Ni-Ce-OMS-2 material: preparation and preliminary catalytic-study
on removing ethanol in the gas phase

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Cryptomelane type manganese oxide K-OMS-2 and Ni-Ce-OMS-2 co-doping materials were synthesized by one-step preparation with refluxing system. The crystalline structure, and morphology were characterized by X-ray diffraction analysis and SEM images. Ni (II) and Ce (III) were incorporated into cryptomelane, substituted for Mn (III) and Mn (IV) resulting an increase of Mn-average-oxidation-state from 3.6 to 3.8 for un-doped and co-doped samples, respectively. With different amount of precursor-cerium concentration, NiCe1.0 improved the ethanol conversion by a factor of 8 compared to unmodified K-OMS-2. Additionally, NiCe1.0 showed a significant increase of ethanol conversion with reaction temperature. Over above 90% of ethanol was total oxidized at 150 °C suggesting a potential Ni-Ce-OMS-2 catalyst for removing volatile organic compounds at low temperature.
1. Introduction

The rapid growth of human population, urbanization and industrialization have greatly contributed to the volatile organic compounds (VOCs) emission threatening our living environment [Kamal et al., 2016]. VOCs are classified as indoor air pollutants causing many detrimental effects on both the environment and human health [Kamal et al., 2016 and Mølhave et al., 1991]. CO was concerned as indoor air pollutant which is deadly poisonous when inhaled in large amount [Zhou et al., 2014]. Formaldehyde can cause illness, soreness of the eyes, nose and throat, even at low levels or short periods [Robert et al., 2021]. Long-term exposure to toluene has been reported to suffer from neurological disorders [Kyzas et al., 2022]. Ethanol, which is one of the most common VOCs, is widely presented in industrial and consumer products such as dyes, inks, polishes, biofuels, cosmetics, perfumes, etc [Li et al., 2020]. Moreover, due to Covid-19 pandemic, the use of alcohol-based hand rubs or ethanol 70% for sterilization significantly surges in homes, medical centers and hospitals. Exposing to high level of ethanol vapor for long period time causes headache, irritation of mucous membrane, lack of concentration and drowsiness [Hautemanière et al., 2013 and Criddle et al., 2019]. At present, various technologies of VOCs treatment have been applied, namely adsorption, thermal oxidation and catalytic oxidation [Zhu et al., 2020, He et al., 2019 and Khan et al., 2000]. Among them, the most feasible and energy-saving approach to remove VOCs under mild operating conditions is
oxidation catalysis. Nowadays, metal oxide-based catalyst is being used thanks to its cost-effectiveness, less toxicity, also having good thermal stability and high surface area. And manganese oxide-based catalysts are known as low-cost materials exhibiting high activity of VOCs total oxidation [He et al., 2019, Khan et al., 2000, Luo et al., 2000 and Dinh et al., 2021].

Manganese oxides, an octahedral molecular sieve (OMS), have been much attracted as a promising catalyst due to their acceptable cost, high catalytic performance compared to noble metal ones [Suib et al., 2008 and Gandhe et al., 2007]. This material has manganese oxides framework with structural unit of MnO$_6$ octahedra connecting by sharing vertices and edges, creating a tunnel structure. The OMS materials are varied through the arrangement of MnO$_6$ octahedra units that define the tunnel structure with dimensions ranging from (2.3 x 2.3) Å to (4.6 x 11.5) Å [Sabaté et al., 2021]. Manganese oxide octahedral molecular sieve cryptomelane (K-OMS-2) is an one-dimensional manganese oxide, formed a 2 x 2 tunnel structure having dimensions of 4.6 Å with K$^+$ ions inside for a charge balance system [Yin et al., 1994].

The modification of cryptomelane by doping foreign metal cations could tune the physicochemical properties assigned to creation of more surface defects and oxygen vacancies [18]. Different cations such as Cr$^{3+}$, Ce$^{3+}$, Co$^{2+}$, Ni$^{2+}$ and Ag$^+$ have been substituted successfully into the OMS-2 structure for a promotion of catalytic performance [Tran et al., 2012, Tran-Thuy et al., 2021, Huang et al., 2020 and Sun et al., 2014]. However, studies on modification of the cryptomelane surface with two dopants (co-
doping cryptomelane) are still little concerns. In this work, nickel and cerium will be co
doped into cryptomelane structure via one-step preparation and the oxidation catalysis in
removal of ethanol vapor will be investigated.

