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Au/MgO catalysts modified with ascorbic acid for low temperature CO oxidation

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Abstract

$Au/Mg(OH)_2$ catalyst was modified with different amounts of ascorbic acid. After dehydration at 350 °C, in various atmospheres, the modified Au/MgO catalysts were characterized and tested in the oxidation of CO. It has been shown for the first time that at high CO pressure supported gold chemisorbs CO and the apparent gold dispersion can be determined. The oxidation of CO was investigated in the temperature range between −30 and 250 °C using both temperature-programmed oxidation technique and time on stream experiments. A characteristic feature of Au/MgO catalysts is the decrease of the activity upon increasing the reaction temperature from −30 to 110–120 °C. The results showed that the introduction of ascorbic acid had a definite positive effect on the activity of Au/MgO catalyst in low temperature CO oxidation. This effect strongly depended on the amount of ascorbic acid introduced and had a distinct optimum. Based on diffuse reflection UV–VIS and in situ FTIR spectroscopic data it is suggested that the addition of ascorbic acid (i) slightly alters the (ionic gold)/(metallic gold) ratio in both the parent ($Au/Mg(OH)_2$) and the working catalysts (Au/MgO) and (ii) suppresses the carbonate formation responsible for the deactivation. It is proposed that the activation of CO requires the formation of "$(Au^{\delta+})_m$–Au_n" ensemble sites, in which the ionic gold is involved in the activation of CO molecule via $Au^{\delta+}$–carbonyl oxygen interaction.

Keywords: Au/MgO catalyst; CO oxidation; Low temperature oxidation; Catalyst modification; Ascorbic acid

1. Introduction

Recently, supported gold catalysts have received great academic interest, due to their high activity in low temperature CO oxidation [1–11]. In these studies different gold precursor compounds and miscellaneous support materials, such as TiO_2 [2,3,7,8], NiO [1], Fe_2O_3 [1,2], Co_3O_4, [1,2], CuO [1] ZrO_2 [7,9], $Mg(OH)_2$ [6,8] and various transition metal hydroxides [4] have been investigated. From these recent studies the following main conclusions can be drawn: (i) supported gold catalysts are highly active even at −70 °C, (ii) only nanoclusters with particle sizes in the range 1–6 nm show high activity, (iii) not only the size, but the shape of the nanoclusters has a significant influence on the activity of supported gold catalysts, (iv) supports with redox properties strongly enhance the activity of supported gold catalysts, (v) a number of different reaction mechanisms can be involved in low temperature CO oxidation.

In the literature there has been no report of an attempt to investigate the role of additives or modifiers on the activity of supported gold catalysts in low temperature CO oxidation. The aim of this work is

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to demonstrate that ascorbic acid can be considered as a good modifier for Au/MgO catalysts used in this reaction.

2. Experimental

2.1. Reagents

Magnesia (>99%) and $HAuCl_4 \cdot xH_2O$ (gold chloride hydrate with 50% Au content) were Aldrich products, while ascorbic acid (>99.99%) was purchased from Reanal.

2.2. Catalyst preparation

2.2.1. Rehydration of MgO

The commercial magnesia powder (BET surface area = 140 m^2/g) was suspended in distilled water (10 ml of water per 1 g of magnesia), stirred and heated to 95 °C for 22 h in an oil bath. After filtration the solid was dried overnight at 100 °C under vacuum. The hydrated magnesia was calcined for 24 h at 400 °C and atmospheric pressure in a static oven resulting in magnesia with a BET surface area of 174 m^2/g.

2.2.2. Adsorption of gold chloride hydrate onto rehydrated MgO

High surface area magnesia (5 g), prepared as above, was slurried under vigorous stirring at room temperature in 400 ml distilled water containing 0.532 g $HAuCl_4 \cdot xH_2O$. After 3 h the colorless aqueous phase was removed on a rotary evaporator at 60 °C. The beige solid obtained was dried for 24 h in an oven at 100 °C resulting in base $Au/Mg(OH)_2{}^{base}$ catalyst. The same preparation procedure has also been employed to prepare supported gold catalysts using MgO as received. This catalyst will be denoted as "base* Au/$Mg(OH)_2$ catalyst" ($Au/Mg(OH)_2{}^{base^*}$).

2.2.3. Preparation of resuspended Au/Mg(OH)$_2$ catalysts ($Au/Mg(OH)_2{}^{resusp}$)

Two grams $Au/Mg(OH)_2{}^{base}$ catalyst was suspended in 200 ml distilled water, stirred for 2 h at room temperature. After filtration the solid was washed three times with 100 ml portions of distilled water, and dried overnight at 100 °C in an oven. The $Au/Mg(OH)_2{}^{resusp}$ catalyst was also prepared in different amounts between 0.3 and 2 g.

2.2.4. Modification of $Au/Mg(OH)_2{}^{resusp}$ catalyst with ascorbic acid

In standard experiments 0.65 g $Au/Mg(OH)_2{}^{resusp}$ catalyst was used in the modification with L(+)-ascorbic acid. The $Au/Mg(OH)_2{}^{resusp}$ catalyst was slurried in 200 ml distilled water. The solution of calculated amount of the L(+)-ascorbic acid in 50 ml distilled water was added to the catalyst under vigorous stirring. The slurry was stirred for additional 2 h at room temperature. After filtration the solid was dried for 5 h at 100 °C in an oven resulting in "modified Au/$Mg(OH)_2$ catalysts" (n-$Au/Mg(OH)_2{}^{mod}$). The number n indicates the amount of ascorbic acid in milligrams used for the modification of 1 g Au/$Mg(OH)_2$ catalyst.

2.2.5. Thermal treatment of Au/Mg(OH)$_2$ catalysts

Different thermal treatment procedures have been used, such as reduction in hydrogen, calcination in air or helium, and calcination in air followed by reduction in hydrogen, to transform the $Mg(OH)_2$ support into MgO and reduce the gold precursor compound. The calcination was performed for 90 min in dried air, while the reduction was carried out in pure hydrogen for 1 h. After subsequent thermal treatment at 350 °C all $Au/Mg(OH)_2$ type catalysts were transformed onto Au/MgO catalysts (Au/MgO^{base}, Au/MgO^{resusp} and n-Au/MgO^{mod} catalysts, respectively). The thermal treatment procedure was performed before the chemisorption and/or the activity test. Prior to the corresponding tests, the catalyst was cooled down from 350 °C to room temperature in an inert gas atmosphere (flow rate: 50 cm^3/min).

