Effect of pretreatment atmosphere on CO oxidation over $\alpha$-Mn$_2$O$_3$ supported gold catalysts

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The microstructural properties of Au/$\alpha$-Mn$_2$O$_3$ catalysts moderately pretreated under different atmospheres, i.e., O$_2$, He and H$_2$, in relation to their activities and stabilities on CO oxidation were investigated. The highest initial activity was obtained for the He-pretreated catalyst, which, however, suffered the most severe deactivation with time on stream. Pretreatment with O$_2$ resulted in the best stability and had the highest steady-state activity among the three catalysts. TEM results revealed that the pretreatment has a negligible effect on the gold particle size. While the formation of moderate surface oxygen vacancies before reaction was suggested to be responsible for the highest initial activity of He-Au/$\alpha$-Mn$_2$O$_3$, overreduction of the oxide support could explain the inferior activity of the H$_2$-pretreated catalyst. Based on the XPS and in situ DRIFTS studies, the superior performance of the O$_2$-pretreated O$_2$-Au/$\alpha$-Mn$_2$O$_3$ catalyst can be attributed to the creation of a specific oxygen-enriched interface leading to an enhanced metal–support synergy.

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1. Introduction

Recently, oxide-supported gold catalysts have attracted tremendous research interest owing to their unique catalytic properties for various redox reactions, in particular, for CO oxidation under ambient conditions [1,2]. It is generally accepted that gold dispersed on reducible oxides is more active and stable than that supported on non-reducible oxides [SiO$_2$, Al$_2$O$_3$] [3]. Exceptionally high activities for CO oxidation have been reported for finely dispersed Au on reducible oxides, such as TiO$_2$ [4], CeO$_2$ [5], Fe$_2$O$_3$ [3,4], Co$_3$O$_4$ [4] and Mn$_2$O$_3$ [6,7]. The gold particle size along with the metal–support interaction/synergy has been suggested to play a decisive role in controlling the activity of the gold catalysts [1,2,8]. These two factors are largely determined by the preparation method and the activation or pretreatment conditions before reaction [4–8].

Among the various techniques used to prepare supported gold catalysts, deposition–precipitation (DP) with the most common gold precursor, H$_2$AuCl$_4$, appeared to be the most suitable method to achieve highly active catalysts [1–4]. With this method, it is possible to obtain very small gold metal particles (2–3 nm) that are highly active for CO oxidation. The main feature in the DP technique is the deposition of the gold precursor on the support, in which one of the major factors is the appropriate pH value [9]. Subsequent thermal treatment following the drying step is generally required for the genesis of active Au species [10,11]. Although there is no general agreement on the optimal calcination temperature for the supported Au particles for CO oxidation, it is frequently observed that calcination at temperatures above 673 K results in a deteriorated activity, which has been attributed to sintering and/or a change in the shape of the particle [10–13].

As for the additional pretreatment to activate the gold catalysts, it has been reported that pretreatment gas conditions can exert a significant influence on the final structure and activity of the supported gold catalysts [14–18]. For example, Gardner et al. [14,15] reported that the pretreatment of Au–MnO$_x$ in He at 328 K resulted in a significant enhancement in the activity for CO oxidation, which may be due to enrichment in the Au and O contents on the surface of this catalyst as revealed by XPS. Zanella and Louis [10] and Tsu-bota et al. [16] showed that a moderate thermal treatment of Au/TiO$_2$ catalyst under hydrogen or argon leads to smaller gold particles than that under air. On the other hand, Park and Lee [17] found that the rate of CO oxidation over Au/TiO$_2$ pretreated in H$_2$ is lower than that inertly pretreated, and the preoxidized one yields the highest activity. More recently, Ho and Yeung [18] have reported that O$_2$-pretreated Au/TiO$_2$ catalyst exhibited a better Au dispersion and enhanced stability compared with O$_2$-pretreated Au/TiO$_2$.

Notwithstanding the extensive research on Au catalysts, the structural effects associated with the activation process have not been well understood, in particular, the oxidation state of gold and the effect on the metal–support interface. In the present paper, we focus on the effect of pretreatment atmosphere on the
activation, deactivation and regeneration of a model Au/\(\alpha\)-Mn\(_2\)O\(_3\) catalyst, which is one of the best catalysts for CO oxidation, even in the presence of water or hydrogen [6,7]. We use XPS, TEM, XRD and in situ DRIFTS coupled with CO adsorption to study the effect of various pre-treatments, i.e., reductive, oxidative and inert atmosphere, on the structure and morphology of the gold particles, manganese oxide support and the metal–support interaction.

