Short communication

Preferential catalytic oxidation of carbon monoxide in presence of hydrogen over bimetallic AuPt supported on zeolite catalysts

Pattarasuda Naknam [a], Apanee Luengnaruemitchai [a,*],
Sujitra Wongkasemjit [a], Somchai Osuwan [b]

[a] *The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok 10330, Thailand*
[b] *The Petroleum and Petrochemical Technology Consortium, Bangkok 10330, Thailand*

Abstract

A series of AuPt/A zeolite and Pt/A zeolite catalysts prepared by incipient wetness impregnation are investigated for the preferential oxidation (PROX) of carbon monoxide in the presence of hydrogen over the temperature range of 50–310 °C under atmospheric pressure. The results indicate that when a small amount of gold is added to the Pt/A zeolite catalyst, the CO selectivity is improved at low temperatures, and 1% AuPt/A zeolite (at a weight ratio of Au:Pt = 1:2) gives the best performance, which provides a high CO conversion in combination with a high CO selectivity. In more realistic simulated reformate gases containing 10% CO_2 and 10% H_2O, there is not much difference between those in the presence and the absence of CO_2 and H_2O. Transmission electron microscopic and X-ray diffraction studies show that the two metals, Au and Pt, appear to be severely phase separated, which is confirmed by energy dispersive investigations.
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1. Introduction

Minor concentrations of CO can cause Pt-based catalysts to deactivate by strongly binding to the Pt surface. This results in dramatic losses in the efficiency of proton-exchange membrane fuel cells (PEMFCs). Therefore, the content of CO in the H_2 stream must be reduced to the ppm level, which is the acceptable limit of CO in the H_2-rich stream obtained from the reforming of hydrocarbons. One of the most effective methods for removing CO from reformate is preferential catalytic oxidation (PROX). The catalysts used for this process usually consist of a noble metal [1–4] and active oxygen [5,6]. Among the catalysts studied, gold is generally regarded as being the least useful of the noble metals for catalytic purposes. Nevertheless, Haruta et al. [7] have reported that suitable catalyst are highly dispersed nanosized Au particles supported on transition metal oxides that can catalyze the oxidation of CO to CO_2 at temperatures as low as −70 °C. Thus, Au may catalyze a wide variety of reac-

tions under comparatively mild conditions. Several gold-based catalysts have been investigated for the selective CO oxidation reaction, e.g., Au/Fe_2O_3 [8,9], Au/Al_2O_3 [10], Au/ZrO_2 and Au/TiO_2 [11]. Other studies have investigated the influence of H_2O and CO_2 [12], as well as of particle size, on the activity and selectivity [13,14] of the PROX reaction over supported Au catalysts. Research in our laboratories has shown that supported Au catalysts, prepared via a co-precipitation technique and using different supports, exhibit a similar or even higher activity at comparatively low temperatures [15,16]. Recently, bimetallic catalysts have been used extensively in many important industrial processes and are often preferred to their mono-metallic counterparts in terms of catalytic activity and/or selectivity because of their unique catalytic properties. For example, Pt-Pd/CeO_2 [17] and Pt-Au/CeO_2 [18] catalysts have been studied for the PROX reaction and found to give better performance than mono-metallic catalysts. Therefore, the previous results can be related to differences in the activity of the Au crystallite sizes in the final catalysts.

Metal oxides have been mainly used as a support for the PROX reaction, whereas zeolite has not been widely investigated. The supported A zeolite catalyst has been shown [19] to

* Corresponding author. Tel.: +66 2 218 4148; fax: +66 2 215 4459.
E-mail address: apanee.l@chula.ac.th (A. Luengnaruemitchai).

give higher selectivity for CO oxidation than supported mordenite, X-zeolite and alumina catalysts [19]. Our preliminary results showed that a Pt/zeolite catalyst can be used to oxidize CO with high activity in the H_2-rich stream around 200 °C, but gives quite low selectivity [20].

