In-situ synthesis of monolithic Cu-Mn-Ce/cordierite catalysts towards VOCs combustion

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Abstract: A monolithic series of Cu-Mn-Ce oxides supported on cordierites with different Cu/Mn/Ce molar ratios were prepared by the *in-situ* sol-gel method without any binder. The catalysts were characterized by scanning electron microscopy (SEM), energy dispersive spectrometer (EDS), X-ray diffraction (XRD), and Brunauer-Emmett-Teller method (BET) and examined in the catalytic combustion of volatile organic compounds (VOCs). The results showed that the well-dispersed nanometer particles of mixed oxides adhered firmly to the cordierite surface. $Cu_{0.15}Mn_{0.3}Ce_{55}$/cordierite was identified as the most active catalyst. Compared with commercial Pd/Al_2O_3, $Cu_{0.15}Mn_{0.3}Ce_{55}$/cordierite showed higher activities for the combustion of various types of VOCs, especially for oxy-derivative compounds which could be lighted off below 200 ºC.

Keywords: catalytic combustion; volatile organic compounds (VOCs); monolithic catalysts; Cu-Mn-Ce mixed oxides; rare earths

Volatile organic compounds (VOCs) are recognized contributors to air pollution[1,2]. Catalytic combustion is a widely used technology for the abatement of VOC emission. Compared with thermal combustion techniques, higher efficiencies at lower operating temperatures are achieved with the presence of catalysts, obtaining considerable environmental and economic benefits[3]. Platinum and palladium are the most commonly used catalysts[4,5]. Although noble metal catalysts are very active for catalytic combustion, these materials are rather expensive and susceptible to deactivation by poisoning[6,7]. Therefore, there is significant interest on the replacement of noble metal catalysts with cheaper ones. The development of transition metal oxides for catalytic combustion has been widely reported in the literature[8–11]. Among metal oxide catalysts, manganese, copper and cerium oxides have been considered as the most active and promising catalysts for the combustion of VOCs. Therefore, much effort has been taken to improve the catalytic performance of these three oxides and their composites. But the activity shown by these catalysts is generally lower than that of noble metal catalysts[12–16].

In addition to practical applications, catalyst should have a structured support to treat large gas flows with a low pressure drop[17,18]. For the preparation of monolithic metal oxide catalysts, a slurry coating procedure using catalyst particles (5–10 μm) produces an easily accessible coated layer. A problem that arises from coating an existing catalyst on the monolithic support is related to the adherence quality of the layer on the monolithic carrier surface. Binding material commonly employed in catalyst coating slurries may also cover the active phase and block catalysts pores. Moreover, the catalysts on the surface of a monolithic substrate easily fall off the surface after calcinations[19–23].

It has been reported that the sol-gel method is an effective, one-step technique for the preparation of ready-to-use mixed oxide catalysts with favorable characteristics and catalytic properties for catalytic combustion of VOCs[13,24]. In present work, Cu, Mn, Ce oxides, or their mixed oxides were supported directly on cordierite honeycomb and prepared by *in situ* sol-gel synthesis. This procedure is an easy and rapid method for the preparation of structure catalysts without the need for a binder or a pre-coating process. The activities of these monolithic catalysts were investigated in the catalytic combustion of toluene. The best catalyst was also examined in the catalytic combustion of various types of VOCs; the results were compared to the commercial honeycomb Pd/Al_2O_3 catalyst.

1 Experimental

1.1 Catalysts preparation

All cordierite honeycombs used were in cylindrical shape with a diameter of 10 mm and a length of 50 mm. They were obtained by cutting commercial cordierite straight-channel monoliths with a square cell density of 81 cpsi (cells per square inch) and a wall thickness of 0.5 mm. Copper nitrate, manganese nitrate, and cerium nitrate were mixed in appropriate molar ratios in an appropriate volume of distilled water to obtain a transparent solution (metal ion concentration

of 1.0 mol/L). The same moles of citric acid were added into the nitrate solution. The cordierite monolith was immersed in this viscous solution for 1 h. Excess liquid in the monolith channels was then blown out by hot air ejected from a heat fan. By this way, excess water was evaporated, and a uniform, thin gel film was formed on the surface of the monolith followed by calcination at 500 °C in air for 5 h. The procedure was repeated several times to achieve the desired loading. In this work, some monolithic catalysts were prepared (Table 1). The loading of the total amount of the deposited active phase is the actual value in relation to the initial weight of the cordierite honeycombs; the Cu/Mn/Ce molar ratio is the material ratio of the impregnating solution used. The following encoding of catalysts was used: $Cu_{0.15}Mn_{0.85-x}Ce_x/CH$ (x=0, 0.3, 0.55, 0.85).

