Preparation of Cu-Mn and Cu-Mn-Ce Oxide-incorporated Mesoporous Silica via Silicate Exfoliation for the Removal of NO and Hg$^0$

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ABSTRACT

Cu-Mn and Cu-Mn-Ce oxide-incorporated mesoporous silica was formed by hydrothermally exfoliating silicate, and the physicochemical properties and NO/Hg$^0$ removal efficiency were investigated. The exfoliation induced structural reformation, resulting in a large specific surface area and the uniform dispersion of metal oxides on the surface. The transfer of valences between Cu$^{2+}$ and Mn$^{3+}$ in the Cu-Mn silica contributed to the single reduction peak displayed in the $H_2$ temperature-programmed reduction profiles and the high Mn$^{4+}$/Mn and Cu$^+/Cu$ ratios observed via X-ray photoelectron spectroscopy (XPS). The high oxygen lability of the Cu-Mn silica may have inhibited its ability to remove NO. By contrast, when SO$_2$ was present, incorporating Ce enhanced the NO removal efficiency due to the increased number of Bronsted acid sites. Cu2Mn8 exhibited the highest Hg removal efficiency, suggesting that Ce’s enhancing effect on Hg$^0$ adsorption was diminished when a large amount of Mn was present. Of the gaseous components, the adsorbed HCl was mainly responsible for the oxidation and subsequent adsorption of Hg$^0$. Furthermore, with the addition of SO$_2$, the competitive adsorption of SO$_2$ and the resulting HgCl$_2$ did not decrease the Cu-Mn silica’s efficiency in oxidizing Hg$^0$, but the oxidized Hg was less adsorptive.

Keywords: Silicate exfoliation; Coal combustion; Mercury; Multi-pollutant; Metal oxide.

INTRODUCTION

Coal-fired power plants (CFPPs) have been reported as one of the major anthropogenic emission sources of NO$_x$, SO$_2$, and heavy metals, such as mercury (U.S. EPA, 2012; UNEP, 2013). NO$_x$ plays a major role in the photochemical reactions in the troposphere and stratosphere, which further cause severe environmental impacts, namely, acid rain and photochemical smog (Roy et al., 2009). Mercury has received great concerns on its influences on both human health and the living environment due to its high toxicity, persistence, and long-distance transport (Chen et al., 2016; Marusczak et al., 2016; Guo et al., 2017). In CFPPs, mercury mainly exists in three forms in the gas streams: elemental mercury (Hg$^0$), oxidized mercury (Hg$^{2+}$), and particle-bound mercury (Hg$^0$) (Galbreath and Zygarlicke, 2000). Most of Hg$^{2+}$ and Hg$^0$ could be adequately removed by the conventional air pollution control devices. Hg$^{2+}$ can be removed by wet flue gas desulfurization and Hg$^0$ is primarily removed by electrostatic precipitator and fiber filter. However, Hg$^0$ is difficult to be removed due to its high stability and volatility (Zhao et al., 2019).

Instead of using the high-cost activated carbon injection for direct adsorption to transform Hg$^0$ into Hg$^0$ (Chou et al., 2018), catalytic oxidation of Hg$^0$ to Hg$^{2+}$ and subsequently to Hg$^0$ over selective catalytic reduction (SCR) catalysts could be a co-benefit during traditional NO removal by metal oxide catalysts. Hg$^0$ catalytic oxidation by various metal oxide catalysts in simulated flue gas has also been examined (Wang et al., 2014; Xiong et al., 2017). Some research has also been done on understanding the simultaneous removal of Hg$^0$ and NO (He et al., 2013; Chang et al., 2015; Li et al., 2015; Zhao et al., 2016; Song et al., 2018). The removal effectiveness of Hg$^0$ by the catalysts depends on the operating environment (flue gas composition and temperature) and the properties of the catalysts (Li et al., 2011a). The addition of ammonia for reduction of NO$_x$ may inhibit the Hg$^0$ removal due to competition of adsorption sites on the catalyst surface (Chang et al., 2015).

Mn-Ce oxides have been widely studied as low-
temperature SCR catalysts due to the presence of various valence states for Mn/Ce and their labile oxygen (Wang et al., 2014). Kang et al. (2006) showed that the NO conversion of MnO could keep over 95% at temperature below 175°C; in the same study, Cu-Mn mixed oxides showed over 95% NO removal efficiency at a broader temperature window (50–250°C). Fang et al. (2014) addressed that CuMnO spinel in Cu-Mn mixed oxide catalysts could promote the valence transition between Cu²⁺ and Mn³⁺ that promoted the SCR performance. The mixture of metallic species can enhance the effects towards an increment in the mobility of the oxygen, as well as stabilizing the active species and favoring the redox cycles that permits the reactivation of the catalyst (Aguilera et al., 2011). Ce oxide has also been known to have a great oxygen storage capacity and outstanding redox characteristics and can be a promising additive for low-temperature NH₃-SCR (Xu et al., 2018). Our earlier studies have also shown that activated carbon and zeolite impregnated with Cu oxide and Cu chloride had great Hg⁰ adsorption performance (Chiu et al., 2014, 2015; Tsai et al., 2017). Therefore, a combination of Cu-Mn or Cu-Mn-Ce oxides supported by porous materials, such as SiO₂, could possess great effectiveness in NO reduction and Hg⁰ oxidation followed by subsequent adsorption. A summary of selected studies on Cu and Mn oxide catalysts for NO and Hg⁰ removal is shown in Table 1.

