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CO oxidation in the presence of hydrogen on Au/TiO_2 catalyst: an FTIR–MS study

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Oxidation of CO in the absence and in the presence of H_2 was studied on TiO_2 and 1% Au/TiO_2 catalysts with the help of Fourier transform infrared spectroscopy and mass spectroscopy at 300–373 K. It was found that CO adsorbed on edged and kinked Au atoms are the active surface species for CO oxidation. Oxygen adsorbs on Au particles, too. Activation of hydrogen on the metallic part of the catalyst reduces the extent of CO oxidation. Formation of formaldehyde (both on the surface and in the gas phase) was observed, which also contributes to the decrease of the extent of CO oxidation. It was stated that Au/TiO_2 catalyst – although it is very active in CO oxidation in the absence of hydrogen – is not appropriate for the preferential oxidation of CO in CO + O_2 + H_2 gas mixtures.

KEY WORDS: CO adsorption; CO oxidation; effect of H_2; TiO_2 and Au/TiO_2 catalysts; FTIR; mass spectrometry.

1. Introduction

Hydrogen produced by the catalytic transformations (steam reforming or partial oxidation) of natural gas or alcohols [1,2] always contains significant amount of CO together with H_2O, CO_2 and CH_4. Before using hydrogen the concentration of CO (ca. 5–15%) must be lowered to 1–100 ppm for the proper operation of fuel cell producing energy with low environmental impact [3]. The most powerful process for the removal of CO proved to be the preferential oxidation (PROX) and/or the methanation of CO. Among other catalytic formulations supported Au catalysts have been tentatively tested in the PROX reaction [4–7] based on the high activity of dispersed gold on certain metal oxides for the low temperature oxidation of CO [8–10]. The important role of a reducible support in the PROX reaction has been demonstrated [9,11–14]. Although Au supported on TiO_2 (as a reducible support) has been found to be one of the most active catalysts for low temperature CO oxidation [9,14], little is known on the catalytic behavior of Au/TiO_2 catalyst in the PROX reaction.

In the present work an attempt was made to assign the surface species formed in CO oxidation and in the PROX reaction on Au/TiO_2 and to detect the changes in the gas phase composition as a function of the reacting gas mixture composition and the reaction temperature (300–373 K).

2. Experimental

TiO_2 was the product of Degussa (P25, 50 m^2/g). For the preparation of 1% Au/TiO_2 catalyst, the pH of the $HAuCl_4$ aqueous solution (Fluka AG) was adjusted to pH = 7.5 by adding droplets of 1 M NaOH solution, and the fine powder of the oxide support was suspended in this solution. The suspension was kept at 353 K for 1 h during continuous stirring. The suspension was aged for 24 h at room temperature and washed with distilled water repeatedly, dried at 353 K and then calcined in air at 573 K for 4 h. CO (99.97%), H_2 (99.999%) and O_2 (99.995%) were the products of Linde.

For IR studies the catalysts powders were pressed onto a Ta-mesh (30×10 mm, 5 mg/cm^2). The mesh was fixed to the bottom of a conventional UHV sample manipulator. It was resistively heated and the temperature of the sample was measured by NiCr–Ni thermocouple spot-welded directly to the mesh. The pretreatments of the samples were performed in a stainless steel UV IR cell (base pressure 1.33×10^{-5} Pa): the sample was heated in 1.33 hPa H_2 up to 573 K and it was kept at this temperature for 1 h, this was followed by degassing at the same temperature for 30 min and by cooling the sample to the temperature of the experiment.

Infrared spectra were recorded with a Genesis (Mattson) FTIR spectrometer with a wavenumber accuracy of ± 4 cm^{-1}. Typically 136 scans were collected. The whole optical path was purged with CO_2- and H_2O-free air generated by a Balston 75-62 FT-IR purge gas generator. The spectrum of the pretreated sample (background spectrum) and the actual vapor spectrum were subtracted from the spectrum registered in the presence of gas or gas mixtures. All subtractions were taken without use of a scaling factor (f = 1.000). Mass spectrometric analysis was performed with the help of a QMS 200 (Balzers) quadrupole mass-spectrometer. The volume around the head of QMS 200 was

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continuously evacuated and it was connected with the UV IR cell via a leak valve producing 2.66×10^{-3} Pa around the MS head when reacting gases were present in the cell. The changes in the signal intensity of the main fragments of CO, H_2, O_2 and those of the possible products were simultaneously followed.

3. Results

3.1. Infrared studies

Bands of very low intensity appeared on the spectra due to CO adsorption on TiO_2 at 300 K (Figure 1). (Note that the spectra of the reduced sample and of the gas phase were subtracted from the spectrum of TiO_2 taken in the presence of CO). In the 2400–1800 cm^{-1} region only one band at 2178 cm^{-1} was detected, the intensity of which slightly increased with the increase of CO pressure. The 2178 cm^{-1} band was completely eliminated by a short evacuation at 300 K; in harmony with earlier assignment [15] this band is attributed to CO adsorbed on TiO_2. The intensities of the bands detected below 1800 cm^{-1} were unchanged with increasing CO pressure. The possible assignments of the above bands were given in Table 1.