2. Materials and methods

2.1. Preparation of K-OMS-2 and Ni-Ce-OMS-2 materials

All chemicals were purchased from Shanghai Zhanyun Chemical Co., Ltd and Duc Giang
Detergent-Chemical JSC, Vietnam without further purification. A solution of Mn$^{2+}$, Ni$^{2+}$
and Ce$^{3+}$ cations was mixed with potassium permanganate at room temperature, at pH < 2.
Typically, 1.0 M of Ni$^{2+}$ cation in the reactant mixture and 1.4 of the molar ratio of Mn$^{2+}$
and Mn$^{7+}$ were prepared before that. Amount of Ce$^{3+}$ cations in the precursor mixture was
adjusted with 1.0 and 1.5 M; correspondingly to NiCe1.0 and NiCe1.5 for the received-
final products. The mixture was further refluxed in a one-step at 100 °C for 24 hours. After
that, the brown slurry was washed many times with distilled water, filtered and dried over
night at 120 °C. For a comparison, an un-doped cryptomelane (K-OMS-2, K0) was
prepared following the protocol reported in our previous work [Tran-Thuy et al., 2021].

2.2 Material characterization analysis

The materials’ characteristics were analyzed using XRD, SEM, AOS, and ICP-MS
methods. X-ray diffraction analysis was carried out on a Bruker D8 Advance diffractometer
using Cu-Kα radiation. Morphologies were analyzed by using a Hitachi-S4800 FE-SEM
for scanning electron microscopy. The chemical composition was determined by the
inductively coupled-plasma mass spectrometry (ICP-MS, OptimaTM 8000 ICP-OES). The manganese average oxidation state (Mn-AOS) was determined by titration method [Tran-Thuy et al., 2021].

2.3 Catalytic performance testing

The catalytic testing in ethanol total oxidation was conducted under atmospheric pressure in a glass fix-bed reactor, which was placed in an electric furnace connected to a reaction temperature controller. Typically, 0.05g of catalyst and 0.05g of SiO₂ quartz were mixed and loaded in the reactor.

Ethanol vapor was carried by adding an inert nitrogen gas into an impinger containing absoluted ethanol kept at 0 °C. The ethanol vapor flow was mixed with a pure O₂ flow and another N₂ one passing through a water tank maintained at 30 °C to simulate an airflow with flowrate of 50 mL/min and relative humidity (RH) of 20%. The feeding flow was introduced in the reactor and the reaction temperature was controlled in the range of 30-150 °C by a water bath. Ethanol vapor removal efficiency (H₄th%) was calculated as the following equation:

\[
H_{Eth}\% = \frac{[EtOH]_{in} - [EtOH]_{out}}{[EtOH]_{in}} \times 100\%
\]

Wherein, [EtOH]_{in} and [EtOH]_{out} are representative for the concentration of ethanol in the inlet and outlet gas stream of the reactor.

3. Results and Discussion
3.1. Characterizations of catalysts

The elemental compositions of synthesized materials from ICP-MS analysis are displayed in Table 1. The K, Mn, Ni and Ce elements were all presented in the Ni-Ce-OMS-2 samples. When the cerium precursor concentration rose from 0.1 to 0.15M, the manganese content in NiCe1.0 and NiCe1.5 decreased from 49.8 to 44.9 wt.%. The manganese percentage of these samples were noticeable dropped when compared with ~59 wt.% of manganese for un-doped cryptomelane K0 sample. The dopants Ni and Ce greatly reduced the amount of potassium ion presenting in the tunnels of OMS-2 structure since the molar ratio of potassium over manganese elements dropped from 0.86/8 (K0 sample) to 0.40/8 (NiCe1.5 sample). Consistently, molar ratio of cerium and manganese increased from 0.43/8 to 0.71/8 for NiCe1.0 and NiCe1.5, respectively. The amount of nickel dopant was recorded at constant value as 0.02/8 of the molar ratio of nickel over manganese, regarding to the same nickel precursor concentration in preparation of co-doping samples.

Figure. 1 shows that K0, NiCe1.0, NiCe1.5 samples have all the signature diffraction patterns at 2θ of 12.6°, 17.9°, 28.7°, 37.5°, 41.9°, 49.9° and 60.1°; representing the cryptomelane structure (JCPDS 29-1020). Nickel and cerium dopants created some interferences in the diffractogram picture resulting broader and shorter peaks over NiCe1.0, NiCe1.5 samples in comparison to the un-doped one. This indicates the cerium loading affects the cryptomelane crystal of synthesized materials.
### Table 1. ICP – MS results and Mn-AOS of synthesized materials

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mn [wt%]</th>
<th>Molar ratio</th>
<th>Mn-AOS</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>K0</td>
<td>59.59</td>
<td>0.86/8/-/-</td>
<td>3.60</td>
<td>[14]</td>
</tr>
<tr>
<td>NiCe1.0</td>
<td>49.80</td>
<td>0.65/8/0.43/0.02</td>
<td>3.83</td>
<td>This work</td>
</tr>
<tr>
<td>NiCe1.5</td>
<td>44.88</td>
<td>0.40/8/0.71/0.02</td>
<td>3.84</td>
<td>This work</td>
</tr>
</tbody>
</table>