The main purpose of this study is to present results for the PROX of CO when using bimetallic Au-Pt supported on A zeolite. The catalytic activities are presented in the terms of CO conversion and CO selectivity as a function of temperature in order to find a catalyst that is able to convert CO completely to CO_2 over a relatively low temperature range for application in an on-board H_2 generator for fuel cell operation. Many effects on the catalytic activity are presented, namely, the effect of Au on the Pt/A zeolite performance, sequential metal loading and metal-loading ratio. Additionally, the performance of the best catalyst is investigated under a realistic reformate containing CO_2 and H_2O.

2. Experimental

2.1. Catalyst preparation

Mono-metallic Pt/A zeolite (designated as Pt/A) with a Pt loading of 1 wt.% was prepared by incipient wetness impregnation of the NaA zeolite with an aqueous solution of $H_2PtCl_6\cdot xH_2O$. Additionally, bimetallics containing Pt and Au with a total metal loading of 1 wt.% were prepared by incipient wetness impregnation. The appropriate concentrations of the $HAuCl_4\cdot3H_2O$ and $H_2PtCl_6\cdot xH_2O$ precursor aqueous solutions were impregnated on to a NaA zeolite support. Both co-impregnation and sequential impregnation were used for catalyst preparation. If Au is firstly loaded on the A zeolite, followed by Pt loading, it will be denoted as Pt-Au/A. On the other hand, if Pt is first loaded on the A zeolite, followed by Au loading, it will be denoted as Au-Pt/A. For co-impregnation, the notation of AuPt/A will be used. All catalysts were dried in an oven at 110 °C overnight and subsequently calcined in air for 5 h at 500 °C.

2.2. Catalytic characterization

The crystallite size of Au and Pt on the surface and the crystalline structure of the A zeolite support were analyzed by means of a Rigaku X-ray diffractometer system (RINT-2200) with a Cu tube for generating Cu Kα radiation (1.5406 Å). Hydrogen pulse chemisorption analysis determined the percent metal dispersion by applying measured pulses of H_2 gas to the prepared catalysts. A transmission electron microscope (TEM) was employed to identify the microstructure of the prepared catalysts. The instrument was a JEM 2010 unit operating at an accelerating voltage of 200 kV.

2.3. Catalytic activity

The PROX reaction was conducted in a fixed-bed, U-tube, micro-reactor by packing with 100 mg of the catalyst. The activity was investigated at various temperatures over the range of 50–310 °C under gas mixture conditions of 1% CO, 1% O_2 and 40% H_2 balanced in He with a total flow rate of 50 ml min^{-1}. The effluent gas from the reactor was analyzed both qualitatively and quantitatively by auto-sampling in an on-line gas chromatograph equipped with a packed carbosphere column, 80/100 mesh, 10 ft × 1/8 in. and a thermal conductivity detector (TCD). Calculation of the CO conversion was based on the formation of carbon dioxide. The selectivity of CO oxidation was defined as the oxygen consumption for CO oxidation divided by the total consumption of oxygen.

3. Results and discussion

3.1. Catalyst characterization

The XRD patterns of AuPt/A catalysts prepared by the incipient wetness impregnation method at different Au:Pt ratios are given in Fig. 1, together with that for A zeolite. The Au and Pt peaks indicate the metals in the prepared catalysts and the crystallite size of the metals was calculated by use of the Scherrer equation. The Au and Pt peaks observed at 2θ values of 38.5° and 39.8° correspond to Au(1 1 1) and Pt(1 1 1) for Cu Kα (1.5406 Å) radiation, respectively. This result indicates that the metal particles of Au and Pt are not mixed to alloy form. For the AuPt catalysts, the substitution of Au by Pt is observed to increase the intensity of the Pt(1 1 1) peak. The substitution of Au by Pt tends to decrease the Au(1 1 1) diffraction peak intensity due to the dilution of Au by Pt. In addition, the total metal loadings of all catalysts are almost the same, as confirmed by ICP results.