The presence of gold (1%) on titania greatly enhanced the intensities of the above mentioned bands below 1800 cm^{-1} in the room temperature CO adsorption experiments. Besides the 2180 cm^{-1} band (CO adsorbed on TiO_2), bands at 2130, 2094, 2051, 2026, 1968 and 1918 cm^{-1} appeared in the range of 2400–1800 cm^{-1} during the low pressure (1.33 Pa–1.33 hPa) CO adsorption. At the highest CO pressure applied here (13.3 hPa) one band with dramatically increased intensity at 2032 cm^{-1} appeared instead of the 2051 and 2026 cm^{-1} bands. The spectral features observed between 2400 and 1800 cm^{-1} are directly due to the presence of gold (Figure 2). It has to be noted that the intense 2032 cm^{-1} band disappeared after a short evacuation at 300 K, and bands with small intensities at 2094, 2051, 2026, 1968 and 1918 cm^{-1} remained on the spectrum (the same bands were observed in low pressure CO adsorption).

The spectra of the reduced 1% Au/TiO_2 sample in 13.3 hPa CO at different temperatures are shown on Figure 3. The intensities of the bands in the range of 2200–1800 cm^{-1} dramatically decreased, when the adsorption temperature was higher than 300 K, showing the dramatic decrease in the surface concentration of Au–CO species at 323–373 K. The 2352 cm^{-1} band (due to adsorbed CO_2) appeared first at 323 K. The appearance of the band due to adsorbed CO_2 in CO alone shows that the oxidation of CO with the active oxygen of the TiO_2 surface proceeds even at 323 K on 1% Au/TiO_2. We note that the 2352 cm^{-1} band did not appear at any temperature on reduced TiO_2 without gold during CO adsorption.

The intensities of the bands due to Au–CO species in CO adsorption (Figure 4 spectrum 1) dramatically decreased when oxygen was added to carbon monoxide and this gas mixture was contacted with reduced 1% Au/TiO_2 at 300 K for 60 min (Figure 4 spectrum 2). The presence of H_2 (13.3 Pa and 1.33 hPa) in the $CO:O_2$ (10:1) gas mixture did not affect the surface concentrations of the species causing the appearance of the bands in the 2200–1800 cm^{-1} region (Figure 4

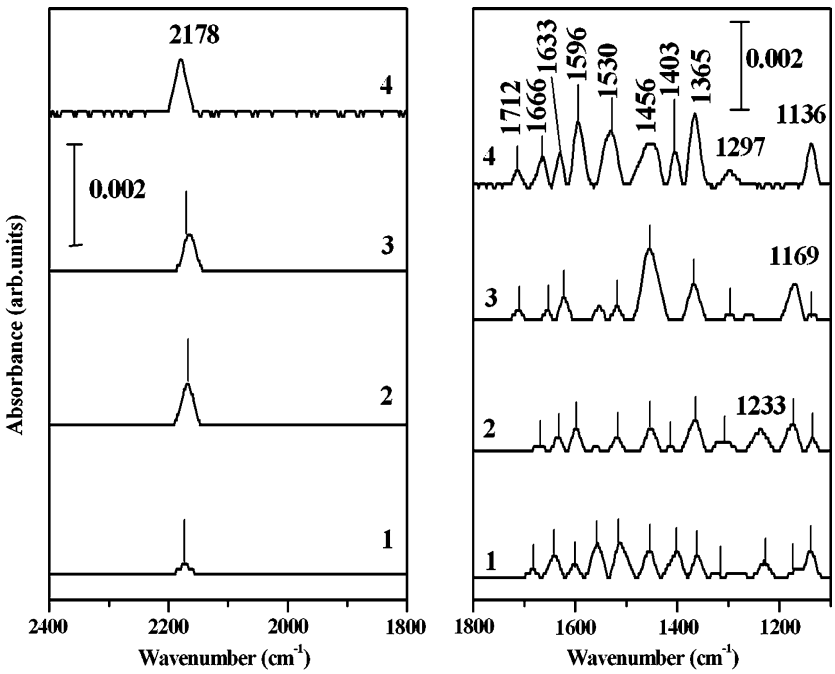

Figure 1. Infrared spectra of CO adsorbed on TiO_2 at 300 K for 15 min: 1 – 1.33 Pa; 2 – 13.3 Pa; 3 – 1.33 hPa and 4 – 13.3 hPa.

