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SURFACE SPECIES AND GAS PHASE PRODUCTS IN THE PREFERENTIAL OXIDATION OF CO ON TiO_2-SUPPORTED Au-Rh BIMETALLIC CATALYSTS

János Raskó and János Kiss[*]
Reaction Kinetics Research Group, Chemical Research Center of the Hungarian Academy of Sciences, University of Szeged, H-6701 Szeged, P. O. Box 168, Hungary

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Abstract

The oxidation of CO in the presence of hydrogen (PROX process) was investigated on bimetallic Au-Rh catalysts at 300-373 K by Fourier transform infrared spectroscopy and mass spectroscopy. The effects of catalyst composition, reaction temperature and composition of the reacting gas mixtures have been studied. The IR studies revealed the formation of bi- and monodentate carbonates, bicarbonates and hydrocarbonates on the catalysts surfaces; these surface species proved to be not involved in the surface reactions. The formation of adsorbed formaldehyde was observed on all surfaces, except 1% (0.25Au+0.75Rh)/TiO_2. Adsorbed CO_2 (as the surface product of CO oxidation) was not detected on any surface. The presence of both O_2 and H_2 reduced the surface concentration of CO adsorbed on the metallic sites. Mass spectroscopic analysis of the gas phase showed that gaseous CO_2 was formed in the highest amount in the CO+O_2 mixture, the presence of H_2 suppressed the amount of CO_2 produced. This negative effect of H_2 was the lowest on the 1% Rh/TiO_2 and 1% (0.25Au+0.75Rh)/TiO_2 catalysts.

Keywords: PROX of CO, bimetallic Au-Rh catalysts, FTIR, mass spectroscopy, surface species, gas phase products

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[*] Corresponding author. Fax: +36-62-420-678; E-mail: jkiss@chem.u-szeged.hu

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INTRODUCTION

Hydrogen produced by catalytic transformations (steam reforming or partial oxidation) of natural gas or alcohols [1, 2] contains always significant amounts of CO together with H_2O, CO_2 and CH_4. Before using hydrogen, the concentration of CO (cca. 5-15%) must be lowered to 1-100 ppm for the proper operation of a 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 has been found to be one of the most active catalysts for low temperature CO oxidation (9, 14), relatively little is known on the catalytic behavior of Au/TiO_2 catalysts in the PROX reaction [4-7].

Another approximation for overcoming the problem caused by the relatively high concentration of CO in the fuel cell is to find a CO-tolerant H_2 oxidation catalyst, which works as an anode catalyst that oxidizes CO while maintaining high activity for H_2 electrooxidation under 373 K. For this purpose, Pt-Sn/C, Pt-Rh supported on MoO_3 and on TiO_2 [15] and γ-Al_2O_3-supported Au-Pt [16] bimetallic systems might be good candidates.

In the present work, an attempt was made to assign the surface species formed in CO oxidation and in the PROX reaction on Au-Rh/TiO_2 bimetallic catalysts 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).

EXPERIMENTAL

TiO_2 was the product of Degussa (P25, 50 m^2/g). The preparation of 1 w.% Au/TiO_2 and 1 w.% Rh/TiO_2 catalysts has been previously published in details (18, 19, 21). The bimetallic Au – Rh catalysts with three different compositions were produced by impregnating TiO_2 with the mixtures of calculated volumes of $HAuCl_4$ and $RhCl_3$ x 3 H_2O solutions to yield 1 w.% metal content. The impregnated powders were dried in air at 383 K for 3 h. CO (99.97%), and H_2 (99.999%) were the products of Linde.

For IR studies the catalyst powders were pressed onto a Ta-mesh (30 x 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 a 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 $1.33x10^{-5}$ Pa): the sample was heated in 1.33 hPa H_2 up to 573 K and it was kept at this temperature for 1 hour, 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 vapour 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 by means of a QMS 200 (Balzers) quadrupole mass-spectrometer. The volume around the head of the QMS 200 apparatus was continuously evacuated and it was connected to the UV IR cell via a leak valve producing 2.67×10^{-3} Pa around the MS head when reacting gases were present in the cell.