Hydrogen temperature programmed reduction (TPR) is an effective technique to provide information on the character of the above interactions. The TPR profiles of the different samples are given in Fig. 2. All samples exhibit one reduction peak with
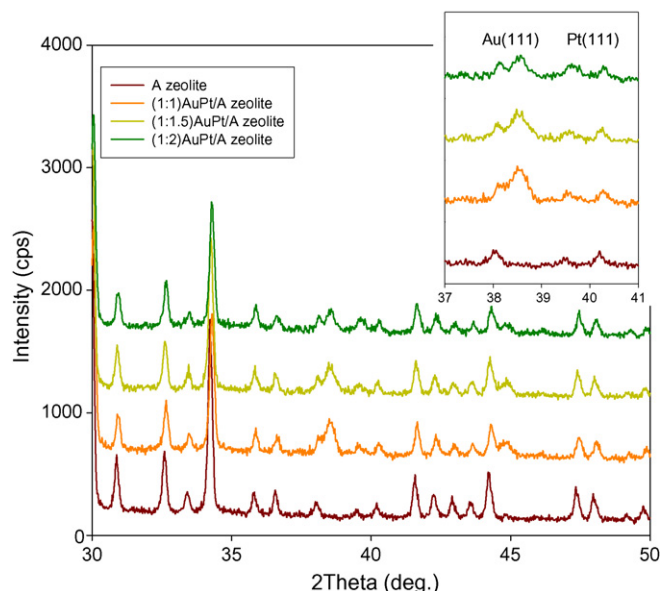

Fig. 1. X-ray diffraction patterns of unloaded A zeolite and AuPt supported on A zeolite with different Au:Pt ratios.
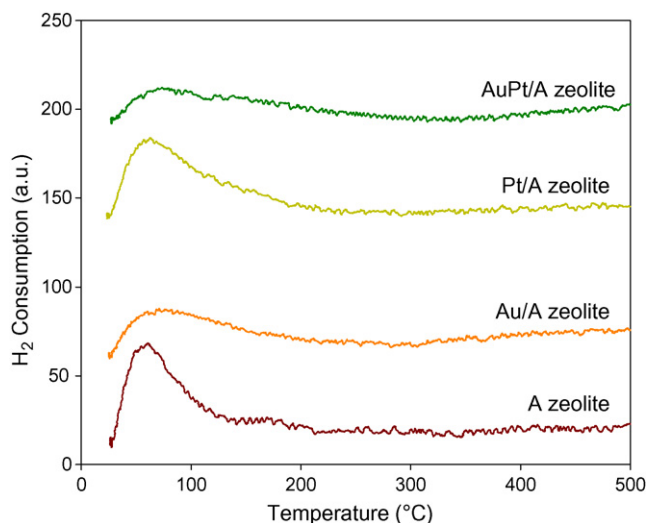
Fig. 2. Temperature programmed profiles of unloaded A zeolite, Pt/A, Au/A and AuPt/A catalysts.

a maximum temperature at ~50–150 °C. The reduction peak at ~70 °C can be ascribed to the reduction of gold ions in the Au/A catalyst. It is interesting to note that the corresponding hydrogen consumption peak around the reduction of gold species of AuPt/A almost overlaps those for the Au/A and Pt/A catalysts, and the reduced amount of adsorbed H_2 on AuPt/A is possibly a possible reason for the higher activity.

