

Cite this: *RSC Adv.*, 2014, 4, 55202

Catalytic activity and stability of porous Co–Cu–Mn mixed oxide modified microfibrus-structured ZSM-5 membrane/PSSF catalyst for VOCs oxidation†

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A porous cobalt–copper–manganese mixed oxide modified microfibrus-structured ZSM-5 membrane/PSSF (paper-like sintered stainless steel fibers) catalyst was fabricated by the incipient wetness impregnating method. Catalytic oxidation performances of VOCs in single component (isopropanol or ethyl acetate) and in binary mixtures (isopropanol and toluene, ethyl acetate and toluene) were investigated over the microfibrus-structured ZSM-5 membrane/PSSF catalyst. The stability and durability of the microfibrus-structured ZSM-5 membrane/PSSF catalyst for isopropanol oxidation were also evaluated. The as-synthesized and tested (after being used at 260 °C for 550 h) microfibrus-structured ZSM-5 membrane catalysts have been characterized by a series of techniques including SEM, EDS mapping, XRD, N₂ adsorption–desorption, XPS and H₂-TPR methods. Experimental results indicated that the total destruction of isopropanol or ethyl acetate alone over the microfibrus-structured ZSM-5 membrane/PSSF catalysts can be achieved at a temperature of 280 °C. In the case of binary mixtures, the total conversion temperatures for toluene are above 300 °C. The porous microfibrus-structured ZSM-5 membrane/PSSF catalyst possesses excellent reaction stability, demonstrating by a high catalytic activity (>90%) during the 550 h long-term catalytic oxidation reaction of isopropanol. After being used at 260 °C for 550 h, the structural and textural properties of the catalyst were changed slightly during the long-term catalytic oxidation process.

Received 16th August 2014
Accepted 15th October 2014

DOI: 10.1039/c4ra08769k

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1. Introduction

Volatile organic compounds (VOCs) such as isopropanol constitute a significant fraction of the hazardous gaseous pollutants due to their harmful effects to human health and environmental safety.^{1–3} A low-temperature catalytic oxidation technique has been recently identified as the most efficient method to completely eliminate VOCs from air due to its low operational cost and high efficiency.^{4–7} However, the phenomena of relatively higher mass/heat transfer resistance, and lower contacting efficiency as well as higher bed pressure drop always exist in the traditional fixed bed reactor due to the

use of pellet shaped or powder catalysts.^{8–10} Several previous investigations^{10–13} indicated that porous modified zeolite membranes as high efficiency catalyst can offer a much higher catalytic activity and contacting efficiency.

Investigations of the catalytic oxidation performances for VOCs in single component have been widely reported. However, catalytic oxidation activity of catalyst for VOCs in single component partially presents the catalyst application.¹⁴ Therefore, it should be of interest to investigate the catalytic oxidation performances of catalysts in the reaction of VOCs in multi-component mixtures. Aguero *et al.*¹⁴ investigated the catalytic combustion of VOCs in binary mixture (ethanol–ethyl acetate) over MnO_x/Al₂O₃ catalyst. It can be noted that there is a competition for the adsorption sites between ethanol and ethyl acetate. Catalytic oxidation behaviors of isopropanol and *o*-xylene in binary mixture over basic zeolites catalysts have been also studied by Beauchet *et al.*^{1,3} It has been confirmed that the presence of isopropanol has promoting effects on the oxidation of *o*-xylene.¹ Abdullah *et al.*¹⁵ also investigated the catalytic combustion of VOCs binary mixture (ethyl acetate–benzene) over Cr-ZSM-5 catalysts, an inhibiting effect can be observed. Therefore, it is very important to study the catalytic oxidation activity of the catalysts for VOCs mixtures in the air stream.

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† Electronic supplementary information (ESI) available: Characterization results of the as-synthesized and tested microfibrus-structured ZSM-5 membrane/PSSF catalyst; catalytic combustion performances of isopropanol over microfibrus-structured ZSM-5 membrane/PSSF catalyst and ZSM-5 powder catalyst; catalytic combustion performances of isopropanol, ethyl acetate, and toluene in single component over microfibrus-structured ZSM-5 membrane/PSSF catalyst. See DOI: 10.1039/c4ra08769k

It is also well known that the catalyst stability or durability in the catalytic oxidation of VOCs is a key factor for the industrial applicability.¹⁶ The catalyst stability or durability in the catalytic oxidation of VOCs has been investigated in a lower extent than the catalyst activity.¹⁷ Several pioneer works dealing with the stability of protonic zeolites (H-ZSM-5, H-MOR and H-BEA) in the catalytic oxidation of chlorinated VOCs were presented by Aranzabal *et al.*^{16,17} During the catalytic oxidation of VOCs over porous catalysts, the catalyst deactivation may be caused by several reasons including physical and chemical. According to Chatterjee *et al.*,^{16,18} during the catalytic oxidation of chlorinated VOC over the protonic and metal exchanged zeolites, the formation of coke is the main reason for the catalysts deactivation. The thermal sintering has been also reported to be the main factor for the deactivation of Ce/Zr mixed oxides by Dai *et al.*¹⁹ and de Rivas *et al.*²⁰ The formation of water during catalytic oxidation of VOCs has been also taken into account as main reasons for the catalysts deactivation in most research works.^{21–23} However, literature about the stability and durability of modified microfibrillar-structured ZSM-5 membrane/PSSF catalyst employed in the oxidation of VOCs is not yet reported.

The aim of this work is (1) to study the catalytic activity of microfibrillar-structured ZSM-5 membrane/PSSF catalyst for VOCs alone or in binary mixtures oxidation; (2) to investigate the stability and durability of microfibrillar-structured ZSM-5 membrane/PSSF catalyst in the catalytic oxidation of VOCs.