RESULTS AND DISCUSSION

CO adsorbs very weakly on TiO_2: in the range of 2400-2000 cm^{-1} only a band around 2180 cm^{-1} with very low intensity was detected, which can be due to CO adsorbed on TiO_2 [17] Its intensity decreased with the increase of the adsorption temperature. No band(s) due to adsorbed CO_2 appeared at 300-373 K during CO adsorption. Bands due to surface formiate (see Table 1) were registered, and a band at 1712-1720 cm^{-1} (due to $CH_2O_{(a)}$ [18g]) was observed on TiO_2 at 300-373 K.

The presence of oxygen led to the intensity increase of bi- and monodentate carbonates' bands and to the decrease of the 2180 cm^{-1} band. An IR feature due to adsorbed formaldehyde (1715 cm^{-1}) was observed even at 373 K in the CO-O_2 gas mixture. Bands due to adsorbed CO_2 were not detected.

When H_2 (13.3 Pa and 1.33 hPa) was also present in the CO-O_2 gas mixtures, new bands with relatively high intensities at 1611, 1546, 1510 and 1460 cm^{-1} were detected, which are probably due to adsorbed hydrocarbonates, bicarbonates, bi- and monodentate carbonates (12, 13, 19). A band assigned to adsorbed formiate appeared at 1693 cm^{-1} in these gas mixtures, and a band at 1646 cm^{-1} due to δ ($H_2O_{(a)}$) was clearly observable. No IR features due to CO_2 adsorbed on TiO_2 were observed in these cases.

As no IR features due to adsorbed CO_2 were observed on TiO_2, it can be supposed that TiO_2 alone cannot oxidize CO to CO_2, neither by its active surface oxygen, nor with the help of gaseous oxygen. The adsorption of CO through the lattice oxygen of TiO_2 led to the formation of bi- and monodentate

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] 1671[19]		1675-1666
bicarbonate			1613,1391,1045[23] 1611,1393,1043[12]	
ν_a(OCO) in $HCOO^-_{(a)}$ on TiO_2		1590,1554[17-22] 1556[19]		1596-1597,1551
bidentate carbonate			1562,1286,1028[24] 1565,1298,1014[12]	1560-1534, 1280-1287
unidentate carbonate			1545,1348,1062[24] 1514,1316[12]	1546-1537, 1354-1365
carbonate polydentate polymer			1462,1353,1066[23] 1463,1353,1050[12]	1465, 1356
ω(CH_2) in DOM	1403-1411			1396-1403
ν_s(OCO) in $HCOO^-_{(a)}$		1374[19]		
τ(CH_2) in DOM	1293-1299			1275-1299
ω(CH_2) in $H_2CO_{(a)}$	1251			1233
ρ(CH_2) in $H_2CO_{(a)}$	1155-1164			1150-1169
ρ(CH_2) in DOM	1112			1136

DOM = dioxymethylene (formed in the reaction of surface oxygen ion and formaldehyde) carbonates and – in the presence of H_2 – to the formation of hydrocarbonate on the titania surface. The formation of adsorbed formaldehyde on TiO_2 seems to be promoted by hydrogen; the presence of formaldehyde in the adsorbed layer and in the gas phase (see later) negatively affects the preferential oxidation of CO [19].

The above experiments were performed on TiO_2-supported metal catalysts, too. The main difference between TiO_2 and metal/TiO_2 catalysts was the appearance of the bands attributed to metal-CO surface species on the latter samples. Bands due to CO adsorbed on the metal sites appearing in the interaction of different gases and gas mixtures with the metal/TiO_2 catalysts are characteristic of the actual state of surface metal centres.