3.2. Activity of AuPt/A and Pt/A catalysts

The preferential oxidation of CO versus temperature curves obtained over Pt/A and AuPt (1:2)/A catalysts are shown in Fig. 3(a and b). Carbon monoxide conversions of 100% are obtained over both catalysts, but the catalytic activity of Pt/A is improved slightly in the presence of Au. The temperature at the maximum CO conversion of AuPt/A is shifted approximately 50 °C to a lower temperature (~170 °C), which suggests that CO adsorption on Au is much weaker than that on Pt [21,22]. Carbon monoxide can be weakly adsorbed on Au and is therefore easily desorbed off the surface. Moreover, adsorbed CO is generally observed only at low temperatures. The fact is that Au has fully occupied d-orbitals and exhibits weak coordination ability toward CO. As a result of this adsorption, the temperature for the maximum conversion of CO on a AuPt/A catalyst is shifted to a lower value. The bimetallic sample displays slightly different activity to mono-metallic Pt, which suggests that the addition of Au by co-impregnation yields large Au particles that are unable to oxidize CO in the presence of H_2. This conclusion is consistent with the Au crystallite sizes determined from XRD data. Similarly, at high temperature, both catalysts exhibit similar selectivity in the range of ~40–50%. At low temperatures, however, the AuPt/A catalyst provided 35% higher CO selectivity than the Pt/A catalyst. This shows that a small amount of Au added to the Pt/A catalyst causes the particle size of the Pt metal to decrease (from ~59.9 to 51.1 nm) and results in the higher dispersion of AuPt/A on the catalyst support (~27%), as compared with the Pt/A catalyst (~21%). Higher dispersion values equate
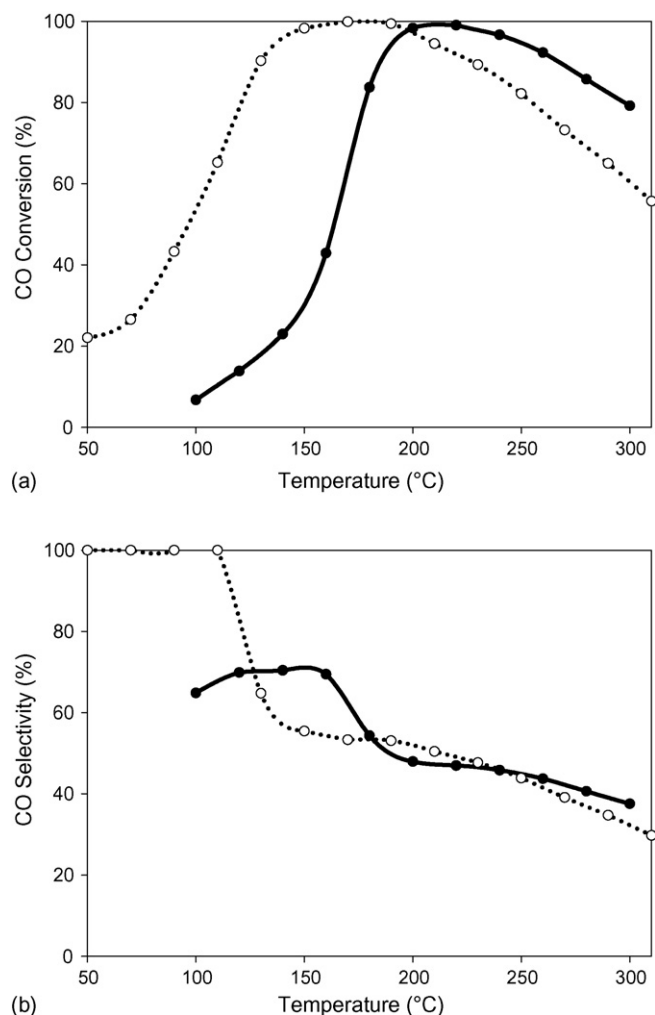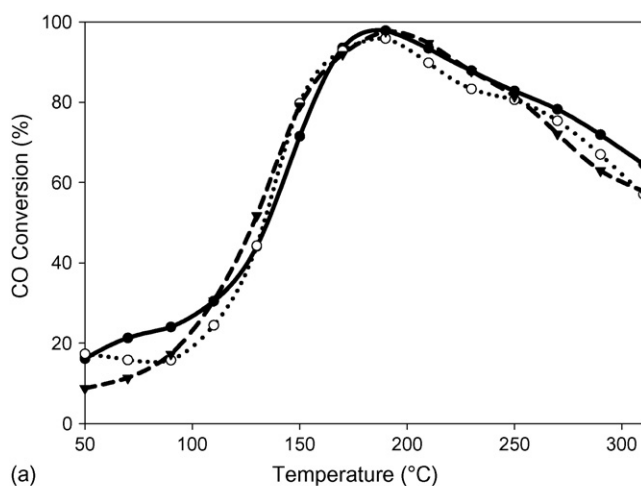

Fig. 3. Catalytic activity of Pt/A zeolite (●) and AuPt (1:2)/A zeolite (○) catalysts. Gas composition: 1% CO, 1% O_2, 40% H_2 and He as balance: (a) CO conversion; (b) CO selectivity.

to more efficient metal atom usage for the catalytic reaction which provides an optimal CO conversion and CO selectivity at relatively low temperatures. The mono-metallic Au/A catalyst displays almost no activity towards CO oxidation at this temperature range.