2. Experimental

Porous microfibrillar-structured ZSM-5 membrane/PSSF composites were prepared by the wet lay-up papermaking process and secondary growth process according to our previous reports.^{8,9} The Co–Cu–Mn (1 : 1 : 1)/ZSM-5 membrane/PSSF catalysts with total metal loading of 28 wt% were prepared by incipient wetness impregnation method. The as-synthesized samples were dried at 100 °C for 12 h and calcined at 350 °C for 6 h. The detailed synthesis process of Co–Cu–Mn (1 : 1 : 1)/ZSM-5 membrane/PSSF catalysts can be found in our previous report.¹⁰

The morphologies of the catalysts were observed by scanning electron microscopy (SEM, Hitachi S-3700N). All of the samples were coated with an ultra-thin film of gold to make them conductive before analysis. The EDS mapping images of catalysts were also obtained by Energy dispersive X-ray spectrometer (EDS, Quantax, Bruker Co., Germany) coupled with the microscope chamber. X-ray diffraction (XRD) patterns of catalysts were recorded on a D8 Advance (Bruker Co.) diffractometer using Cu K α radiation (40 kV, 40 mA) with 2θ range of 5–80°. The X-ray tube was operated at 40 kV and 40 mA. N₂ adsorption-desorption isotherms of catalysts were tested using an ASAP 2020 (Micromeritics Instrument Co., USA) at 77 K. Before measurements, all of the samples were out-gassed at 523 K for 8 h. The X-ray photoelectron spectra (XPS) results were obtained by a Kratos Axis Ultra (DLD) spectrometer with an Al K α (1486.6 eV) radiation source operated at 15 kV and 10 mA. The binding energy (BE) of C1s peak at 284.6 eV was taken as a reference. Temperature programmed reduction (TPR) tests were performed on Quantachrom Automated Chemisorption Analyzer. A 50 mg of each sample was loaded into the reactor and purged with 30 ml min⁻¹ of helium at 300 °C for 1 h to eliminate contaminants, and then cooled down to room temperature. The temperature was increased to 700 °C at a heating rate of 10 °C min⁻¹ with flowing of 10% H₂ and 90% Ar.

As shown in Fig. 1, catalytic oxidation tests were measured in a continuous flow experimental apparatus at atmospheric pressure. The reactor based on Co–Cu–Mn (1 : 1 : 1)/ZSM-5 membrane/PSSF catalysts with bed height of 2 cm was consisted of a 10 mm i.d stainless steel tube located inside an electrical furnace. The vapor of VOCs in single component or binary component was generated by passing air at a certain flow rate through the generator. Each reaction temperature was kept 20 min until reaching the steady state of system and the data were determined by using gas chromatographs (Agilent 7890A, Palo Alto, CA) equipped with FID and TCD detectors for the quantitative analysis of the reactants and products. The data were the average of at least three measurements. In the present work, although a small amount of intermediate species is detected by GC at low temperature during the catalytic

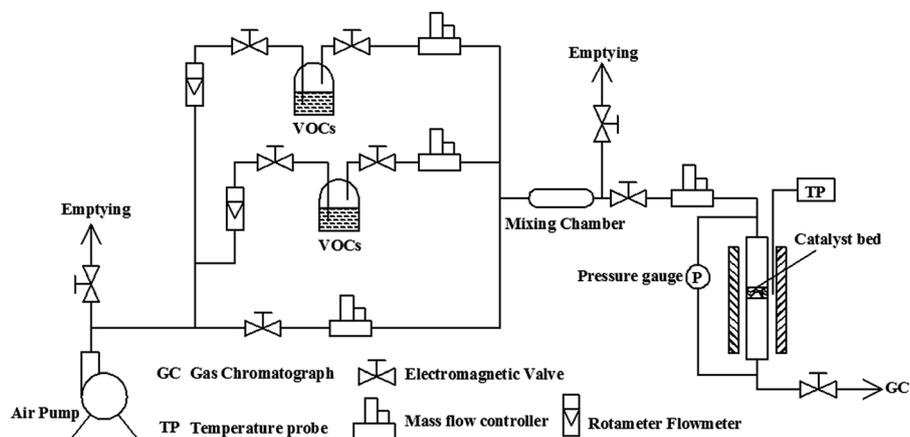


Fig. 1 A schematic diagram of the catalytic combustion test setup.

oxidation process, the only final products were CO_2 and H_2O and no other by-products were observed under the experimental conditions.

3. Results and discussion

3.1 Catalytic oxidation of single VOCs over Co–Cu–Mn (1 : 1 : 1)/ZSM-5 membrane/PSSF catalyst

Catalytic oxidation performances of VOCs in single component (isopropanol, ethyl acetate) over the Co–Cu–Mn (1 : 1 : 1)/ZSM-5 membrane/PSSF catalysts were investigated. Firstly, the effects of the bed height on catalytic oxidation performances of isopropanol were studied. Secondly, catalytic oxidation performances of ethyl acetate in single component were measured over the catalysts using different inlet concentrations and flow rates. Catalytic combustion performances of isopropanol over the microfibrinous-structured ZSM-5 membrane/PSSF catalyst and ZSM-5 powder catalyst under the same experimental conditions (4.7 mg L^{-1} of isopropanol in the feed gas, GHSV of 7643 h^{-1}) are also shown in Fig. S7 (see ESI†). Moreover, catalytic oxidation performance of toluene in single component over the microfibrinous-structured ZSM-5 membrane/PSSF catalyst under the experimental conditions (4.1 mg L^{-1} of toluene in the feed gas, GHSV of 7643 h^{-1}) is shown in Fig. S8 (see ESI†).

Catalytic oxidation performances of isopropanol were studied over the Co–Cu–Mn (1 : 1 : 1)/ZSM-5 membrane/PSSF catalysts with different bed heights (1 cm and 2 cm) using the inlet concentration of 4.1 mg L^{-1} and GHSV of 7643 h^{-1} , and the conversion profiles are presented in Fig. 2. Fig. 2 shows that the $T_{50\%}$ (the value of the temperature at conversions approach 50%) for isopropanol oxidation decrease clearly as the bed height increased. However, the $T_{90\%}$ values (the value of the temperature at conversions approach 90%) for isopropanol oxidation over the catalysts with bed height of 1 cm and 2 cm are similar. The possible reasons are that the residence time of

VOCs molecules in the reactor was extended, and the contacting efficiency was obviously enhanced because of a relatively larger catalyst bed height. In other words, for the 2 cm catalyst bed height, VOCs molecules had sufficient time to contact with active sites of catalyst due to much more catalyst active sites in the reactor.