2. Experimental

2.1. Catalyst preparation

\(\alpha\)-Mn\(_2\)O\(_3\) was prepared by the direct thermal decomposition of MnCO\(_3\) powder (Aldrich) in static air [19]. Gold was deposited on the as-synthesized \(\alpha\)-Mn\(_2\)O\(_3\) by DP using urea as the precipitating agent [20]. Typically, 0.55 g of \(\alpha\)-Mn\(_2\)O\(_3\) was added to an aqueous solution with the desired amount of HAuCl\(_4\) and urea (urea/Au = 100, molar ratio). The suspension was then heated to 363 K and stirred for 4 h, followed by filtering and washing several times with deionized water to remove Cl\(^-\). The resulting solid product was dried overnight before calcination at 573 K for 4 h in static air. The gold loading of the as-prepared catalyst was 2.9 wt% as determined by ICP-AES.

2.2. Catalyst activity tests and kinetic measurements

The catalysts were evaluated at atmospheric pressure using a fixed bed quartz reactor (i.d. 3 mm). The weight of the catalyst was 20 mg, and the total flow rate of the reaction gas was 50 mL min\(^{-1}\), with a composition of 1%CO–20%O\(_2\) (balanced with He). Prior to the reaction, the catalysts were pretreated with 30 mL min\(^{-1}\) of He, O\(_2\) or H\(_2\) at 473 K for 0.5 h. For the sake of clarity, the three as-prepared catalysts were referred to as He–Au/\(\alpha\)-Mn\(_2\)O\(_3\), O\(_2\)–Au/\(\alpha\)-Mn\(_2\)O\(_3\) and H\(_2\)–Au/\(\alpha\)-Mn\(_2\)O\(_3\). Kinetic measurements were performed under differential reaction conditions, with typically 2 mg catalyst powder. To limit the conversion to values typically between 5% and 20%, the catalysts were diluted with chemically inert \(\alpha\)-Al\(_2\)O\(_3\). The reactions were carried out with 100 mL min\(^{-1}\) of 1%CO–20%O\(_2\) balanced with He. Kinetic data were acquired after 120-min reaction. The composition of the influent and effluent gas was detected with an online GC-17A gas chromatograph equipped with a TDX-01 column. The conversion of CO was calculated from the change in CO concentrations in the inlet and outlet gases.

2.3. Catalyst characterization

The BET specific surface areas of the calcined catalysts were determined by adsorption–desorption of nitrogen at liquid nitrogen temperature, using Micromeritics TriStar 3000 equipment. The X-ray powder diffraction (XRD) was carried out on a Bruker AXS D8 Avance X-ray diffractometer with nickel-filtered Cu K\(\alpha_1\) radiation (\(\lambda = 1.540562\) Å) with a voltage and current of 40 kV and 20 mA, respectively. Chemical analysis was performed by inductively coupled plasma (ICP) atomic emission spectroscopy using a Thermo Electron IRIS Intrepid II XSP spectrometer. A JEOL 2011 microscope operating at 200 kV equipped with an EDX unit (Si(Li) detector) was used for the TEM investigations.

XPS data were obtained with a Perkin Elmer PHI 5000C system equipped with a hemispherical electron energy analyzer. The adventitious carbonaceous C 1s line (284.6 eV) was used as the reference to calibrate the binding energies (BEs). Prior to the XPS characterization, the Au/\(\alpha\)-Mn\(_2\)O\(_3\) catalyst was pretreated under different atmospheres as in the case of activity measurements. The diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) experiments were carried out on a Bruker Vector 22 FT-IR spectrometer equipped with a MCT detector and Harrick diffuse reflectance accessory. In situ pretreatment was performed with 30 mL min\(^{-1}\) of He, O\(_2\) or H\(_2\) at 473 K for 0.5 h, as in the case of activity measurements. Background signals from gas-phase CO were subtracted before the spectra were reported.

3. Results and discussion

3.1. Structural characterization

Fig. 1 shows the XRD patterns of various Au/\(\alpha\)-Mn\(_2\)O\(_3\) catalysts. For the samples pretreated in O\(_2\) or He, only the well-defined diffraction peaks of \(\alpha\)-Mn\(_2\)O\(_3\) (bixbyte, JCPDS 41-1442) can be identified. In contrast, additional peaks at 2\(\theta\) = 36.2\(^\circ\) and 44.4\(^\circ\) characteristic of Mn\(_3\)O\(_4\) phase emerged in the XRD pattern of the H\(_2\)-pretreated sample (Fig. 1c), indicating that a partial reduction of the parent support has occurred. In addition, no distinct Au reflections are visible in the XRD patterns of any samples, owing to the fact that the strongest reflection from gold overlaps with that of \(\alpha\)-Mn\(_2\)O\(_3\) at 2\(\theta\) = 38.2\(^\circ\) [6]. TEM was then used as a complementary technique to examine the structures of Au particles. Representative TEM images for various catalysts are shown in Fig. 2. It can be observed that for all samples, gold particles with a narrow size distribution in the range of 1–3 nm are finely dispersed on the surface of the support. The average gold particle size is estimated to be ca. 2.0, 2.0 and 1.9 nm for the samples pretreated in O\(_2\), He and H\(_2\), respectively (see Table 1), which clearly indicates that the nature of gas has a negligible effect on the gold particle size.