3.3. Effect of sequential metal loading

The sequential order of metal loading does not have a significant effect on CO conversion, as shown in Fig. 4. Maximum CO conversion takes place at a temperature around 190 °C. By contrast, the sequential order of metal loading has a significant effect on CO selectivity at low temperatures (lower than 170 °C). It can be seen that a higher CO selectivity is obtained at low temperatures for all tested catalysts. These results can be explained by the fact that the average metal crystallite sizes do not differ greatly among the prepared catalysts (~71 nm). The same metal crystallite sizes lead to the same metal dispersion, resulting in similar catalytic activities among all samples (Pt-Au/A, Au-Pt/A and AuPt/A catalysts). This suggests that if either Au or Pt is initially loaded in the sequential metal loading or if co-
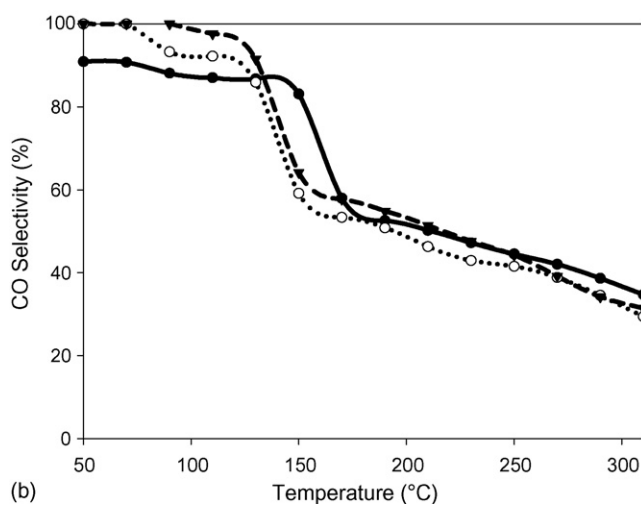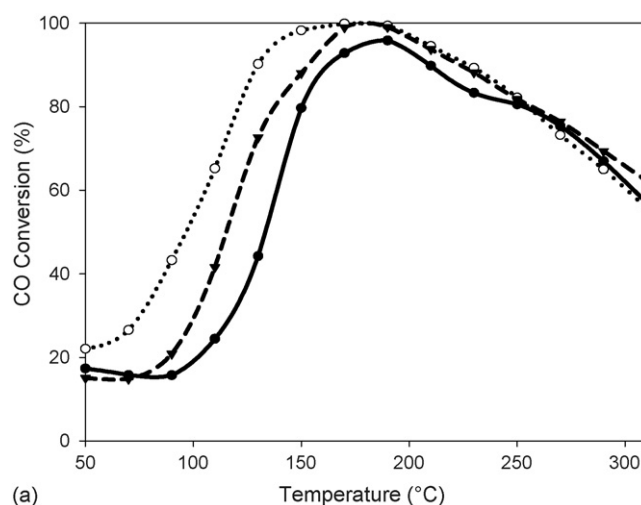
Fig. 4. Catalytic activities of Pt-Au (●), AuPt (○) and Au-Pt (▼) supported on A zeolite catalysts with a Au/Pt ratio of 1. Gas composition: 1% CO, 1% O_2, 40% H_2 and He as balance: (a) CO conversion; (b) CO selectivity.