Table 1
Bands (in cm^{-1}) and their assignments

Assignment	Formaldehyde on Au/TiO_2 [16]	Formic acid on TiO_2 and Au/TiO_2	PROX on CeO_2 and Pt/CeO_2	Present work
ν(CO) in $H_2CO_{(a)}$	1706–1710			1712–1714
$HCOOH_{(a)}$ on TiO_2		1690–1695 [17,18] and 1671 [19]		1675–1666
Bicarbonate			1613,1391,1045 [23] and 1611,1393,1043 [12]	
ν_a(OCO) in $HCOO^-_{(a)}$ on TiO_2		1590,1554 [17–22] and 1556 [19]		1596–1597,1551
Bidentate carbonate			1562,1286,1028 [24] and 1565,1298,1014 [12]	1560–1534, 1280–1287
Unidentate carbonate			1545,1348,1062 [24] and 1514,1316 [12]	1546–1537, 1354–1365
Carbonate polydentate polymer			1462,1353,1066 [23] and 1463,1353,1050 [12]	1465, 1356
$\omega(CH_2)$ in DOM	1403–1411			1396–1403
ν_s(OCO) in $HCOO^-_{(a)}$		1374 [19]		
$\tau(CH_2)$ in DOM	1293–1299			1275–1299
$\omega(CH_2)$ in $H_2CO_{(a)}$	1251			1233
$\rho(CH_2)$ in $H_2CO_{(a)}$	1155–1164			1150–1169
$\rho(CH_2)$ in DOM	1112			1136

DOM – dioxymethylene (formed in the reaction of surface oxygen ion and formaldehyde).

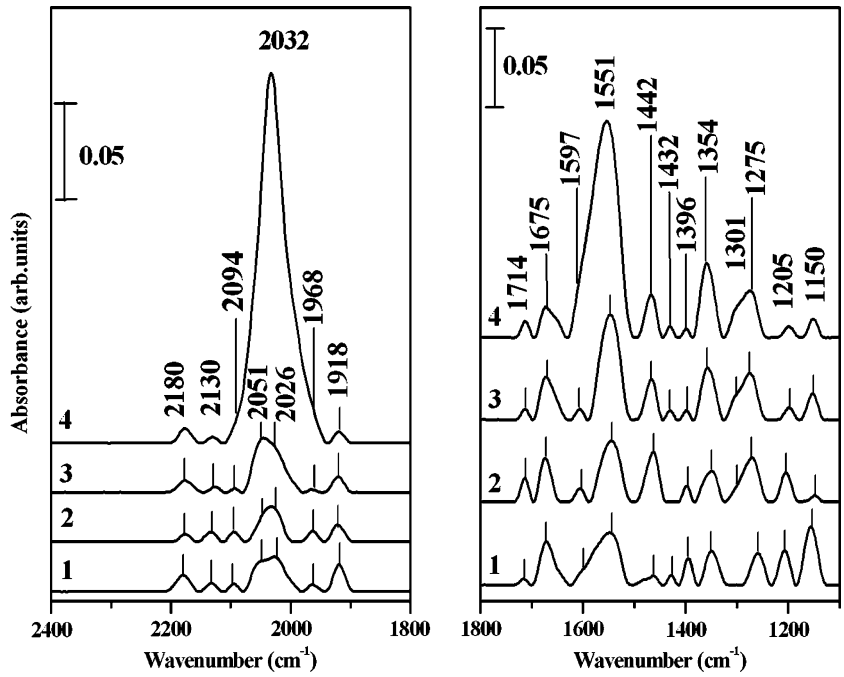

Figure 2. Infrared spectra of CO adsorbed on 1% Au/TiO_2 at 300 K for 15 min: 1 – 1.33 Pa; 2 – 13.3 Pa; 3 – 1.33 hPa and 4 – 13.3 hPa.

spectra 3–4). The band at 2358 cm^{-1} due to adsorbed CO_2 was observed with the highest intensity in the $CO–O_2$ mixture, its intensity strongly reduced in $CO–O_2–H_2$ gas mixtures and its position shifted to lower wavenumbers due to the presence of hydrogen. Below 1800 cm^{-1} the bands at 1560 and 1540 cm^{-1} appreciably increased in $CO–O_2–H_2$ mixtures. At higher temperatures (323–373 K) the intensities of the bands of adsorbed CO_2 and CO adsorbed on Au sites were smaller than at 300 K. In $CO–O_2–H_2$ mixtures the bands at 1560 and 1540 cm^{-1} became dominant below 1800 cm^{-1} at 323–373 K.

The band due to adsorbed CO_2 ($\sim$2350 cm^{-1}) was not detected on TiO_2 at any temperatures and in any gas mixtures. Similarly to the features observed on 1% Au/TiO_2, the bands at 1560 and 1540 cm^{-1} were also dominant in $CO–O_2–H_2$ mixtures on the spectra of TiO_2 at all temperatures.