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 metallic phase. CO adsorption on gold is very weak, which is manifested in a low steady state CO coverage at operational conditions [5–7]

A detailed description of preferential CO oxidation on Au/TiO_2 has recently been given (19). Similarly to the previous findings [5-7], CO adsorption proved to be weak on this sample. It was postulated that the increase of the reaction temperature, the presence of oxygen and hydrogen lowered the surface concentration of adsorbed CO. It was also suggested that Au/TiO_2 is not a suitable catalyst for preferential CO oxidation, as the amount of CO_2 (both in the adsorbed layer and in the gas phase) was highly suppressed by the presence of hydrogen. This was interpreted by the formation of formaldehyde [19].

Data obtained in the present work on 1% (0.75Au+0.25Rh)/TiO_2 sample were similar in many respects to those experienced on 1% Au/TiO_2.

On the other monometallic catalyst (1% Rh/TiO_2), CO adsorbs in higher quantity than on the 1% Au/TiO_2. Bands due to symmetric stretching (2101 cm^{-1}) and asymmetric stretching (2033 cm^{-1}) of $Rh^+(CO)_2$ surface species, due to linearly bonded CO (2066 cm^{-1}), as well as bands due to bridge-bonded CO (1965 cm^{-1}) and CO adsorbed on threefold coordinated hollow sites (1863 cm^{-1}) could be seen on the spectra taken at 300 K. With the increase of the adsorption temperature, the intensities of the CO bands drastically decreased, and the state of surface Rh sites changed: at 323 K Rh^+ sites (corresponding IR bands are at 2088 and 2033 cm^{-1} of $Rh^+(CO)_2$) and hollow sites threefold coordinated by Rh^0 atoms (1863 cm^{-1}) are available for CO adsorption. At 373 K bands due to CO adsorbed on zerovalent Rh atoms (linearly bonded CO on Rh^0 – 2066 cm^{-1} and $(Rh^0)_2(CO)_3$ surface species [20] – 2003 cm^{-1}) were only observed possibly due to the reduction of Rh^+ centres by CO at this temperature.

In the CO+O_2 gas mixtures, the intensities of the CO bands decreased, which shows that oxygen adsorption blocks a remarkable part of Rh sites at 300 K. At higher temperatures (323-373 K) the intensities of the bands due to $Rh^+(CO)_2$

species increased and practically no IR features due to CO adsorbed on zerovalent Rh sites were observed in CO+O_2 mixtures. This is possibly due to the oxidation of Rh^0 centres to Rh^+ by gaseous oxygen.

Addition of H_2 into the CO+O_2 mixtures caused a further dramatic decrease in the intensities of CO bands, which may be due to H_2 activation on the metallic sites. Thus a part of Rh surface sites may be occupied by H_2 dissociation reducing thereby the number of active Rh sites in CO adsorption and its further oxidation.