Commercial monolithic Pd/Al_2O_3 catalyst with Al_2O_3 coating was from the Hangzhou Kai-Te Environment and Technology Company. The Pd/Al_2O_3 catalyst was in the same shape as the metal oxide monolithic samples.

1.2 Activity test

Catalytic activity test was conducted in a fixed-bed flow reactor of quartz tube. Monolithic catalysts were loaded into the tube with an inner diameter of 1.0 cm. The reactor was housed in an electric heating furnace 1.5 cm in diameter and 50 cm in length, which provided uniform heating of the catalyst bed. Gaseous VOCs were generated by flowing air coming from a mass-flow controller through liquid organics in an incubator placed in an ice bath. The VOC-containing stream was mixed with the main air stream introduced through another mass-flow controller. The gas hourly space velocity (GHSV) was 10000 h^{-1}. Effluents from the reactor were analyzed by an online HP 6890 gas chromatograph equipped with an FID detector.

1.3 Catalyst characterization

Textural properties were studied by N_2 adsorption measurement at liquid nitrogen temperature in a micromeritics ASAP 2010. Before analysis, the catalysts were degassed for 2 h at 473 K in vacuum. SEM was performed with a Hitachi S-4700 II scanning electron microscope operated at 1.0 kV. Energy dispersed spectroscopy (EDS), which was used to determine elemental composition in a selected area of the specimen, was conducted on the same SEM instrument. X-ray diffraction (XRD) patterns were collected on an ARL SCINTAG X'TRA powder diffractometer using Cu Ka radiation. The working voltage of the instrument was 45 kV and the current was 40 mA. The intensity data were collected at room temperature in a 2θ range from 5° to 60° with a scan rate of 0.02 (°)/s.

Ultrasonic test was performed to evaluate the cohesive capability of the active phase. The samples were subjected to ultrasonic cleaning by being immersed in water inside a glass vessel and in an ultrasonic vibration cleaner at 40 KHz for 60 min. After ultrasonic cleaning, the samples were calcinated at 500 ℃ and weighed, and the mass losses of the active phase were calculated using

$$\Delta w = \frac{w_{\text{before}} - w_{\text{after}}}{w_{\text{before}}} \times 100 \qquad (1)$$

2 Results and discussion

2.1 Catalyst characterization

The morphology of the bare substrate (cordierite honeycomb) and the Cu-Mn-Ce monolithic catalyst is shown in Fig. 1. The surface of cordierite (Fig.1 (a)) is irregular with various pore structures; this feature benefits the adhesion between the active phase and the substrate. Fig. 1(b–d) show the morphology of the monolithic $Cu_{0.15}Mn_{0.85-x}Ce_x/CH$ (x=0, 0.55, 0.85) catalysts. As can be seen in the figure, the pores of cordierite disappeared, and a uniform catalytic layer of mixed oxides covering the substrate was formed. Ultrasonic test was employed as a severe method to test adherence. The mass losses of the monolithic catalysts are listed in Table 1. The mass losses of all oxide catalysts are less than 0.9 wt.%. This is an indication that the active phase anchors onto the cordierite substrate and has strong vibration-shock resistance. Table 1 also demonstrates that the loading of metal oxides on cordierite can reach up to 6 wt.%– 9 wt.% after two impregnations and that loading increases with Ce^{4+} content. The EDS characterization confirmed that surface ratio of the metal ion was proportional to that of the dipping solution. This indicates that the same amount of metal ions in the solution will be attached into the cordierite surface upon first immersion, and have no selective adsorption. The BET surface areas of the cordierite substrate and monolithic catalysts are listed in Table 1. The surface area of cordierite is only 0.6 m^2/g, which is rather lower than the specific surface area of $Cu_{0.15}Mn_{0.85-x}Ce_x/CH$ monolithic catalysts (from 2.0 to 9.0 m^2/g), indicating that metal oxide coating dramatically increases the surface porosity of cordierite substrate.