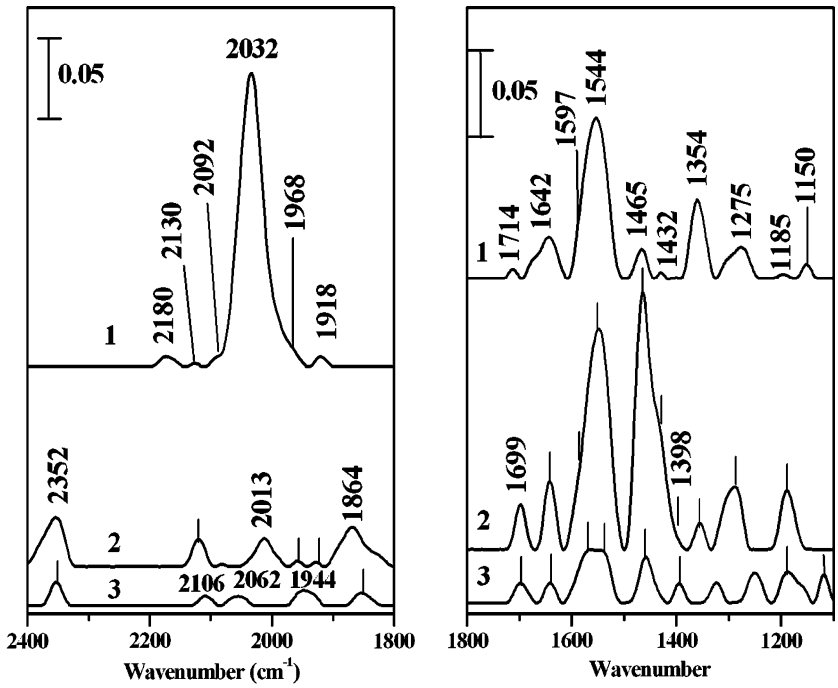

Figure 3. Infrared spectra of 13.3 hPa CO adsorbed on 1% Au/TiO_2 at different temperatures: 1 – 300 K; 2 – 323 K and 3 – 373 K. The spectra were taken at the temperatures of adsorption.

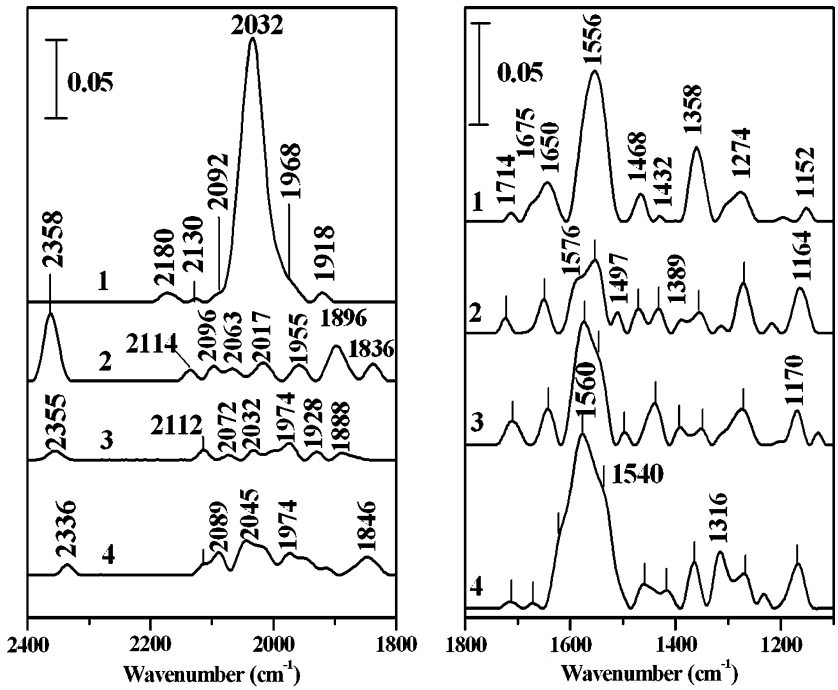

Figure 4. Infrared spectra of different gas mixtures adsorbed on 1% Au/TiO_2 at 300 K for 60 min: 1 – 13.3 hPa CO; 2 – 13.3 hPa CO + 1.33 hPa O_2; 3 – 13.3 hPa CO + 1.33 hPa O_2 + 13.3 Pa H_2 and 4 – 13.3 hPa CO + 1.33 hPa O_2 + 1.33 hPa H_2.

3.2. Mass spectrometric studies

During the above FTIR experiments the changes of the gas phase composition have been monitored by mass spectrometer. Some characteristics and informative curves registered at 300 K during the interactions of different gas mixtures with reduced 1% Au/TiO_2 are shown on Figure 5.