2.3. Catalyst characterization

2.3.1. CO chemisorption and temperature-programmed treatment procedures

In both characterization methods the ASDI RXM 100 equipment (Advanced Scientific Designs) was used. The amount of chemisorbed CO was determined as a difference of total and physical adsorption by measuring the adsorption isotherms up to 1000 Torr CO pressure. The low value of the sticking coefficient for CO on gold [12] made it necessary to use an unusually high pressure for the chemisorption measurements. To the best of our knowledge this is the first attempt to measure CO chemisorption on supported gold catalysts.

In temperature-programmed treatment procedures a number of gases, such as hydrogen, air or helium were used. In standard experiments the heating rate was 5 °C/min.

2.3.2. FTIR measurements

FTIR spectra were obtained at room temperature using a Nicolet 5PC FTIR instrument. Two spectral ranges were investigated: (i) the carbonyl region at 1800–2200 cm^{-1} and (ii) the carbonate region at 1300–1700 cm^{-1}. In these spectral regions the resolution was 4 cm^{-1}. The description of the cell and the high vacuum apparatus used can be found elsewhere [13]. Catalyst samples were pressed onto self-supporting wafers and were mounted in the sample holder. The weight of the self-supporting disks was about 5–8 mg/cm^2. The treatment of the sample in oxygen and/or in hydrogen was accomplished in a built-on furnace located above the IR cell. The catalysts were cooled to room temperature in flowing He (flow rate: 30 ml/min). FTIR spectra were measured under CO flow (3 vol.% CO in He, flow rate: 30 ml/min). The spectra were obtained after accumulating 256 scans. First the spectrum of the IR cell with the gas phase was measured as the background spectrum, then the spectrum of the catalyst sample was measured. The spectrum of the adsorbed species was obtained by subtracting the spectrum measured in He flow from the spectrum obtained in CO/He. In the presence of CO spectra were taken after 10, 30 and 60 min time on stream (TOS).

2.3.3. UV–VIS spectra

Diffuse reflectance UV–VIS spectra were recorded under ambient conditions on a Cary 300 Scan (Varian) spectrometer with a standard diffuse reflectance unit using MgO as reference.

2.4. Catalytic experiments

Two methods were used to investigate the activity of supported gold catalysts. In both methods the ASDI RXM 100 equipment was used. A temperature-programmed oxidation (TPO) technique was applied in the temperature range of −30 to 270 °C. The relevance of this technique was demonstrated in our recent study on low temperature CO oxidation over tin modified Pt/SiO_2 catalysts [14]. In TPO runs the following conditions were used: amount of catalysts = 50–150 mg, carrier gas: helium, gas mixture = 16 Torr CO and 44 O_2, total flow rate = 70 ml/min, heating rate = 5 °C/min. The purity of gases used (helium and hydrogen) was 99.9995 vol.%. The water content of the gases used was below 1 ppm.

The TPO experiments were carried out in the following way. The catalyst after its thermal treatment was cooled down to −30 °C and kept at this temperature for 5 min under the helium flow. The helium flow was switched to the gas mixture containing CO and oxygen and kept at this temperature for additional 3 min, allowing the stabilization of the gas flow through the reactor. The temperature ramp was started after this short stabilization period. In all the TPO studies the heating rate was 5 °C/min.

The TOS experiments were carried out under isothermal conditions in the temperature range of −50 and +25 °C. In the standard TOS experiments the following experimental conditions were used: amount of catalysts = 50–150 mg, gas mixture = 16 Torr CO and 44 O_2, total flow rate = 70 ml/min. These parameters corresponded to the space velocity of 39.2–117.6 $l\,h^{-1}\,g_{cat}{}^{-1}$.

Both TPO and TOS experiments were monitored recording the m/e = 28, 32 and 44 signals of CO, oxygen consumed and CO_2 formed, respectively. In catalytic runs the fractional conversion values were calculated.

3. Results and discussion

3.1. Modification of $Au/Mg(OH)_2$ catalyst with ascorbic acid

The modification of $Au/Mg(OH)_2{}^{base}$ catalyst with ascorbic acid is associated with a slight color change. The color of the $Au/Mg(OH)_2{}^{resusp}$ catalyst after drying at 100 °C is beige with a light gray tone. The n-$Au/Mg(OH)_2{}^{mod}$ catalyst samples after modification with ascorbic acid and subsequent drying at 100 °C were light bluish-violet or light pinkish-red. Ascorbic acid is considered to be a mild reducing agent, consequently it is suggested that in its presence the spontaneous auto-reduction of the gold precursor compound is further enhanced.

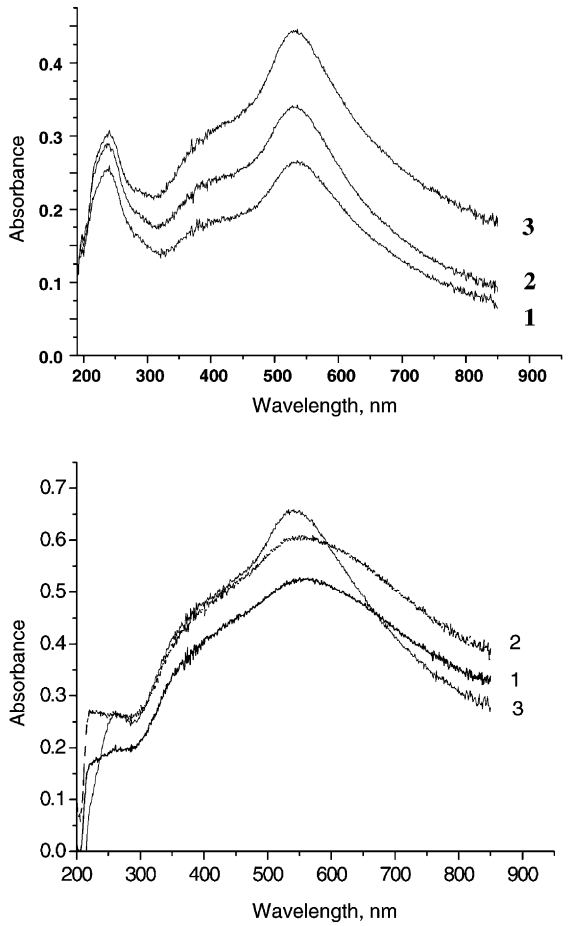

Fig. 1. Diffuse reflectance UV–VIS spectra of different gold catalysts. (A) Catalysts prior to reduction: (1) $Au/Mg(OH)_2^{resusp}$, (2) $0.7\text{-}Au/Mg(OH)_2^{mod}$ and (3) $2.4\text{-}Au/Mg(OH)_2^{mod}$. (B) Catalysts after reduction in hydrogen at 350 °C: (1) Au/MgO^{resusp}, (2) $0.7\text{-}Au/MgO^{mod}$ and (3) $2.4\text{-}Au/MgO^{mod}$.