3.2. Chemical state and surface composition

XPS characterization was performed to investigate the chemical state of various Au/\(\alpha\)-Mn\(_2\)O\(_3\) catalysts. The Au 4f, Mn 2p and O 1s XP spectra of all three samples are presented in Fig. 3a–c, respectively. The detailed XPS parameters are summarized in Table 2. As illustrated in Fig. 3a, quantitative deconvolution of the Au 4f peaks revealed ca. 25% contribution from partially oxidized Au species (85.6 eV) [21] for the O\(_2\)-pretreated sample and the amount of positively charged gold species in the three samples decreased in the following order: O\(_2\)-Au/\(\alpha\)-Mn\(_2\)O\(_3\) > He–Au/\(\alpha\)-Mn\(_2\)O\(_3\) > H\(_2\)-Au/\(\alpha\)-Mn\(_2\)O\(_3\) (see Table 2). This indicates that conditioning in reductive atmosphere can lead to the formation of higher fraction of metallic MnO\(_4\) and \(\alpha\)-Mn\(_2\)O\(_3\).
Physicochemical properties, catalytic activities and activation energies for various Au/\(\text{Mn}_2\text{O}_3\) catalysts pretreated under different atmospheres.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>(d_{\text{ag}}) (nm)</th>
<th>(T_{50}) (K)</th>
<th>(r_{\text{av}}) (mmol\textit{CO} g\textit{Au}^{-1} s^{-1})</th>
<th>(E_a) (kJ mol^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{O}_2)-Au/(\text{Mn}_2\text{O}_3)</td>
<td>2.0 ± 0.3</td>
<td>261</td>
<td>2.97</td>
<td>24</td>
</tr>
<tr>
<td>(\text{He})-Au/(\text{Mn}_2\text{O}_3)</td>
<td>2.0 ± 0.4</td>
<td>252</td>
<td>2.31</td>
<td>19</td>
</tr>
<tr>
<td>(\text{H}_2)-Au/(\text{Mn}_2\text{O}_3)</td>
<td>1.9 ± 0.4</td>
<td>283</td>
<td>1.36</td>
<td>21</td>
</tr>
</tbody>
</table>

\(d_{\text{ag}}\) - Average gold particle size estimated by statistical analysis from TEM results.  
\(T_{50}\) - The temperature at which the conversion was 50%.  
\(r_{\text{av}}\) - The mass specific reaction rate of CO oxidation at 323 K.  
\(E_a\) - Activation energy of \(\text{CO}\) oxidation.

It may be noted that the high vacuum required for XPS and the energy of the soft X-rays could lead to the reduction of a fraction of cationic gold species [22]. Therefore, the real percentages of positive gold atoms that are present before analysis may be underestimated by XPS. Furthermore, it is worthwhile to note that it is difficult to determine the chemical state of Mn in the support, because the Mn 2p XPS spectra for the three samples in Fig. 3b show very similar Mn 2p\(_{3/2}\) peaks with the same binding energy (BE) at 641.3 eV. In addition, the extent of Mn 3s multiple splitting commonly used in the determination of Mn valences [23] cannot be obtained for the present system due to the superposition of Au 4f and Mn 3s peaks.

The surface compositions in Table 2 show that the pretreatment of \(\text{Au}/\text{Mn}_2\text{O}_3\) under \(\text{H}_2\) resulted in much smaller Au/Mn molar ratio than the treatment under \(\text{O}_2\) or \(\text{He}\), while similar Au/Mn ratios were obtained with the latter two gases. Considering the slightly smaller gold particle size of \(\text{H}_2\)-Au/\(\text{Mn}_2\text{O}_3\) (see Fig. 2 and Table 1), one possible explanation could be the partial encapsulation of Au nanoparticles by manganese oxides as a result of strong metal-support interaction (SMSI). This scenario is reinforced by the fact that the in situ DRIFT CO adsorption studies (see below) show an obviously reduced intensity for \(\text{H}_2\)-Au/\(\text{Mn}_2\text{O}_3\) as compared with other samples. Recently, by using XPS coupled with UV photoelectron spectroscopy (UPS), Guczi et al. [24] have observed a gradual decrease in the photoemission intensity for Au as opposed to Fe species upon vacuum annealing of a Au/FeO\(\text{SiO}_2/\text{Si}(100)\) model system at temperatures above 773 K. Such a phenomenon has been rationalized by migration of the partially reduced iron oxide species leading to a partial encapsulation of Au particles.