The difference in crystallinity, oxidation state, and the amount of specific surface area and pore volume of metal oxides supported by porous materials could influence the NO and Hg⁰ removal performance. Therefore, a novel silicate exfoliation method was applied in this study to synthesize the Cu-Mn and Cu-Mn-Ce mixed oxides supported by mesoporous silica. During the silicate exfoliation method, the proper hydrothermal treatment could cause the surface structure of SiO₂ to reform. The surface reformation leads to (1) uniform dispersion of metal oxides on the silica surface, (2) a high Cu-Mn and Cu-Mn-Ce loading, and (3) large surface area and pore volume, all of which could be highly beneficial for Hg⁰ adsorption and NO reduction by NH₃, but not thoroughly understood by previous research.

**EXPERIMENTAL SECTION**

**Preparation of Metal Oxide-incorporated Mesoporous Silica via Silicate Exfoliation**

The CuOₓ-MnOₓ/SiO₂ samples were prepared by the silicate exfoliation method with a mole ratio of the precursor metal nitrate set at (Cu + Mn)/Si = 1. Firstly, stoichiometric amounts of Cu(NO₃)₂ and Mn(NO₃)₂ were dissolved in deionized water. The mixture was then neutralized with Na₂CO₃ aqueous solution to form the metal template at a deionized water. The mixture was then neutralized with conversion of MnOₓ by subsequent adsorption. A summary of selected studies reconstruct and incorporate with the silicate during the hydrothermal process. After filtration and drying, calcination at 100°C was employed for 3 days. The metal oxide would treated at 100°C for 3 days. The metal oxide would at 400°C was employed for 3 h in air to yield Cu-Mn oxides supported by porous materials could influence the surface chemical compositions and valence states of metal oxides on the samples. For XPS analysis, all binding energies were referenced to C₁s peak at 285 eV. The catalytic properties of resulting samples were characterized by H₂ temperature-programmed reduction (H₂-TPR) and NH₃ temperature-programmed desorption (NH₃-TPD) experiments. In H₂-TPR and NH₃-TPD, samples were firstly pretreated in a pure Ar flow at 150°C. H₂-TPR experiments were conducted on a Micromeritics II Autochem 2920 by increasing the temperature to 600°C at a rate of 10 °C min⁻¹ with 50 mL min⁻¹ of 10% H₂/Ar. For NH₃-TPD experiments, samples were treated with 10% NH₃/Ar for 1 h and then heated up to 750°C at a heating rate of 10 °C min⁻¹. The amount of NH₃ desorption from samples was detected by the Micromeritics II Autochem 2920.

**NO and Hg⁰ Removal Tests**

Hg⁰ removal performance was examined in a fixed-bed testing apparatus (Fig. 1), similar to our previous study (Chiu et al., 2014), using a simulated flue gas containing 30 μg Nm⁻³ Hg⁰. Hg⁰ was generated with a certified Hg⁰ permeation tube (VICI Metronics) in a gas generator at specific temperature to ensure a constant Hg⁰ diffusion rate. 12% CO₂, 10% H₂O, 6% O₂, 50 ppmv HCl, 200 ppmv SO₂, 200 ppmv NO, and balanced N₂ were applied as the simulated CFPP flue gas condition. The resulting gas was then passed through a temperature-controlled fixed-bed column (i.d.: 0.5") containing 10 mg sample and 0.5 g quartz sand. The gas flow through an empty column was about 1.5 L min⁻¹ at 25°C. The column length of sample/sand mixture was about 1.5 cm, and the time for gas stream to...
Table 1. Summary of studies on Cu/Mn and other metal oxide catalysts for NO and Hg\(^0\) removal.