Fig. 2 presents the XRD spectra of $Cu_{0.15}Mn_{0.85-x}Ce_x/CH$ catalysts prepared on cordierite honeycomb. Despite the strong presence of the diffraction lines of cordierite, which overlapped with most of the reflections of the oxide phases of the catalysts, there are a few observable XRD peaks due to catalyst phases. The diffraction peaks of the $Cu_{0.15}Mn_{0.85}/CH$ catalyst correspond mainly to Mn_2O_3 phase. The XRD patterns of $Cu_{0.15}Mn_{0.3}Ce_{0.55}/CH$ and $Cu_{0.15}Ce_{0.85}/CH$ catalysts show that single CeO_2 phase, XRD peaks due to CuO and MnO_x oxides are not detected in the catalyst, most probably due to incorporation of the copper and manganese ions into the CeO_2 lattice.

2.2 Catalytic combustion of toluene on monolithic metal oxide catalysts

The catalytic activity in the catalytic combustion of toluene is shown in Fig. 3. Mixed metal oxide catalysts are more active than pure oxides catalysts. The performance of the CuO/CH in the total oxidation of toluene is quite poor,
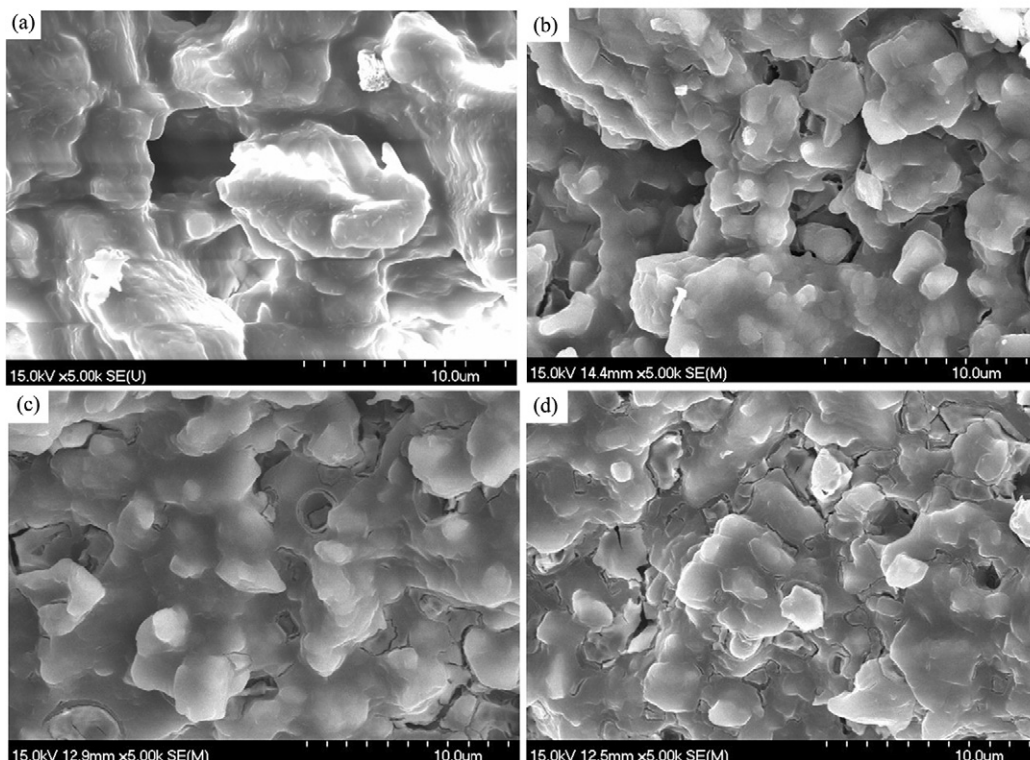
Fig. 1 SEM images of cordierite and Cu-Mn-Ce/CH catalysts

(a) CH (cordierite honeycomb); (b) $Cu_{0.15}Mn_{0.85}$/CH; (c) $Cu_{0.15}Mn_{0.3}Ce_{0.55}$/CH; (d) $Cu_{0.15}Ce_{0.85}$/CH

