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A comparative study of ceria-supported gold and copper oxide catalysts for preferential CO oxidation reaction

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Abstract

In this paper we compare the catalytic performance of ceria-supported gold and copper oxide catalysts for the preferential CO oxidation (PROX) in the presence of excess hydrogen. The catalytic properties are strongly affected by the synthesis procedure, i.e. deposition–precipitation (DP) and modified deposition–precipitation (MDP), mainly in the case of gold. The DP method leads to the preparation of more active PROX catalysts than the MDP one. Highly dispersed and more easily reducible gold or copper oxide species are formed on the catalyst surface and enhance the catalytic activity. Au/ceria catalysts are significantly more active, while CuO/ceria ones are remarkably more selective. The presence of CO_2 and H_2O causes a significant decrease in the catalytic activity, especially in the case of the gold catalyst. However, this deactivation is fully reversible. Both catalysts exhibit a perfectly constant behaviour with the reaction time.

Keywords: Copper oxide; Gold catalysts; Ceria; Deposition–precipitation method; Hydrogen; Preferential CO oxidation; PROX

1. Introduction

The development of efficient catalysts for the preferential CO oxidation has become an important research topic during the last decade due to their application in H_2-fuelled solid polymer fuel cell (SPFC) systems. In order to avoid technical problems associated with the use of pure H_2, especially in vehicle applications, a H_2-rich gas mixture can be obtained from liquid fuels such as methanol or natural gas, via a fuel processor. The gas mixture produced from the steam reforming and water gas shift processes contains 0.5–2 vol.% CO, which degrades the fuel cell performance and its concentration should be reduced to less than 10 ppm [1,2]. The catalytic preferential CO oxidation with molecular oxygen, i.e. the PROX reaction, is the simplest and most cost effective method for removing CO from H_2-rich fuels [1]. An efficient PROX catalyst must fulfill three important requirements: (i) high oxidation rate, (ii) high selectivity with respect to the undesired H_2 oxidation side reaction and (iii) stability with reaction time.

Various catalytic systems have been proposed in the literature for the preferential CO oxidation reaction. Most of the reports are related to Pt group metal-based catalysts [3–7]. The only drawback of these systems is that they cannot avoid significant losses of H_2 due to oxidation. On the other hand, highly dispersed Au nanoparticles supported on selected reducible metal oxides such as Fe_2O_3, MnO_x, TiO_2 and CeO_2 [7–15], were found to be superior than Pt group catalysts, since they are able to remove CO from reformed fuels with an extraordinarily high oxidation rate and a better selectivity at much lower temperatures, ca. <100 °C. However, the presence of both CO_2 and H_2O lowers the CO conversion, especially in the lower temperature region [7,8,11,13]. In what concerns the catalyst deactivation with reaction time, Au/ceria catalysts were found to be quite stable [8,13], in contrast with other gold catalysts, such as Au/Fe_2O_3 [7,9] or Au/TiO_2 [16], which lost a significant portion of their initial activity during the first hours of reaction. A few papers have studied selective CO oxidation activity of Au/ceria catalysts [8,12,13]. Panzera et al. have reported that calcination of an Au/ceria catalyst prepared by coprecipitation significantly enhances CO conversion with a selectivity of about 40% in any reaction condition [8]. Deng et al. have pointed

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out the role of cationic gold on PROX activity of low content (<0.6 at.%) gold–ceria catalyst [12]. Luengnaruemitchai et al. have used coprecipitation, impregnation and sol–gel methods for the preparation of 1% Au/ceria catalyst [13].

CuO–CeO_2 catalysts have been also proposed as one of the best candidates for the preferential removal of CO from reformed fuels [1,17–23]. These catalysts are able to operate in a temperature range of 100–200 °C with almost ideal selectivity. They are also very stable under reaction conditions and can tolerate high concentrations of CO_2 and H_2O. Compared to the Pt group-based catalysts, they exhibit superior activity and selectivity [7]. That high catalytic activity was attributed to the strong interaction between the copper oxide nanoparticles and ceria [24]. High oxygen mobility and redox properties of ceria can enhance the catalytic performance of copper oxide in CO oxidation reaction, since additional active sites, generated from oxygen vacancies, are formed at the interface of two phases [1,19–24]. Various additives, such as samaria, lanthana or zirconia have been incorporated in Cu–Ce oxide catalysts in order to improve their performance in PROX reaction [21,22].