Catalytic oxidation performances for ethyl acetate alone over the Co–Cu–Mn (1 : 1 : 1)/ZSM-5 membrane/PSSF catalysts with a bed height of 2 cm were carried out using different inlet concentrations ($6.3\text{--}9.2 \text{ mg L}^{-1}$) at a constant GHSV of 7643 h^{-1} . Fig. 3 represents that the $T_{50\%}$ and $T_{90\%}$ for ethyl acetate oxidation in relatively low inlet concentration ($6.3\text{--}8.0 \text{ mg L}^{-1}$) over the catalysts are similar. However, the $T_{50\%}$ for ethyl acetate oxidation in a high inlet concentration (9.2 mg L^{-1}) increases obviously. The possible explanations are that the unit catalysts bed in a reactor offers limited active sites for ethyl acetate

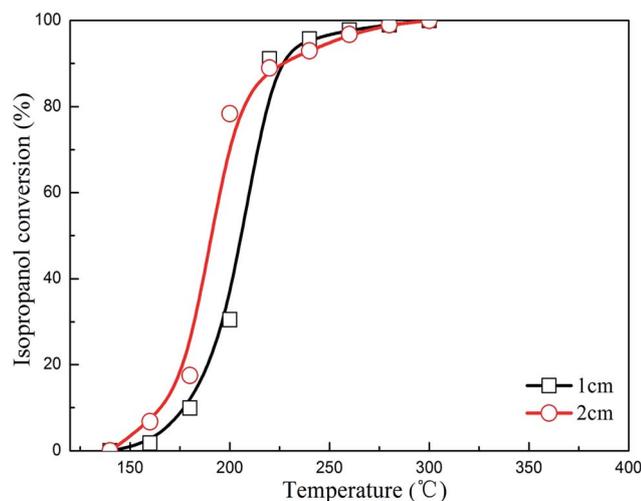


Fig. 2 Catalytic oxidation performances for isopropanol over the Co–Cu–Mn (1 : 1 : 1)/ZSM-5 membrane/PSSF catalysts with different bed heights (4.1 mg L^{-1} of isopropanol in the feed gas, GHSV of 7643 h^{-1} in all cases).

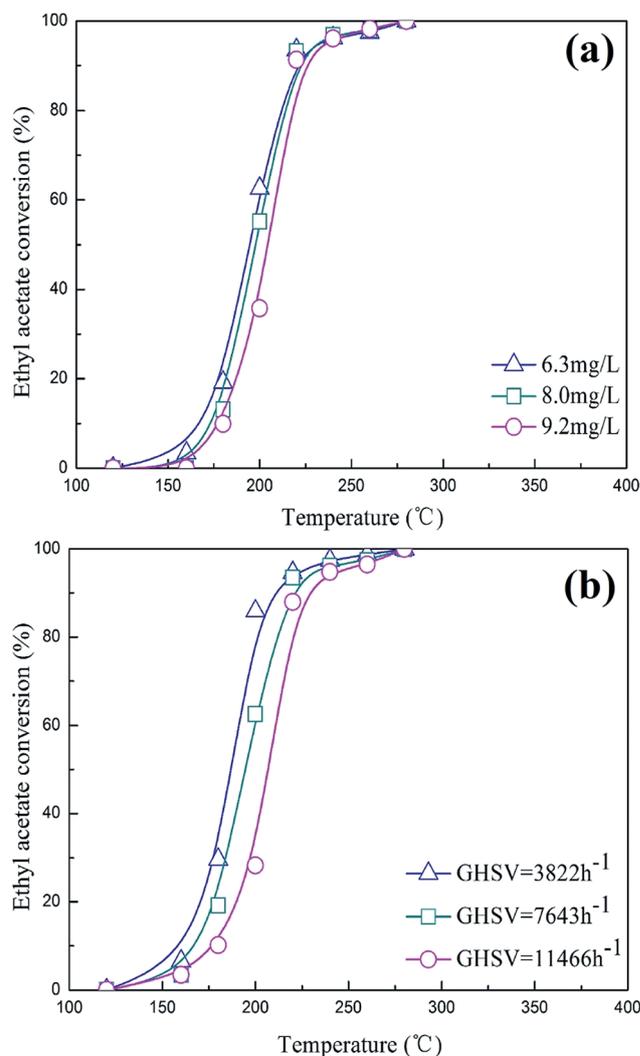


Fig. 3 Catalytic oxidation performance of ethyl acetate over the Co–Cu–Mn (1 : 1 : 1)/ZSM-5 membrane/PSSF catalysts at different inlet concentrations ($6.3\text{--}9.2 \text{ mg L}^{-1}$ of ethyl acetate in the feed gas, GHSV of 7643 h^{-1} in all cases), and different GHSV (GHSV of $3822\text{--}11466 \text{ h}^{-1}$, 6.3 mg L^{-1} of ethyl acetate in the feed gas).

oxidation, however, the treated ethyl acetate quantity in a unit catalysts bed increases at a higher inlet concentration of VOCs.¹¹ Therefore, a decrease of catalytic oxidation conversion of ethyl acetate can be observed at a higher inlet concentration. Fig. 3(a) also indicates that catalytic conversion of ethyl acetate over the catalysts can reach 100% below the temperature of 280 °C.