Fig. 5. Catalytic activity of AuPt/A zeolite at various Au:Pt ratios, 1:1 (●), 1:1.5 (▼) and 1:2 (○) supported on A zeolite catalysts. Gas composition: 1% CO, 1% O_2, 40% H_2 and He as balance: (a) CO conversion; (b) CO selectivity.
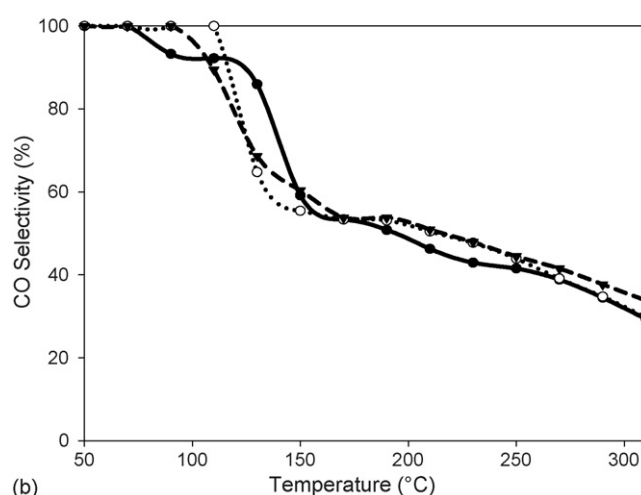
impregnation is used, there is no effect on the metal coverage on each metal.

3.4. Effect of metal-loading ratio

To improve the catalytic activity of the AuPt/A catalyst, the effect of the addition of Au to the Pt/A was investigated. The AuPt/A catalysts were prepared by co-impregnation. The Au:Pt ratios were 1:1, 1:1.5 and 1:2. As shown in Fig. 5, the presence of Au on the Pt/A catalyst improves both the CO conversion and selectivity. The results indicate that although both a Au and Pt are present in the samples, the ratio of Pt and Au exerts an effect on the catalytic activity. The AuPt/A catalyst containing a Au to Pt ratio of 1:2 gives the highest CO conversion (100%) and selectivity. Moreover, the temperature at maximum CO conversion is also shifted to a lower temperature compared with other Au/Pt ratios. This behavior can be attributed to the crystallite size of Au in the samples because the presence of small crystallites of Au enhances CO oxidation, as shown in Fig. 1. Consequently a ratio of Pt:Au = 1:1, gives the lowest activity. The catalyst performance depends on many variables, however,

such as the support, the actual total metal loading and the metal dispersion of the metal. Therefore, additional studies are needed to quantify these results. In addition, the metal particles of Au and Pt are not mixed to form an alloy because TEM observations of AuPt/A (not shown here) suggest that the two metals appear to be severely phase separated, as confirmed by the EDS technique. This result is in a good agreement with that reported by Chandler et al. [23], who showed that the co-impregnation of Au with Pt from chloride salts yielded catalysts with little or no interaction between the two metals.