A slight increase in the gas phase concentration of CO_2 was experienced in the interaction of CO alone with the Au/TiO_2. The highest amount of gaseous CO_2 was

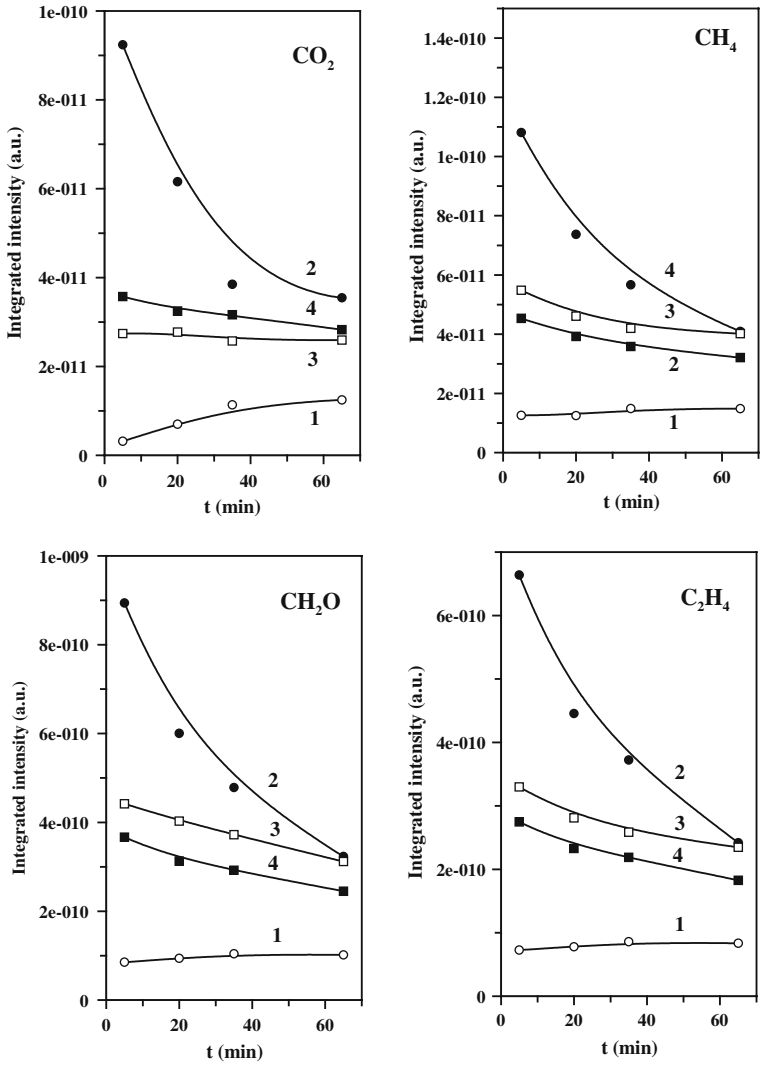

Figure 5. Changes in the gas phase composition during the interaction of different gas mixtures with 1% Au/TiO_2 at 300 K: 1 – 13.3 hPa CO; 2–13.3 hPa CO + 1.33 hPa O_2; 3 – 13.3 hPa CO + 1.33 hPa O_2 + 13.3 Pa H_2 and 4 – 13.3 hPa CO + 1.33 hPa O_2 + 1.33 hPa H_2.

measured when the CO + O_2 gas mixture reacted with the catalyst. An important observation is that the amount of gas phase CO_2 was reduced by the presence of H_2 in the CO–O_2 gas mixture.

Interestingly formaldehyde appeared in the gas phase when the Au/TiO_2 sample reacted with CO–O_2 and CO–O_2–H_2 gas mixtures. As the decomposition products of formaldehyde [19], gas phase methane and ethylene were also detected in these experiments. Formaldehyde and consequently its decomposition products (methane and ethylene) were not experienced in the interaction of CO with Au/TiO_2. It has to be mentioned that gaseous formic acid (HCOOH) was not detected in any interaction at 300 K.

The increase of the reaction temperature did not modify the ranking of the changes in the gas phase presented above at 300 K. The amounts of the above mentioned products were slightly higher at 323 K than at 300 K; at 373 K, however, their amounts were the smallest.

In the reaction of CO with reduced TiO_2 at 300–373 K the formation of gaseous CO_2, CH_2O, CH_4 and C_2H_4 was not observed. In CO–O_2 and CO–O_2–H_2 gas mixtures, however, the above products appeared in the gas phase; their amounts were smaller than those detected on 1% Au/TiO_2 sample.

The changes in the gaseous concentrations of CO and O_2 on TiO_2 (A) and on 1% Au/TiO_2 (B), respectively, at 300 K using different gas mixtures were plotted on Figure 6. From the characteristic curves it can be concluded that TiO_2 and 1% Au/TiO_2 utilized differently the two main components (CO and O_2) of the reacting gas mixtures. Practically no change in the gas phase CO concentration was observed in the reaction of CO (alone) on TiO_2. In any other gas mixtures the original CO concentration decreased dramatically on TiO_2. In