To investigate the effects of the GHSV on the catalytic performance, the conversions of ethyl acetate in single component over the Co–Cu–Mn (1 : 1 : 1)/ZSM-5 membrane/PSSF catalysts with bed height of 2 cm were also measured using different GHSV (3822–11 466 h⁻¹) but at a constant inlet concentration (6.3 mg L⁻¹). As can be seen in Fig. 3(b), the $T_{50\%}$ and $T_{90\%}$ for single ethyl acetate oxidation over the catalysts increase slightly with increasing GHSV. The possible reasons are that the residence time of ethyl acetate molecules on the surface of catalysts was shortened at a relatively higher GHSV, ethyl acetate molecules had insufficient time to contact with the active sites of catalyst.¹¹ However, complete conversion can be obtained essentially under all GHSV values at the temperatures above 250 °C. The possible reasons are that the catalysts possessed a higher contacting efficiency, lower mass/heat transfer resistance as well as shorter diffusion path.¹¹

3.2 Mixture effect of toluene

Catalytic oxidation behaviors of VOCs in binary component (isopropanol–toluene, ethyl acetate–toluene) over the Co–Cu–Mn (1 : 1 : 1)/ZSM-5 membrane/PSSF catalysts with bed height of 2 cm were also studied. Firstly, catalytic oxidation performances of isopropanol (5.8 mg L⁻¹) with the addition of gradual concentration of toluene (0–10.1 mg L⁻¹ of toluene) were measured at a constant GHSV of 7643 h⁻¹. Secondly, catalytic oxidation performances of ethyl acetate (8.0 mg L⁻¹) with the addition of gradual concentration of toluene (0–10.1 mg L⁻¹ of toluene) were measured at a constant GHSV of 7643 h⁻¹. Finally, VOCs destruction in binary component (isopropanol and toluene, ethyl acetate and toluene) was also performed using different GHSV (3822–11 466 h⁻¹).

Fig. 4 shows that over the Co–Cu–Mn (1 : 1 : 1)/ZSM-5 membrane/PSSF catalysts, very low temperatures are needed to destroy isopropanol alone (toluene: 0 mg L⁻¹). We can notice that the $T_{50\%}$ for isopropanol oxidation alone over the catalysts is 200 °C and the total destruction can be obtained at the temperature of 280 °C. It can be also observed in Fig. 4 that the $T_{50\%}$ and $T_{90\%}$ for isopropanol oxidation over the catalysts increase slightly when toluene is added (3.4–10.1 mg L⁻¹). Complete destruction of isopropanol in binary component can be achieved below the temperature of 300 °C. However, the $T_{50\%}$ and $T_{90\%}$ for toluene oxidation increase obviously as the concentration of toluene increased, shifting to higher temperatures by about 10 °C. A higher temperature above 300 °C was needed to totally destroy toluene in binary mixture. The possible reasons are that a competition phenomenon between isopropanol and toluene exists on the same active sites of the catalyst, and toluene possesses inhibiting effects on the isopropanol destruction.¹¹ Another possible explanation is that the

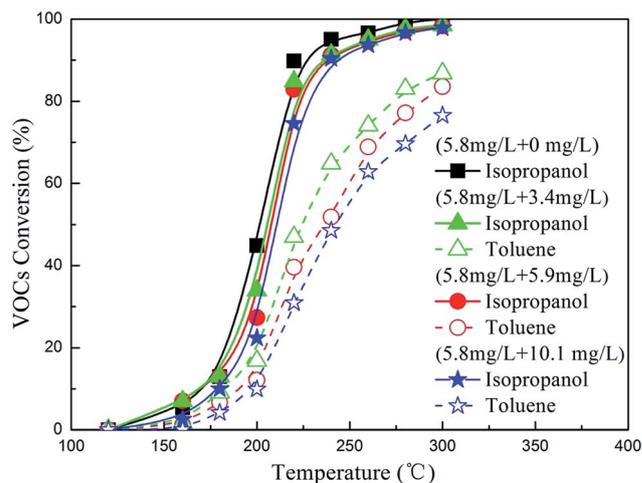


Fig. 4 Catalytic oxidation conversion of VOCs in binary component (isopropanol and toluene) over Co–Cu–Mn (1 : 1 : 1)/ZSM-5 membrane/PSSF catalysts (5.8 mg L⁻¹ of isopropanol and 0–10.1 mg L⁻¹ of toluene in the feed mixture gas, GHSV of 7643 h⁻¹ in all cases).

kinetic diameter of isopropanol (0.47 nm) is smaller than that of toluene (0.58 nm).²⁴ Similar phenomena have been also observed by Burgos *et al.*²⁴ during the catalytic oxidation of a binary VOCs mixture (isopropanol and toluene) over the Pt/Al₂O₃ catalysts. The similar phenomena for catalytic oxidation of isopropanol and *o*-xylene in binary mixture have been also reported by Beauchet.³ As can be seen in Fig. 5, the $T_{50\%}$ and $T_{90\%}$ for isopropanol and toluene in binary mixture slightly increase as the GHSV increased (3822–7643 h⁻¹), shifting to higher temperatures by approximately 10–20 °C.

Catalytic oxidation performances of VOCs in binary component (8.0 mg L⁻¹ of ethyl acetate plus 0–10.1 mg L⁻¹ of toluene) over the Co–Cu–Mn (1 : 1 : 1)/ZSM-5 membrane/PSSF catalysts

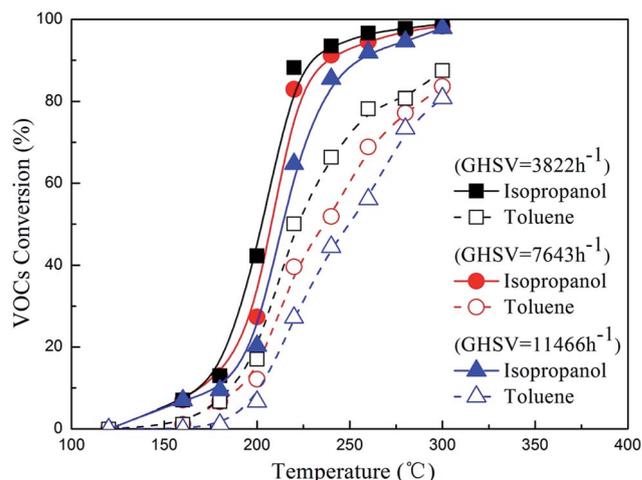


Fig. 5 Catalytic oxidation conversion of VOCs in binary component (isopropanol and toluene) over Co–Cu–Mn (1 : 1 : 1)/ZSM-5 membrane/PSSF catalysts (GHSV of 3822–11 466 h⁻¹, 5.8 mg L⁻¹ of isopropanol and 5.6 mg L⁻¹ of toluene in the feed mixture gas in all cases).