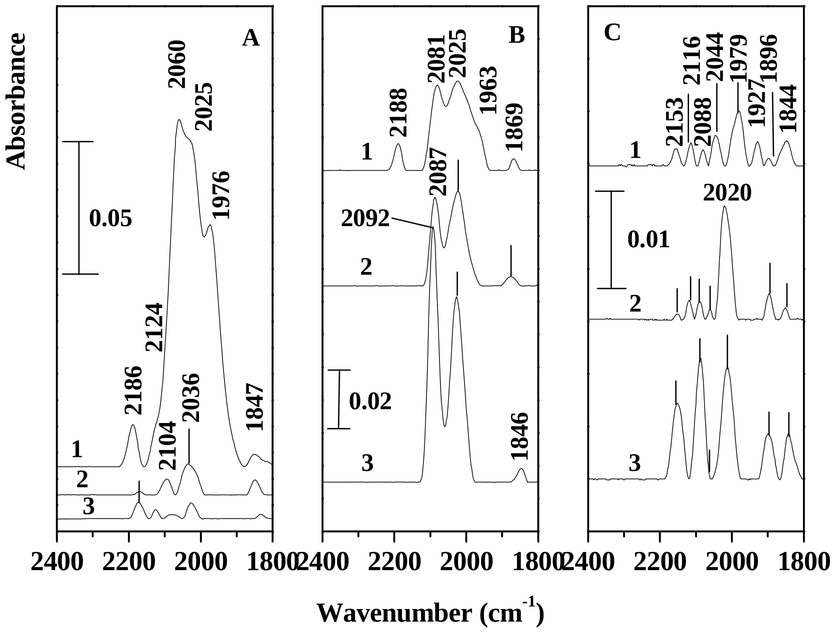

Fig. 1. Infrared spectra of 1% (0.25Au+0.75Rh)/TiO_2 detected in (A) – 1.33 hPa CO; (B) - 1.33 hPa CO + 13.3 Pa O_2 and (C) - 1.33 hPa CO + 13.3 Pa O_2 + 13.3 Pa H_2 at different temperatures: 1 – 300 K; 2 – 323 K and 3 – 373 K. Adsorption time 60 min

The results obtained on 1% (0.5Au+0.5Rh)/TiO_2 and on 1% (0.25Au+0.75Rh)/TiO_2 samples were very similar to those observed on 1% Rh/TiO_2 catalysts. This is illustrated by the spectra registered on 1% (0.25Au+0.75Rh)/TiO_2 in different gases and gas mixtures at different temperatures (Fig. 1). We have recently found [21] the enrichment of Rh in the outer surface layers of bimetallic (Au-Rh) crystallites on TiO_2. On this basis it can be expected that the bimetallic Au-Rh catalysts show a CO adsorptive behavior similar to that observed on TiO_2-supported monometallic Rh sample. It has to be emphasized that no IR feature due to adsorbed CO_2 was registered on Rh-rich bimetallic samples and on monometallic Rh/TiO_2 catalyst.

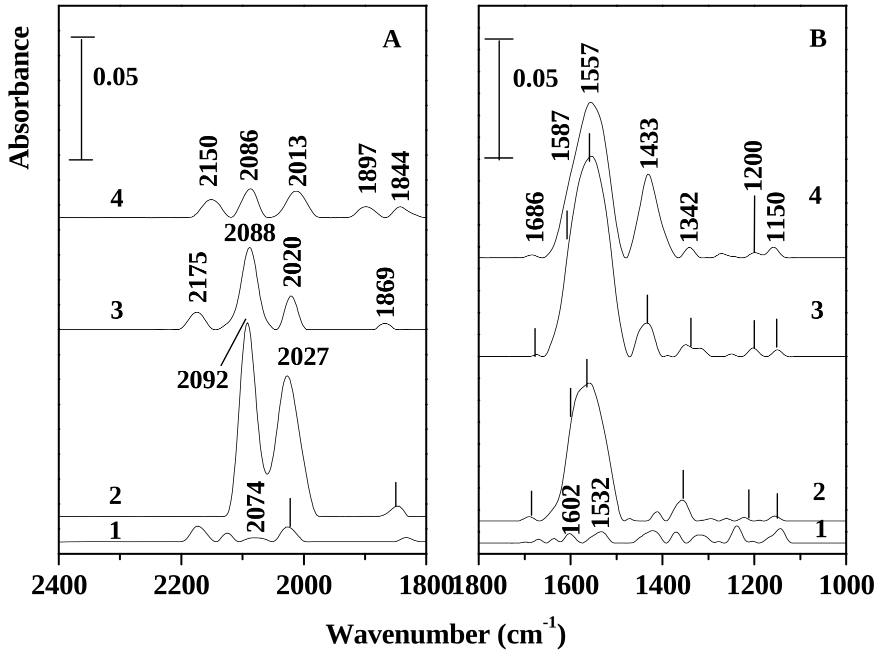

Fig. 2. Infrared spectra of 1% (0.25Au+0.75Rh)TiO_2 registered in different gases at 373 K (adsorption time 60 min): 1 – 1.33 hPa CO; 2 - 1.33 hPa CO + 13.3 Pa O_2; 3 - 1.33 hPa CO + 13.3 Pa O_2 + 1.33 Pa H_2 and 4 - 1.33 hPa CO + 13.3 Pa O_2 + 13.3 Pa H_2