Further information can be obtained from the O 1s spectra as shown in Fig. 3c. For each sample, the O 1s spectrum contains a main peak at ca. 529.4 eV characteristic of the lattice oxygen [14] along with a distinct shoulder at ca. 531.5 eV assignable to a mixture of hydroxyl groups and adsorbed water on the surface of the catalysts [14, 25]. The peak deconvolution results as shown in Table 2 indicate a higher fraction of surface hydroxyl groups or chemisorbed water on the reductively pretreated sample compared with those pretreated in oxidative or inert atmosphere. On the other hand, the molar ratios of surface lattice oxygen (\(O_1\), 529. 4 eV) to Mn for all samples are smaller than the stoichiometric value in \(\text{Mn}_2\text{O}_3\) (1.5), inferring the presence of oxygen vacancies on the surface of the catalysts, which, however, are filled by water or hydroxyl groups. The smallest \(O_1/\text{Mn}\) ratio was detected for \(\text{H}_2\)-Au/\(\text{Mn}_2\text{O}_3\) (0.88), indicating a substantial reduction in the oxide support, in good agreement with the XRD results.

3.3. CO oxidation activity, reaction kinetics and stability

Fig. 4a displays the temperature dependence of the CO conversions for various catalysts. For comparison, the activity of the as-synthesized \(\text{Au}/\text{Mn}_2\text{O}_3\) without pretreatment is also included. It is clear that the activity of \(\text{Au}/\text{Mn}_2\text{O}_3\) is highly sensitive to the pretreatment atmosphere. Pretreatment in He or \(\text{O}_2\) led to notably improved activity as compared with the unpretreated catalyst, whereas reductive pretreatment deteriorated the activity. Of all \(\text{Au}/\text{Mn}_2\text{O}_3\) catalysts investigated, \(\text{He}-\text{Au}/\text{Mn}_2\text{O}_3\) shows the highest activity for CO oxidation. The temperature at which the conversion was 50% (\(T_{50}\)) for \(\text{He}-\text{Au}/\text{Mn}_2\text{O}_3\) is 252 K (Table 1), ca. 30 K below that for \(\text{H}_2\)-Au/\(\text{Mn}_2\text{O}_3\). On the other hand, kinetic studies showed that all catalysts have similar activation energies (\(E_a\)), as reflected by the Arrhenius plots presented in Fig. 4b. This result suggests that different pretreatment conditions do not change the reaction mechanism of CO oxidation over the \(\text{Au}/\text{Mn}_2\text{O}_3\) catalysts. It is also interesting to note that in contrast to the activity trend (light-off test) obtained from Fig. 4a, the...
and the activity loss for \( \text{H}_2 \)-Au/\( \text{Mn}_2\text{O}_3 \), on the other hand, the deactivation rate slowed down significantly afterwards, suggesting that the steady-state activity follows the decreasing trend of \( \text{O}_2 \)-Au/\( \text{Mn}_2\text{O}_3 \) and shows a much smaller reaction rate. Interestingly, the stability of the regenerated catalysts was significantly improved, with activity decayed by 89% after 120 min on stream. This is in good agreement with the XPS results. Moreover, the \( \text{H}_2 \)-pretreated sample also shows much stronger bands in the carbonate region (1200–1700 cm\(^{-1}\)) as compared with the He- or \( \text{O}_2 \)-pretreated samples, indicating promoted surface carbonate decomposition in the presence of \( \text{O}_2 \) or He. These findings are in line with the results reported by Denkwitz et al. for CO oxidation over Au/TiO\(_2\) catalyst [30], where the growth of carbonate species was found markedly suppressed in an \( \text{O}_2 \)-rich atmosphere. It is worth mentioning here that hydrogen has also been suggested to have beneficial effects in the removal of surface carbonates during CO oxidation for various gold catalysts [30,31]. However, it should be pointed out that this effect only works indirectly by producing water through hydrogen oxidation, based on the fact that water can facilitate the conversion of poisoning carbonates into thermally less stable bicarbonates [30–32].