with bed height of 2 cm were also investigated at a constant GHSV of 7643 h^{-1} and were shown in Fig. 6. The effects of space velocity on the catalytic behaviors were also studied using different GHSV ($3822\text{--}11\,466\text{ h}^{-1}$) but at a constant inlet concentration (8.0 mg L^{-1} of ethyl acetate and 7.1 mg L^{-1} of toluene) and were shown in Fig. 7. Results in Fig. 6 and 7 show that ethyl acetate alone (toluene: 0 mg L^{-1}) and in binary mixture is totally destroyed below the temperature of $300\text{ }^{\circ}\text{C}$. It seems that the presence of toluene ($3.2\text{--}7.1\text{ mg L}^{-1}$) has no effect on the ethyl acetate conversion and that slightly variation of the $T_{50\%}$ (shifting to higher temperature by approximately $20\text{ }^{\circ}\text{C}$) for ethyl acetate is observed when inlet concentration of toluene reached 10.1 mg L^{-1} . The addition of toluene in the binary mixture had

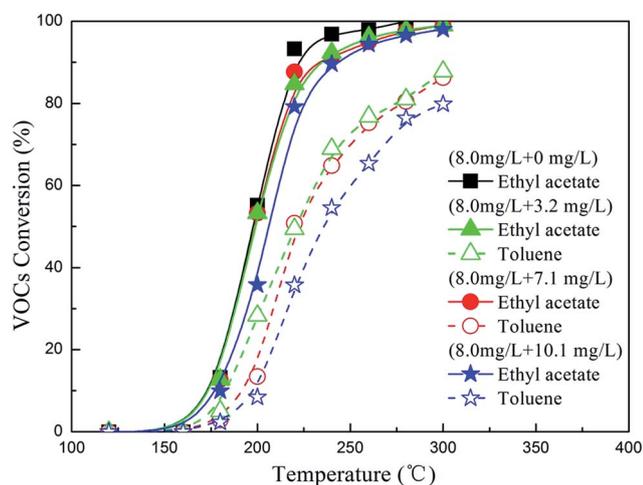


Fig. 6 Catalytic oxidation conversion of VOCs in binary component (ethyl acetate and toluene) over Co–Cu–Mn (1 : 1 : 1)/ZSM-5 membrane/PSSF catalysts (8.0 mg L^{-1} of ethyl acetate and $0\text{--}10.1\text{ mg L}^{-1}$ of toluene in the feed mixture gas, GHSV of 7643 h^{-1} in all cases).

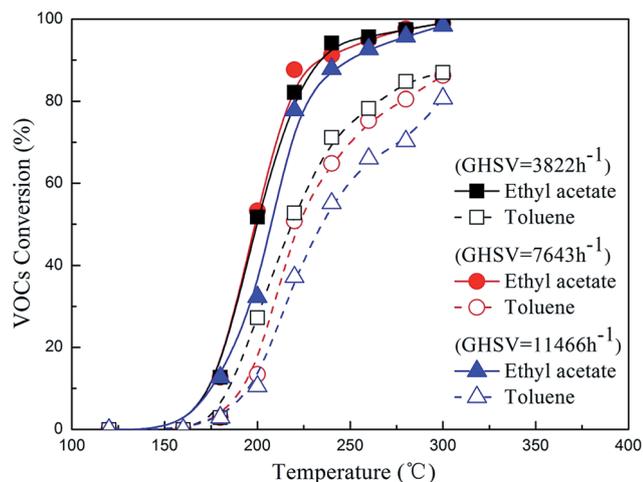


Fig. 7 Catalytic oxidation conversion of VOCs in binary component (ethyl acetate and toluene) over Co–Cu–Mn (1 : 1 : 1)/ZSM-5 membrane/PSSF catalysts (GHSV of $3822\text{--}11\,466\text{ h}^{-1}$, 8.0 mg L^{-1} of ethyl acetate and 7.1 mg L^{-1} of toluene in the feed mixture gas in all cases).

minimal inhibiting effects on the ethyl acetate destruction. We can also notice that the conversion curves of toluene are shifted slightly to higher temperatures as the inlet concentration of toluene increased and the higher temperature above $300\text{ }^{\circ}\text{C}$ was needed to completely destroy toluene in the binary mixture. These results are in agreement with the observations reported by Abdullah *et al.*¹⁵ during catalytic oxidation of a binary VOCs mixture (ethyl acetate and benzene) over the Cr-ZSM-5 catalysts. It can be found that the destruction of ethyl acetate in the binary mixture was easier than that of toluene, attributing to its nucleophilic property, smaller kinetic diameter as well as linear molecule type.¹¹ Catalytic oxidation behaviors of the binary VOCs mixture (ethyl acetate and toluene) over the catalysts were also carried out by changing GHSV from 3822 h^{-1} to $11\,466\text{ h}^{-1}$. It can be clearly observed from Fig. 7 that a slight negative effect of enhancing space velocity on VOCs conversions is obtained, shifting the conversion curves to higher temperatures by approximately $10\text{ }^{\circ}\text{C}$.