Below 1800 cm^{-1}, bands due to formiate, bi- and monodentate carbonates and formaldehyde appeared on the spectra (Table 1). The formation of the above surface species was limited to CO alone on all catalysts, possibly due to the limited amount of surface active oxygen on the TiO_2 surface. In the presence of oxygen and hydrogen, however, the intensities of the bands due to bi- and monodentate carbonates appreciably increased. Characteristic spectra registered on 1% (0.25Au+0.75Rh)/TiO_2 were collected in Fig. 2. Similar bands were

Fig.3

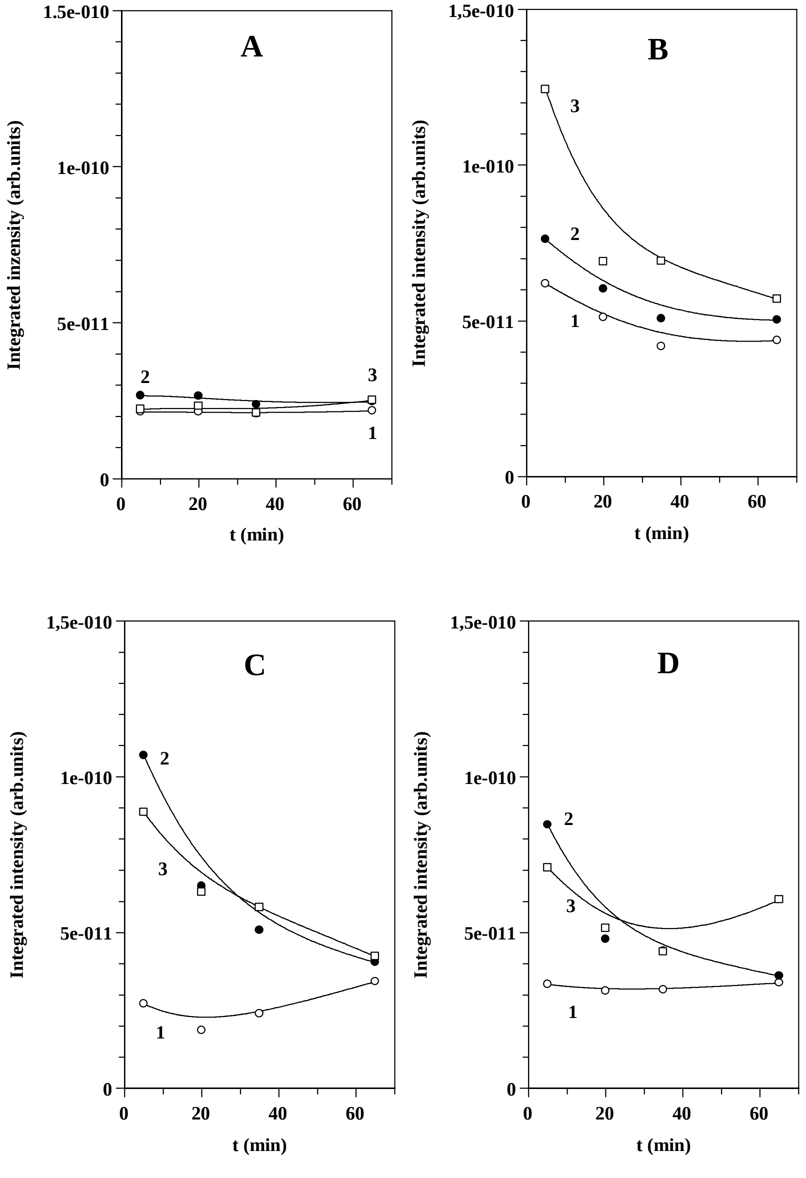

Fig. 3. Amounts of gaseous CO_2 (detected by MS) at 373 K in (A) – 1.33 hPa CO; (B) - 1.33 hPa CO + 13.3 Pa O_2; (C) - 1.33 hPa CO + 13.3 Pa O_2 + 1.33 Pa H_2 and (D) - 1.33 hPa CO + 13.3 Pa O_2 + 13.3 Pa H_2 on: 1 – 1% Au/TiO_2; 2 - 1% (0.25Au+0.75Rh)TiO_2 and 3 - 1% Rh/TiO_2

detected on other bimetallic samples. The above finding clearly shows the decisive role of gaseous oxygen in the formation of carbonates, which contradicts the former suggestion [22] that gas phase oxygen does not participate in the production of carbonate-like species. The intensities of the above bands were not affected by the composition of the reacting gas mixture and by the adsorption time. Based upon these findings it can be suggested that these species are not involved in the surface reactions, similarly to the former proposal (23). In the presence of hydrogen, a new band around 1433 cm^{-1} appeared the intensity of which depended on the amount of H_2 in the gas phase. This band is tentatively assigned to a surface hydrocarbonate species.