The aim of the present work is the comparative study of gold and copper oxide catalysts supported on ceria for the CO abatement from realistic H_2-rich fuels by preferential oxidation. The catalysts were prepared by two different methods: deposition–precipitation and modified deposition–precipitation. Some of us have recently reported on the effect of the synthesis procedure on the physicochemical properties of these catalysts with respect to their catalytic performance in the WGS reaction [25]. In this paper, we compare, under realistic reaction conditions, the catalytic activity and selectivity of these catalysts in the PROX reaction. The deactivation in the presence of CO_2 and H_2O is also investigated and the reason for the decrease of activity is discussed.

2. Experimental

Au/ceria and CuO/ceria catalysts were prepared via two different techniques, namely the deposition–precipitation (DP) and a modified version of the deposition–precipitation (MDP) method. The difference between the two methods lies on the type of ceria employed, i.e. precalcined ceria in the DP method and freshly precipitated cerium hydroxide in the MDP method. Details of the preparation procedures and characterization techniques (N_2 physisorption, XRD, HRTEM, FTIR and H_2–TPR) have been reported elsewhere [25]. Either gold or copper oxide loading for each catalyst was 3 wt.%, on the basis of our previous investigations [25,26]. Depending on the preparation method, the samples are labelled as AuCeDP, CuCeDP and AuCeMDP, CuCeMDP.

The preferential CO oxidation reaction was carried out in a conventional fixed-bed reactor system, which has been described previously [1,18]. Prior to all catalytic tests, the samples were heated in a flowing 20 vol.% O_2/He mixture at 400 °C for 30 min as a standard pretreatment, in order to yield clean surfaces. The catalyst weight was 50–120 mg and the total flow rate of the reaction mixture was 50–100 $cm^3\ min^{-1}$, yielding contact times (*W/F*) in the range of 0.03–0.144 $g\ s\ cm^{-3}$. The feed contained 1 vol.% CO, 1.25 vol.% O_2, 50 vol.% H_2, 0–15 vol.% CO_2, 0–10 vol.% H_2O and He as balance. Product and reactant analysis was carried out by a gas chromatograph (Shimadzu GC-14B) equipped with a TCD. Both CO hydrogenation and water-gas shift reactions were found to be negligible at temperatures less than 250 °C.

3. Results and discussion

The structural and morphological properties of ceria-supported gold and copper oxide catalysts were investigated and discussed in detail in a previous paper by Tabakova et al. [25]. Characterization by several techniques (N_2 physisorption, XRD, XPS, FTIR, HRTEM and H_2–TPR) revealed that the deposition–precipitation method is more suitable than the modified one for the preparation of active WGS ceria-supported catalysts, because it allows a larger fraction of nanosized gold and copper species to be exposed on the catalytic surface. It was found that copper oxide is highly and uniformly dispersed on both CuCeDP and CuCeMDP catalysts. On the other hand, the presence of highly dispersed gold clusters (average size of ∼1 nm) was revealed only in the case of the AuCeDP catalyst, while large agglomerates (average size of ∼15 nm) of gold particles were observed in the AuCeMDP catalyst. TPR studies indicated that the DP method results in the formation of more easily reducible copper oxide species. The TPR peak of the

