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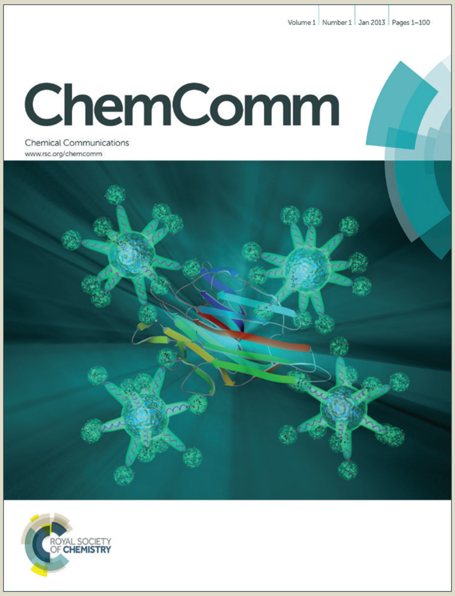

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COMMUNICATION

La-doped Al_2O_3 Supported Au Nano-particles: A Highly Active and Selective Catalyst for PROX at PEMFC Operation Conditions

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A La-doped γ-Al_2O_3 supported Au catalyst shows high activity and selectivity for the PROX reaction at PEMFC operation conditions. The superior performance is attributed to the formation of $LaAlO_3$, which suppresses H_2 oxidation and strengthens CO adsorption on Au sites, thereby improves competitive oxidation of CO at elevated temperature.

The proton-exchange membrane fuel cells (PEMFCs) have aroused extensive interest due to their efficiency in clean energy conversion.[1] However, one of the major barriers to the commercialization of PEMFC is that small amount of residual CO in the H_2 stream poisons the anode and thus decreases the PEMFC performance.[2] Preferential oxidation of CO in H_2-rich stream (PROX) is regarded as the most promising solution.[3]

Compared with other catalysts,[4] supported Au catalysts seem to be the most suitable and promising one for PROX reaction because they are highly active for CO oxidation[5, 6] at low-temperature but less active for H_2 oxidation.[5a] However, for the PROX reaction on supported Au catalysts, a big issue is that the CO conversion decreases dramatically with temperature rise due to the competitive oxidation of H_2,[6] especially in the presence of H_2O and CO_2. This performance will seriously limit the application of supported Au catalysts to PROX reaction at PEMFC operation conditions (50 ~ 100 °C in the presence of H_2O and CO_2). In fact, to the best of our knowledge, there have been no reports so far to realize CO total conversion on supported Au catalyst at PEMFC operation conditions except an Au/Fe_2O_3 catalyst[7] that showed 99.5% CO conversion. It is therefore highly desirable to develop more selective gold catalysts that show total conversion of CO at PEMFC operation conditions.[8]

Alumina supported gold catalysts have shown potential application in the PROX reaction because the presence of H_2 or water vapor could accelerate the CO oxidation rate and effectively inhibit the deactivation of the catalysts.[9] Moreover, alumina is one of the most used commercial supports owing to its high surface area, thermal stability, mechanical strength, etc., which make the alumina supported Au catalyst more practical and attractive. However, although alumina supported Au catalysts were found active enough for the PROX reaction,[10] their selectivity at elevated temperature is extremely low. Modification with oxides could improve the CO_2 selectivity,[11] while the CO conversion was still far from the desired target.[12]

In this communication, we reported a La-doped γ-Al_2O_3 (denoted as LA-Al_2O_3) supported Au catalyst which was not only highly active for the PROX reaction but also gave total CO conversion in a wide temperature range, even with the presence of H_2O and CO_2. To our knowledge, this is the best result reported so far for PROX over supported gold catalysts. Further studies revealed that the enhanced CO adsorption strength and the significantly decreased H_2 oxidation rate caused by the doping of La accounted for the promoted performance.