Table 1 Physical-chemical properties of monolithic Cu-Mn-Ce catalysts

Catalysts	Loading/ wt.%	BET/ (m^2/g)	Δw/ %	Surface ion content*		
				Cu atom/ %	Mn atom/ %	Ce atom/ %
CH	/	0.6	/	/	/	/
CuO/CH	6.47	2.4	0.36	/	/	/
$Cu_{0.15}Mn_{0.85}$/CH	7.02	5.9	0.65	1.63	9.92	/
MnO_x/CH	6.83	3.8	0.41	/	/	/
$Cu_{0.15}Mn_{0.55}Ce_{0.3}$/CH	7.63	7.0	0.89	1.09	4.69	2.25
$Cu_{0.15}Mn_{0.3}Ce_{0.55}$/CH	8.18	7.8	0.74	1.08	1.77	3.85
$Cu_{0.15}Ce_{0.85}$/CH	8.65	8.1	0.78	1.12	/	9.86
CeO_2/CH	8.56	8.9	0.52	/	/	/

* Measured via EDS

even at 320 ℃, the conversion only reaches 40%. When the Mn content continues to increase, a significant increase in the catalytic performances is observed. The temperature at which the conversion reaches 50% (T_{50}) is 270 ℃ for $Cu_{0.15}Mn_{0.85}$/CH catalyst. Whereas pure MnO_x/CH shows a sharp decline in activity, which indicates that a small amount of copper is necessary to keep the high activity of Cu/Mn mixed oxides. It agrees well with reports of the literature for total oxidation of ethanol[25].

CeO_2 has been widely used in automobile exhaust three-way catalysts due to its outstanding oxygen storage capacity[26]. In the catalytic combustion of toluene, pure CeO_2/CH catalyst also shows very high activity at low temperature; 10% toluene conversion can be achieved at 250 ℃. However, total toluene conversion is achieved at 360 ℃ due to the
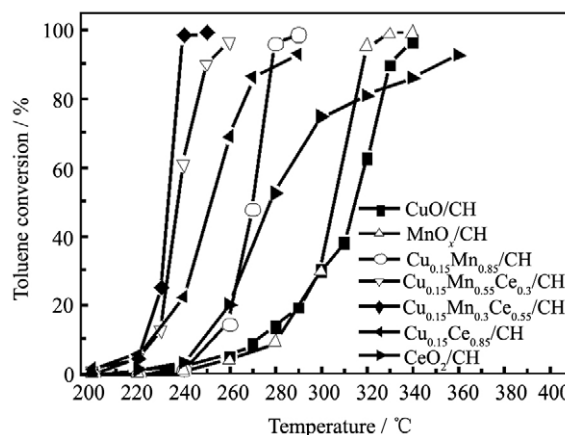

Fig. 2 XRD patterns of $Cu_{0.15}Mn_{0.85-x}Ce_x$/CH catalysts

Fig. 3 Light-off curves of toluene catalytic combustion on monolithic oxides catalysts

poor oxygen mobility of CeO_2. The substitution of Ce^{4+} by other transition metal ions favors the creation of structural defects, accelerates oxygen diffusion, and induces more surface active oxygen species[13,27]. In the catalysts studied, Cu-Mn-Ce three-component mixed oxide catalysts show better activity than Cu-Mn and Cu-Ce catalysts. About 99% toluene conversion was achieved when the temperature rose to 240 ºC on the $Cu_{0.15}Mn_{0.3}Ce_{0.55}$/CH catalyst.

Prolonged catalytic tests are required to investigate the long-term stability of our catalysts. Fig. 4 shows the conversion vs. time at 260 and 300 ºC for $Cu_{0.15}Mn_{0.3}Ce_{0.55}$/CH catalyst. During the first 50 h, some deactivation is observed at 260 ºC, the toluene conversion decreases from 98% to 96%, but it can remain stable after 40 h. When the temperature increases to 300 ºC, the conversion of toluene is maintained at about 100%. After reaction at 300 ºC for 50 h, the temperature back to 260 ºC, the toluene conversion can still be maintained at 96%, and no deactivation is found. This indicated that $Cu_{0.15}Mn_{0.3}Ce_{0.55}$/CH has excellent stability for catalytic combustion of toluene at 260–300 ºC.