<table>
<thead>
<tr>
<th>Material</th>
<th>Reaction condition</th>
<th>Target pollutant</th>
<th>Experimental results</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-Mn oxide (molar ratio Cu/Mn = 50, 25, 1, 1/25, and 1/50)</td>
<td>1. 500 ppm NO, 500 ppm NH(_3), 5 vol.% O(_2) balanced by N(_2); 100 ppm SO(_2), 11 vol.% H(_2)O when needed</td>
<td>NO</td>
<td>1. Cu0.01Mn0.25 showed the best performance at temperature range from 25 to 200°C. 2. Catalyst activity primarily depended on the calcination temperature which resulted in increasing pore volume and metal species in high oxidation state. 3. The NO conversion decreased from 95% to 64% in the presence of SO(_2) and H(_2)O.</td>
<td>Kang et al. (2006)</td>
</tr>
<tr>
<td>MnO(_x)/Alumina</td>
<td>1. 200–2000 ppm SO(_2), 5 vol.% O(_2) balanced by N(_2); 2.4 g MnO(_x)/γ-Al(_2)O(_3)</td>
<td>Hg(^0)</td>
<td>1. The effect of NO, CO(_2), and 0–5% H(_2)O was not obvious on the mercury removal. 2. HCl enhanced the mercury oxidation. The desorption of pre-adsorbed mercury occurred in the presence of HCl; the species in the outlet was mostly Hg(^{2+}). 3. SO(_2) slightly inhibited the mercury removal in the presence of HCl and strongly decreased the Hg(^0) adsorption ability.</td>
<td>Qiao et al. (2009)</td>
</tr>
<tr>
<td>CuO-MnO(_x)-FeO(_y)/γ-Al(_2)O(_3) (CMFA)</td>
<td>1. SFG condition: 10% CO(_2), 5% O(_2), 400 ppm SO(_2), 10 ppm HCl, 200 ppm NO, 8% H(_2)O balanced by N(_2); 0.3 g of sample</td>
<td>Hg(^0)</td>
<td>1. Hg(^0) concentration slightly dropped (from 75 to 55 µg m(^{-3})) in the condition only O(_2) and N(_2) was purged in. 2. For 3-day test (in SFG condition), CMFA could adsorbed all of Hg(^{2+}) in the beginning; Hg(^{2+}) was first detected after 10 hours. 3. CMFA pre-adsorbed HCl strongly enhanced Hg(^0) adsorption (about 95% efficiency in 120-minute test).</td>
<td>Wang et al. (2013)</td>
</tr>
<tr>
<td>Cu-MnO(_x)/TiO(_2) (molar ratio Cu/Mn = 0.025, 0.05, 0.1, 0.15, and 0.2)</td>
<td>1. 720 ppm NO, 800 ppm NH(_3), 3 vol.% O(_2) balanced by N(_2); 8 vol.% H(_2)O when used; 200 mg sample</td>
<td>NO</td>
<td>1. Over 95% NO conversion was shown on 0.05Cu-MnO(_x)/TiO(_2) at 180°C for 18-hour test. 2. Copper improved the resistance of potassium poisoning over MnO(_x)/TiO(_2). 3. H(_2)O caused the reversible inhibition on 0.2Cu-MnO(_x)/TiO(_2). The conversion decreased from 95% to 85%.</td>
<td>Fang et al. (2014)</td>
</tr>
<tr>
<td>Ce-Cu modified (V_2O_5/TiO_2) based commercial SCR catalysts</td>
<td>1. 500 ppm NO, 500 ppm NH(_3), 1000 ppm SO(_2), and 5% O(_2) balanced by N(_2)</td>
<td>Hg(^0)/NO</td>
<td>1. 7%Ce-1%Cu/SCR showed the best removal efficiency on mercury and NO. 2. Commercial SCR modified with 7%Ce-1%Cu improved the SCR activity in the presence of SO(_2) (recovery from 65% to 90%).</td>
<td>Chi et al. (2017)</td>
</tr>
<tr>
<td>Material Reaction condition</td>
<td>Target pollutant</td>
<td>Experimental results</td>
<td>References</td>
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| Cu-Mn/ordered mesoporous carbon (prepared by three different methods: self-assembly (S), ultrasound-assisted impregnation (I), and mechanical mixing (M)). | NO | 1. Cu-Mn/OMC(S) performed the highest NO conversion (88%) at 250°C.  
2. XRD indicated manganese oxides are highly dispersed on the surface of the Cu-Mn/OMC(S).  
3. According to XPS, the self-assembly method provided the highest ratio of Mn⁴⁺/Mn³⁺, Cu²⁺/Cu⁺, and chemisorbed oxygen. | Yu et al. (2017) |
| MnOₓ supported by TiO₂, Al₂O₃, SiO₂, and MK 10 (montmorillonite K 10) | Hg⁰ | 1. The removal mechanism was divided into three parts: physical adsorption, chemical adsorption, and oxidation. Chemical adsorption was dominant at 350°C.  
2. According to XPS, stronger electron transition between Mn⁴⁺ and Mn³⁺ (or Mn³⁺ and Mn²⁺) corresponded to either the adsorption or oxidation. Among four supports, MK 10 improved redox ability of Mn most. | Wu et al. (2018) |
| CuₓMnᵧAl₁₋ₓOₓ mixed oxide | NO | 1. CuₓMn₀.₅Al₀.₅Oₓ exhibited the highest NO conversion (91%) at 150°C.  
2. Cu reduced the crystallinity of manganese oxide and increased the ratio of Mn⁴⁺/Mn³⁺ on the surface.  
3. According to FTIR, NO conversion strongly depended on the quantity of Lewis acid sites. | Yan et al. (2018) |
pass the mixture was approximately 0.08 s. The effluent gas from the fixed-bed column was heated by heating tapes and divided into two streams. One stream flowed to an impinger containing SnCl$_2$(aq). SnCl$_2$(aq) was applied to reduce any oxidized Hg compounds to Hg$^0$ to comprehend the adsorption effect of samples; CTHg refers to the total Hg (THg) concentration (i.e., Hg$^0$ + oxidized Hg) in the inlet or outlet stream. The other stream went through an impinger with KCl(aq) with an attempt to completely capture oxidized Hg to understand the oxidation effect to the outlet Hg by the samples; CHg$^0$ represents the Hg$^0$ concentration in the inlet or outlet stream. The Hg$^0$ concentration in the two stream outlets was detected by two individual cold vapor atomic absorption spectrophotometers (CV AAS; EMP-2 coupled with SGM-8 Mercury Monitor, Nippon Instruments Corp.). The experiment was performed for 840 min or ceased when 100% breakthrough was achieved. The Hg adsorption capacities of samples were then calculated based on the breakthrough curves obtained from the CTHg experiment. By determining the difference between the Hg$^0$ concentration monitored by the two spectrophotometers (i.e., CTHg and CHg$^0$), the amount of oxidized Hg in the outlet stream could be estimated. The normalized Hg$^0$ concentration of the THg and Hg$^0$ removal tests and the outlet oxidized Hg ratio were calculated as follows:

$$\text{Normalized Hg}^0 \text{ concentration} = \frac{\text{CTHg}_{\text{outlet}} - \text{CHg}^0_{\text{outlet}}}{\text{CTHg}_{\text{outlet}}} \quad \text{or} \quad \frac{\text{CHg}^0_{\text{outlet}}}{\text{CTHg}_{\text{inlet}}}$$