3.4. Initial states of various catalysts

To examine the initial surface feature of various Au/\( \text{Mn}_2\text{O}_3 \) catalysts, DRIFT spectra were collected as shown in Fig. 6. It can be seen that with reductive pretreatment, the broad band at 3300–3500 cm\(^{-1}\), characteristic of molecularly adsorbed water or surface OH groups, is significantly stronger than those pretreated with oxidative and inert atmospheres. This is in good agreement with the XPS results. Moreover, the \( \text{H}_2 \)-pretreated sample also shows much stronger bands in the carbonate region (1200–1700 cm\(^{-1}\)) as compared with the He- or \( \text{O}_2 \)-pretreated samples, indicating promoted surface carbonate decomposition in the presence of \( \text{O}_2 \) or He. These findings are in line with the results reported by Denkwitz et al. for CO oxidation over Au/TiO\(_2\) catalyst [30], where the growth of carbonate species was found markedly suppressed in an \( \text{O}_2 \)-rich atmosphere. It is worth mentioning here that hydrogen has also been suggested to have beneficial effects in the removal of surface carbonates during CO oxidation for various gold catalysts [30,31]. However, it should be pointed out that this effect only works indirectly by producing water through hydrogen oxidation, based on the fact that water can facilitate the conversion of poisoning carbonates into thermally less stable bicarbonates [30–32].

3.4.2. CO adsorption studies

Fig. 7 shows the DRIFT spectra for CO adsorption on various catalysts after in situ pretreatment under different atmospheres. The adsorption of CO on \( \text{O}_2 \)-Au/\( \text{Mn}_2\text{O}_3 \) for 5 min resulted in a strong band at ca. 2108 cm\(^{-1}\) with a small shoulder at higher frequency of ca. 2123 cm\(^{-1}\). The former band is generally attributed to CO adsorption on negatively polarized gold species (Au\(^{\text{IV}}\)-CO) [33,34], while the latter is associated with CO adsorption on positively polarized gold species (Au\(^{\text{II}}\)-CO), which most likely result from the spillover of oxygen or OH groups from the support onto the Au nanoparticles [27,35]. Such CO

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**Table 2**

XPS results of various Au/\( \text{Mn}_2\text{O}_3 \) catalysts pretreated under different atmospheres.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>BE of Au(^{4f})/( \text{eV} )</th>
<th>BE of Mn(^{2p})/( \text{eV} )</th>
<th>( \text{OH} + \text{H}_2\text{O} )/( % )</th>
<th>Au/( % )</th>
<th>O/( \text{Mn} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{O}_2 )-Au/( \text{Mn}_2\text{O}_3 )</td>
<td>83.9</td>
<td>641.4</td>
<td>35</td>
<td>0.093</td>
<td>1.45</td>
</tr>
<tr>
<td>( \text{He} )-Au/( \text{Mn}_2\text{O}_3 )</td>
<td>84.0</td>
<td>641.4</td>
<td>36</td>
<td>0.091</td>
<td>1.30</td>
</tr>
<tr>
<td>( \text{H}_2 )-Au/( \text{Mn}_2\text{O}_3 )</td>
<td>83.9</td>
<td>641.3</td>
<td>54</td>
<td>0.082</td>
<td>0.88</td>
</tr>
</tbody>
</table>

\(^{a}\) Proportion of \( \text{OH} \) groups and chemisorbed \( \text{H}_2\text{O} \) estimated from the O 1s spectra. \(^{b}\) \( \text{O}_2 \)/\( \text{Mn}_2\text{O}_3 \) surface lattice oxygen.
adsorption bands have also been observed on the Au/TiO2 [36] and Au/CeO2 [5] catalysts under similar conditions.

As compared with the O2-pretreated sample, the Au0–CO band is considerably weaker on He–Au/α-Mn2O3. This observation indicates less presence of defective gold sites on the He-pretreated sample. CO adsorption was also performed on the regenerated He–Au/α-Mn2O3. It is interesting to find that the intensity of the Au3+–CO band increased notably, with that of the Au0–CO band almost unaltered as compared with that of the fresh He–Au/α-Mn2O3. An increase in the positively charged gold sites can be understood by the fact that excess oxygen is present under reaction conditions. The H2–Au/α-Mn2O3 sample shows the weakest CO adsorption at 2101 cm⁻¹ along with a shoulder at lower frequency of 2087 cm⁻¹. This shoulder peak could be ascribed to CO adsorption on negatively charged gold species (Au3+–CO). Bands in a similar region have also been reported by Boccuzzi et al. [26] in a study of CO adsorption on a prereduced Au/TiO2 sample, in addition to the “normal” peak at 2100 cm⁻¹. This distinct feature was proposed to arise from the reduction of the support by H2 with transferring negative charge to the gold particles [26], which leads to an increased back-donation and hence to a weakening of the C–O bond.