Fig. 1A and B shows the diffuse reflection UV–VIS spectra of the different gold catalysts prior to and after reduction in hydrogen at 350 °C, respectively. All the samples give rise to three adsorption bands around 240, 390 and 565 nm. These bands correspond to: (i) Au^+ cations, (ii) $(Au)_n^{\delta+}$ small clusters and (iii) $(Au)_n$ metallic Au particles, respectively [15]. Fig. 1A shows unambiguously that during the preparation of these samples spontaneous auto-reduction of the gold precursor compound takes place. In this auto-reduction both ionic and metallic forms of gold are formed. The spectra reveal that (i) auto-reduction begins under the resuspension conditions (see sample (1) in Fig. 1A, (ii) there is a certain amount of ascorbic acid which is not involved in the auto-reduction (compare samples (1) and (2) in Fig. 1A) and (iii) above a minimum level the addition of ascorbic acid increases the amount of both metallic gold and the positively charged gold nanoclusters $(Au)_n$ and $(Au)_m^{\delta+}$, respectively, while the amount of Au^+ cations is practically constant.

The reduction of samples in hydrogen resulted in further increases in the intensity of bands at around 390 and 560 nm, whilst the band at around 240 nm completely disappeared. The spectra of samples Au/MgO^{susp} and $0.7\text{-}Au/MgO^{mod}$ are almost identical: this indicates that the amount of ascorbic acid added was not sufficient to change the forms of gold in the modified catalyst.

After reduction in hydrogen the character of the gold-containing species is similar to that formed prior to the reduction. However, it can be seen from Fig. 1B that for samples Au/MgO^{resusp} and $0.7\text{-}Au/MgO^{mod}$, the band at around 560 nm is broader than in the corresponding samples shown in Fig. 1A.

In sample $2.4\text{-}Au/MgO^{mod}$ the plasma-resonance peak is shifted to a lower wavelength (ca. 545 nm) and the peak is narrower compared with the corresponding peak in the other two samples. These facts indicate that the addition of ascorbic acid enhances the stabilization of supported gold nanoparticles in the sizes below 50 Å required for low temperature CO oxidation.

We cannot of course exclude the possibility of formation of larger gold clusters in addition, but our CO chemisorption results (see Section 2.2) indicate that the *average* gold particle size is below 50 Å. This result was further supported by preliminary XRD data.

It should be noted that the reduction in hydrogen does not lead to the disappearance of $(Au)_n^{\delta+}$ species. We consider that the positively charged gold nanoclusters play a crucial role in the activation of CO.

3.2. Catalyst characterization

3.2.1. Temperature-programmed treatments and CO chemisorption

The temperature and the duration of the thermal treatment processes were chosen so that the transformation of $Mg(OH)_2$ to MgO could be achieved.

The temperature-programmed treatment of all types of $Au/Mg(OH)_2$ catalysts either in helium or hydrogen

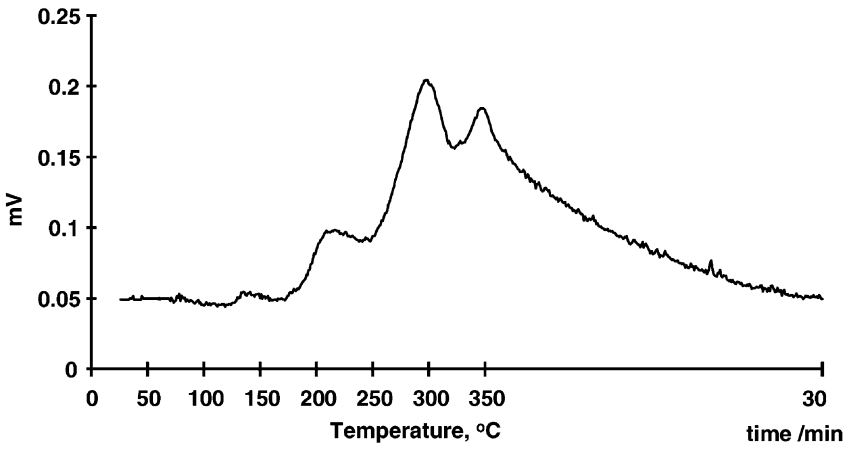

Fig. 2. Temperature-programmed reduction of an Au/MgO^{resusp} sample treated in air at 350 °C.

was performed with a heating rate of 5 °C/min up to 350 °C followed by heating at this temperature for 1 h. The quantitative formation of water in the quantity corresponding to the dehydration of $Mg(OH)_2$ to MgO has been achieved in all cases. The water formation started at 335–345 °C and was completed at 350 °C within 40–60 min. In samples modified with ascorbic acid, evolution of CO_2 and trace amount of CO was also observed in addition to the water formation.

Temperature-programmed reduction of Au/MgO^{resusp} sample treated in air at 350 °C for 1.5 h is shown in Fig. 2. This figure shows a complex TPR pattern and the amount of hydrogen consumed is 0.054 mmol/g, corresponding to 0.036 mmol of gold in the form of Au_2O_3. Consequently, our Au/MgO catalyst shows an unusual behavior compared with results reported earlier. In recent studies [6,8] it was shown that after calcination metallic gold was obtained on an $Mg(OH)_2$ support.

After thermal treatment in hydrogen or in air and hydrogen at 350 °C further color changes occurred in the catalyst samples. The reduced samples had a color between purple, light violet or light bluish-violet. Based on literature data [16] this indicates the relatively high dispersion achieved in our Au/MgO catalysts.