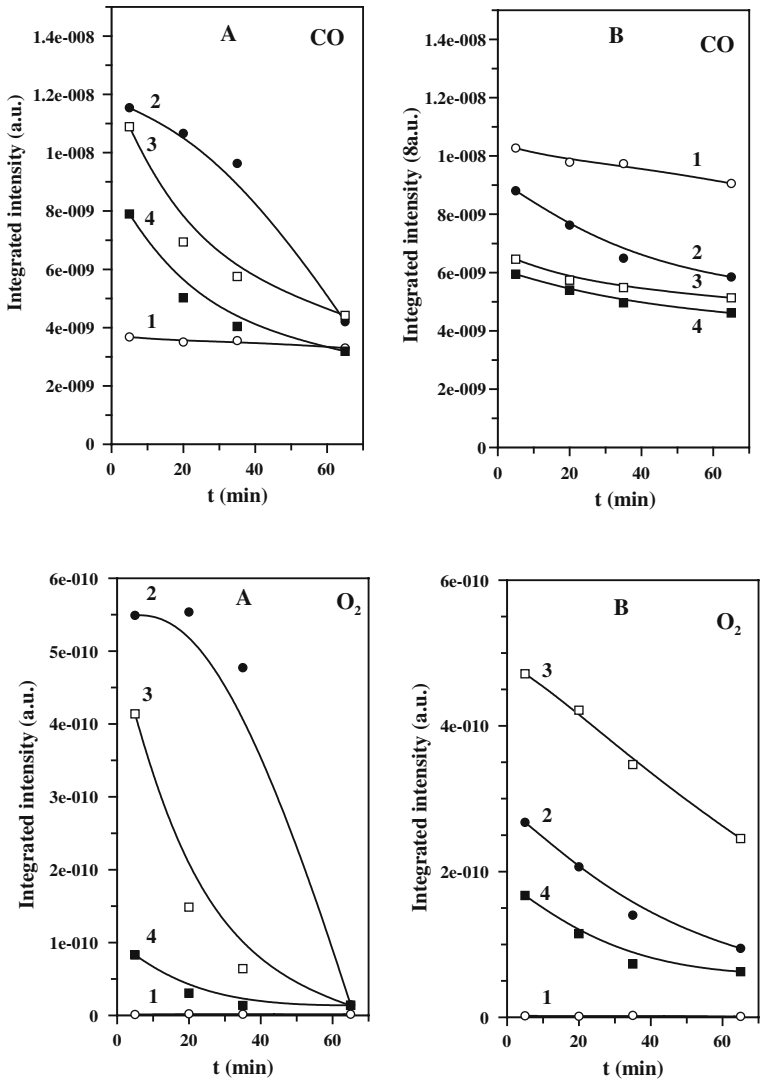

Figure 6. Changes in the gas phase concentration of CO and O_2 during the interaction of different gas mixtures with TiO_2 (a) and 1% Au/TiO_2 (b) at 300 K: 1 – 13.3 hPa CO; 2 – 13.3 hPa CO + 1.33 hPa O_2; 3 – 13.3 hPa CO + 1.33 hPa O_2 + 13.3 Pa H_2 and 4 – 13.3 hPa CO + 1.33 hPa O_2 + 1.33 hPa H_2.

the reactions of O_2-containing gas mixtures oxygen disappeared from the gas phase in the 60th min. The highest extent of O_2 consumption was observed in CO–O_2 gas mixture on TiO_2. Very probably on TiO_2 a huge part of gaseous oxygen reacts with the oxygen vacancies produced at high temperature reduction.

An appreciable decrease in the concentration of gaseous CO was observed when CO alone reacted at 300 K on 1% Au/TiO_2 sample. The extent of O_2 disappearance was relatively higher in the reaction of CO–O_2 gas mixture, while the consumption of gaseous carbon monoxide was smaller in CO–O_2–H_2 mixtures. The rate of O_2 disappearance was slower, the extent of oxygen consumption was smaller on 1% Au/TiO_2 than on TiO_2.

The changes in the amount of gaseous H_2 (if any) on TiO_2 and on 1% Au/TiO_2 differ considerably. Only slight decrease in gaseous H_2 concentrations was detected on TiO_2 at 300–373 K using CO–O_2–H_2 gas mixtures. The amount of the gaseous H_2 decreased in the highest extent at 300 K on 1% Au/TiO_2 in CO–O_2–H_2 mixtures. At higher temperatures the extent of H_2 consumption was smaller than at 300 K. An interesting feature was: the higher the reaction temperature, the higher the amount of gas phase H_2.

4. Discussion

Numerous studies on the oxidation of CO on TiO_2-supported Au catalysts have been published; for instance, Haruta [25,26] reported zero-order kinetics for CO oxidation over Au/TiO_2. Zero-order kinetics suggests that CO and O_2 are adsorbed to saturation and that reaction of adsorbed CO and oxygen ($O_{(a)}$ or $O_{2(a)}$) is the rate determining step.

Vannice and coworkers [10,27] used kinetic modeling and DRIFTS to elucidate the reaction mechanism of

CO oxidation on Au/TiO_2. A two site model, with CO adsorbing on Au and O_2 adsorbing on TiO_2, that is consistent with Langmuir–Hinselwood kinetics for noncompetitive adsorption, was found to fit the partial pressure data well.

Although it is generally accepted that the high catalytic activity of supported gold catalysts in low temperature CO oxidation can be attributed to the presence of small gold particles [28–30], the nature of the active gold sites remains a matter of discussion. While some authors believe that ionic gold provides the active sites for CO oxidation [31,32], others claim metallic gold to be the active species [28,29]. However, according to many papers, the gold/support interface plays an important role [33–35].

