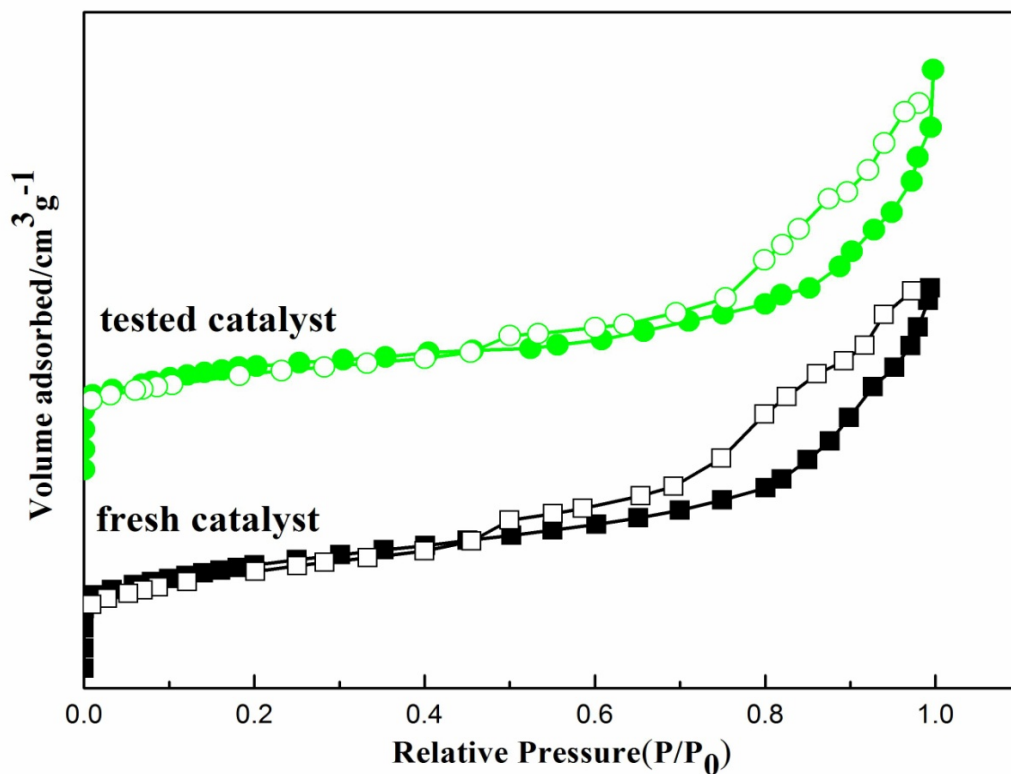
1 micro-pore volume ( $0.016 \text{ cm}^3/\text{g}$ ) and meso-pore volume ( $0.119 \text{ cm}^3/\text{g}$ ). Comparing to the as-  
2 synthesized catalyst, the tested catalyst exhibits a similar BET specific surface area ( $109 \text{ m}^2/\text{g}$ ) and  
3 relatively lower total pore volume ( $0.120 \text{ cm}^3/\text{g}$ ), micro-pore volume ( $0.02 \text{ cm}^3/\text{g}$ ) as well as meso-  
4 pore volume ( $0.101 \text{ cm}^3/\text{g}$ ). The experimental results indicate that the surface characteristics and  
5 pore structures of catalyst were slightly changed during the long-term catalytic oxidation process.

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8 **Fig. S5** X-ray diffraction patterns of the as-synthesized and tested Co-Cu-Mn (1:1:1)/ZSM-5  
9 membrane/PSSF catalyst



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2 **Fig. S6** N<sub>2</sub> adsorption-desorption isotherms of the as-synthesized and tested Co-Cu-Mn (1:1:1)/ZSM-  
 3 5 membrane/PSSF catalysts at 77 K

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5 **Table S1** Physicochemical properties of the as-synthesized and tested Co-Cu-Mn (1:1:1)/ZSM-5  
 6 membrane/PSSF catalysts

Samples	V <sub>Micro-pore</sub> (cm <sup>3</sup> g <sup>-1</sup> )	V <sub>Meso-pore</sub> (cm <sup>3</sup> g <sup>-1</sup> )	V <sub>Total</sub> (cm <sup>3</sup> g <sup>-1</sup> )	S <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> )
Co-Cu-Mn(1:1:1)/ZSM-5/PSSF (as-synthesized)	0.016	0.119	0.133	109
Co-Cu-Mn(1:1:1)/ZSM-5/PSSF (tested in 550h)	0.020	0.101	0.120	109

