Selective oxidation of CO in rich hydrogen stream over Ag/OMS-2 catalyst

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ABSTRACT
The Ag/OMS-2 catalysts prepared by the simple reflux method show high activity and stability for the CO selective oxidation in rich H2 stream. The catalysts are characterized by means of XRD, BET, XRF, XPS, SEM, TEM and H2-TPR. The results show that the materials have the cryptomelane type structure with a one-dimensional channel and Ag ions are well dispersed in the micropores of the cryptomelane structure. The catalytic activity for CO selective oxidation was increased after Ag introduction. In the longtime stability test under the realistic reaction condition, 100% CO conversion can maintain for 250 h at 120 °C with about 90% selectivity. The main reason for the deactivation of the Ag/OMS-2 catalysts is that the fine-dispersed silver species are agglomerated to form Ag2O and parts of OMS-2 are reduced to Mn2O3, accompanied with a structure reordering.

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1. Introduction

One of the major technical challenges for the commercialization of PEMFCs is to reduce the carbon monoxide concentration to an extremely low level in fuel systems, because only a trace amount of CO could shut down fuel cell operation due to poisoning of the Pt on the anode of a PEM fuel cell. Intensive work has been devoted in the last three decades to finding new technologies to remove CO from hydrogen-rich feed streams in fuel cells and new materials that are tolerant to the CO in the hydrogen at suitable operating temperatures. Possible approaches for the removal of CO from hydrogen-rich feed streams down to very low levels include adsorption, reduction, or oxidation. Among these, selective CO removal by catalytic oxidation appears to be the most promising approach [1,2].

Catalysts developed for the selective oxidation of CO are mainly grouped into non-noble metal oxides [3–7], supported Pt catalysts [8–10], supported Pd catalysts [11–13], supported Ru catalysts [14–16] and supported Au catalysts [17–19]. Supported noble metal catalysts, such as Pt, Pd and Ru, usually are a high conversion of CO and CO can be totally converted to CO2 but the hydrogen-oxidation side reaction also simultaneously occurs in the presence of excess H2 [8,11,16]. Another class of the CO selective oxidation catalysts, the supported gold catalysts own a remarkable activity and selectivity at low temperature while its activity is strongly dependent on the preparation method and deactivation is more rapid upon long-term operation [20–23]. So, the preferential character of the catalysts of selective oxidation is a high oxidation rate of CO and a high selectivity with respect to the side oxidation reaction of H2 since fuels being used for PEMFCs are mainly
reformats which contain a high concentration of hydrogen. Meanwhile, such catalysts should also have a good stability and be able to tolerate the presence of CO2 and H2O.

Cryptomelane, a manganese oxide octahedral molecular sieves having a well-defined 2 × 2 tunnel structure (OMS-2), has attracted a great deal of attention because of its excellent catalytic activities towards oxidation reactions [24–38]. The OMS-2 materials doped by metal cations such as Cu [24,25], Co [26], Ag [27,28], Ti [29], Ce [30], Zr [31], V [32] and Pb [33] have been successfully applied to the oxidation of CO [25,27,28], HCHO [32], alcohol [34], phenol [30,33], cyclohexane [35] and so on [27,30,37,38]. Our previous researches [24] have reported a series of Ag-doped manganese oxide octahedral molecular catalysts and determined their activation energies for CO desorption, CO2 desorption and CO oxidation by the temporal conductivity detector (TCD) technique. In this work, we focus on the evaluation of the preferential oxidation performances CO in rich hydrogen over the Ag/OMS-2 catalysts. The activity and selectivity of these Ag/OMS-2 catalysts, the long-term stability, as well as the deactivation were investigated in paper.

2. Experimental

2.1. Sample preparation

The Ag/OMS-2 catalysts were synthesized by the reflux method. 3 mL of 0.5 M MnSO4 solution at room temperature to provide an aqueous reaction medium having a pH of 1.0. The solution was then added dropwise into 100 mL aqueous solution containing 5.89 g KMnO4 and an appropriate amount of AgNO3. The resulting black precipitate was stirred vigorously and refluxed at 100 °C for 48 h. The solid obtained was filtered and washed with distilled water, followed by drying at 120 °C for 6 h and calcination at 300 °C in static air.