According to the above statements, different adsorbed CO species were assigned in the IR studies of CO oxidation. The band that appeared at 2106 cm^{-1} could be attributed to CO chemisorbed on gold metallic part [10,36–37]. The bands at 2060 and 1998 cm^{-1} were reported for supported gold catalysts after reduction treatment. The 2060 cm^{-1} band was assigned to CO adsorbed on very small gold clusters, negatively charged as a consequence of an electron transfer from the reduced support to the small clusters, while the band at 1998 cm^{-1} is due to CO adsorbed on Au in bridge form [40].

It has been reported [41,42] that the increased electron density on gold resulted in an enhanced CO adsorption by increased backdonation from gold d bands to the $2\pi^*$ orbital of the CO molecule. It has also been suggested that the increase in the electron density of gold is the result of the migration of an electron from the reactant oxygen, thus this electron transfer to the gold particle increased the CO oxidation activity.

On the basis of the data obtained in studying the poisoning effect of SO_2 on the catalytic activity of Au/TiO_2 in CO oxidation [43], the above explanation has been criticized. It was postulated [43] that the electron transfer to the Au particles occurs from surface sulfate formed in SO_2 treatment, the consequence of which was the decrease in the catalytic activity. Hence, it would be reasonable to claim that the catalytic activity of Au/TiO_2 is not solely depended on the electronic state of Au. The increase of the adsorption strength (caused by SO_2 treatment) between CO and the Au particles is thought to be one of the reasons for decreasing the CO oxidation activity by suppressing the migration of CO adsorbed on the Au particles to the $Au–TiO_2$ perimeter sites to form CO_2.

Only weak IR features grew at 1600–1700 cm^{-1} during CO adsorption, indicating that very low adsorption or formation of carbonate species was detected on TiO_2 support. No features were observed in the range of 2000–2400 cm^{-1} that could be indicative of adsorbed CO or CO_2, demonstrating that no reactions occur on the bare TiO_2 (i.e. no gold) [44]. Strong IR absorption bands were observed on Au/TiO_2 in the presence of $CO–O_2$ gas mixture. These results suggest that Au is necessary for the facile adsorption of CO and subsequent formation of carbonate species either on Au or TiO_2 support. Similar carbonate bands on Au/TiO_2 were observed in CO alone, suggesting that the presence of O_2 is not necessary for carbonate formation on this sample [44].

Bands near 1620 cm^{-1} have been previously assigned to bidentate carbonate species on anatase [10,45] and to carbonate-like species on Au/TiO_2 samples [46]. The band near 1500 cm^{-1} could be due to a carboxilate species or a bidentate carbonate species bound to a single Ti atom [47]. Monodentate carbonate species may also be present, because they have band positions typically around 1530–1470 and 1370–1300 cm^{-1} [47].

Isotopic substitution studies of $^{12}CO–^{16}O_2$ and $^{12}CO–^{18}O_2$ interactions have suggested that gas phase oxygen does not participate in the formation of carbonate-like species, and thus the oxygen involved in the formation of carbonates is from the oxide-support, not from gas phase O_2 [48].

As the intensities of all species (carboxilate, bidentate and monodentate carbonates) grew together after switching on and evolved little except for a slow uniform decrease in all bands after switching off of the reacting $CO–O_2$ mixture, it has been suggested that these species are spectators and are not involved in the surface reaction [44].

In general, the suitable catalyst for preferential CO oxidation in hydrogen must adsorb CO and provide activated oxygen, while hydrogen adsorption must be suppressed [12,13]. CO is thought to adsorb on the metal phase (in our case on Au). CO adsorption on gold is very weak, which is manifested in low steady state CO coverage at operational conditions [5–7]. But oxygen does not adsorb on Au because of its very low sticking coefficient [49]. In this way, oxygen activated on TiO_2 should diffuse to interface sites and subsequently reacts either at the perimeter or – after a spillover process of one of the components – on the adjecent metal–oxide site [12].

In harmony with the previous findings [5–7], we have also found weak CO adsorption on gold, which is manifested in low steady-state intensities of the IR bands in the range of 2200–1800 cm^{-1} due to adsorbed CO species. At the CO pressure of 1.33–133 Pa the stable bands at 1968 and 1918 cm^{-1} might be assigned to 2-fold (bridge bonded) and 3-fold adsorbed CO. The 2180 cm^{-1} band belongs to CO adsorbed on titania (see figure 1), while the band at 2130 cm^{-1} can be due to CO adsorbed on highly-valent (Au^{n+}) metal site (existing in a small quantity after the reduction at 573 K).

The most striking feature obtained in this work was the detection of a three band structure (similar to that

observed on supported Rh) in low CO pressures at 300 K. The classical assignment of the three bands detected in the case of supported Rh (~2100 and ~2030 cm^{-1} bands are due to symmetric and asymmetric stretchings of $Rh^{+1}(CO)_2$ and the ~2060 cm^{-1} band is due to on top CO [50]), however, is not applicable to Au/TiO_2, as the three bands behaved differently with the changes of the experimental conditions.