Fig. 3 shows the adsorption isotherms of CO over Au/MgO^{resusp} catalyst. The calculated amount of chemisorbed CO shows a saturation level around 800–1000 Torr of CO. It is worth mentioning that on a Pt/SiO_2 catalyst, a similar saturation level has been observed in the pressure range of 20–30 Torr.

Preliminary results of CO chemisorption are summarized in Table 1. These indicate that Au/MgO^{resusp} and Au/MgO^{mod} catalysts and the MgO support chemisorb CO. However, the latter has much less chemisorption capacity than the gold-containing samples. The chemisorption results show good reproducibility of the preparation (compare experiments numbers 2 and 3).

The amounts of CO chemisorbed on Au/MgO^{resusp} (I) and (II) catalysts roughly correspond to CO/Au = 0.10–0.12, i.e., the dispersion of gold in Au/MgO^{resusp}

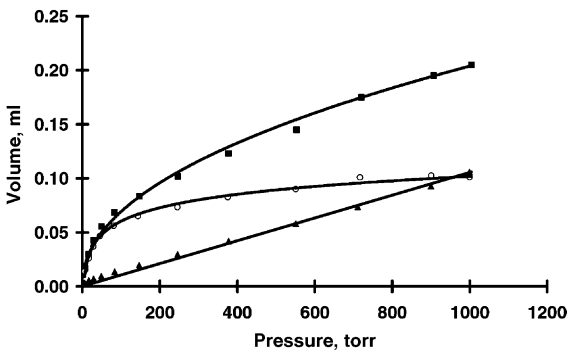

Fig. 3. Adsorption isotherms of CO on Au/MgO^{resusp} catalyst (sample number 3 in Table 1). (■) Total volume of adsorbed CO; (▲) volume of physisorbed CO; (○) volume of chemisorbed CO. Amount of catalyst: 0.13 g.

Table 1
CO chemisorption on MgO and different Au/MgO catalysts

Number	Catalyst	Treatment	V_{CO} (ml/g)		CO/Au (at./at.)
			Measured	Corrected[a]	
1	MgO	Air and H_2 at 350 °C	0.095	–	–
2	Au/MgO^{resusp} (I)[b]	Air and H_2 at 350 °C	0.554	0.642	0.113
3	Au/MgO^{resusp} (II)[c]	Air and H_2 at 350 °C	0.547	0.632	0.111
4	Au/MgO^{resusp} (II)[c]	H_2 at 350 °C	0.569	0.675	0.120
5	0.7-Au/MgO^{mod}	H_2 at 350 °C	0.540	0.630	0.110
6	0.7-Au/MgO^{mod}	Air and H_2 at 350 °C	0.525	0.600	0.103
7	2.2-Au/MgO^{mod}	H_2 at 350 °C	0.813	1.005	0.176

[a] Corrected by the amount of CO chemisorbed on MgO and for the amount of water lost due to transformation of $Mg(OH)_2$ to MgO.
[b] Prepared in amount of 1.3 g.
[c] Reproduction of (I) in amount of 1.3 g, thermal treatment: heating in air to 350 °C and keeping 1.5 h at this temperature followed by reduction in hydrogen for 1 h.

catalysts is about 10–12%. Results presented in Table 1 show that the modification with ascorbic acid resulted in a substantial increase in the amount of CO chemisorbed and the dispersion value increased to 17.6%. This dispersion value corresponds to a particle size below 5 nm, but if the quantity of ascorbic acid used was relatively low (see experiments 5 and 6), the dispersion of gold did not change. This observation is in full agreement with the UV–VIS results (see Fig. 1A and B) as no difference was observed between the Au/MgO^{resusp} and 0.7-Au/MgO^{mod} catalyst samples.

3.3. Preliminary catalytic experiments

Fig. 4 shows preliminary TPO experiments using different types of unmodified Au/MgO catalysts.

The Au/MgO^{base*} catalyst prepared using MgO as received showed very low activity in the temperature range of −30–250 °C. Upon using high surface area MgO the activity increased considerably (see catalyst Au/MgO^{base}). Further increase of the activity was observed upon using Au/MgO^{resusp} catalyst.

These results indicate on the complexity of surface reactions involved in the formation of supported gold

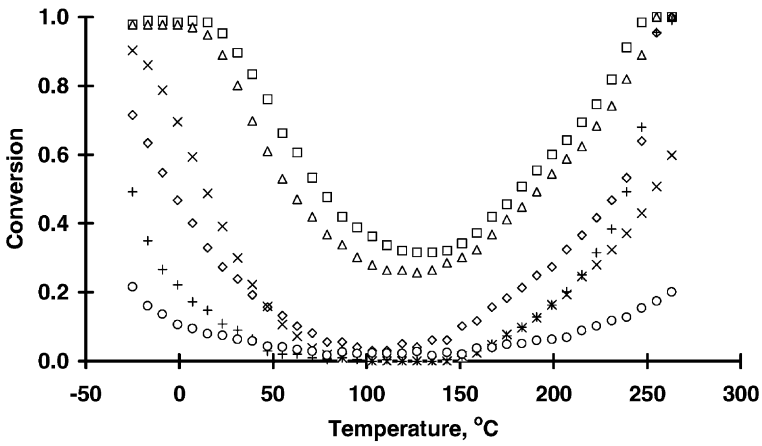

Fig. 4. Oxidation of carbon monoxide on different unmodified Au/MgO catalysts using TPO techniques. Catalysts: (□) Au/MgO^{resusp} (fresh, 0.150 g); (△) Au/MgO^{resusp} (used, 0.150 g); (×) Au/MgO^{resusp} (fresh, 0.075 g); (◇) Au/MgO^{base} (fresh, 0.150 g); (+) Au/MgO^{base} (used, 0.150 g); (○) Au/MgO^{base*} (fresh, 0.075 g). Catalyst pretreatment: calcination in air at 350 °C for 1.5 h followed by reduction in hydrogen at 350 °C for 1 h.

nanoclusters on MgO support. We propose that in the preparation of highly active Au/MgO catalysts the first step is the surface reaction between the surface hydroxyl groups of the support and the gold precursor compound. This is an unknown, anchoring type of surface reaction. This reaction may be analogous to the reaction of H_2PtCl_6 with the surface OH groups in alumina or magnesia. Parallel to this reaction partial and full auto-reduction as well as hydrolysis of both the solvated and the anchored $HAuCl_4$ can take place.