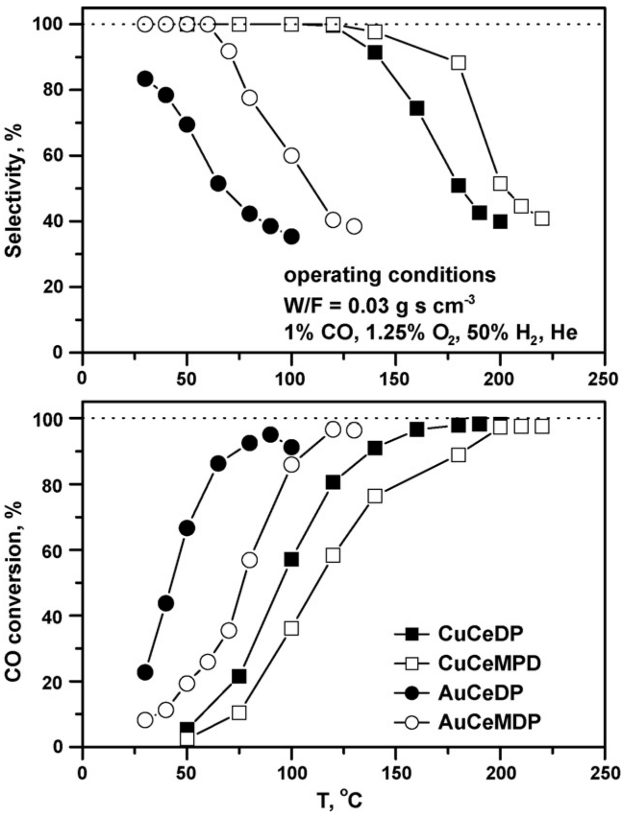

Fig. 1. Activity and selectivity of CuO/ceria (rectangles) and Au/ceria (circles) catalysts prepared by DP (solid symbols) and MDP (open symbols) methods, for the PROX reaction, at $W/F = 0.03\ g\ s\ cm^{-3}$. Feed: 1% CO, 1.25% O_2, 50% H_2, He.

AuCeMDP catalyst was broad and appeared at higher temperatures than the corresponding peak of the AuCeDP catalyst. The resulting behavior was related to the preparation method, which leads to different particle sizes of gold and enhancement of ceria reducibility.

Fig. 1 shows the CO conversion and the selectivity towards CO_2 production of Au/ceria and CuO/ceria catalysts, prepared by the DP and the MDP methods, for the preferential CO oxidation reaction. It can be observed that the activity and the selectivity depend strongly on the nature of the catalyst. Indeed, no hydrogen at all was oxidized at temperatures lower than 120 °C and the selectivity remained constant at 100% over CuO/ceria catalysts, while over the Au/ceria catalysts the selectivity decreased progressively from 85–100% to 35–40%, as the reaction temperature increased from 30 °C to 100–125 °C. On the other hand, it should be noted that in the low-temperature region ($T < 100$ °C), gold catalysts are remarkably more active than the CuO/ceria catalysts, though this high activity is accompanied with poor selectivity. Among the four catalysts tested, the AuCeDP is the most active, while the CuCEMDP is the most selective. The preparation method strongly influences the catalytic performance and a higher efficiency towards CO_2 production was obtained with the DP method. Thus, using a W/F ratio of $0.03\ \mathrm{g\,s\,cm^{-3}}$, the temperature at which 50% CO conversion is obtained (T_{50}), was found equal to 43 °C (76% selectivity), 77 °C (82% selectivity), 95 °C (100% selectivity) and 113 °C (100% selectivity) for the AuCeDP, AuCeMDP, CuCeDP and CuCeMDP catalysts, respectively. The maximum CO conversion achieved over the AuCeDP sample was 96%, with 39% selectivity, at 90 °C, while over the CuCeDP sample, 100 ppm CO were detected in the reactor outlet, with 51% selectivity, at 180 °C.

Based on XPS measurements, reported in detail elsewhere [25], the DP method allows a larger fraction of gold or copper oxide to be exposed on the catalyst surface. The calculations showed 0.69 and 0.20 at.% of Au on the surface of AuCeDP and AuCeMDP catalysts, respectively and 4.32 and 3.65 at.% of Cu on the surface of CuCeDP and CuCeMDP, respectively.

In the case of gold catalysts, a small particle size and a high activity are strongly related. The DP method leads to higher dispersion of gold particles (TEM measurements in Ref. [25]) than the MDP method and this plays a crucial role for the catalytic performance. In what concerns CuO/ceria catalysts, the higher catalytic activity of the DP-prepared sample compared to the MDP-prepared sample is attributed to the formation of more easily reducible well-dispersed copper oxide species strongly interacting with the ceria surface (TPR measurements in Ref. [25]). The copper oxide particle size, on the other hand, remains unaffected by the preparation method (TEM measurements in Ref. [25]).