The LA-Al_2O_3 support was prepared by incipient wetness impregnation of γ-Al_2O_3 with $La(NO_3)_3$ solution followed by calcination at 850 °C for 4 h. Au targeted at 1 wt% was deposited on both γ-Al_2O_3 and LA-Al_2O_3 supports with an adsorption method, and the residual Cl^- anions were subsequently removed by washing with ammonia solution and deionized water (details see Supplementary Information). After drying at 80 °C in air for 12 h, the catalysts were further reduced with H_2 at 300 °C for 1 h prior to the reaction tests. The resultant Au/γ-Al_2O_3 and Au/LA-Al_2O_3 have an actual Au loading of 0.67 wt% and 0.82 wt%, respectively, which were lower than the target value due to gold loss in adsorption process. On the other hand, the slightly higher Au loading obtained with LA-Al_2O_3 than un-doped Al_2O_3 suggests that the former support has more adsorption sites for gold, which was most probably due to the higher isoelectric point originated from the doping of La.[13]

The BET surface area (Table S1) of the Au/LA-Al_2O_3 is 107 $m^2\ g^{-1}$, which is smaller than that of Au/Al_2O_3 (140 $m^2\ g^{-1}$) due to the doping of La (13.2 wt% by weight). The XRD patterns of the two catalysts did not show any gold species (Fig. S1), suggesting that either the gold loading was too low or the gold nano-particles were too small to be detected by XRD measurement. On the other hand, $LaAlO_3$ crystal phase in the Au/LA-Al_2O_3 was formed as a consequence of La doping and the subsequent calcination at high temperature. The X-ray absorption near-edge structure spectra

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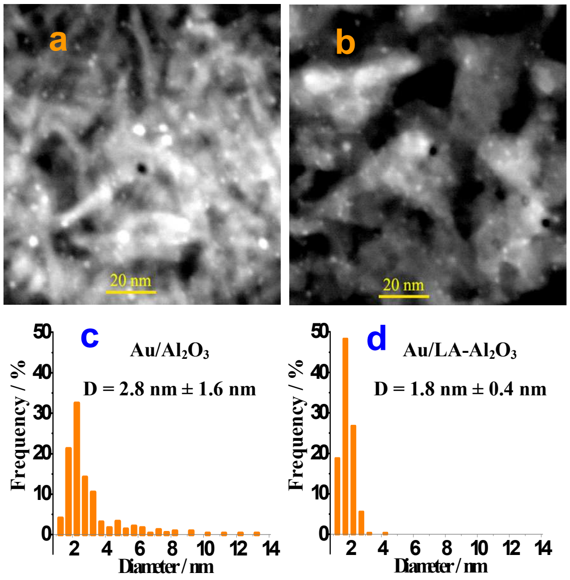

Fig. 1 HAADF-STEM images of Au/Al_2O_3 (a) and Au/LA-Al_2O_3 (b) and their Au particle size distribution (c, d)

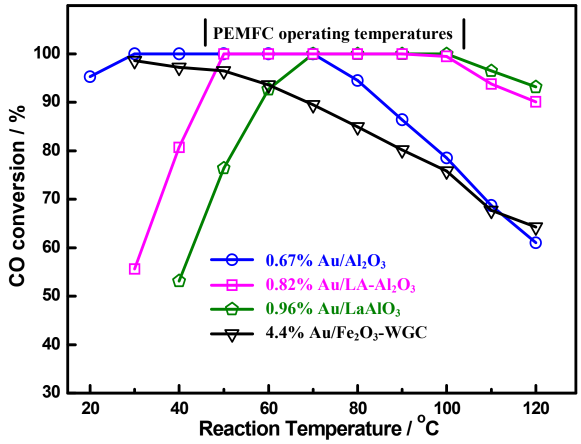

Fig. 2 CO conversions as a function of the reaction temperature Reaction conditions: 1 vol% CO + 1 vol% O_2 + 40 vol % H_2 and balance He. Weight hourly space velocity (WHSV): 60,000 mL g_{cat}^{-1} h^{-1}.

indicate that gold in both samples exists mainly as Au^0 (Fig. S2).

The size of gold nano-particles is one of the most important features that determine the catalyst performance. Therefore, we further examined the samples with scanning transmission electron microscopy (STEM) and some typical images and their Au nanoparticle size distributions are presented in Fig. 1 and Fig. S3 - S5. The low magnification images (Fig. S3) showed that there were nearly no large Au particles (>10 nm) on Au/Al_2O_3 and the gold particles were relatively uniform in size distribution. However, the high magnification images revealed that in some areas the Au nano-particles were uniform in size (Fig. S4a, 4c, 4e), while in other areas (Fig. 1a, Fig. S4b, 4d, 4f) the size distribution of Au nano-particles was non-uniform. On the other hand, for the Au/LA-Al_2O_3 sample, the low magnification images (Fig. S5a, 5b) showed that the Au nano-particles larger than 5 nm were not observed and the high magnification images (Fig. 1b and Fig. S5c - 5f) showed that the Au nano-particles were much uniform in size distribution compared with that of the Au/Al_2O_3. Fig.1d also clearly showed that the particles size distribution in the Au/LA-Al_2O_3 was fairly uniform with mean size of 1.8 nm.