Results presented in Fig. 4 show that the TPO pattern strongly depended on the amount of catalyst used and there were slight activity changes between the fresh and the used catalyst samples.

As can be seen from Fig. 4, all the Au/MgO catalysts show unusual TPO behavior. Upon increasing the reaction temperature from −30 to 100–120 °C the conversion of CO decreases. This decrease is very substantial in all catalysts. Upon further increase of the temperature, the conversion of CO increases and almost full conversion is reached around 250 °C. It is noteworthy that a similar effect, i.e., a decrease in activity on increasing the temperature, has recently been observed on $Au/Mg(OH)_2$ catalyst under dry

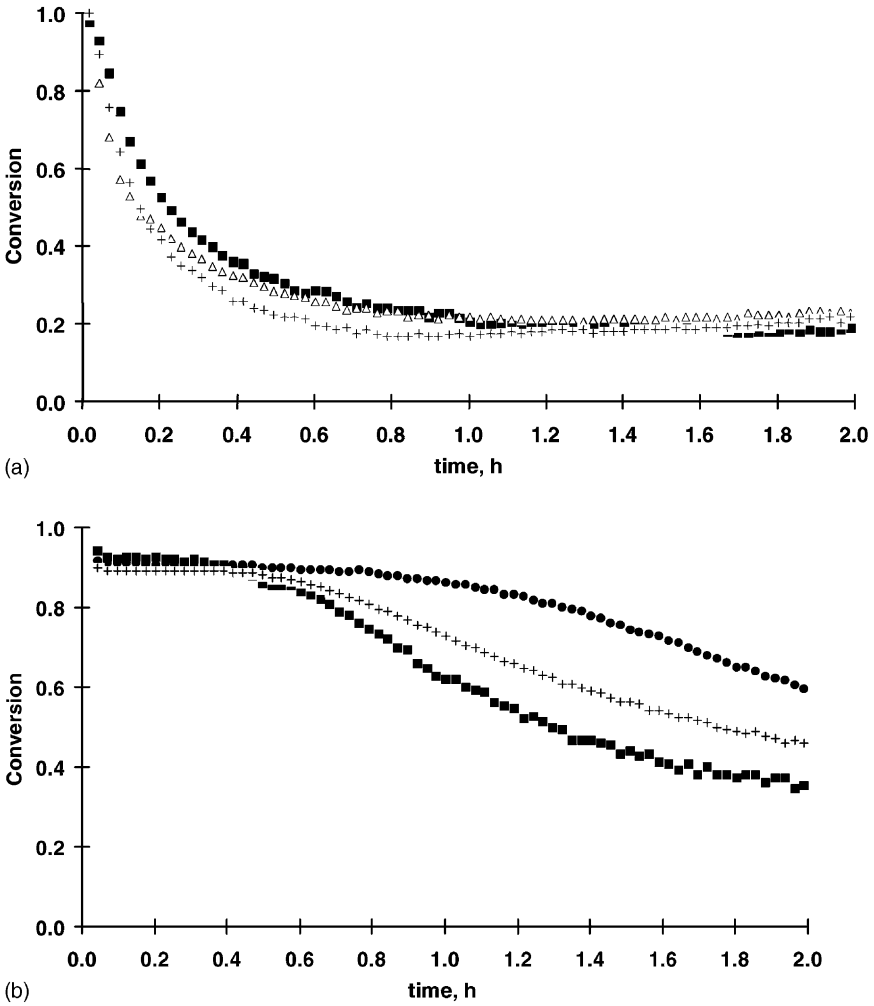

Fig. 5. TOS experiments on (a) Au/MgO^{base} and (b) Au/MgO^{resusp} catalysts at various temperatures. Reaction temperatures: (a) (■) −50 °C; (△) −30 °C; (+) 0 °C; (b) (+) −50 °C; (●) −30 °C; (■) 0 °C. Catalyst pretreatment: calcination in air at 350 °C for 1.5 h followed by reduction in hydrogen at 350 °C for 1 h. Amount of catalyst: 0.15 g.

conditions [8]. The authors attributed this behavior to "negative activation energy". It should be emphasized that no other catalyst systems, such as Au/TiO_2, Au/Fe_2O_3 or Au/ZrO_2 showed similar behavior. We do not accept the hypothesis regarding negative activation energies; and suggest that the activity decrease observed upon increasing the reaction temperature from −30 to 120 °C on both $Au/Mg(OH)_2$ [8] and all of our Au/MgO catalysts can be attributed to deactivation (aging) with the involvement of the support.

With respect to the activity decrease observed upon increasing the temperature, the deactivation of Au/MgO catalysts by surface species *formed* in situ, such as carbonates, cannot be ruled out. Therefore, we tentatively suggest that the unusual behavior of our Au/MgO catalysts in TPO experiments may be ascribed to the poisoning effect induced by surface carbonates.

The catalyst poisoning hypothesis is strongly supported by TOS results obtained at −50, −30 and 0 °C on Au/MgO^{base} catalyst. These results are shown in Fig. 5a. From Fig. 5a it can be seen that the Au/MgO^{base} catalyst does not withstand the temperature of the reaction and deactivates extremely quickly. The strong deactivation of pure Au/MgO catalysts during TOS has recently been reported [17].

Fig. 5b shows the deactivation pattern of Au/MgO^{resusp} catalyst at different temperatures. With the Au/MgO^{resusp} catalyst the rate of deactivation was much lower than that of on Au/MgO^{base} catalyst, although after 2 h of TOS the activity dropped to almost half of the initial value.

Fig. 6 shows the influence of the pretreatment procedures on the activity of Au/MgO^{resusp} catalysts in TPO experiments. In this series the following pretreatment procedures were compared: (i) calcination in air followed by reduction in hydrogen, (ii) reduction in hydrogen and (iii) treatment in helium. The temperature of all the treatment procedures was 350 °C. The highest activity was observed on catalysts treated in hydrogen, while the lowest was obtained with catalysts calcined and reduced. These results indicate that the atmosphere used to decompose the gold precursor compound has a great influence on the activity of the resulting supported gold nanoclusters. In this respect hydrogen has a most positive effect. It is very important to emphasize that in previous studies on $Au/Mg(OH)_2$ catalysts no reduction step was used [6,8] and a simple calcination step at 200–280 °C resulted in highly active Au/MgO gold catalysts at around −50 °C.