3.4.3. State of the catalysts during CO oxidation reaction

The accumulation of adsorbed surface species on various catalysts during CO oxidation reaction was also followed by in situ DRIFT measurements. Fig. 7 illustrates the evolution of the full spectra recorded on O2–Au/α-Mn2O3 during the reaction, with the enlarged details of the carbonate and CO2/CO regions being presented in Fig. 8b–d. The spectra reveal the characteristic peaks of Au3+–CO at 2115 cm⁻¹, the bands of gaseous CO2 at 2340 and 2360 cm⁻¹ and a set of broad bands in the range of 1200–1750 cm⁻¹. The bands at 1517, 1338, 1480 and 1380 cm⁻¹ are commonly assigned to the C=O, asymmetric O–C–O stretch vibration of bidentate carbonates, the symmetric and asymmetric O–C–O stretch vibration of monodentate carbonates [37], respectively. It is important to remark that the general features were
similar for all samples, while the characteristic frequencies and the intensities as well as their evolution during reaction were appreciably different. For instance, the CO related peaks appear at 2113 and 2115 cm\(^{-1}\) on the H\(_2\)-Au/\(\alpha\)-Mn\(_2\)O\(_3\) and He-Au/\(\alpha\)-Mn\(_2\)O\(_3\) catalysts, respectively. In all cases, over the investigated time scale, the location of the Au\(^0\)-CO peak remains constant. Moreover, the general shapes of CO/CO\(_2\) related peaks did not change with time, indicating that the nature of adsorbed CO species and thus of the adsorption sites were not modified by the reaction [30].

The integrated intensity of CO, CO\(_2\) and carbonate-related peaks for various Au/\(\alpha\)-Mn\(_2\)O\(_3\) samples are plotted as a function of time as shown in Fig. 9. The CO and carbonate-related peaks for each sample increased significantly during the first few minutes and then slowly approached a steady state. The intensity of the carbonate related peaks for H\(_2\)-Au/\(\alpha\)-Mn\(_2\)O\(_3\) was much weaker than that of He-Au/\(\alpha\)-Mn\(_2\)O\(_3\). The strongest carbonate peaks were found on O\(_2\)-Au/\(\alpha\)-Mn\(_2\)O\(_3\), the intensity of which, however, was exceeded by that of He-Au/\(\alpha\)-Mn\(_2\)O\(_3\) after 60 min. The CO adsorption peak on O\(_2\)-Au/\(\alpha\)-Mn\(_2\)O\(_3\) was much stronger than those on the H\(_2\)-Au/\(\alpha\)-Mn\(_2\)O\(_3\) and He-Au/\(\alpha\)-Mn\(_2\)O\(_3\) catalysts. As for CO\(_2\) peak evolution, the intensity decreases in the order of O\(_2\)-Au/\(\alpha\)-Mn\(_2\)O\(_3\) > He-Au/\(\alpha\)-Mn\(_2\)O\(_3\) > H\(_2\)-Au/\(\alpha\)-Mn\(_2\)O\(_3\). In general, the evolution trend of the intensity closely resembled that of the deactivation curve as reported above.

3.5. Discussion

3.5.1. Influence of pretreatment atmosphere on the initial activity

Results obtained in this study clearly demonstrate that the pretreatment atmosphere has a significant influence on both structural and catalytic properties of the Au/\(\alpha\)-Mn\(_2\)O\(_3\) system in CO oxidation. Pretreatment in inert atmosphere, i.e., He, leads to a gold catalyst with the highest initial activity, which, however, suffers the most severe deactivation with time on stream. In contrast, oxidative pretreatment affords the most stable catalyst while maintaining high activity. The trend of the initial activity for differently pretreated catalysts follows the order of He-Au/\(\alpha\)-Mn\(_2\)O\(_3\) > O\(_2\)-Au/\(\alpha\)-Mn\(_2\)O\(_3\) > H\(_2\)-Au/\(\alpha\)-Mn\(_2\)O\(_3\), which obviously cannot be simply correlated to the variation of either the oxidation state or the particle size of gold. In fact, XPS results suggested the presence of higher fraction of cationic gold species in the O\(_2\)-Au/\(\alpha\)-Mn\(_2\)O\(_3\) catalyst and TEM images revealed very similar sizes of the gold particles irrespective of the pretreatment conditions.