2.3 Catalytic Combustion of VOCs over $Cu_{0.15}Mn_{0.3}Ce_{0.55}$/CH catalyst

The activity of $Cu_{0.15}Mn_{0.3}Ce_{0.55}$/CH in the catalytic combustion of hydrocarbons and oxygenated compounds is plotted in Figs. 5 and 6, respectively. The catalytic activity was analyzed on the basis of T_{50} and T_{95} (reaction temperatures that correspond to 50% and 95% of VOCs conversion,
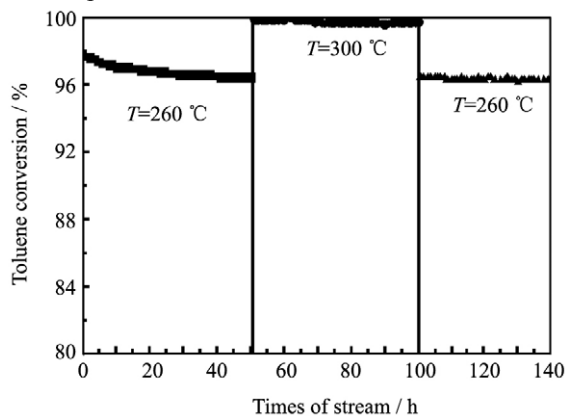

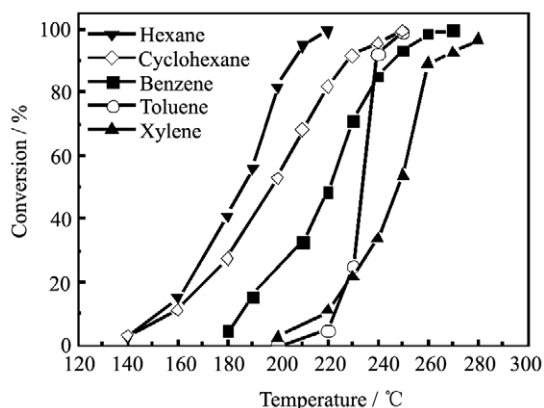Fig. 4 Toluene conversion vs. time for $Cu_{0.15}Mn_{0.3}Ce_{0.55}$/CH at 260 and 300 ºC

Fig. 5 Light-off curves of aromatics and alkanes catalytic combustion on $Cu_{0.15}Mn_{0.3}Ce_{0.55}$/CH
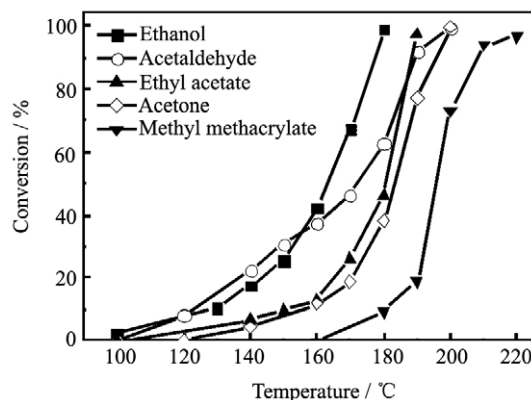

Fig. 6 Light-off curves of oxygenated organics catalytic combustion on $Cu_{0.15}Mn_{0.3}Ce_{0.55}$/CH

respectively). T_{10} was not used because some products at that conversion level was partial oxidation products (such as acetaldehyde was detected as the product of ethanol partial oxidation). The comparison of Figs. 5 and 6 shows that the oxy-derivative compounds are more readily oxidized than hydrocarbons. The temperature of oxygenate total conversion is generally around 40 ºC lower than that of hydrocarbons.

Table 2 shows the temperature required for the 50% and 95% conversion of tested hydrocarbons and oxygenates on monolithic $Cu_{0.15}Mn_{0.3}Ce_{0.55}$/CH metal oxide catalysts. Catalytic activity decreases in the following order with T_{50} as reference:

Ethanol (160 ºC)>acetaldehyde (170 ºC)>ethyl acetate (180 ºC)>acetone (185 ºC)>hexane (190 ºC)>methyl methacrylate (195 ºC)>cyclohexane (200 ºC)>benzene (225 ºC)>toluene (235 ºC)>o-xylene (250 ºC).