3.3 Stability and durability of the Co–Cu–Mn (1 : 1 : 1)/ZSM-5 membrane/PSSF catalyst

The reaction stability and durability tests for VOCs oxidation in single component over the Co–Cu–Mn (1 : 1 : 1)/ZSM-5 membrane/PSSF catalysts were also investigated. The reaction stability of catalyst for ethyl acetate oxidation (6.3 mg L^{-1} of ethyl acetate) was investigated using the reaction temperature of $260\text{ }^{\circ}\text{C}$ and GHSV of 7643 h^{-1} . It can be observed in Fig. 8 that the catalyst possesses excellent reaction stability for ethyl acetate oxidation, and the conversions of ethyl acetate are always remained above 95% during 50 h. The stability and durability test of catalyst were further studied by following the catalytic activity in terms of isopropanol conversion as a function of time-on-stream (550 h). Catalytic oxidation reaction was carried out feeding 4.1 mg L^{-1} of isopropanol in air at the reaction temperature of $260\text{ }^{\circ}\text{C}$ and the space velocity of 7643 h^{-1} . Fig. 8 shows that the Co–Cu–Mn (1 : 1 : 1)/ZSM-5 membrane/PSSF catalysts exhibited excellent stability, within the first 200 h, and relatively higher catalytic activity for isopropanol oxidation, remaining above 95%. After that, the catalytic oxidation conversions of isopropanol present some gradual decrease until the end of experimental run (550 h), ranging between 95% and 90%.

3.4 Characterization of as-synthesized and tested catalyst

The reduction performances of the as-synthesized and tested (after being used at $260\text{ }^{\circ}\text{C}$ for 550 h) Co–Cu–Mn (1 : 1 : 1)/ZSM-5 membrane/PSSF catalyst were investigated, and the TPR curves are presented in Fig. 9. The TPR curve of as synthesized catalyst presents a relatively sharp reduction peak at around $200\text{ }^{\circ}\text{C}$, which could be attributed to the combined reduction of Co–Cu–Mn mixed oxides. However, the TPR curve of tested catalyst changed obviously after being used at $260\text{ }^{\circ}\text{C}$ for 550 h, charactering by the presence of two small reduction peaks. The first peak located at a higher temperature (around $212\text{ }^{\circ}\text{C}$) is similar to the single reduction peak of the as-synthesized catalyst. The second reduction peak moves toward a much higher

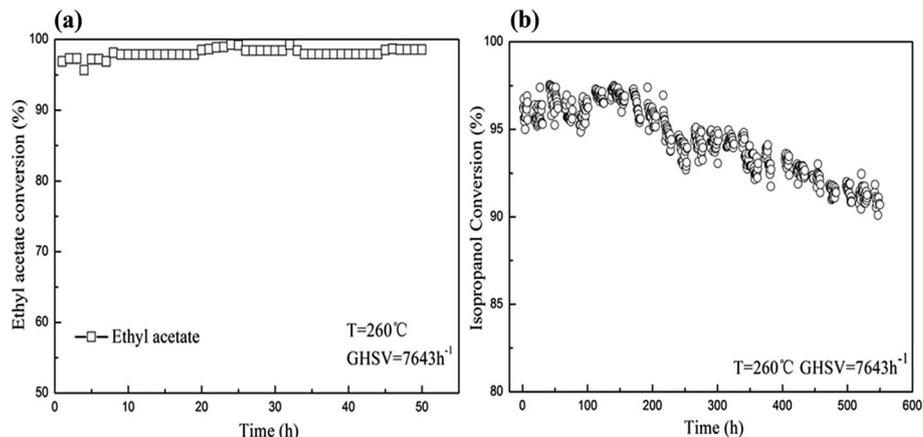


Fig. 8 Stability and durability tests for VOCs oxidation in single component with time-on-stream over the Co–Cu–Mn(1 : 1 : 1)/ZSM-5 membrane/PSSF catalysts: (a) 6.3 mg L⁻¹ of ethyl acetate in the feed gas, reaction temperature of 260 °C, reaction time of 50 h, GHSV of 7643 h⁻¹; (b) 4.1 mg L⁻¹ of isopropanol in the feed gas, reaction temperature of 260 °C, reaction time of 550 h, GHSV of 7643 h⁻¹.

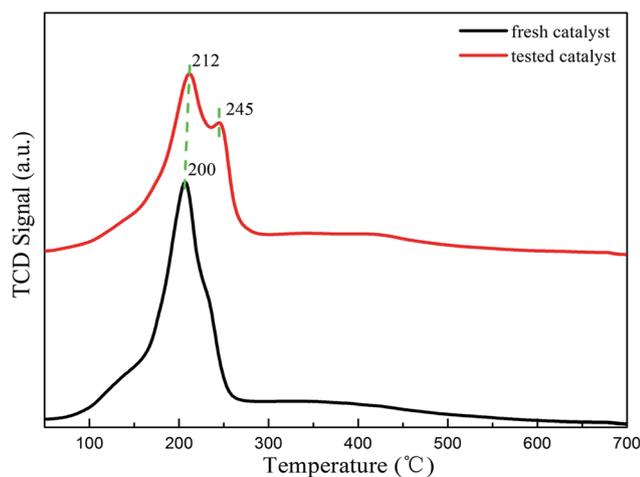


Fig. 9 H₂-TPR profiles of the as-synthesized and tested Co–Cu–Mn (1 : 1 : 1)/ZSM-5 membrane/PSSF catalysts (after being used at 260 °C for 550 h).