The series of catalysts prepared include 0, 0.5, 1.0 and 2.0% Ag/OMS-2. The loading values are nominal loadings.

2.2. Physical and chemical characterization

X-ray powder diffraction (XRD) patterns were recorded with a 2308 powder diffractometer (Rigaku, Japan) operated at 27.5 kV and 25 mA, using nickel-filtered Cu Kα radiation. The scanning range is 2θ = 10°–80°.

The specific surface areas (S_BET) of the catalysts were calculated from N2 adsorption data that obtained from a multipoint Brunauer-Emmett-Teller (BET) analysis of the nitrogen adsorption isotherms at 77K recorded on a Quantachrome Autosorb-1 apparatus.

The element compositions of catalysts were determined by X-ray fluorescence (XRF) analysis equipped with ARL ADVANT’X Intellie Power 4200 scanning X-ray fluorescence spectrometer with a rhodium tubes as the source of radiation.

The morphologies of the samples were investigated by field-emission scanning electron microscopy (SEM) by a JEOL JSM-6700F instrument operated at 1 kV. The transmission electron microscopy (TEM) observations were performed with a JEOL JEM-2010 electron microscope. A drop of the samples suspension diluted in alcohol was placed onto a holey carbon film supported by a 3-mm copper grid and then observed.

The X-ray photo electron spectroscopy (XPS) measurements were performed on a Perkin–Elmer PHI-1600 ESCA spectrometer with Mg Kα source (hv = 1253.6 ev). The catalyst sample was fixed on a sample stage and was evacuated to 2 × 10⁻⁷ Pa for the measurement. The binding energies were corrected by using the contaminant carbon (C1s = 284.6 eV).

The temperature-programmed reduction (TPR) analysis was carried out on a system equipped with a thermal conductivity detector (TCD). The samples (50 mg) were taken in a quartz tube reactor (i.d. = 6 mm) and heated to 150 °C with N2 flowing (40 mL/min) for 2 h. After cooling to the room temperature and introducing the reduction agent of a 5 vol% H2/N2 mixture (40 mL/min), the samples then were heated to 600 °C at a rate of 8 °C/min. The amount of H2 uptake during the reduction was measured by the TCD detector.

2.3. Catalytic activity measurements

The catalytic oxidation of CO was performed in a fixed-bed reactor under atmospheric pressure. 500 mg catalyst was filled in a quartz tube reactor (i.d. = 6 mm). The reacting stream consisted of 1.0% CO (by volume hereinafter), 1% O2, 50% H2, 10% H2O (when used), 10% CO2 (when used) and balanced N2. The total space velocity was 10,000 ml g⁻¹ h⁻¹. The temperature of the reactor was monitored by the thermocouple placed on the catalysts and the heating rate is 6 K/min. The effluent from the outlet of the reactor were analyzed using an online CIs 200 (SRS Company, USA) mass spectrometer and a G7890 (Techcomp Company, China) gas chromatograph equipped with TCD and FID detectors. In this case, the CO conversion, O2 conversion and CO2 selectivity were calculated using the following formulas:

\[
\text{CO conversion(%) } = \frac{[\text{CO}]_{\text{out}} - [\text{CO}]_{\text{in}}}{[\text{CO}]_{\text{in}}} \times 100
\]

Fig. 1 – XRD patterns of catalysts with different Ag loadings. (a) OMS-2, (b) 0.5%Ag/OMS-2, (c) 1.0%Ag/OMS-2, (d) 2%Ag/OMS-2.
O₂ conversion (%) = \frac{|O₂_{\text{in}} - O₂_{\text{out}}|}{O₂_{\text{in}}} \times 100

CO₂ selectivity (%) = 0.5 \times \frac{|CO_{\text{in}} - CO_{\text{out}}|}{O₂_{\text{in}}} \times 100

3. Results and discussions

3.1. Catalyst characterization

The Ag/OMS-2 materials synthesized using the reflux method are dark-brown powders. Fig. 1 shows the XRD patterns of the synthesized Ag/OMS-2 materials. There are clear main diffraction peaks at 2θ = 12.6°, 17.9°, 28.7°, 37.5°, 41.9°, 49.9° and 60.1°, which showed that they all have the typical structures of cryptomelane (KMn₈O₁₆, JCPDS 29-1020) [26]. Noticeably, the intensity of the diffraction peaks of Ag/OMS-2 becomes stronger with the increasing of the Ag loading, indicative of improving crystallizability of the cryptomelane materials. No peaks related to the dopant Ag metal cations are observed, which indicated that Ag ions are well dispersed and have been probably substituted for the framework manganese cations of cryptomelane.