3.3.1. CO oxidation over Au/MgO^{mod} catalysts

Selected TPO curves obtained over Au/MgO^{mod} catalysts, i.e., on catalysts modified with different amount of ascorbic acid, are shown in Fig. 7. These

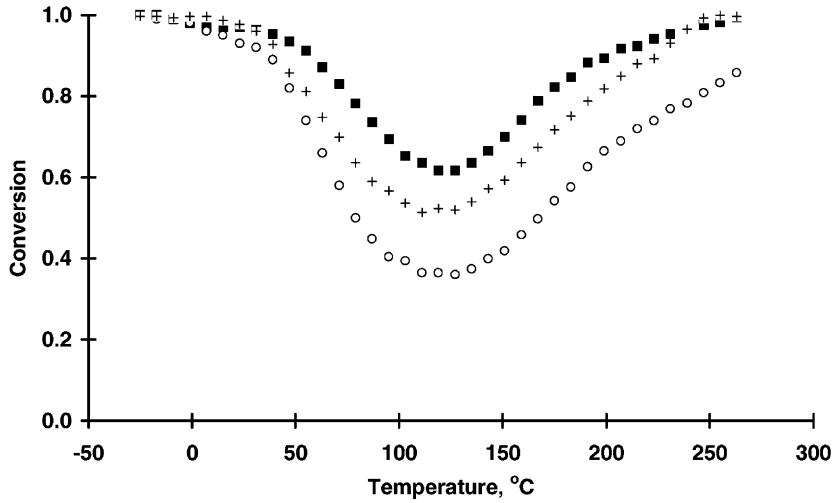

Fig. 6. The influence of the pretreatment procedures on the activity of Au/MgO^{resusp} catalyst investigated by TPO technique. Catalysts: (■) reduced in hydrogen; (○) calcined in air followed by reduction in hydrogen; (+) pretreated in helium. Pretreatment temperature: 350 °C. Duration of the pretreatments: calcination for 1.5 h, reduction for 1 h and in helium for 1.5 h. Amount of catalysts: 0.075 g.

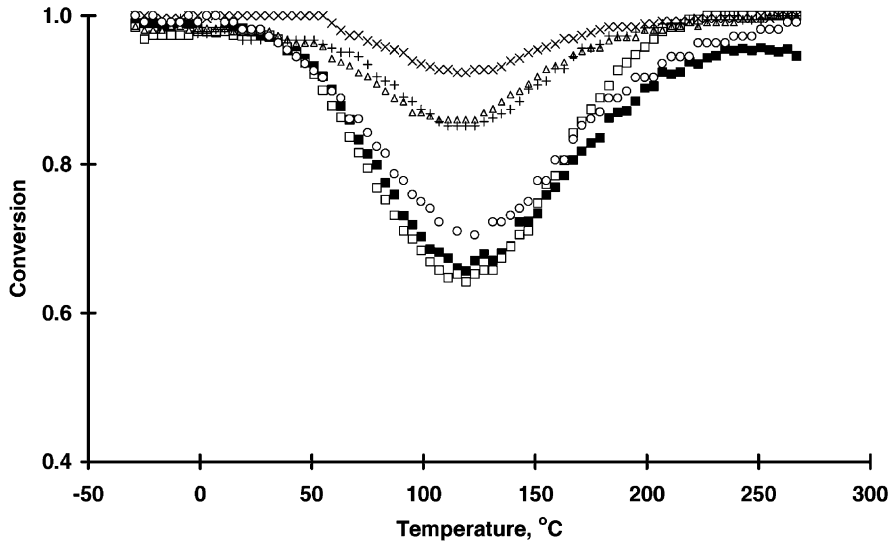

Fig. 7. The influence of the amount of ascorbic acid on the activity of Au/MgO^{mod} catalysts. Results of TPO experiments. Catalysts: (■) Au/MgO^{resusp}; (□) 0.7-Au/MgO^{mod}; (○) 1.2-Au/MgO^{mod}; (△) 2.3-Au/MgO^{mod}; (×) 3.4-Au/MgO^{mod}; (+) 5.3-Au/MgO^{mod} (the corresponding numbers indicate the amount of ascorbic acid in milligrams used to modify 1 g $Au/Mg(OH)_2$ catalyst). Amount of catalyst: 0.075 g. Catalysts pretreated in hydrogen at 350 °C for 1 h.

results show that the addition of ascorbic acid strongly alters the properties of Au/MgO^{resusp} catalyst and leads to substantial activity changes in the whole temperature range. However, the character and the extent of these changes strongly depended on the amount of ascorbic acid introduced.

It should also be mentioned that the resuspension of the Au/MgO^{base} catalyst in water has already been shown to result in a pronounced increase in activity (see Fig. 4). This increased activity was further improved by the addition of ascorbic acid. However, the results presented in Fig. 7 show that the activity increase is related to an optimal amount of ascorbic acid, and an increase in this amount results in an activity decrease. The optimum amount of ascorbic acid, expressed in moles, corresponds to 10–15% of the total gold content.

The Au/MgO^{mod} catalysts were also tested after thermal treatment in air followed by reduction in hydrogen; but his treatment procedure always resulted in lower activity than the treatment in hydrogen, i.e., the behavior of Au/MgO^{mod} catalysts strongly resembled the behavior of Au/MgO^{resusp} catalysts (see Fig. 6).

Summing up the results of the TPO experiments the following conclusions can be drawn: (i) the addition of ascorbic acid up to 3.4 $mg/g_{catalyst}$ onto the Au/MgO^{resusp} catalyst leads to an overall increase of the activity in the sub-ambient temperature region and (ii) the introduction of ascorbic acid exceeding the above level leads to the suppression of the activity both in the sub-ambient and the high temperature region.