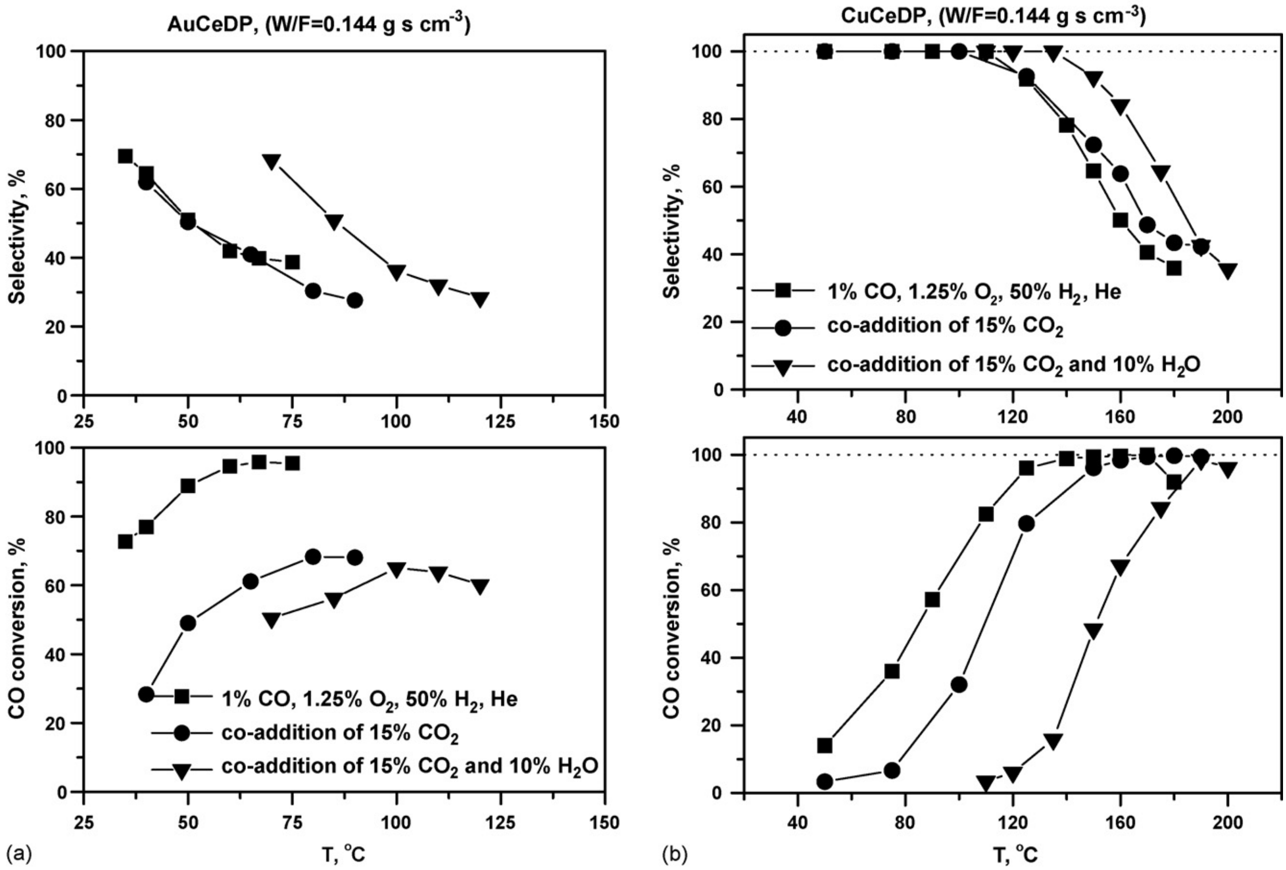

Fig. 2. Activity and selectivity of AuCeDP (a) and CuCeDP (b) catalysts, for the PROX reaction, at $W/F = 0.144\ \mathrm{g\,s\,cm^{-3}}$, in the absence of CO_2 and H_2O (■), in the presence of 15 vol.% CO_2 (●), and in the presence of both 15 vol.% CO_2 and 10 vol.% H_2O (▼) in the feed. Standard feed: 1% CO, 1.25% O_2, 50% H_2, He.

The activity and the selectivity of the AuCeDP and CuCeDP catalysts were also tested at a higher *W*/*F* ratio (0.144 g s cm^{-3}) and the results are presented in Fig. 2a and b, respectively. Under these conditions, 96% CO conversion was obtained with the AuCeDP catalyst at 67 °C with 40% selectivity. The complete removal of CO was achieved over the CuCeDP catalyst, at 180 °C with 50% selectivity. With the same sample, less than 100 ppm CO were already detected at 140 °C with 80% selectivity.