Outlet oxidized Hg ratio = \frac{\text{CTHg}_{\text{outlet}} - \text{CHg}^0_{\text{outlet}}}{\text{CTHg}_{\text{outlet}}}

where CTHg$^{\text{inlet}}$ is the concentration of inlet Hg$^0$ (µg Nm$^{-3}$); CTHg$^{\text{outlet}}$ and CHg$^0_{\text{outlet}}$ are the concentration of outlet Hg$^0$ (µg Nm$^{-3}$) detected by spectrophotometers through the SnCl$_2$ and KCl solution, respectively. Therefore, the Hg$^0$ removal efficiency through adsorption ($\eta$) could be determined:

$$\eta = 1 - \frac{\text{CTHg}^{\text{outlet}}}{\text{CTHg}^{\text{inlet}}}$$

NO removal tests were carried out to determine the optimal mole ratio of Cu/Mn/Ce in the metal oxide-incorporated silica for NO reduction by NH$_3$. The test condition was described as follows: 1 g of sample, 200 ppmv NO, 200 ppmv NH$_3$, 200 ppmv SO$_2$ (when used), 6% O$_2$, and balanced N$_2$ with a total gas flow rate of 1.5 L min$^{-1}$ (25°C) were used. The length of the sample/gas wool mixture in the fixed bed was approximately 5 cm, and the time for the gas flow to pass the mixture was approximately 1 s. NO concentration was continuously monitored with a SICK MAIHAK S710 gas analyzer, which could also monitor the concentration variation of SO$_2$ and O$_2$. The NO concentration at the outlet of reactor was acquired when the NO reduction achieved stability at a given temperature. Because a portion of the downstream NO was captured by the condenser located prior to the flue gas.
analyzer, the NO removal efficiency was determined by:

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\text{NO removal efficiency} = \frac{C_{\text{NO}}^{\text{out}}}{C_{\text{NO}}^{\text{blank}}} \times 100\% 
\]

where \( C_{\text{NO}}^{\text{blank}} \) is the NO concentration obtained from the blank test. The blank test was performed under the simulated condition, without the presence of metal oxide-incorporated SiO\(_2\). \( C_{\text{NO}}^{\text{out}} \) is the NO concentration in the outlet gas stream, when the sample is in the fixed-bed reactor.

Based on our preliminary examination, Cu5Mn5, Cu2Mn8, Cu6Mn4Ce1, and Cu8Mn2Ce1 were selected for further investigation to understand the effects of temperature and presence of SO\(_2\) due to their better NO removal performance within the tested Cu-Mn and Cu-Mn-Ce samples.

### RESULTS AND DISCUSSION

**Characterization of Cu-Mn and Cu-Mn-Ce Incorporated SiO\(_2\)**

The XRD patterns of four samples, including Cu5Mn5, Cu2Mn8, Cu6Mn4Ce1, and Cu8Mn2Ce1 are shown in Fig. 2(a). The broad peak below 30° was denoted as amorphous silica. In addition, no crystalline phase was determined from these patterns. These results suggest that the samples may be amorphous or the metal oxides are highly dispersed on the surface of silica. The weak and broad diffraction peaks at 30.8°, 35°, 57.4°, and 62.4° were attributed to the Cu phyllosilicate in the form of Cu\(_2\)Si\(_2\)O\(_5\)(OH)\(_2\) with poor crystallinity. Cu phyllosilicate is the layered structures composed of polymeric sheets of SiO\(_4\) tetrahedra linked to sheets of Cu(O,OH)\(_6\) octahedra, which are usually divided into 1:1 and 2:1 by layer type.

![Fig. 2.](image-url)
oxide layer may contain the Mn-O-Cu bonds to inhibit the metal oxide aggregation. In contrast, Ce oxide modification caused the decrease of $S_{\text{BET}}$ and pore volume due to the complicated interactions between these metal species, that may result in mesopore blockage, which are suggested by Figs. 4(c)–4(f), in which the original spherical SiO$_2$ particles disappeared and significant aggregation was shown. Di et al. (2016) also suggested that because copper phyllosilicates possess high specific surface area, the larger surface area of Cu-Mn samples may be attributed to more copper phyllosilicates, or special type of copper phyllosilicate species preserved in the samples.