The BET surface areas of the Ag/OMS-2 catalysts are summarized in Table 1. It can be seen that the surface areas of these materials are between 76 and 82 m²/g. The actual content of Ag in the catalysts is also listed in Table 1. It shows that the actual Ag content in the catalyst is close to the nominal value since the catalysts were prepared using an impregnation method.

Fig. 2 shows the SEM and TEM image of the 2% Ag/OMS-2 catalyst. All the four catalysts have the similar morphologies (not shown here). It clearly showed that the synthetic catalysts are needle-like nanorods. The diameters of the nanorods range from 35 to 50 nm, and the lengths are about 600–700 nm.

The H₂-TPR profiles of the Ag/OMS-2 catalysts with different Ag contents are illustrated in Fig. 3. For all catalysts, two obvious reduction peaks (I and II) at 200–500 °C are observed. The low temperature reduction peak I possible represents the reduction of MnO₂ to Mn₃O₄ and the high temperature II one refers to further reduction of Mn₃O₄ to MnO [27]. Noticeably, the reduction peaks (I and II) shift to lower temperatures with the increasing of Ag contents.

![Fig. 3 – TPR profiles for the synthesized catalysts with different Ag loadings. (a) OMS-2, (b) 0.5%Ag/OMS-2, (c) 1.0% Ag/OMS-2, (d) 2%Ag/OMS-2.]

Table 1 – BET surface area and the actual content of Ag.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>BET surface area (m²/g)</th>
<th>Ag content (wt%)</th>
</tr>
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<tbody>
<tr>
<td>OMS-2</td>
<td>76.9</td>
<td></td>
</tr>
<tr>
<td>0.5%Ag/OMS-2</td>
<td>79.7</td>
<td>0.58</td>
</tr>
<tr>
<td>1.5%Ag/OMS-2</td>
<td>81.2</td>
<td>1.13</td>
</tr>
<tr>
<td>2%Ag/OMS-2</td>
<td>81.8</td>
<td>2.07</td>
</tr>
</tbody>
</table>

![Fig. 2 – Representative SEM (a) and TEM (b) images 2%Ag/OMS-2.]

indicating that the presence of silver promotes the reducibility of manganese oxide through a hydrogen spillover effect [29]. In addition, the areas of the reduction peak increase with the increasing of the loading Ag. It could be assigned to the reduction of finely dispersed Ag$^+$ to Ag. The hydrogen consumption amounts estimated from the reduction peaks further confirmed this stepwise reduction of Ag$^+$.

### 3.2. CO selective oxidation in rich hydrogen

Activity and selectivity of the four Ag/OMS-2 catalysts in preferential oxidation of CO with excess hydrogen are illustrated in Fig. 4a and b, respectively. It could be observed that the addition of Ag had a significant influence on the catalytic performance of Ag/OMS-2 catalysts. With the increasing of the Ag loading from 0.5 to 2.0 wt.%, the CO selective oxidation activity of the catalysts is enhanced monotonously. The catalyst of 2%Ag/OMS-2 exhibited the highest catalytic activity and the catalyst of OMS-2 without Ag showed the lowest catalytic activity. The conversion of CO was improved when increasing the temperature in the reactive system. For almost catalysts, 90% conversion of CO was achieved at a temperature as low as 110 °C.

However, the selectivity of CO$_2$ showed a contrary trend with CO conversion with the increase of reaction temperatures. For example, in the case of 2% Ag/OMS-2, the selectivity declined from 100% at 60 °C to about 72.4% at 180 °C. It seems to imply that CO oxidation is superior to hydrogen oxidation at lower temperature because of the nearly 100% selectivity of CO$_2$. That is, displacement of adsorbed hydrogen by carbon monoxide and blocking of hydrogen adsorption by pre-adsorbed carbon monoxide occur during the competing adsorption of hydrogen and carbon monoxide at low temperature [41]. Therefore, the H$_2$O$_2$ reaction could not occur until carbon monoxide desorbed. After carbon monoxide desorbed at high temperatures, hydrogen molecular rapidly adsorbs and occupies the active sites on the surface of the catalysts. Carbon monoxide oxidation and H$_2$O$_2$ reactions started competing.