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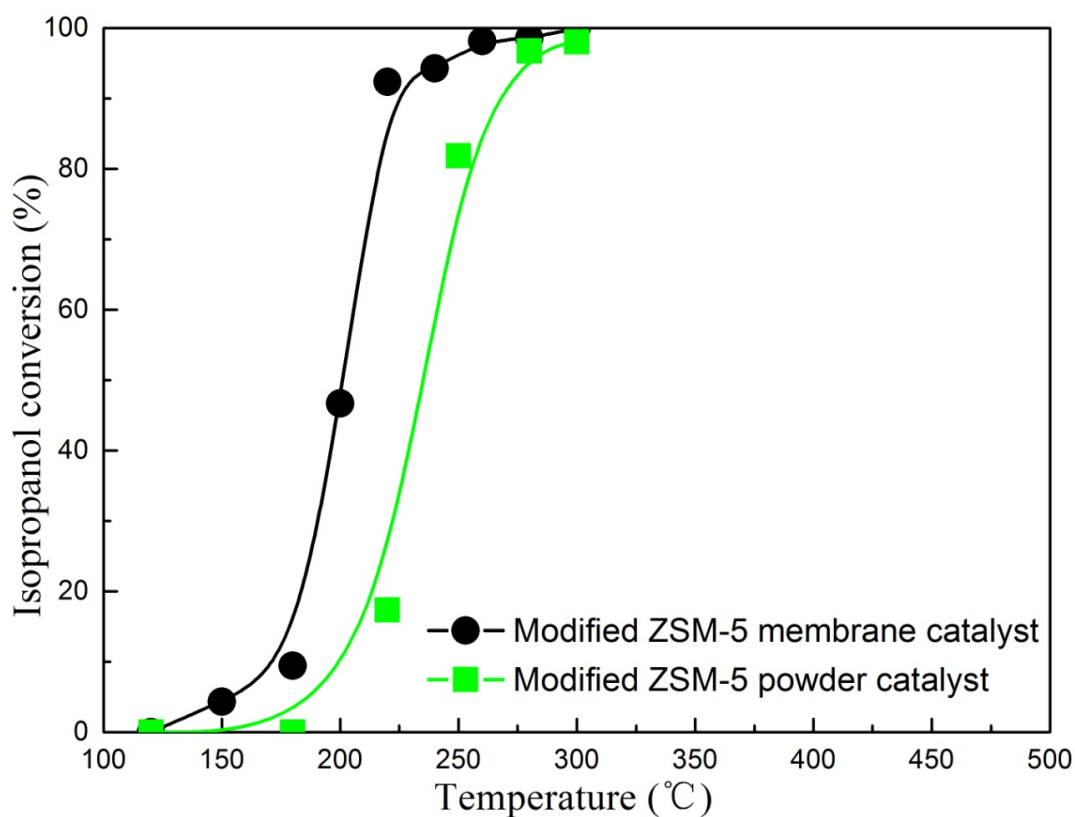
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1 **Supporting Information II: Catalytic combustion performances of isopropanol over**  
2 **microfibrinous-structured ZSM-5 membrane/PSSF catalyst and ZSM-5 powder**  
3 **catalyst**