3.5. Effect of water vapour on catalytic performance

The effect of the water vapour in the feed stream on the catalytic performance of the 1% (1:2) AuPt/A catalyst was investigated. In practice, a reformate stream usually contains up to 10–15% H_2O. Therefore, it is essential to investigate the influence of water vapour on the PROX reaction while maintaining gas conditions. The catalytic activities of the catalyst were tested with a reactant gas composition of 10% H_2O, 1% CO, 1% O_2
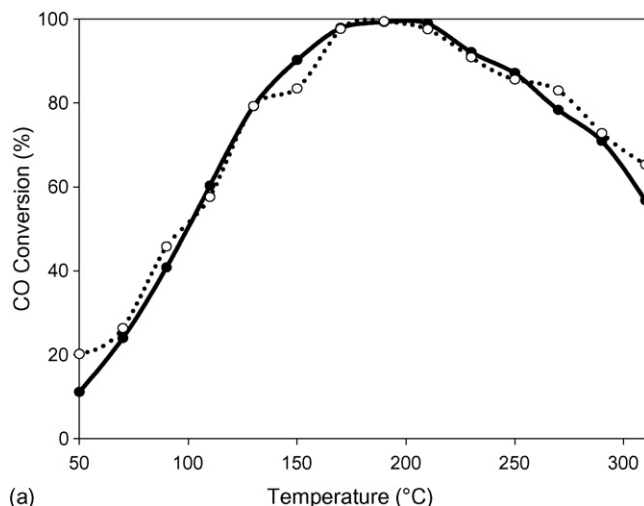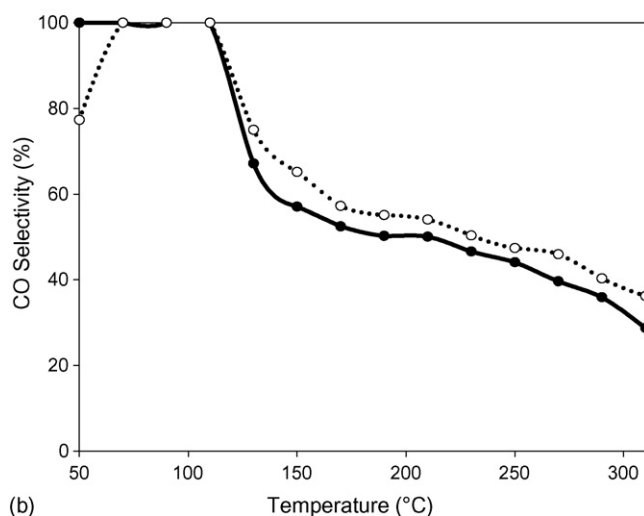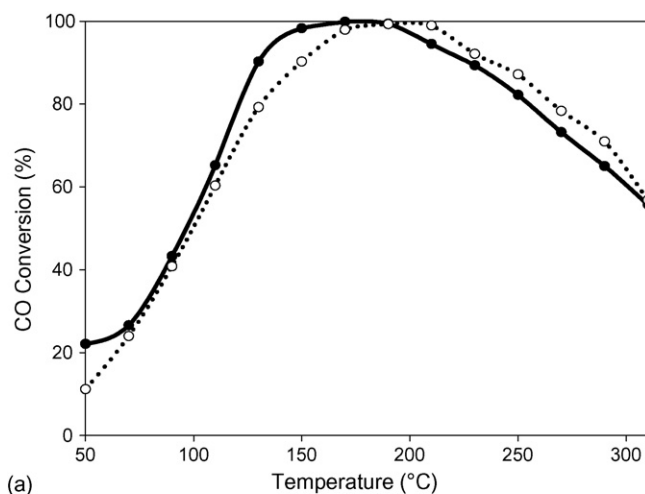
Fig. 6. Effect of H_2O on catalytic activities of 1% (1:2) AuPt/A zeolite catalyst. Gas composition: 1% CO, 1% O_2, 40% H_2, 0–10% H_2O and He as balance: (●) 0% H_2O and (○) 10% H_2O—(a) CO conversion; (b) CO selectivity.

and 40% H_2 balanced in He. As shown in Fig. 6(a and b), the presence of water vapours does not have a significant effect on CO conversion, but has a positive effect on CO selectivity at high temperatures. The CO selectivity increases from 50 to 55% at 190 °C. Schubert et al. [21] examined the influence of CO_2 and H_2O on selective CO oxidation over Au/α-Fe_2O_3. It was concluded that the addition of H_2O exerts a positive effect of the selectivity by suppressing the competing H_2 oxidation reaction and promoting the water–gas shift reaction. As a result, more CO is converted to CO_2 at high temperatures and causes an increase in CO selectivity. Additionally, the presence of H_2O increases the formation of hydroxyl groups on the catalyst support, which makes water a better oxidant than oxygen and increases the oxidation rate of CO and H_2. This result can be confirmed by the reduction of O_2 consumption. On the other hand, Calla et al. [24] found that the presence of H_2O in a feed stream significantly increased the rate of CO oxidation over Au/Al_2O_3 because the activation energy CO oxidation was reduced. By contrast, we found that the presence of H_2O vapour had a negative effect on

the performance of the Pt/A catalyst. Based on these findings, it can be concluded that when a small amount of Au is added to a Pt/A catalyst, the activity of 1% (1:2) AuPt/A does not show much difference in the presence or absence of H_2O vapour in the feed stream.