The Au/MgO^{mod} catalysts were also tested under TOS conditions in a continuous-flow reactor at −30 °C. The results of these TOS experiments are presented in Fig. 8. All the catalysts except Au/MgO^{mod} showed pronounced deactivation. These data indicate that the addition of ascorbic acid not only increases the intrinsic activity of Au/MgO catalyst, but strongly reduces its aging properties, resulting in more stable Au/MgO catalyst in the sub-ambient temperature range.

4. FTIR results

CO chemisorption has been investigated by FTIR spectroscopy on 3.4-Au/MgO^{mod} catalyst after two treatment procedures: (a) catalyst pretreated in air followed by reduction in hydrogen and (b) catalyst

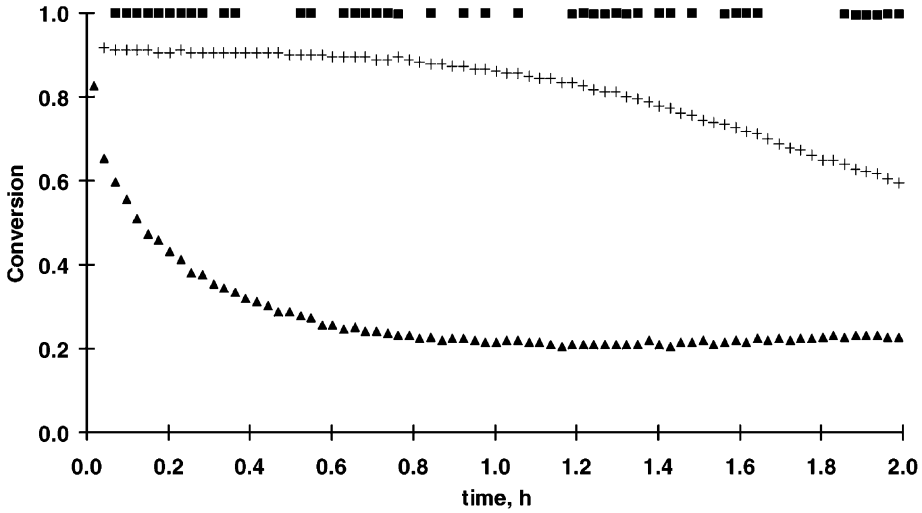

Fig. 8. TOS experiments on different Au/MgO catalysts. (■) 3.4-Au/MgO^{mod}; (+) Au/MgO^{resusp}; (▲) Au/MgO^{base}. Reaction temperature: −30 °C, amount of catalyst: 0.15 g, catalysts pretreated in hydrogen at 350 °C for 1 h. LHSV (ml h^{-1} g$_{cat}^{-1}$): 39 200 for unmodified catalysts, 78.400 for modified catalyst.

reduced in hydrogen. Two spectral regions were investigated: (a) the carbonyl region between 1800 and 2300 cm^{-1} and (b) the carbonate region between 1400 and 1800 cm^{-1}. The corresponding spectra are presented in Figs. 9 and 10, respectively.

Using catalyst pretreated in air and reduced in hydrogen, CO exposure gives rise to one relatively broad carbonyl band at around 2115 cm^{-1} (see Fig. 9a). Upon increasing the duration of CO exposure, the position of this peak shifted slightly to the low frequency region, to 2106 cm^{-1}. Parallel to this shift a broad band appeared in the low frequency region. The switch of the CO flow to pure helium resulted in complete removal of the CO band around 2106 cm^{-1}, but this had no influence on the broad band discussed above. Complete removal of this broad band was observed only after thermal treatment in helium above 250 °C.

The sample treated only in hydrogen showed a broad overlapping CO band at 2125 and 2105 cm^{-1}

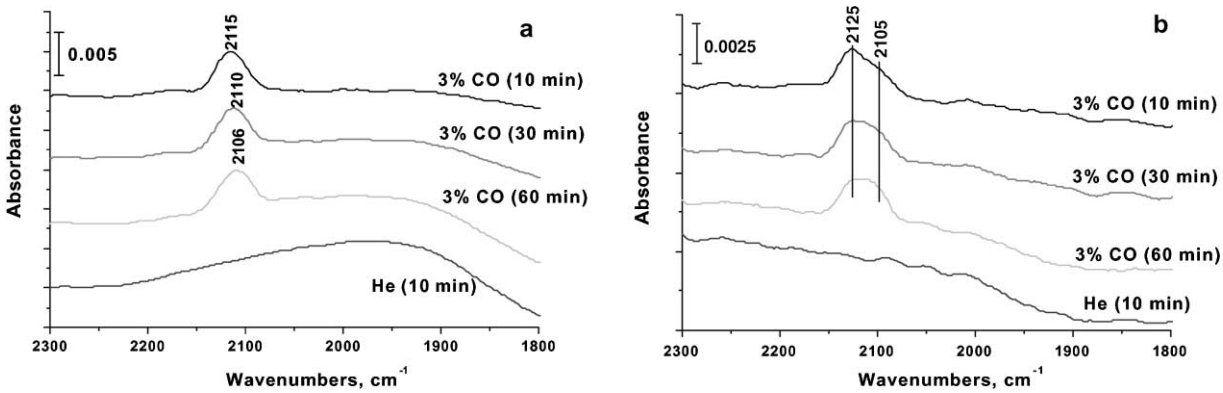

Fig. 9. FTIR spectra of chemisorbed CO on 3.4-Au/MgO^{mod} catalyst, carbonyl region. (a) Catalyst pretreated in air followed by reduction in hydrogen; (b) catalyst pretreated in hydrogen.