Thus the 2094 cm^{-1} band can be more probably assigned to CO adsorbed on monoatomic Au^0, similarly to the assigment made in the case of Pt/TiO_2 [51], where the band at around 2100 cm^{-1} was attributed to the monoatomic Pt^0–CO surface species. The bands at 2051 and 2026 cm^{-1} may belong to CO adsorbed on Au atoms with different coordination numbers (i.e. Au atoms on edges and kinked Au atoms).

Interestingly, the 2051 and 2026 cm^{-1} bands disappeared with the increase of CO pressure at 300 K (Figure 2); only one band at 2032 cm^{-1} with high intensity appeared in 13.3 hPa CO. The appearance of the 2032 cm^{-1} band due to increasing CO pressure suggests the occurrence of agglomeration or recunstruction of surface Au atoms. Very probably, in higher CO pressure edged and kinked Au atoms transform to Au atoms in more ordered position: i.e. they become parts of different smooth Au crystalline facets (reconstruction). At the same time the increase of the Au crystallite size can also be expected (agglomeration).

The above assignments permit to conclude that after reduction at 573 K monoatomic Au^0, small Au clusters with edged and kinked Au atoms and higher-valent Au^{n+} sites are present on the titania surface. CO adsorbed on these surface sites can be regarded as a surface reaction partner for oxidation during the interaction of CO, CO + O_2 and CO + O_2 + H_2 gas mixtures with the catalyst. The surface concentrations of adsorbed CO species were slightly increased with increasing CO pressure and decreased with the increase of the reaction temperature. At 300 K and in 13.3 hPa CO an additional surface species, CO adsorbed on Au atoms of smooth Au crystal facets, increase the surface concentration of adsorbed CO. This type of adsorbed CO was missing in the spectra registered at 323–373 K.

When oxygen was present in the gas mixtures, the intensities of the bands due to adsorbed CO were smaller than in CO alone. Band due to CO adsorbed on Au of smooth crystal facets was missing in CO + O_2 mixture. From this it can be concluded that oxygen competes with CO for surface Au sites, i.e. oxygen adsorbs on the metallic part (Au) of the catalyst, too. This suggests that CO oxidation may proceed on the metallic sites with Langmuir–Hinselwood kinetics for competitive adsorption.

According to the above statements the surface active species for CO oxidation are very probably CO adsorbed on edged and kinked Au sites. The surface concentration of these species is the highest at 300 K in CO + O_2 gas mixture, accordingly the extent of the gas phase CO_2 formation (CO oxidation) is the highest in this case.

An FTIR study revealed dissociation of H_2 at room temperature on Au/TiO_2 [40]. As there are no data on H_2 dissociation on TiO_2 (without metal), it can be concluded that the surface sites for H_2 activation are probably the Au sites on TiO_2. Thus, a part of Au surface sites is occupied by H_2 activation in CO + O_2 + H_2 gas mixtures, which reduces the extent of CO oxidation on these sites, as it was experienced above.

Besides the bands assigned to bidentate and monodentate carbonates, as well as carbonate polydentate polymer (table 1), which can be regarded as spectators and not involved in surface reaction [44], bands due to surface formic acid, formiate and formaldehyde were found in the IR spectra (table 1). The appearance of formaldehyde in the gas phase was also experienced. The formation of formaldehyde temporarily contributes to the consumption of the gaseous CO and H_2, the decomposition of formaldehyde, however, produces mainly CO and H_2 [16], which reduces the efficiency of CO disappearance through its oxidation to CO_2. Thus, the ability of the Au/TiO_2 catalyst to produce formaldehyde on its surface lowered the extent of CO oxidation, that is Au/TiO_2 catalyst is not suitable for the preferential oxidation of CO.

5. Conclusions

1. Monoatomic Au^0, small Au clusters with edged and kinked Au atoms and higher-valent Au^{n+} sites were detected by CO adsorption at 300 K on Au/TiO_2 after its reduction at 573 K. Higher pressure CO caused the transformation of edged and kinked Au atoms to Au atoms in more ordered position: i.e. they become parts of different smooth Au crystalline facets (reconstruction). At the same time the increase of the Au crystallite size can also be expected (agglomeration).
2. Oxygen adsorbs on the metallic part (Au) of the catalyst, too. This suggests that CO oxidation may proceed on the metallic sites with Langmuir–Hinselwood kinetics for competitive adsorption.
3. A part of Au surface sites is occupied by H_2 activation in CO + O_2 + H_2 gas mixtures, which reduces the extent of CO oxidation on these sites.
4. Au/TiO_2 catalyst produces formaldehyde on its surface, which lowers the extent of CO oxidation. Au/TiO_2 catalyst is not suitable for the preferential oxidation of CO.

Acknowledgments

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