Fig. 6 shows the H$_2$-TPR profiles of Cu-Mn and Cu-Mn-Ce samples. Single metal oxide samples, namely Cu- and Mn-silicates, were also prepared and examined for comparison. The reduction peak centered at 225°C for the Cu-silicate was attributed to two reasons: (1) one-step reduction of low interacting species Cu$^{2+}$ to Cu$^0$; and (2) partial reduction of highly dispersed species (Cu$^{2+}$ → Cu$^+$) (Diaz et al., 1999). However, as described by Shi et al. (2018), Cu$^{2+}$ to Cu$^0$ may not likely occur at our experimental condition. There were two reduction peaks over the Mn-silicate: The peaks under 300°C and above 300°C could be denoted as MnO$_2$ species to Mn$_3$O$_4$ and Mn$_2$O$_3$ to MnO, respectively (Shi et al., 2018; Yi et al., 2018). Different from Cu- and Mn-silicate, the broad reduction peak was observed in the results of Cu-Mn samples (except for Cu2Mn8). Yan et al. (2018) proposed that the broad reduction was caused by the synergistic effect, which was related to the electron transfer between Cu and Mn oxides. Furthermore, the trimodal peaks observed over the Cu2Mn8 sample indicated less Cu-Mn interaction on its surface.

NH$_3$-TPD was carried out to characterize the surface acidity and NH$_3$ adsorption ability (Fig. 7). The desorption peak of Cu5Mn5 at 100°C was denoted as the physically adsorbed NH$_3$. Zheng et al. (2013) proposed that the NH$_3$ desorption peak centered at low temperature (<400°C) and the peak at high temperature (>600°C) was assigned to weak acid sites and strong acid sites, respectively. All four samples exhibited the broad peak from 150 to 500°C, ascribed to the multiple desorption NH$_3$ bound to weak or strong Brønsted acid sites. Different from samples with the addition of Ce, weak desorption peak centered at 600°C originated from Lewis acid sites was observed in the results of Cu5Mn5 and Cu2Mn8. Cu6Mn4Ce1 and Cu2Mn8Ce1 had the similar NH$_3$ desorption profile, which was probably related to the corresponding redox properties and texture. The amounts of desorbed NH$_3$ (without counting the physisorbed NH$_3$) over the four samples followed the sequence: Cu2Mn8 (1.00) > Cu6Mn4Ce1 (0.89) > Cu8Mn2Ce1 (0.68) > Cu5Mn5 (0.52). The reason causing the greatest NH$_3$ adsorption capacity over Cu2Mn8 may be due to the less synergistic effect aforementioned, which influences the surface acid strength. The NH$_3$-TPD results also suggest that Ce could promote the NH$_3$ adsorption capacity, which may be mainly caused by increasing the Brønsted acid sites.

To identify the chemical state of surface species, XPS analysis was carried out over the Cu5Mn5, Cu2Mn8, Cu6Mn4Ce1, and Cu8Mn2Ce1 samples (Figs. 8(a) and 8(b)).
The peaks with binding energies corresponding to Cu2p and Mn2p were further deconvoluted. The XPS spectra of Cu2p and Mn2p could be divided into the Cu$^{+}$ and Cu$^{2+}$ peaks at the binding energy of 932.8 and 934.4 eV (Yi et al., 2018) (Fig. 8(a)). According to Fang et al. (2014), Mn2p could be separated into Mn$^{3+}$ peak at 641.8–642.0 eV, and Mn$^{4+}$ peak at 643.2–644.5 eV (Fig. 8(b)). The relative atomic concentration ratios of species are presented in Table 3. For Cu2p XPS results, greater Cu$^{+}$ ratios were observed in the spectra of Cu5Mn5 and Cu2Mn8; large Mn$^{4+}$/Mn$^{3+}$ ratios were observed in the deconvolution results of all samples (Table 3). These experimental results are attributed to the electron transfer between Cu and Mn oxides, which caused the valence transition between Cu$^{2+}$ and Mn$^{3+}$.

The XPS spectra of O1s and Ce3d were also analyzed (Figs. 8(c) and 8(d)). There were three different O species on the sample surface: the lattice oxygen (labeled as O$\alpha$) at 529.3–530 eV, chemisorbed oxygen (labeled as O$\beta$) at 531.2–532 eV, and hydroxyl groups, defect oxide, and adsorbed water species (labeled as O$\gamma$) near 540 eV. In
addition, the complex spectra of Ce3d could be divided into two different Ce cations. The subbands at 886 eV corresponded to Ce3+; those at 901.5, 907, and 917 eV were attributed to Ce4+. The chemisorbed oxygen was considered as a significant species in the catalytic processes (Yan et al., 2018). Cations with high oxidation state (Ce4+) give rise to a reactive ammonia complex to react with NO (Tang et al., 2016); it resulted in the larger activity over the Cu6Mn4Ce1 compared with the performance over Cu8Mn2Ce1. In addition, the possible reason of high Cu2+/Cu ratio over the Cu8Mn2Ce1 was the valence transition between Ce4+ and Ce3+.

**NO Removal Activity of Cu-Mn and Cu-Mn-Ce Samples**

The NO removal performance of Cu-Mn samples is presented in Fig. 9. Without the presence of Cu oxide, Mn-silicate showed great activity at the temperature range of 200–300°C, with a NO conversion over 90%. However,
the NO removal efficiency sharply decreased to 60% with the incorporation of Cu oxides. Corresponding to the H$_2$-TPR, the incorporation of Cu oxide appeared to change the redox properties of Mn-silicate, which caused the inhibition of the SCR activity. Therefore, the greater performance over Cu$_2$Mn$_8$ as compared to other Cu-Mn and Cu-Mn-Ce incorporated silica may be due to a lesser influence of the synergistic effect on its Mn-based active sites.