Figure 2 illustrates profiles of CO conversions as a function of reaction temperatures over the catalysts at a high space velocity (60,000 ml g_{cat}^{-1} h^{-1}). As a standard catalyst to benchmark the activity measurement system, a 4.4 wt% Au/Fe_2O_3-WGC catalyst provided by World Gold Council (WGC) was tested firstly. It gave a CO conversion of 98 % at 30 °C that decreased gradually with elevating the reaction temperature due to competitive oxidation of H_2 with O_2. The Au/Al_2O_3 sample, with only 0.67 wt% Au loading, however, was highly active and selective for the PROX reaction and gave a 100% CO conversion at a temperature window of 30 - 70 °C. More importantly, with introduction of La dopant, the window for CO total conversion shifted to higher temperature and further expanded to 50 - 100 °C, the typical PEMFC operating temperature range, showing an improved selectivity (Fig. S6). In contrast, Au/$LaAlO_3$ catalyst was less active at low temperatures and showed a much narrower temperature window. Compared with other supported gold catalysts reported previously (Table S2), the Au/LA-Al_2O_3 catalyst was actually the best, even with the co-presence of H_2O and CO_2. The stability test showed that the Au/LA-Al_2O_3 catalyst was rather stable over 1200 min run without the presence of CO_2, but adding high concentration of 20 vol% CO_2 made it deactivate gradually for carbonates accumulation[14a] on the catalyst (Fig. S7).

To figure out how the doping of La and the formation of $LaAlO_3$ improved the CO conversion at elevated temperatures, the reaction rates were tested and summarized in Table 1. For Au/Al_2O_3 catalyst, as expected, it was intrinsically more active for the oxidation of H_2 (2.24 mmol g_{Au}^{-1} s^{-1}) than CO (1.95) in the individual oxidation tests, even with the same concentration of H_2 and CO (2 vol%). With a higher concentration of 40 vol%, the specific rate for H_2 oxidation could reach 14.21 mmol g_{Au}^{-1} s^{-1}, which was much higher than that of CO. Thus, when this sample was subjected to the PROX reaction, although the CO activity was significantly enhanced by the presence of H_2 and the H_2 activity was greatly inhibited by the presence of CO, it still gave a comparable H_2 and CO activity (2.37 v.s. 3.89), suggesting that a competitive oxidation of H_2 tends to occur. In contrast, the Au/LA-Al_2O_3 sample was intrinsically less active for H_2 oxidation than for CO oxidation (0.71 v.s. 1.43). Even with 40 vol% H_2, the activity for H_2 oxidation was only slightly higher than for CO oxidation. When subjected to PROX reaction, the CO oxidation activity was also enhanced by the presence of H_2 (from 1.43 to 3.28) and the H_2 oxidation activity was inhibited and was only about one third that of the CO, indicating a less

Table 1 CO and H_2 oxidation specific rates on various samples for the PROX reaction (PROX) and for CO and H_2 individual oxidation (OX) at 80 °C

Samples	Specific rates (mmol g_{Au}^{-1} s^{-1})				
	H_2 (OX)[a]	H_2 (OX)[b]	CO (OX)[c]	H_2 (PROX)[d]	CO (PROX)[d]
0.67 wt% Au/Al_2O_3	2.24	14.21	1.95	2.37	3.89
0.82 wt% Au/LA-Al_2O_3	0.71	2.70	1.43	0.96	3.28
0.96 wt% Au/$LaAlO_3$	0.02	0.38	0.48	0.14	0.52
4.4 wt% Au/Fe_2O_3[e]	--	--	--	--	0.22

[a] Feed gas: 2 vol% H_2 + 2 vol% O_2 balance He; [b] 40 vol% H_2 + 2 vol% O_2 balance He; [c] 2 vol% CO + 2 vol% O_2 balance He; [d] 40 vol% H_2 + 2 vol% CO + 0.4 vol% O_2 balance He; [e] Cited from Ref. 4f.