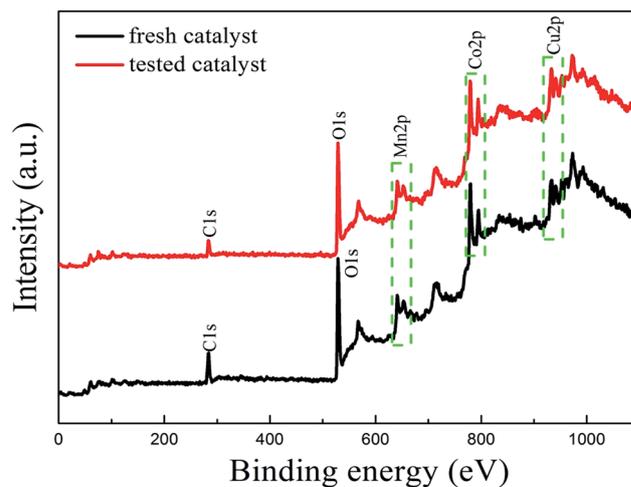


Fig. 10 XPS fully scanned spectra of the as-synthesized and tested Co–Cu–Mn (1 : 1 : 1)/ZSM-5 membrane/PSSF catalysts (after being used at 260 °C for 550 h).

temperature at around 245 °C. The possible reasons are that some mixed metal oxides were partially reduced during the long-term catalytic oxidation process. The XPS fully scanned spectra of as-synthesized and tested (after being used at 260 °C for 550 h) Co–Cu–Mn (1 : 1 : 1)/ZSM-5 membrane/PSSF catalyst are shown in Fig. 10. It can be seen in Fig. 10 that XPS fully scanned spectra of as-synthesized and tested catalysts are similar, characterizing by the presence of several dominant peaks. The peaks of C 1s and O 1s can be observed at 284.6 eV and 533 eV, respectively. The XPS spectra of Co 2p, Cu 2p_{3/2}, Mn 2p and O 1s of the as-synthesized and tested catalysts are also presented in Fig. 11, and the XPS analysis data are summarized in Table 1. As can be seen in Fig. 11(a), the Co 2p spectra of as-synthesized and tested catalysts present two main peaks located at 775–790 and 790–800 eV, which could be ascribed to the Co 2p_{3/2} and Co 2p_{1/2}. The Co 2p_{3/2} could be deconvoluted to two components at 780 and 783 eV, corresponding to the Co³⁺ and Co²⁺, respectively. The Co 2p_{1/2} can be also deconvoluted to two

components at 794 and 797.5 eV, which could be attributed to the Co³⁺ and Co²⁺, respectively. As can be seen in Table 1, the proportion of Co³⁺/Co²⁺ of as-synthesized catalyst (0.73) is higher than that of tested catalyst (0.45). The possible reasons are that most of Co³⁺ species was reduced to Co²⁺ species during the long-term catalytic oxidation process, indicating that the cobalt oxide species as catalytic active components play a role in the catalytic oxidation process of VOCs. In the Cu 2p_{3/2} XPS spectra of as-synthesized and tested catalysts, the peak located at 928–938 eV could be deconvoluted into two main components at 933.5 and 935 eV, attributed to Cu¹⁺ and Cu²⁺, respectively. As can be seen in Table 1, the as-synthesized catalyst possesses a much higher Cu²⁺ content (the proportion of Cu²⁺/Cu¹⁺ is 1.15). However, after being used at 260 °C for 550 h, the Cu²⁺/Cu¹⁺ of tested catalyst decreased obviously to 0.23. These experimental results indicate that a lot of Cu²⁺ species was reduced to Cu¹⁺ species during the long-term catalytic