One possible reason for the different activities of Au catalysts with a similar particle size is the varied Au crystal shapes that resulted from pretreatment under different atmospheres. It is generally accepted that the amount of low-coordinated Au atoms, the key sites for the adsorption and activation of O\(_2\) or CO, depends on both size and shape of the particle [38]. The importance of morphology for Au nanoparticles to obtain a high activity in CO oxidation has been underlined by both theoretical and experimental studies [38–41]. In the present work, although we have no direct evidence on the difference in Au morphology, the variation in the nanoscale Au structures induced by different pretreatments could be inferred from the IR spectra of CO adsorption on the Au/\(\alpha\)-Mn\(_2\)O\(_3\) catalysts. As shown in Fig. 7, the CO adsorption peak is much weaker on inertly or reductively pretreated Au/\(\alpha\)-Mn\(_2\)O\(_3\) samples, indicating less exposure of defective gold sites with respective to the O\(_2\)-Au/\(\alpha\)-Mn\(_2\)O\(_3\) sample. This fact may account for the lowest activity of H\(_2\)-Au/\(\alpha\)-Mn\(_2\)O\(_3\) (although in this case the partial encapsulation of Au clusters by partially reduced support may also play a role in blocking the active gold sites as stated in Section 3.2), but cannot explain the highest initial activity of He-Au/\(\alpha\)-Mn\(_2\)O\(_3\).

Another likely interpretation is related to the surface properties of the support oxide concerning the concentration of oxygen vacancies modified by surface pretreatments. The participation of oxygen vacancies on reducible supports in CO oxidation with Au catalysts was proposed by various groups [42–46]. Applying the technique of quantitative temporal analysis of products (TAPs), Widmann et al. [45] demonstrated that a freshly calcined Au/\(\beta\)-CeO\(_2\) is only slightly active for CO oxidation and the activity is significantly increased on the removal of about 7% of the surface oxygen, whereas overreduction leads to a lower initial activity. They proposed that the surface oxygen vacancies play an important role in activating the CO oxidation reaction on ceria-supported Au catalysts. As for the Au/\(\alpha\)-Mn\(_2\)O\(_3\) system in the present study, the highest activity achieved by He-pretreatment may be explained in the same manner. It is reasonable that an optimal amount of surface oxygen vacancies was produced by mild He-pretreatment. In contrast, for the sample pretreated in H\(_2\), the Mn\(_2\)O\(_3\) support was overreduced into manganese oxides with lower valence states, leading to deteriorated activity. This assumption is corroborated by the XPS results with respect to the O\(_{\text{L}}$/Mn ratio (see Table 2)
as well as the XRD pattern (see Fig. 1) of H2–Au/\(\alpha\)-Mn2O3, which clearly indicated the presence of Mn3O4 phase.

3.5.2. Influence of pretreatment atmosphere on the stability

It has been proposed that two main factors may contribute to the deactivation of Au catalysts in CO oxidation, i.e., the growth of gold particle size induced by the exothermic nature of the reaction and the accumulation of carbonates blocking the active sites [30,31,47–49]. Recently, on investigating the effect of reaction atmospheres on the catalytic performance of a set of unconditioned Au/TiO2 catalysts, Denkwitz et al. [30] suggested that the dominant reason for the deactivation of Au/TiO2 is not due to the reaction-induced growth of the very small Au particles (ca. 1.3–1.8 nm), but rather the buildup of surface carbonates on the support during reaction. More recently, by monitoring three activation-deactivation cycles of a Au/MgO catalyst by in situ IR, Hao et al. [48] have shown that the buildup of carbonate-like species on gold particles rather than on the oxide support is responsible for the deactivation. As for the differently pretreated Au/\(\alpha\)-Mn2O3 catalysts in the present study, investigation by means of in situ DRIFTS clearly shows that substantial amount of surface carbonate species is produced during the reaction, especially for the He–Au/\(\alpha\)-Mn2O3 and O2–Au/\(\alpha\)-Mn2O3 catalysts (Fig. 9). While the rapid deactivation of the He–Au/\(\alpha\)-Mn2O3 catalyst can be well understood by the continuous accumulation of carbonate-like species, we emphasize that the present DRIFTS data do not provide an explanation for the marginal activity loss of the O2–Au/\(\alpha\)-Mn2O3 sample. Moreover, it is noteworthy that the deactivated He–Au/\(\alpha\)-Mn2O3 catalyst could be regenerated to a large extent along with an even improved stability. All these results strongly suggest that apart from the carbonate accumulation, other factors may also play a crucial role in controlling the deactivation behaviour of the Au/\(\alpha\)-Mn2O3 catalyst.