**Fig. 7.** NH$_3$-TPD profiles of Cu-Mn and Cu-Mn-Ce incorporated SiO$_2$ samples.

**Fig. 8.** (a) Cu$_{2p}$; (b) Mn$_{2p}$; (c) O$_{1s}$; (d) Ce$_{3d}$ XPS spectra of Cu$_5$Mn$_5$, Cu$_2$Mn$_8$, Cu$_8$Mn$_2$Ce$_1$, and Cu$_6$Mn$_4$Ce$_1$ samples.
Table 3. The relative concentration ratios of specific states of the surface elements on the Cu-Mn-incorporated mesoporous silica.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cu&lt;sup&gt;2+&lt;/sup&gt;/Cu</th>
<th>Mn&lt;sup&gt;4+&lt;/sup&gt;/Mn</th>
<th>O&lt;sub&gt;α&lt;/sub&gt;/O</th>
<th>O&lt;sub&gt;β&lt;/sub&gt;/O</th>
<th>O&lt;sub&gt;γ&lt;/sub&gt;/O</th>
<th>Ce&lt;sup&gt;4+&lt;/sup&gt;/Ce&lt;sup&gt;3+&lt;/sup&gt;</th>
</tr>
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<tbody>
<tr>
<td>Cu5Mn5</td>
<td>0.141</td>
<td>0.926</td>
<td>0.166</td>
<td>0.478</td>
<td>0.406</td>
<td>-</td>
</tr>
<tr>
<td>Cu2Mn8</td>
<td>0.122</td>
<td>0.600</td>
<td>0.120</td>
<td>0.500</td>
<td>0.380</td>
<td>-</td>
</tr>
<tr>
<td>Cu8Mn2Ce1</td>
<td>0.935</td>
<td>0.923</td>
<td>0.503</td>
<td>0.350</td>
<td>0.147</td>
<td>1.443</td>
</tr>
<tr>
<td>Cu6Mn4Ce1</td>
<td>0.535</td>
<td>0.628</td>
<td>0.049</td>
<td>0.595</td>
<td>0.356</td>
<td>1.962</td>
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</table>

The NH<sub>3</sub> adsorption capacity of Cu6Mn4Ce1 was similar with that for Cu2Mn8 based on the NH<sub>3</sub>-TPD results. It is because the high ratio of Ce<sup>4+</sup> coordinates with NH<sub>3</sub>. It was reported that SO<sub>2</sub> would occupy the acid sites on the catalyst causing poisoning (Wei et al., 2016); the addition of Ce could trap the sulfation of the active sites (Jin et al., 2014). In order to understand the effect of Ce on limiting SO<sub>2</sub> poisoning, Cu2Mn8 and Cu6Mn4Ce1 having large NH<sub>3</sub> adsorption ability were selected to evaluate the NO removal efficiency at the temperature range from 150 to 350°C with presence of 200 ppmv SO<sub>2</sub> (Fig. 10). The obvious inhibition in NO reduction by SO<sub>2</sub> (i.e., 30% decrease in NO removal) was shown over Cu2Mn8. On contrary, there were no obvious decrease in NO removal for Cu6Mn4Ce1; instead, the removal efficiency at 250–350°C was further enhanced. As reported by Jin et al. (2014), the Ce modification causes more Brønsted acid sites, which attribute to the promotion of the SCR performance at 250–350°C. Yang et al. (2013) also showed that CeO<sub>2</sub> had an excellent SCR activity in the presence of SO<sub>2</sub> at 300–500°C. The promotion of SO<sub>2</sub> on the SCR reaction over CeO<sub>2</sub> was mainly due to the sulfation of CeO<sub>2</sub>, which could be the reason for the promotion of NO removal by Cu6Mn4Ce1.
Fig. 9. NO removal efficiency of Cu-Mn incorporated samples as compared to Mn-silicate.

Hg° Removal Test on Cu-Mn and Cu-Mn-Ce Incorporated Silica

Fig. 11(a) shows the results of THg and Hg° removal tests over Cu2Mn8 under the baseline condition (i.e., at Hg° = 30 µg m⁻³ and 150°C). There was no noticeable difference between CTHg and CHg0 for the 14-h test. The similar results also showed in other three samples, including Cu5Mn5, Cu6Mn4Ce1, and Cu8Mn2Ce1. These experimental results suggest that either the Hg° catalytic oxidation are not obvious on the sample surface, or, more likely, the oxidized Hg is immediately captured on the surface of the Cu-Mn and Cu-Mn-Ce silica samples. Consequently, the Hg° removal is primarily dependent on the oxidation followed by immediate adsorption. Furthermore, the experimental results also showed that 100% breakthrough was hardly achieved, which may be due to the poor adsorption kinetics between Hg and the tested samples.