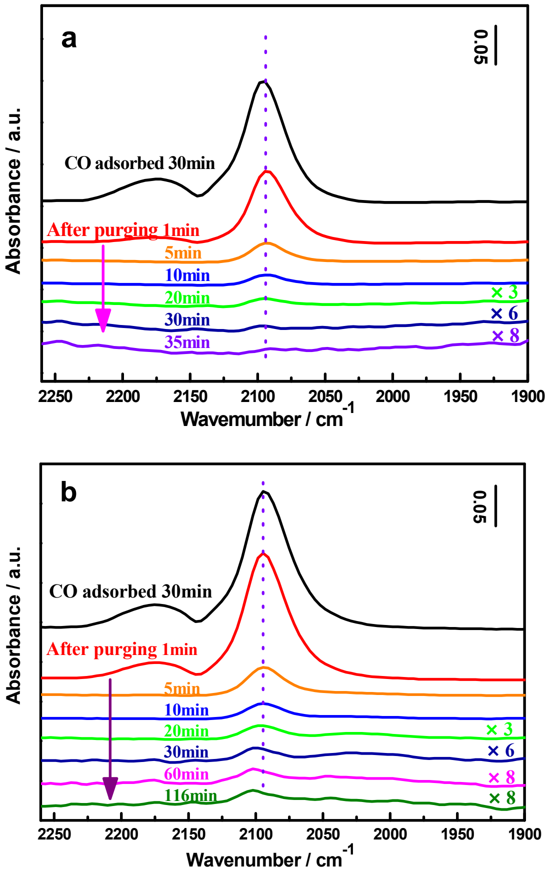

Fig. 3 In situ DRIFTS spectra of CO adsorption on Au/Al_2O_3 (a) and $Au/LA\text{-}Al_2O_3$ (b) at 80 °C and then purged with 40 vol% H_2-He

competitive oxidation of H_2. Since the difference mainly came from the La doping and subsequently the formation of $LaAlO_3$ on Al_2O_3 between these two samples, it is reasonable to conjecture that the intrinsic lower activity of H_2 oxidation originates from the $LaAlO_3$ support. We therefore tested the $Au/LaAlO_3$ sample and the results showed that the activity for H_2 oxidation (0.02 mmol g_{Au}^{-1} s^{-1}) was one order of magnitude lower than that for CO oxidation (0.48). Even with 40 vol% H_2, the reaction rate for H_2 oxidation was still lower than that of CO oxidation. This result clearly demonstrates that the doping of La, by the formation of $LaAlO_3$ on Al_2O_3, significantly suppressed the H_2 oxidation on $Au/LA\text{-}Al_2O_3$, giving rise to a less competitive oxidation of H_2 in PROX reaction.

In addition to limiting the H_2 oxidation, doping of La on the Al_2O_3 support also changed CO adsorption strength on Au. As shown in Fig. 3, after 30 min CO adsorption at 80 °C, a band centered at ~2098 cm^{-1} was observed on both Au/Al_2O_3 and $Au/LA\text{-}Al_2O_3$ which can be ascribed to the CO adsorption on small Au nano-particles.[14b] Upon purging with 40% H_2/He gas, the CO band decreased gradually with the purging time on both samples. However, as shown in Fig. S8 the ratio of the residual peak intensity to that of the original one on the $Au/LA\text{-}Al_2O_3$ was always higher than that on the Au/Al_2O_3 at the same purging time. Furthermore, on the Au/Al_2O_3 sample the CO adsorption band vanished after 35 min purge while on $Au/LA\text{-}Al_2O_3$ sample the band maintained even after about 120 min. This result provides solid evidence that the adsorption of CO was stronger on $Au/LA\text{-}Al_2O_3$ than that on Au/Al_2O_3. Similarly, the CO adsorption on $Au/LaAlO_3$ catalyst was also stronger than that on the Au/Al_2O_3 sample as shown in Fig. S9. These results indicate clearly that the formation of $LaAlO_3$ on Al_2O_3 enhanced the CO adsorption strength on $Au/LA\text{-}Al_2O_3$, thus promoted CO competitive oxidation in H_2-rich stream at elevated temperatures.

In summary, we have developed a La-doped γ-Al_2O_3 supported Au catalyst, which was not only highly active for PROX reaction but also showed a wide temperature range for the total conversion of CO, even with the presence of H_2O and CO_2. It was suggested that the introduction of La, by forming $LaAlO_3$ on Al_2O_3, could strengthen the CO adsorption on Au meanwhile significantly decrease the intrinsic activity for H_2 oxidation, giving rise to the enhancement of competitive oxidation of CO at PEMFC operation conditions. The commercial Al_2O_3 support and the lower Au loadings would make it more practical and may have great potential application.

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