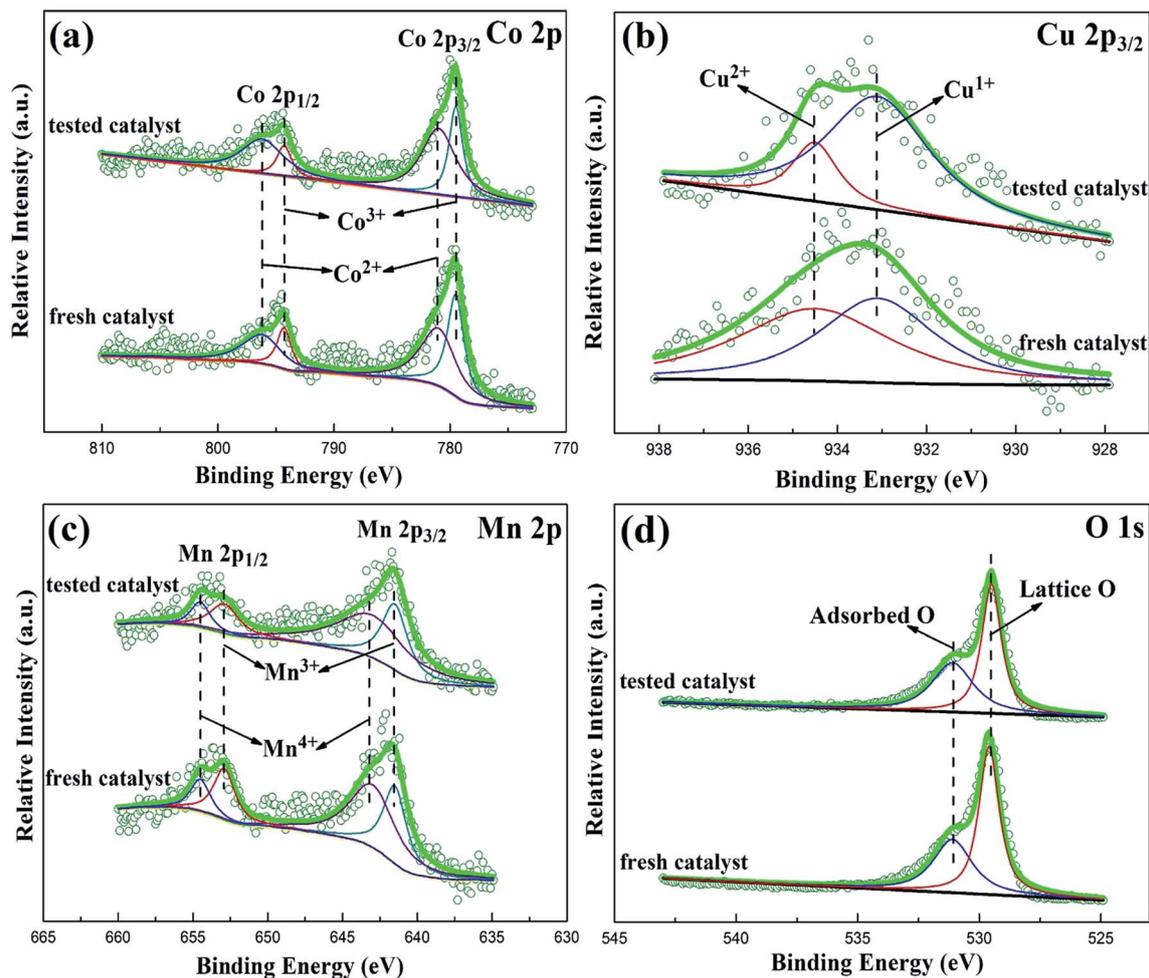


Fig. 11 XPS analysis of the as-synthesized and tested Co–Cu–Mn (1 : 1 : 1)/ZSM-5 membrane/PSSF catalysts (after being used at 260 °C for 550 h): (a) fitted Co 2p_{1/2} and Co 2p_{3/2} photoelectron peaks; (b) fitted Cu 2p_{3/2} photoelectron peaks; (c) fitted Mn 2p_{1/2} and Mn 2p_{3/2} photoelectron peaks; (d) fitted O 1s photoelectron peaks.

Table 1 Surface element compositions of the as-synthesized and tested catalysts (after being used at 260 °C for 550 h)

Samples	Co ³⁺ /Co ²⁺ ^a	Cu ²⁺ /Cu ¹⁺ ^a	Mn ⁴⁺ /Mn ³⁺ ^a	O _{adsorbed} /O _{lattice} ^a
Co–Cu–Mn (1 : 1 : 1)/ZSM-5/PSSF (as-synthesized)	0.73	1.15	0.83	0.68
Co–Cu–Mn (1 : 1 : 1)/ZSM-5/PSSF (tested in 550 h)	0.45	0.23	0.72	0.80

^a Calculated from the XPS results.

oxidation process. The possible explanations are that the copper oxide species could be the dominant catalytic active components for isopropanol oxidation, playing the vital role in the catalytic oxidation reaction. Fig. 11(c) clearly displays the XPS spectra of Mn 2p for the as-synthesized and tested catalyst. All the Mn 2p spectra present two main peaks located at 640–645 and 650–655 eV, corresponding to the Mn 2p_{3/2} and Mn 2p_{1/2}. The Mn 2p_{3/2} signal can be further deconvoluted to two main components at 641.5 and 643 eV, attributed to Mn³⁺ and Mn⁴⁺. The Mn 2p_{1/2} signal of each catalyst could be also deconvoluted to two main components at 652.5 and 654 eV, corresponding to Mn³⁺ and Mn⁴⁺. It can be observed in Table 1

that the actual ratio of Mn⁴⁺/Mn³⁺ for as-synthesized catalyst is 0.83. After being used at 260 °C for 550 h, the ratio of Mn⁴⁺/Mn³⁺ for tested catalyst (0.72) is slight lower than that of as-synthesized catalyst, indicating that a small quotient of Mn⁴⁺ species was reduced during the long-term catalytic oxidation process. The XPS spectra of O1s for as-synthesized and tested catalysts are also presented in Fig. 11(d). As can be seen in Fig. 11(d), asymmetric two band structures can be observed, the sharp peak at lower binding energy of about 529.8 eV is attributed to the lattice oxygen and the wide peak at higher binding energy of 532 eV is characteristic of the adsorbed oxygen. As can be seen in Table 1, the ratio of O_{adsorbed}/O_{lattice} for as-

synthesized catalyst is 0.68, indicating that the lattice oxygen is the main presence form of oxygen in modified ZSM-5 membrane catalyst. However, the ratio of $O_{\text{adsorbed}}/O_{\text{lattice}}$ for tested catalyst (0.8) is much higher than that of as-synthesized catalyst. The XPS analysis results indicate that the Co and Cu species in Co–Cu–Mn mixed oxides modified ZSM-5 membrane catalysts are the dominating catalytic active sites for isopropanol oxidation, however, the Mn species offer small catalytic activity for isopropanol oxidation.¹⁰ Moreover, the SEM (Fig. S1†), EDS (Fig. S2†), XRD (Fig. S3†), N_2 adsorption-desorption (Fig. S4, Table S1†) characterization results of modified ZSM-5 membrane catalyst and their detailed analysis were also clearly presented in ESI.†

4. Conclusion

Porous microfibrillar-structured Co–Cu–Mn (1 : 1 : 1)/ZSM-5 membrane/PSSF catalyst was developed for VOCs removal. Catalytic oxidation performances of VOCs alone or in binary component mixtures (isopropanol–toluene, ethyl acetate–toluene) were evaluated at different inlet concentration and space velocity. The stability and durability of catalyst were also assessed feeding 4.1 mg L⁻¹ of isopropanol in air, using the reaction temperature of 260 °C and the space velocity of 7643 h⁻¹. The as-synthesized and tested catalysts were characterized by using SEM, EDS mapping, XRD, N_2 adsorption-desorption, XPS as well as H₂-TPR techniques. Experimental results indicated that the complete destruction of VOCs alone (isopropanol or ethyl acetate) can be all achieved below the temperature of 300 °C. Isopropanol and ethyl acetate were found to be more reactive than toluene in the catalytic oxidation of VOCs in binary mixtures. Toluene in binary mixtures possessed slight inhibiting effects on the destruction of isopropanol and ethyl acetate due to the competitive adsorption phenomenon. The porous modified microfibrillar-structured ZSM-5 membrane catalyst also possesses excellent reaction stability, demonstrating by a high catalytic activity (90%) during the 550 h long-term catalytic oxidation reaction. After being used at 260 °C for 550 h, the structural and textural properties of catalyst were changed slightly during the long-term catalytic oxidation process.

Acknowledgements

We are grateful for the financial support from the National Natural Science Foundation of China (Grant no. 21176086 and 21376101).

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