**Figure 1.** XRD patterns of OMS-2 materials

The Mn-AOS (as shown in Table 1) of NiCe1.0 and NiCe1.5 samples increased to around 3.8 comparing to 3.6 of the un-doped K0 sample possibly performing a partial replacement of Ni$^{2+}$ and Ce$^{3+}$ for lower oxidation state of manganese sites. This consisted with increase
of chromium loading resulting an incline of Mn-AOS over Cr-doped cryptomelane. This also figured out that chromium dopant took part in weakening the Mn-O bonds leading a positive effect on enhancement of formaldehyde-total oxidation [Tran-Thuy et al., 2021]. SEM images for Ni-Ce-OMS-2 materials are shown in Figure. 2 and Figure. 3, respectively. K-OMS-2 prepared by reflux method have nanorod-like morphology [Wang et al., 2009] which are agglomerated as clusters in the presence of nickel and cerium for preparation of cryptomelane. These clusters distribute randomly, not in any certain order, creating numerous voids in Ni-Ce-OMS-2 samples. The surface morphology of OMS-2 materials remains unchanged nanorod-like over NiCe1.0 sample (n_{Ce}/n_{Mn} = 0.41/8) having diameter at 20 ± 5 nm agglomerating into many clusters with the average size at 436 ± 19 nm (Figure 4a and Figure 4b) [Wang et al., 2009 and Dong et al., 2021]. When increasing the percentage of cerium loading in NiCe1.5 sample (n_{Ce}/n_{Mn} = 0.71/8), the clusters are clearly observed with various sizes, ranging from 200 nm to 2000 nm with the average diameter at 550 ± 58 nm (Figure 4c) and the nanorod-like shape disappears due to a slight aggregation (Figure. 3).
Figure 2. SEM images of NiCe1.0 samples at (a) 200 nm, (b) 500 nm and (c) 2 \( \mu \)m of scales.
Figure 3. SEM images of NiCe1.5 samples at (a) 200 nm, (b) 500 nm and (c) 2 μm of scales.
3.2. Removal of ethanol vapor by K-OMS-2 and modified cryptomelane catalysts

A skimming investigation of ethanol oxidation shows that K0 and NiCe1.5 materials had no efficiency in oxidizing ethanol vapor as less than 3.0% of removed ethanol during reaction at 30 °C. However, the NiCe1.0 presents a remarkable performance in removing ethanol vapor at 30 °C of reaction temperature, which is 9.6 ± 1.0 %. This indicates the worth effect of Ni and Ce co-dopant in the cryptomelane structure and a certain amount of the dopants dominates the catalytic activity. Figure. 5 presents the incline of NiCe1.0-catalytic performance versus the reaction temperature. 19 ± 5.2 % of ethanol vapor removal efficiency ($H_{\text{Eth}}\%$) is recorded at 50 °C and the $H_{\text{Eth}}\%$ gets 44.6 ± 3.3 % at 120 °C of the
reaction temperature. The notable increase in $H_{\text{Eth}}$% to $91 \pm 0.8$ % could be observed at 150 °C of the reaction temperature revealing a possible NiCe1.0 catalyst in ethanol deep-oxidation at low temperature. It was reported that less than 25% of ethanol was total converted on Mn-Cu oxide catalysts [Morales et al., 2006] and only ~5% of ethanol was total oxidized over manganese oxide catalyst [Bastos et al., 2009] at 150 °C of oxidation temperature. This evidences a comparable NiCe1.0 material for efficient removal of VOCs, in general and in particular of ethanol vapor at low temperature.

![Conversion of ethanol (%) vs Reaction temperature (°C)](image)

**Figure 5.** Ethanol conversion on NiCe1.0 catalyst at different reaction temperature

4. Conclusions

The co-doped Ni-Ce-OMS-2 materials are synthesized via one-step method in the assistance of reflux system. SEM images show the aggregation of cryptomelane nanorod-like morphology after loading Ni and Ce dopants to the K-OMS-2 structure. The dopants
also give rise to AOS of manganese from 3.60 to around 3.80, showing that Ni and Ce dopants partly take over the positions of manganese with lower oxidation state in the OMS-2 framework. The ethanol vapor conversion over NiCe1.0 is enhanced compared to the undoped K-OMS-2. At 150 °C of the reaction temperature, the co-doped catalyst effectively removes over 90% ethanol in the feeding stream.

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References