For data comparison, the Hg removal performance was presented as the average THg removal efficiency and the Hg adsorption capacity over 14 h (Fig. 11(b)). The deviation represented the variation of the removal efficiency over the test. The average THg removal efficiency is determined by:

\[
\text{Average THg removal efficiency} = \frac{\text{CTHg_{outlet} } - \text{CTHg_{inlet}}} {\text{CTHg_{inlet,average}}} \times 100\%
\]

where CTHg_{inlet,average} is the average Hg° concentration at the outlet over the THg test. The experimental results for Cu2Mn8 had the greatest average THg removal efficiency, indicating that the effect of Ce modification on enhancing Hg° adsorption was less significant when Mn was present in a great amount. Notably, Cu6Mn4Ce1 and Cu8Mn2Ce1 had greater average THg removal than Cu5Mn5, indicating that Ce modification enhanced Hg° adsorption when Mn was present in a smaller amount. Furthermore, the Hg° adsorption capacity of the tested samples decreased in the same order of acid site content obtained from NH₃-TPD data: Cu2Mn8 > Cu6Mn4Ce1 > Cu8Mn2Ce1 > Cu5Mn5. These results, in agreement with previous studies (Chang et al., 2015; Liu et al., 2017), suggest that the amount of the acid sites verified by NH₃ adsorption plays an important role in Hg° oxidation and removal. These results also suggest that the extent of surface area and pore volume should not be the determining factor on Hg° removal for the tested metal-oxide silica.

Because of its greater NO and Hg° removal performance as compared to the others, Cu2Mn8 was further tested to evaluate the effect of temperature and inlet concentration on the Hg° adsorption. The test temperatures were set at 150, 250, and 350°C and the experimental results are shown in Fig. 12(a). Again, the effect of the catalytic oxidation over Cu2Mn8 was not obviously shown in the outlet stream even at 350°C, implying that if Hg oxidation occurs on the surface of Cu-Mn silica, the oxidized Hg would be immediately adsorbed. The average Hg° removal efficiency decreased with the increase of the temperature. The decrease in THg removal efficiency at 350°C was expected because the adsorption of Hg is thermodynamically unfavorable at elevated temperature (Chiu et al., 2015).

The effect of concentration on Hg adsorption over Cu2Mn8 was investigated in the similar gas condition at three inlet Hg° concentrations: 30, 65, and 100 µg m⁻³ at 150°C (Fig. 12(b)). Again, oxidized Hg was not observed in the outlet stream even as the inlet Hg° was at 100 µg m⁻³. The greatest THg removal efficiency was observed when the inlet Hg° increased to 65 µg m⁻³. The largest adsorption capacity was obtained when the inlet Hg° concentration increased to 100 µg m⁻³.
Because of the complex composition of the simulated coal-combustion flue gas, the transient response test was further performed on Cu2Mn8 to investigate the effect of flue gas components on Hg\textsuperscript{0} adsorption at 150°C. Fig. 13(a) shows the effect of pure N\textsubscript{2}, 6% O\textsubscript{2}, 12% CO\textsubscript{2}, and 200 ppmv NO on Hg\textsuperscript{0} adsorption. Firstly, there was only 10% THg removal efficiency for Cu2Mn8 in pure N\textsubscript{2} condition. It is related to the reaction of Hg\textsuperscript{0} with a limited amount of lattice oxygen, which may follow the Mars-Massen mechanism (Qiao et al., 2009). Hg\textsuperscript{0} firstly adsorbed on the surface to form Hg\textsuperscript{0(ad)}. The Hg\textsuperscript{0(ad)} then bonded with the lattice oxygen on the samples to form HgO\textsuperscript{(ad)}. The uptake of the lattice oxygen by Hg would be compensated by chemisorbed oxygen due to the high mobility.

With the addition of 6% O\textsubscript{2} at 4.5 h, the Hg\textsuperscript{0} removal efficiency increased slightly (Fig. 13(a)) because the gas-phase oxygen would replenish the uptake of the lattice oxygen and chemisorbed oxygen. At around 5.8 h, 12% CO\textsubscript{2} was introduced and there was no significant difference. Then, 200 ppmv NO was added in at 6 h. The THg removal efficiency increased to 25% and small amount of oxidized Hg was observed at the outlet. NO could be adsorbed on the basic sites of metal-oxide catalysts and give rise to active species, such as NO\textsubscript{2} and NO\textsubscript{2}\textsuperscript{+} for Hg oxidation. Li et al. (2011b) also suggested the oxidized Hg detected at the outlet was some volatile mercuric compounds, such as Hg(NO\textsubscript{3})\textsubscript{2}.

Following the test, 50 ppmv HCl was added in at 9 h (Fig. 13(a)). The THg and Hg\textsuperscript{0} removal efficiency sharply increased to 80 and 95%, respectively. The high Hg
oxidation by HCl, which may stem from formation of HgCl₂, has been proposed by several studies (Presto and Granite, 2006; Wang et al., 2014). Therefore, further investigation for better understanding the enhancing behavior of Hg⁰ adsorption by HCl at 150°C was done on Cu2Mn8, shown in Fig. 13(b). Firstly, the Cu2Mn8 sample was pretreated with 50 ppmv HCl for 1 h and purged with N₂ for 0.5 h; then, 30 µg m⁻³ Hg⁰ carried by N₂ was applied to the HCl-pretreated sample. The THg removal efficiency was shown to slowly decrease from 55 to 35% for 7 h. Consequently, HCl was confirmed to be strongly adsorbed on the surface of Cu2Mn8 and further oxidized and captured Hg⁰. At 7 h, the addition of oxygen, as mentioned above, replenished the deficiency of the surface oxygen that further enhanced the Hg⁰ adsorption again.