It has been reported that the pretreatment of Au/TiO2 catalyst in oxidative atmosphere can lead to the formation of positive gold species affording a stronger metal–support interaction and better stability against sintering [18]. In addition, a recent model study on the nucleation of Au clusters on TiO2(110) surfaces showed a much stronger Au oxide–support adhesion on O-rich Au–support interfaces [50]. Accordingly, based on the results of XPS analysis (Table 2), it is reasonable to speculate that the pretreatment of Au/\(\alpha\)-Mn2O3 sample in the oxidative atmosphere could also lead to the formation of an oxygen-rich Au–support interface bearing strong bonding strength, which is a likely reason for the superior stability of O2–Au/\(\alpha\)-Mn2O3. Indeed, our XPS results clearly indicate that the O2-pretreated O2–Au/\(\alpha\)-Mn2O3 sample is featured with the largest fraction of positively charged gold species. Moreover, the improved stability of the regenerated He–Au/\(\alpha\)-Mn2O3 can also be well understood based on the fact that oxygen is present in an excess amount in the reactant gas. This is further confirmed by the enhanced signals of the cationic gold species after regeneration, as revealed by the CO adsorption data in Fig. 7.

At this juncture, it is also interesting to point out that there are greater activity differences between catalysts as a function of time on stream (up to about 2 h) than the differences seen between the catalysts as a result of different pretreatments. Notably, the former involve factors of up to 5–6, whereas the latter involve factors of up to only three at the most (see Fig. 5a). The fact that an even larger difference could be identified in the final steady activity allows concluding that the surface pretreatment can have profound influence on the intrinsic activity of the Au/\(\alpha\)-Mn2O3 system. Such catalytic characteristic could be of great importance for a potential practical application. While further work is needed to fully understand such a remarkable pretreatment-dependent catalytic behaviour, it is important to remark that the steady activity can be well correlated to the significant differences in the corresponding COad.

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**Fig. 8.** Sequence of in situ DRIFT spectra recorded during CO oxidation on H2–Au/\(\alpha\)-Mn2O3 (reaction times: 2, 10, 20, 60 and 120 min). (a) full spectra, (b) enlarged details of the carbonate region, (c) enlarged details of the C–O stretch region characteristic for CO adsorption and (d) enlarged details of the C–O stretch region characteristic for CO2.
pretreatment under different atmospheres, we would like to comment on the intensity of adsorbed CO (see Fig. 9b). Similar correlations have also been adopted by Denkwitz et al. to explain the evolution trend of the activity of Au/TiO2 catalyst in CO oxidation [30]. In other words, the steady state activity is mainly determined by the amount of the active gold sites available for CO adsorption.

Although the main purpose of this paper was to present a detailed investigation of the structural variation of both Au and \(\alpha\)-Mn2O3 phases in the specific Au/\(\alpha\)-Mn2O3 catalyst system upon pretreatment under different atmospheres, we would like to comment on the practical implications of the present results. It is well known that many supported metal nanoparticles, such as Cu [51], Pt [52], Pd [53] and Rh [54], can undergo substantial geometric/electronic changes when treated in oxidative or reductive atmosphere at moderate temperatures. In the specific case of supported gold nanoparticles, such geometric/electronic variations may also occur upon various pretreatments, thus leading to greatly modified catalytic properties. While it is not yet possible to achieve a complete understanding of the catalytic origin and the very nature of the Au species for CO oxidation [55,56], results obtained in this study indicate that the pretreatment–dependent catalytic behaviour of the Au/\(\alpha\)-Mn2O3 system arises largely from the structure-sensitivity of the metal–support interface. We believe that this rationalization may be readily extended to gold supported on other reducible oxides [3–5], over which significantly discrepant catalytic activities have been frequently identified with even the same composition or similar Au particle size. This highlights new opportunities in the development of highly active and stable Au-based catalysts for a range of catalytic applications.

4. Conclusions

In this study, the effect of the pretreatment atmosphere on the structural and catalytic properties of the Au/\(\alpha\)-Mn2O3 system in the low temperature CO oxidation reaction was investigated. TEM results showed that the pretreatment atmosphere had a negligible effect on the gold particle size distribution, while XPS revealed a higher fraction of positively charged gold species in the catalyst pretreated with \(\text{O}_2\). It is proposed that the highest initial activity obtained on He–Au/\(\alpha\)-Mn2O3 is due to the moderate formation of surface oxygen vacancies prior to the reaction, while the over-reduction of the oxide support evidenced by XRD may account for the lowest activity of \(\text{H}_2\text{–Au}/\alpha\text{-Mn}_2\text{O}_3\). As compared with the He-pretreated sample, the superior stability of \(\text{O}_2\text{–Au}/\alpha\text{-Mn}_2\text{O}_3\) has been attributed to its enhanced metal–support synergy rather than suppressed accumulation of carbonate-like surface species as revealed by in situ DRIFTS studies.

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