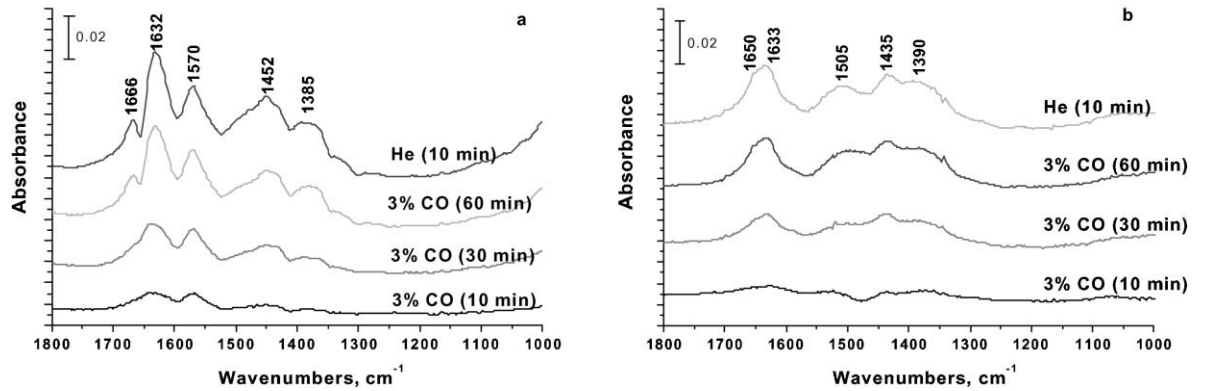

Fig. 10. FTIR spectra of chemisorbed CO on 3.4-Au/MgO^{mod} catalyst, carbonate region. (a) Catalyst pretreated in air followed by reduction in hydrogen; (b) catalyst pretreated in hydrogen.

(see Fig. 9b). Almost similar overlapping CO bands have been obtained on Au/Al_2O_3 catalyst after its treatment with oxygen [18]. The increase of the CO exposure time resulted in slight changes in the ratio of these two bands in favor of the lower frequency one. It should be emphasized that on this sample the appearance of the broad carbonyl band between 1900 and 2200 cm^{-1} is negligible.

The exposure to CO resulted in substantial changes in the carbonate region, too. As emerges from Fig. 10a and b different surface carbonate species are formed on both samples; however the intensity of these changes, especially in the 1550–1700 cm^{-1} region is more pronounced on a sample treated both in air and hydrogen.

Based on literature data, the carbonyl bands at 2105 and 2125 cm^{-1} can be attributed to CO chemisorbed on gold nanoclusters [9,19], while the broad band between 1800 and 2200 cm^{-1} can be assigned to chemisorbed CO, or spilled over to MgO. It should be emphasized that no similar band has been observed on pure MgO. The amount of this form of CO was strongly reduced on a catalyst sample treated only in hydrogen. This band was removed only after high temperature treatment in helium (at 300 °C for 1 h).

The spectra shown in Fig. 10a and b indicate that carbonate formation was more intensive when the catalyst was treated both in air and hydrogen. Evidence for carbonate formation has also been found on Au/TiO_2 catalysts [19,20]. Based on these results, it is suggested that the lower activity of catalysts pretreated both in air and hydrogen can be related to the carbonate formation induced by CO spilled over to MgO.

According to Boccuzzi et al. [19], the linear CO band appears at 2106–2116 cm^{-1} on small gold particles. Grünwald et al. [9] ascribed the bands around 2111–2123 cm^{-1} to CO chemisorbed on step and kink sites, while the bands around 2128–2135 cm^{-1} were assigned to CO chemisorbed on positively polarized gold sites. Consequently, the appearance of a CO band at 2125 cm^{-1} and above, obtained on 3.4-Au/MgO^{mod} sample pretreated only in hydrogen indicates that this catalyst might contain more ionic forms of gold than the one treated both in oxygen and hydrogen. This form of gold seems to be quite stable as the duration of CO exposure did not result in a notable intensity change (see Fig. 9b). The asymmetric character of the CO band on a sample pretreated both in air and hydrogen indicates that the Au/MgO catalyst might also have ionic gold species, but the proportion of the ionic gold is relatively low.

Further FTIR studies will be needed to produce more exact assignments for the bands in both the carbonyl and carbonate region and correlate the activity of Au/MgO catalysts with the intensity and the frequency of IR bands.

5. Conclusions

Different types of Au/MgO catalysts were prepared using $HAuCl_4 \cdot xH_2O$ as a gold precursor compound.

A new method has been developed to measure the CO chemisorption on the Au/MgO catalysts. These Au/MgO catalysts had high activity for low temperature CO oxidation. In contrast to earlier findings [8], the highest activity was found after reduction in hydrogen, omitting the calcination step.

The activity of Au/MgO catalysts was further increased by its modification with ascorbic acid. The positive influence of ascorbic acid was observed in a relatively narrow concentration range. As far as we are aware, we have obtained the first experimental verification that (i) the dispersion of supported gold catalysts can be measured and (ii) supported gold catalysts can be effectively modified.

With respect to the action of the modifier the following possible factors may play an important role: (i) control of the auto-reduction of the gold precursor compound, (ii) stabilization of the size of gold nanoclusters supported on magnesia, (iii) stabilization of ionic forms of gold in the form of positively polarized gold sites and (iv) the suppression of the deactivation of the Au/MgO catalyst induced by surface carbonate formation via spillover of CO to the support.

We consider that the high activity of this type of Au/MgO catalyst can be attributed to the presence of positively polarized gold sites in the neighborhood of supported gold nanocluster. UV–VIS spectra of reduced Au/MgO samples provided new evidence for the formation and stabilization of ionic forms of gold after reduction at 350 °C. We believe that ionic forms of gold play a crucial role in the activation of the triple bond of carbon monoxide.

In our recent studies in low temperature oxidation of CO over Sn–Pt/SiO_2 catalysts we have demonstrated the importance of the interaction between Sn^{n+} moieties and the lone pair of electrons in the oxygen atom of CO [14]. This interaction was also modeled and calculated [21].

As far as in this present study is concerned, clear experimental evidence has been obtained for the stabilization of positively charged gold species in all the Au/MgO samples, the analogy between the "Sn^{n+}–Pt_n" and "$Au_m{}^{\delta+}$–Au_n" ensemble sites seems relevant. Our UV–VIS and FTIR spectroscopic evidence indicates that the experimental conditions applied in this study, i.e., the use of ascorbic acid as modifier and the proper choice of the pretreatment procedure, increases the chances of stabilizing gold in a positively polarized form. It should be emphasized that evidence for the presence of ionic forms of gold in Au/MgO catalysts has been found in earlier studies [22–24], but the role of these positively charged surface species in the activation of CO has not been discussed.

Further studies will be needed to elucidate the role of ascorbic acid and other potential reducing agents and to clarify the character of the activity decrease observed upon increasing the reaction temperature. These further studies will provide additional information with respect to the decrease of the activity in the temperature range between −30 and 120 °C, observed both over Au/$Mg(OH)_2$ [5,6,8] and our Au/MgO catalysts.

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