According to the transient response and HCl pretreatment test, the adsorbed HCl is confirmed to play the dominant role in the Hg⁰ oxidation/adsorption over the Cu-Mn samples. HCl would be adsorbed on the surface through two pathways (He et al., 2009; Chang et al., 2015): (1) The adsorbed HCl on the original basic sites of Cu-Mn samples would modify the chemical environments of samples, which caused the shift of the valence due to the strong electronegativity of Cl (Eq. (5)), and (2) the adsorbed HCl could bond with neighboring sites (Eq. (6)).

\[
\begin{align*}
M^{(n-1)+} + OH + Cl^- & \rightarrow Cl-M^n+ + OH \quad (5) \\
M^{n+} + HCl & \rightarrow Cl-M^{n+} + OH \quad (6)
\end{align*}
\]

where M could be Mn or Cu in this study.

Based on the aforementioned results, the Hg⁰ removal mechanism may be explained by the Langmuir-Hinshelwood mechanism:

\[
\begin{align*}
HCl + 4Mn^{4+} = O & \rightarrow Cl-Mn^{4+} + OH \quad (7) \\
Cl^- + Cu^{+} + OH & \rightarrow Cl-Cu^{2+} + OH \quad (8)
\end{align*}
\]
$\text{Hg} + \text{Mn}^{4+} = \text{O} \rightarrow \text{Mn}^{4+} - \text{O} - \text{Hg}$  \hspace{1cm} (9)  \\
$\text{Mn}^{4+} - \text{O} - \text{Hg} + \text{Cl} - \text{Cu}^{2+} - \text{OH} \rightarrow \text{Mn}^{4+} - \text{O} - \text{HgCl} + \text{Cu}^{+} - \text{OH}$  \hspace{1cm} (10)  \\
$\text{Mn}^{4+} - \text{O} - \text{HgCl} + \text{Cl} - \text{Mn}^{4+} - \text{OH} \rightarrow \text{HgCl}_2 + \text{Mn}^{4+} = \text{O} + \text{Mn}^{3+} - \text{OH}$  \hspace{1cm} (11)  \\
$\text{Mn}^{3+} - \text{OH} + 1/4\text{O}_2 \rightarrow \text{Mn}^{4+} = \text{O} + 1/2\text{H}_2\text{O}$  \hspace{1cm} (12)

Fig. 12. (a) Temperature dependence of average THg removal efficiency and the adsorption capacity with the inlet Hg$^0$ concentration of 30 µg m$^{-3}$ for Cu2Mn8. (b) Concentration dependence of average THg removal efficiency and the adsorption capacity at 150°C for Cu2Mn8.

Because of a low energy barrier in the reaction between Hg and Cl, the probable reactions would occur between reactive Cl and Hg$^0$ on the surface of samples (Presto and Granite, 2006). First, HCl would adsorb on the surface basic sites and generate the reactive Cl. The low ratios of Cu$^{2+}$/Cu and high ratios of Mn$^{4+}$/Mn in the XPS results indicate that the probable sites are Cu$^+$, which is activated by the reactive Cl, and Mn$^{4+}$ would bond with HCl. Furthermore, the correspondence between the results of the NH$_3$-TPD and the Hg$^0$ removal test suggest that the acid sites, both the Brønsted and Lewis acid sites, could be the activated Cl species. Then, the adsorbed Hg$^0$ would react with the reactive Cl to form HgCl$_2$, which is quickly adsorbed by the samples. The reoxidation of the Mn$^{3+}$–OH species by oxygen replenishes Mn$^{4+}$–O. Notably, Hg$^0$ oxidation may also follow the Eley-Rideal mechanism (Xiong et al., 2017), for which gaseous Hg$^0$ directly reacts with the adsorbed reactive Cl to form HgCl$_2$ and the formed HgCl$_2$.
are mostly released back to the gas phase and leads to significant Hg\(_0\) oxidation in the outlet stream. This may not be the case observed in our experiments because most of the formed oxidized Hg are speculated to adsorb on the sample surface.

The transient response test implied that the THg removal efficiency could achieve over 95% with the flue gas condition without the presence of SO\(_2\) and H\(_2\)O vapor. Therefore, the effect of SO\(_2\) was further investigated (Fig. 14). The results showed that the Hg\(_0\) oxidation kept over 90%, but the Hg capture efficiency gradually decreased from 80 to 60%.

These experimental results indicate that the competitive...
adsorption between the possibly formed HgCl₂ and SO₂ did not inhibit the Hg⁰ oxidation, but the oxidized Hg is less adsorptive, and a portion of it is released into the outlet stream. H₂O has also been reported to inhibit Hg⁰ oxidation and removal over metal or metal oxide based catalysts due to the competitive adsorption with reactive species, which caused the decrease of the overall Hg⁰ oxidation efficiency (Li et al., 2011b).

CONCLUSIONS

We hydrothermally exfoliated silicate to create mesoporous SiO₂ with a large specific surface area and well-dispersed Cu-Mn and Cu-Mn-Ce oxides. The presence of Cu phyllosilicate, detected via XRD, in the SiO₂ indicated that CuO-SiO₂ with a large specific surface area and well-dispersed phyllosilicate catalysts for acetic ester hydrogenation to ethanol.

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