As we have mentioned, a good catalyst for the CO selective oxidation should also be able to tolerate the presence of CO$_2$ and H$_2$O since the reformate H$_2$-rich stream contains 10–25% CO$_2$ and about 10% H$_2$O. The variations of CO conversion and selectivity with the reaction temperature for the CO selective oxidation over the 2% Ag/OMS-2 catalyst in the presence of 10% H$_2$O and 10% CO$_2$ are shown in Fig. 5. An obvious change could be observed that the complete removal of CO can be received at higher temperature than that in the absence of CO$_2$ and H$_2$O. 99.3% CO conversion is obtained at 160 °C with 68% selectivity, while the same conversion is achieved at 120 °C with 91% selectivity in the absence of H$_2$O and CO$_2$. The possible reason for the decrease of catalytic activity with CO$_2$ and CO$_2$ is that the blockage of the adsorbed molecular water on the active sites and the competitive adsorption of CO and CO$_2$ on the catalyst surface.

### 3.3. Deactivation

#### 3.3.1. Long-time stability test

Fig. 6 illustrates the longtime stability test on 2% Ag/OMS-2 catalyst for CO selective oxidation in a hydrogen-rich stream.
during the first 250h of time on stream, 100% CO conversion maintains with about 90% selectivity under a space velocity of 10,000 ml g\(^{-1}\) h\(^{-1}\) at 120\(^\circ\)C. However, in the subsequent 50 h, the decrease in both O\(_2\) and CO conversion speeded up. The CO conversion and CO\(_2\) selectivity decreased drastically from 95% to 46.8% and 82% to 50%, respectively. When tested at 160\(^\circ\)C, the deactivation of the 2% Ag/OMS-2 catalyst is more speedy. The CO conversion decreased significantly from 100% at the initial stage to 82% at 90 h. The fast deactivation probably implies that there are possible changes in the physical and chemical properties of the catalyst during the reaction process.

3.3.2. Surface characterization of the deactivated catalyst

XRD patterns of the fresh and deactivated 2% Ag/OMS-2 catalysts are shown in Fig. 7. It is shown that the fresh catalyst has the typical structures of cryptomelane and no peaks related to the dopant Ag metal cations are observed. After longtime reaction, the intensities of peaks of cryptomelane decrease significantly, indicating that such crystals in the bulk may transfer to amorphous phase. The characteristic peaks of Ag\(_2\)O are observed in the deactivated catalyst, indicating silver ions which were highly dispersed in the micropores of the cryptomelane structure have agglomerated and formed a new phase. Meanwhile, a new phase ascribed to Mn\(_2\)O\(_3\) is observed in the deactivated catalyst, indicating a phase transformation from KMn\(_4\)O\(_8\) to Mn\(_2\)O\(_3\). The transformation of the phases reveals that the chemical state of the manganese oxides changes, and that the catalyst surface restructure is present during the longtime stability test.

To examine the chemical species on the fresh and deactivated catalysts, XPS measurement was performed. The XP spectra in the Ag 3d region of the fresh and deactivated catalysts are shown in Fig. 8a. The binding energies of Ag 3d\(_{5/2}\) and Ag 3d\(_{3/2}\) are 367.8 eV and 373.8 eV, respectively, which could be attributed to the characteristics of Ag\(^{+}\) [42]. In accord with the results of XRD, it could be observed two weak peaks ascribed to Ag\(^+\) in the fresh catalyst, which demonstrates again the silver ions are probably highly dispersed in the micropores of the cryptomelane structure of the bulk since XPS is a surface analysis technique. The intensity of the peaks of Ag\(^+\) in the deactivated catalyst is more obvious. It is in good agreement with the XRD result, where silver ions transferring from the bulk to the surface of the catalyst and agglomerating to form a new phase is detected. Since the silver species well dispersed in the micropores of the cryptomelane structure is considered to be the promoter species for CO oxidation, the assemblage of the surface Ag\(^+\) of the catalyst is one of the reasons for the deactivation.