The effect of the presence of CO_2 and H_2O in the feed on the activity and on the selectivity of the DP-prepared catalysts for the PROX reaction was also examined and the results are presented in Fig. 2. The addition of 15 vol.% CO_2 or both 15 vol.% CO_2 and 10 vol.% H_2O provoked a decrease in both activity and selectivity of the catalysts, due to the competitive adsorption of CO, CO_2 and H_2O on the catalyst surface [1,5,8,11,13,14,27]. The deactivation is not caused by modification of the physicochemical properties of the catalysts, since the activity is fully recovered by switching to a CO_2–H_2O free feed. Thus, the inhibition observed in the presence of CO_2 and H_2O is not irreversible. Since, both CO_2 and H_2O are adsorbed on the catalysts surface and block the active sites, the inhibition will be eliminated at high temperatures where the surface coverage of CO_2 or H_2O will become quite low. Park et al. [27] performed TPD experiments of preadsorbed CO_2 and H_2O over CuO–CeO_2/Al_2O_3 catalysts, and concluded that the inhibiting effects of CO_2 and/or H_2O were temporally significant at low temperatures, where CO_2 and H_2O have not yet been desorbed from the catalyst surface. Formation of carbonates, carboxylates and linear adsorbed CO with exposure of CeO_2 to CO at room temperature has been also reported [28,29]. Hilaire et al. [30] have found that carbonate species are formed upon exposure of a Pd/CeO_2 catalyst to CO at 400 °C. These carbonate species are quite stable on a reduced ceria surface, but decompose rapidly with exposure in oxygen.

The magnitude of the inhibiting effect provoked by CO_2 and H_2O is strongly dependent on the nature of the catalyst. Thus, the CuO/ceria catalyst is able to tolerate significant amounts of CO_2 and H_2O, while the gold catalyst is more sensitive. For example, using a *W*/*F* ratio of 0.144 g s cm^{-3}, 99% CO conversion was obtained over the CuCeDP catalyst at 140 °C, with 80% selectivity in the absence of CO_2 and H_2O in the feed, while the same conversion was achieved at 160 °C (64% selectivity) and at 190 °C (43% selectivity) in the presence of 15 vol.% CO_2 or both 15 vol.% CO_2 and 10 vol.% H_2O in the feed, respectively (Fig. 2b). On the other hand, 96% CO conversion was obtained over the gold catalyst at 67 °C, with 40% selectivity in the absence of CO_2 and H_2O in the feed, while in the presence of 15 vol.% CO_2 or both 15 vol.% CO_2 and 10 vol.% H_2O in the feed, the maximum CO conversion obtained was only 68% (at 80 °C with 30% selectivity) and 65% (at 100 °C with 37% selectivity), respectively.

The deactivation caused by the presence of CO_2 and H_2O is accompanied to a smaller extent by a decrease of selectivity in the case of the CuO/ceria catalyst. The desired CO concentration in the reactor outlet can be obtained albeit at a lower selectivity with operation at higher reaction temperature. The CuO/ceria catalyst was tested in a 3-day catalytic run and exhibited excellent stability under realistic reaction conditions.

It is obvious that higher values of contact time are required for the gold catalyst in order to achieve high CO conversion in the presence of CO_2 and H_2O, since the gradual drop of selectivity with temperature makes the operation at higher temperatures prohibitive. The poor selectivity in combination with the low resistance towards deactivation by CO_2 and H_2O present in the feed and the high cost of gold, limit the practical use of Au/ceria catalyst in fuel processors. The high CO oxidation activity of the gold catalyst at low temperatures cannot be considered as an advantage, since the presence of water vapor in the reformed fuel limits the operation of the PROX reactor at temperatures higher than 60–70 °C, where significant losses of hydrogen, due to oxidation, cannot be avoided. However, the Au/ceria catalyst was found to be stable with the reaction time (in a 3-day catalytic run), in contrast to other gold catalysts, such as Au/Fe_2O_3 [7,9] or Au/TiO_2 [16], which lost a significant portion of their initial activity during the first hours in the reaction stream.

4. Conclusions

The deposition–precipitation method compared to the modified one, leads to the formation of more active ceria-supported CuO and Au catalysts for the preferential CO oxidation reaction. By employing DP method, highly dispersed gold clusters are formed, which enhance the reducibility of ceria surface and the catalytic activity towards CO_2 production. In the case of copper oxide catalysts, the higher catalytic performance of the CuCeDP sample is attributed to the formation of more easily reduced, well-dispersed copper oxide species strongly interacting with the ceria surface.

Au/ceria catalysts showed higher activity than CuO/ceria for the PROX reaction at temperatures lower than 120 °C, while the CuO/ceria catalysts were able to operate at higher temperatures, with a remarkably better selectivity. The presence of CO_2 and H_2O caused a significant decrease in the catalytic performance of the gold catalyst, while the CuO/ceria catalyst could still achieve complete removal of CO in the presence of CO_2 and H_2O, albeit at higher temperatures and with lower selectivity. The inhibition caused by CO_2 and H_2O is reversible and initial activity is fully restored after removal of CO_2 and H_2O from the reaction mixture. Both catalysts exhibited a perfectly constant behaviour with the reaction time.

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