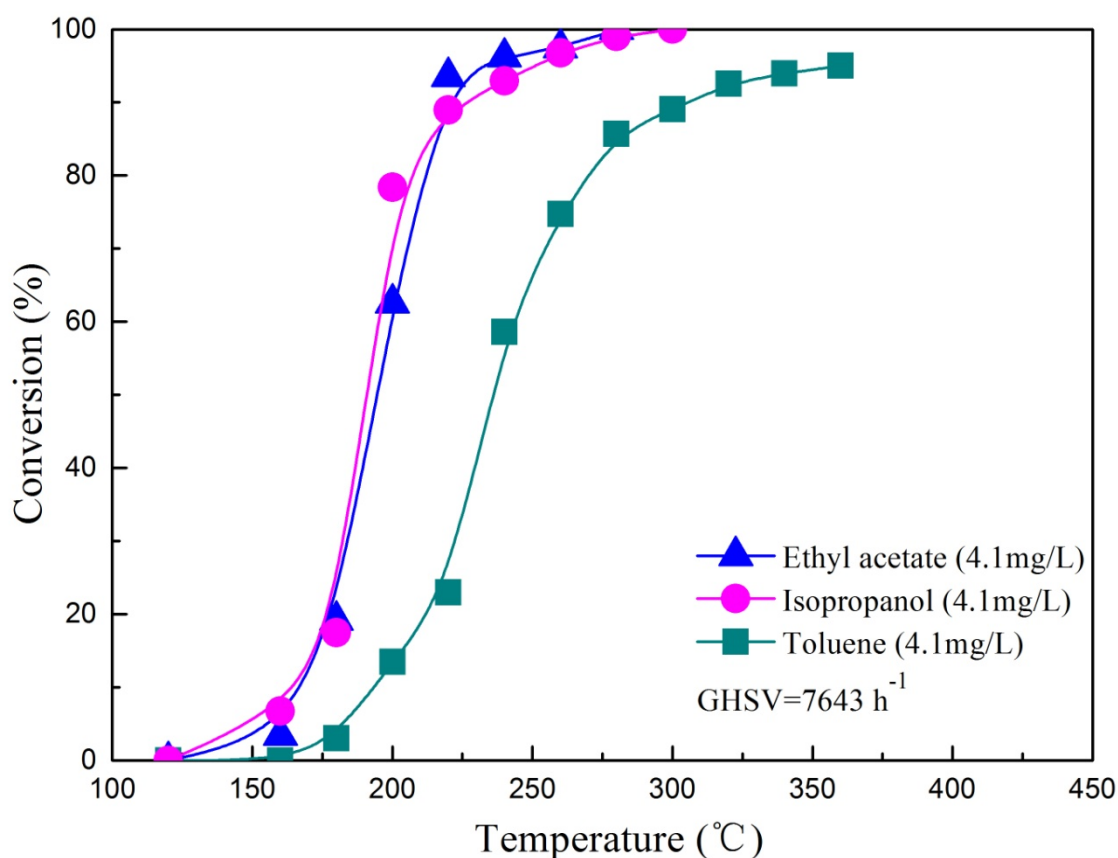
4 Catalytic oxidation performances of isopropanol over the microfibrinous-structured ZSM-5  
5 membrane/PSSF catalyst and ZSM-5 powder catalyst under the same experimental conditions (4.7  
6 mg/L of isopropanol in the feed gas, GHSV of 7643 h<sup>-1</sup>) are shown in Fig. S7. It can be seen in Fig.  
7 S7 that the  $T_{50\%}$  and  $T_{90\%}$  of isopropanol conversion over the microfibrinous-structured ZSM-5  
8 membrane/PSSF catalyst bed are consistently below their equivalent counterparts over ZSM-5  
9 powder catalyst bed, indicating that the microfibrinous-structured ZSM-5 membrane/PSSF catalyst  
10 offers a relatively higher catalytic oxidation activity. This is an expected result because of that the  
11 microfibrinous-structured ZSM-5 membrane/PSSF catalyst offers great advantages of high mass/heat  
12 transfer, shorter diffusion path, lower bed pressure drop, higher contacting efficiency, and higher  
13 catalyst active sites dispersion.



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15 **Fig. S7** Catalytic oxidation performances of isopropanol over microfibrinous-structured ZSM-5  
16 membrane/PSSF catalyst and ZSM-5 powder catalyst (4.7 mg/L of isopropanol in the feed gas,  
17 GHSV of 7643 h<sup>-1</sup> in both cases)

1 **Supporting Information III: Catalytic combustion performances of isopropanol,**  
2 **ethyl acetate, and toluene in single component over microfibrinous-structured ZSM-5**  
3 **membrane/PSSF catalyst**

4 Catalytic oxidation performances of isopropanol, ethyl acetate, and toluene in single component  
5 over the microfibrinous-structured ZSM-5 membrane/PSSF catalyst under the same experimental  
6 conditions (4.1 mg/L of VOCs in the feed gas, GHSV of 7643 h<sup>-1</sup>) are shown in Fig. S8. It can be  
7 seen in Fig. S8 that the  $T_{50\%}$  and  $T_{90\%}$  of isopropanol and ethyl acetate conversion over the  
8 microfibrinous-structured ZSM-5 membrane/PSSF catalyst bed are more lower than that of toluene.  
9 The isopropanol and ethyl acetate were found to be more reactive than toluene. The destructions of  
10 isopropanol and ethyl acetate in single component were much easier than that of toluene, which  
11 should be attributed to their nucleophilic property and smaller kinetic diameter as well as linear  
12 molecule type.



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14 **Fig. S8** Catalytic oxidation performances of isopropanol, ethyl acetate, and toluene over  
15 microfibrinous-structured ZSM-5 membrane/PSSF catalyst (4.1 mg/L of VOCs in the feed gas, GHSV  
16 of 7643 h<sup>-1</sup> in all cases)

1 **References**

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- 3 1. M. M. Treacy and J. B. Higgins, *Collection of Simulated XRD Powder Patterns for Zeolites Fifth*  
4 *(5th) Revised Edition*, Elsevier, 2007.

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