Special attention has been paid to the formation of formaldehyde in the adsorbed layer. Recently it has been shown (19) that the formation of formaldehyde dramatically reduced the effectivity of the PROX process on Au/TiO_2 catalyst. On the monometallic Rh/TiO_2 no formation of adsorbed formaldehyde was observed in CO and in $CO+O_2$ gas mixtures at 300-373 K; in $CO+O_2+H_2$ gas mixtures, however, infrared bands due to surface formaldehyde were detected. On the 1% $(0.75Au+0.25Rh)/TiO_2$ bimetallic sample, bands due to adsorbed formaldehyde were registered in all reacting gases at 300-373 K. The decrease of the Au content in the bimetallic catalysts led to the disappearance of IR features assigned to $CH_2O_{(a)}$. On 1% $(0.5Au+0.5Rh)/TiO_2$ these bands appeared only in CO and in $CO+O_2+H_2$ gas mixtures and on 1% $(0.25Au+0.75Rh)/TiO_2$ these bands were missing in all reacting gas mixtures and at any temperature. If we accept the former statement [19] that the formation of formaldehyde is disadvantageous in the PROX process, its absence on 1% $(0.25Au+0.75Rh)/TiO_2$ would make this sample a promising catalyst for the oxidation of CO in the presence of hydrogen.

Besides the registration of the IR spectra, mass spectrometric analysis of the gas phase was continuously performed in the above experiments. Among the MS data the intensity changes of gas phase CO_2 on selected catalysts at 373 K were depicted on Fig. 3. The highest amount of gaseous CO_2 was detected in the $CO+O_2$ gas mixture on all catalysts. The data clearly show that the effectivity of monometallic Au/TiO_2 in CO oxidation is significantly suppressed by the presence of hydrogen; on 1% Rh/TiO_2 and on 1% $(0.25Au+0.75Rh)/TiO_2$ catalysts, however, the negative effects were experienced only in the presence of higher amounts of gaseous hydrogen.

CONCLUSIONS

1. The interaction of gaseous CO with the lattice oxygen of titania leads to the formation of bi- and monodentate carbonates, bicarbonates and hydrocarbonate. The presence of H_2 in the gas phase increases the surface concentration of

hydrocarbonate. All these surface species are not involved in the surface reactions.