Fig. 8b displays the XP spectra of Mn 2p in the fresh and deactivated catalysts. The binding energies of Mn 2p\(_{3/2}\) and Mn 2p\(_{1/2}\) in the Ag/OMS-2 catalysts are about 642.0 eV and 654.0 eV, respectively, which could be simply attributed to a mixture of Mn\(^{3+}\) and Mn\(^{4+}\) species [25]. The detailed peak fitting results of Mn 2p features for the two materials are listed in Table 2. It is found that these samples contain both Mn\(^{3+}\) and Mn\(^{4+}\) species. Quantitative analysis of the surface components shows that the deactivated catalyst contain more Mn\(^{3+}\) (about 48%) than the fresh catalyst (about 39%), indicating that Mn species in the
fresh catalyst have higher average oxidation state than the deactivated catalyst.

The XP spectra of O 1s shown in Fig. 8c show two BE peaks for both the fresh and deactivated catalysts. The lower BE bond of 529.0–530.0 eV could be ascribed to lattice oxygen ions bonded to metal cations (O_l) and the higher BE bond of 531.0–532.0 eV might be assigned to surface oxygen ions (O_s) bonded to metal cations [32]. From Fig. 5C, it could be observed that the surface oxygen ions (O_s) have a distinct increase on the deactivated catalyst than on the fresh catalyst, indicative of the diffusion of the oxygen from the lattice or bulk to the surface, which is then further indicated the catalyst surface have been restructured and some of the crystal structure has collapsed by O_2 evolution.

![X-ray photoelectron spectra in the Ag 3d (a), Mn 2p (b), O 1s (c) and C 1s (d) regions for the fresh and deactivated 2% Ag/OMS-2 catalysts.](image)

The C 1s spectra shown in Fig. 8d indicate the presence of two different carbon species on the catalyst surface: adventitious carbon (284.6 eV) and formate or carbonate (284.6 eV). The peak at 288.8 eV ascribed to the formate or/and carbonate species [23] increases significantly on the fresh catalyst than on the deactivated catalysts, which is taken as evidence that both carbonate or/and formate species form during the CO selective oxidation process on the 2% Ag/OMS-2 catalysts.

In summary, the results of XRD and XPS demonstrate that the structure and the species on 2% Ag/OMS-2 catalyst have changed after the longtime reaction. The silver species well dispersed in the surface of catalysts are agglomerated to form Ag_2O and parts of the manganese oxide molecular sieve are reduced to Mn_2O_3. That is, the surface Ag/OMS-2 structure is destroyed and the chemical or structural reordering may be responsible for the deactivation of the Ag/OMS-2 catalysts.

### 4. Conclusions

The Ag/OMS-2 catalysts prepared by the simple reflux method show high activity and stability for the CO selective oxidation in rich H_2 stream. The catalysts are characterized by means of XRD, BET, XRF, XPS, SEM, TEM and H_2-TPR. The results show that the materials have the cryptomelane type structure with

<table>
<thead>
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<th>Catalyst</th>
<th>BE (eV)</th>
<th>Mn^{3+}/(Mn^{4+} + Mn^{3+}) (atomic %)</th>
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<tbody>
<tr>
<td></td>
<td>2p_{3/2}</td>
<td>2p_{1/2}</td>
</tr>
<tr>
<td>Deactivated</td>
<td>641.9</td>
<td>653.5</td>
</tr>
<tr>
<td>Fresh</td>
<td>641.8</td>
<td>653.3</td>
</tr>
</tbody>
</table>
a one-dimensional channel and Ag ions are well dispersed in the micropores of the cryptomelane structure. The catalytic activity for CO selective oxidation was increased after Ag introduction. In the longtime stability test under the realistic reaction condition, 100% CO conversion can maintain for 250 h at 120 °C with about 90% selectivity. The main reason for the deactivation of the Ag/OMS-2 catalysts is that the fine-dispersed silver species are agglomerated to form Ag2O and parts of OMS-2 are reduced to Mn3O4, accompanied with a structure reordering.

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