Among oxygenated compounds, the activity of organics with similar carbon numbers has the following order: alcohol>aldehyde>ester≅ketone. Among hydrocarbons, alkanes are more easily oxidized than aromatics, and the methyl group on aromatic rings reduces the reactivity of aromatic oxidation. In the case of VOCs, many authors suggest that weak C–H bonds and molecular polarity are associated with the reactivity of oxidation. Table 2 presents the C–H bond

Table 2 Results of VOCs combustion on $Cu_{0.15}Mn_{0.3}Ce_{0.55}$/CH and commercial Pd/Al_2O_3 catalyst

VOCs name	Weakest C–H bond/(kJ/mol)	Polarity	$Cu_{0.15}Mn_3Ce_{0.55}$/CH		Commercial Pd/Al_2O_3	
			T_{50}/ºC*	T_{95}/ºC*	T_{50}/ºC	T_{95}/ºC
Benzene	426.2	0	225	250	245	270
Toluene	370.3	0.45	235	240	225	235
O-xylene	/	0.33	250	280	215	225
Hexane	395.0	0	190	210	330	345
Cyclohexane	399.0	0	200	240	330	325
Ethanol	396.6	1.69	160	175	220	245
Acetaldehyde	394.3	2.71	170	190	240	250
Ethyl acetate	/	1.78	180	190	260	270
Methyl methacrylate	/	1.68	195	210	210	220
Acetone	411.5	2.77	185	195	230	250

* Temperature for the conversion of VOCs reaches 50% or 95%

and molecular polarity of hydrocarbons and oxygenates. There are no linear correlations between the weakest C–H bonds and T_{50}. As for molecular polarity, oxygenates are much higher than hydrocarbons, and this is consistent with experimental results. However, the polarity of hydrocarbons or oxygenates has no direct correlation with reactivity. This result indicates that polarity is not the only factor determining activity. The mechanistic process during catalytic oxidation is more complex; other factors such as molecular weight and boiling point of compounds can directly affect adsorption and activation on metal oxide catalyst.

Comparisons between $Cu_{0.15}Mn_{0.3}Ce_{0.55}/CH$ and other catalysts are very difficult to conduct because the results depend on experimental conditions which are always different in each publication. For activity tests performed at the same reaction conditions, a monolithic commercial Pd catalyst was selected as reference catalyst and cut in the same shape as the $Cu_{0.15}Mn_{0.3}Ce_{0.55}/CH$ samples. The results of the catalytic combustion of various VOCs on commercial monolithic Pd/Al_2O_3 are shown in Table 2. The reactivity of VOCs decreases as follows: methyl methacrylate (210 ℃)> o-xylene (215 ℃)>ethanol (220 ℃)>toluene (225 ℃)>acetone (230 ℃)>acetaldehyde (240 ℃)>benzene (245 ℃)>ethyl acetate (260 ℃)>cyclohexane (290 ℃)>hexane (330 ℃)

T_{50} and T_{90} of VOCs except for toluene and o-xylene under the Pd/Al_2O_3 catalyst are higher than those under the $Cu_{0.15}Mn_{0.3}Ce_{0.55}/CH$ catalyst. This indicates that $Cu_{0.15}Mn_{0.3}Ce_{0.55}/CH$ is more suitable for applications in the catalytic combustion of alkane and oxygenates. In addition, the catalytic activity of Pd/Al_2O_3 catalyst appears to be totally different from that of $Cu_{0.15}Mn_{0.3}Ce_{0.55}/CH$ catalysts. Alkanes such as hexane and cyclo-hexane are the most difficult species to destroy over the Pd catalyst, followed by oxygenated compounds and aromatics. There is essentially a different reaction mechanism for the catalytic combustion of VOCs over Pd and metal oxide catalysts. Further research is needed to achieve a better understanding of the catalytic mechanism of precious metals and oxide catalysts.

3   Conclusions

A novel monolithic metal oxide supported by cordierite honeycomb was prepared by *in situ* sol-gel method. The active phase of metal oxides dispersed and anchored onto the cordierite substrate and had strong vibration-shock resistance. Activity tests showed that the $Cu_{0.15}Mn_{0.3}Ce_{0.55}/CH$ catalyst had the highest activity in the catalytic combustion of toluene. Compared with commercial Pd catalyst, $Cu_{0.15}Mn_{0.3}Ce_{0.55}/CH$ had excellent activity in the catalytic combustion of VOCs, especially for alkanes and oxygenates. Therefore, low-cost $Cu_{0.15}Mn_{0.3}Ce_{0.55}/CH$ had great potential for replacing noble metal catalysts in the industry.

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