3.6. Effect of combination of CO_2 and H_2O on catalytic performance

The effect of the presence of CO_2 and H_2O in the feed stream on the catalytic performance of the 1% (1:2) AuPt/A catalyst was also examined because reformate typically contains up to 25% CO_2 and 10–15% H_2O. It is essential, therefore, to investigate the influence of both CO_2 and H_2O on the preferential oxidation of CO in order to evaluate whether the high activity and selectivity observed in simulated reformate are still maintained under more realistic conditions. From the CO conversion profiles in Fig. 7(a), the presence of CO_2 and H_2O in the feed stream has a slightly negative effect on the CO conversion profile of the 1% (1:2) AuPt/A catalyst. The maximum CO conversion is shifted
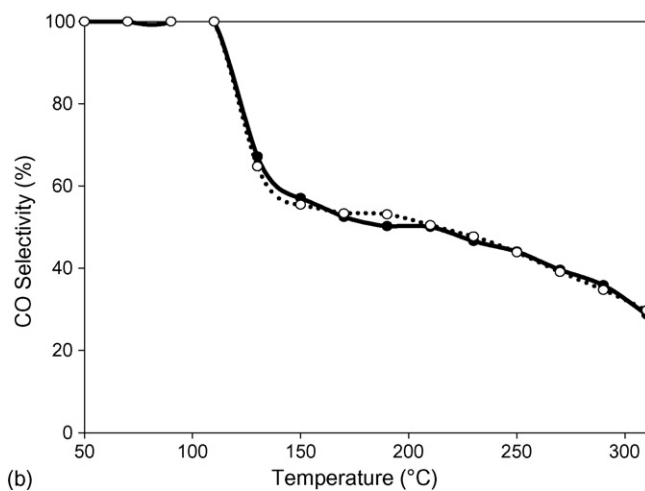
Fig. 7. Effect of CO_2 and H_2O on catalytic activity of 1% (1:2) AuPt/A zeolite catalyst. Gas composition: 1% CO, 1% O_2, 40% H_2, 0–10% CO_2, 0–10% H_2O and He as balance: (●) 0% CO_2 + 0% H_2O and (○) 10% CO_2 + 10% H_2O—(a) CO conversion; (b) CO selectivity.

to a higher temperature by approximately $10\,^\circ$C. The CO selectivity of the catalyst is not significantly changed by the presence of CO_2 and H_2O in the feed stream. Avgouropoulos et al. [9] investigated the influence of CO_2 and H_2O on catalyst activity for the preferential oxidation of CO over a Au/α-Fe$_2$O$_3$ catalyst. They reported that the presence of CO_2 and H_2O further reduced CO conversion, but increased CO selectivity. In addition, the Pt/γ-Al$_2$O$_3$ catalyst is more resistant than Au/α-Fe$_2$O$_3$ and CuO-CeO$_2$ catalysts towards deactivation. Based on these results, it can be concluded that the presence of Au in the Pt/A catalyst can slightly reduce the influence of CO_2 and H_2O.

4. Conclusions

A bimetallic catalyst prepared by incipient wetness impregnation, which is a conventional synthesis, results in catalysts containing segregated Pt and Au particles. When a small amount of Au is added to the Pt/A catalyst, CO selectivity is improved at low temperatures. Additionally, the temperature at maximum CO conversion on AuPt (1:2)/A is shifted by $50\,^\circ$C to a lower temperature. These differences are the result of the presence of Au in the Au-Pt bimetallic particles. The sequential order of metal loading has no significant effect on the catalytic activity. The AuPt/A catalyst containing a Au to Pt ratio of 1:2 provides the best performance; it completely removes CO from the H$_2$-rich stream and achieves a high selectivity. Moreover, the temperature of maximum CO conversion is also shifted to lower temperatures. Under practical conditions, the presence of CO_2 and H_2O in the feed stream has a negative effect on CO conversion and slightly effects CO selectivity.

Acknowledgements

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