2. Formation of adsorbed formaldehyde was also observed, which negatively affects the effectivity of the catalysts in CO oxidation.
3. The surface concentration of CO adsorbed on metallic sites was reduced by the presence of both O_2 and H_2.
4. No IR features due to adsorbed CO_2 were registered, which shows that the product of surface oxidation of CO desorbs immediately from the surfaces.
5. The amount of gaseous CO_2 was suppressed by the presence of H_2 in the gas phase.
6. Based upon the data on the formation of surface species and of gaseous products, the 1% (0.25Au+0.75Rh)/TiO_2 sample seems to be a promising candidate among the Au-Rh bimetallic catalysts for the oxidation of CO in the presence of H_2.

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REFERENCES

1. J.N. Armor: *Appl. Catal.*, **176**, 159 (1999).
2. F. Aupretre, C. Descorme, D. Duprez: *Catal. Commun.*, **3**, 263 (2002).
3. A.J. Appleby, F.R. Foulkes: Fuel Cell Handbook, Van Nostrand Reinhold, New York, 1989.
4. G. Avgouropoulos, T. Ioannides, Ch. Papadopoulou, J. Battita, S. Hocevar, H.K. Martalis: *Catal. Today*, **75**, 157 (2002).
5. G.K. Bethke, H.H. Kung: *Appl. Catal.*, **194**, 43 (2000).
6. M.J. Kahlich, H. Gasteiger, R.J. Behm: *J. Catal.*, **182,** 430 (2000).
7. M.M Schubert, M.J. Kahlich, H. Gasteiger, R.J. Behm: *J. Power Sources*, **84,** 175 (1999).
8. M. Haruta, T. Kobayashi, S. Iijama, F. Delannay: *Proc. 9th Int. Congr. Catal.*, **3,** 1206 (1988).
9. D. Cunningham, S. Tsubota, N. Kamijo, M. Haruta: *Res. Chem. Intermed.*, **19,** 1 (1993).
10. M.A. Bollinger, M.A. Vannice: *Appl. Catal. B: Environmental*, **8,** 417 (1996).
11. A. Wootsch, C. Descorme, D. Duprez: *J. Catal.*, **225**, 259 (2004).
12. O. Pozdnyakova, D. Teschner, A. Wootsch, J. Krönert, B. Steinhauer, H. Sauer, L. Tóth, F.C. Jenthoft, A. Knop-Gericke, Z. Paál, R. Schlögl: *J. Catal.*, **237,** 1 (2006).
13. O. Pozdnyakova, D. Teschner, A. Wootsch, J. Krönert, B. Steinhauer, H. Sauer, L. Tóth, F.C. Jenthoft, A. Knop-Gericke, Z. Paál, R. Schlögl: *J. Catal.*, **237**, 17 (2006).
14. S. Lin, M.A. Bollinger, M.A. Vannice: *Catal. Lett.*, **17**, 245 (1993).
15. G. Avgouropoulus, T. Ioannides: *Appl. Catal. B: Environmental*, **56**, 77 (2005).
16. S. Zhou. K. McIlwrath, G. Jackson, B. Eichhorn: *J. Am. Chem. Soc.*, **126,** 1780 (2006).

17. J. Raskó, Z. Szabó, T. Bánsági, F. Solymosi: *Phys. Chem. Chem. Phys.*, **3,** 4437 (2001).
18. T. Kecskés, J. Raskó, J. Kiss: *Appl. Catal. A: General*, **273**, 55 (2004).
19. J. Raskó, J. Kiss: *Catal. Lett.*, **111**, 87 (2006).
20. F. Boccuzzi, A. Chiorino, M. Manzoli, D. Andreeva, T. Tabakova: *J. Catal.*, **188**, 176 (1999).
21. J. Raskó, J. Kiss: *Reakt. Kinet. Catal. Lett.*, **90**, 187 (2007).
22. F. Boccuzzi, A. Chiorino, S. Tsubota, M. Haruta: *J. Phys. Chem.*, **100**, 3625 (1996).
23. B.-K. Chang, B.W. Jang, S. Dai, S.H. Overbury: *J. Catal.*, **236,** 392 (2005).