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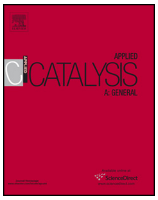

# Catalytic and photocatalytic reactions of $H_2 + CO_2$ on supported Au catalysts

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ABSTRACT

The interaction and the reaction between $H_2 + CO_2$ have been investigated on supported Au catalysts. By means of infrared spectroscopy, the formation of formate species was detected. The reaction between $H_2 + CO_2$ occurred above 475–500 K. The main reaction pathway was the formation of CO. The catalytic efficiency of Au sensitively depended upon the nature of the support. Highest conversion of $CO_2$ was found on Au particles dispersed on n-type oxides, $TiO_2$, ZnO, and $CeO_2$. Au deposited on insulating oxides exhibited much less activity. At higher pressure, at 8.5 atm, a small amount of $CH_4$ and $CH_3OH$ were also produced. Illumination of the active catalysts induced the reaction even at room temperature resulting in the formation of $CH_4$. The high activity of Au particles supported by n-type semiconducting oxides was ascribed to the electronic interaction between Au and oxides leading to the activation of $CO_2$.

## 1. Introduction

The activation of $CO_2$ and its conversion into more valuable compounds is a great challenge for heterogeneous catalysis [1–5]. We became involved in this subject in early 80s [6–9]. Our main findings were as follows: in contrast to the earlier belief $CO_2$ does not dissociate on supported Rh at 300 K, but addition of $H_2$ to $CO_2$ induces its dissociation even at room temperature and leads to the formation of formate species. This result was confirmed on Rh(1 1 1) in UHV by several electrons spectroscopic measurements [10]. It was an important finding that the catalytic performance of the Pt metals in the hydrogenation of $CO_2$ is strongly affected by the nature of the supports. $TiO_2$ was found to be the most effective one, which was attributed to the electronic interaction between metals and $TiO_2$ [9]. This explanation was based on our early finding namely that variation of the work function of $TiO_2$ appreciably affected the catalytic performance of Ni evaporated on $TiO_2$ [11–13]. It appears that the interest in the carrier effect became more intensive nowadays thanks to the modern surface science methods, and the possible role of oxygen vacancy of $TiO_2$ came into prominence [14–16].

After discovery that Au in nanosize exhibits a surprisingly high catalytic activity in many reactions [17–19], its influence has been also tested in the catalytic chemistry of $CO_2$ [20–23]. Au deposited on $TiO_2$ and titanate nanotube were found to be inactive in $CO_2$ hydrogenation [21]. At high pressure (50 atm) and at relatively low space velocity (3000 $h^{-1}$ ml $g^{-1}$), however, a significant amount of methanol was found [22,23].

In the present work, we examine the surface interaction and reaction between $H_2$ and $CO_2$ on Au catalysts. Attention is paid to the effects of supports, promotors and illumination. We expect that the Au in nanosize (1–3 nm) deposited on n-type semiconducting oxides might be able to activate the rather inert $CO_2$ and induces its thermal and photoreactions with $H_2$ even at low pressure. Recently, it was found the Au/$TiO_2$ is a very effective catalyst even for the photoinduced reactions of NO + $C_2H_5OH$ and in the decomposition of several organic compounds at room temperature [24]. As regards the activation of $CO_2$, recently we found that the deposition of K on Au(1 1 1) single crystal leads to the formation of negatively charged $CO_2$ and its dissociation even above 300 K [25]. Illumination of the $CO_2$ + K/Au(1 1 1) system greatly promoted the dissociation of $CO_2$ [26].

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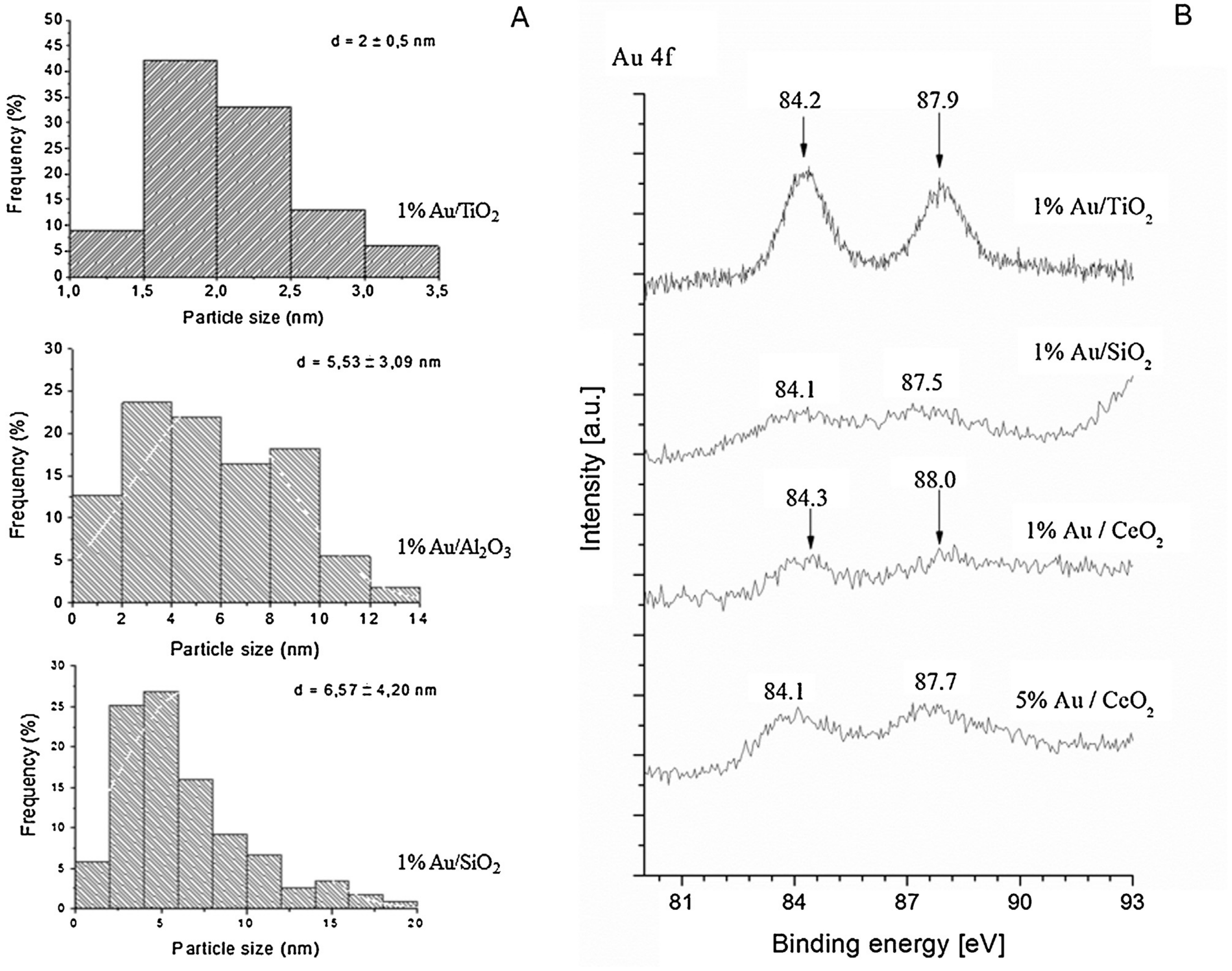

**Fig. 1.** Sizes of Au particles on different supports (A), XPS spectra of different Au catalysts (B).

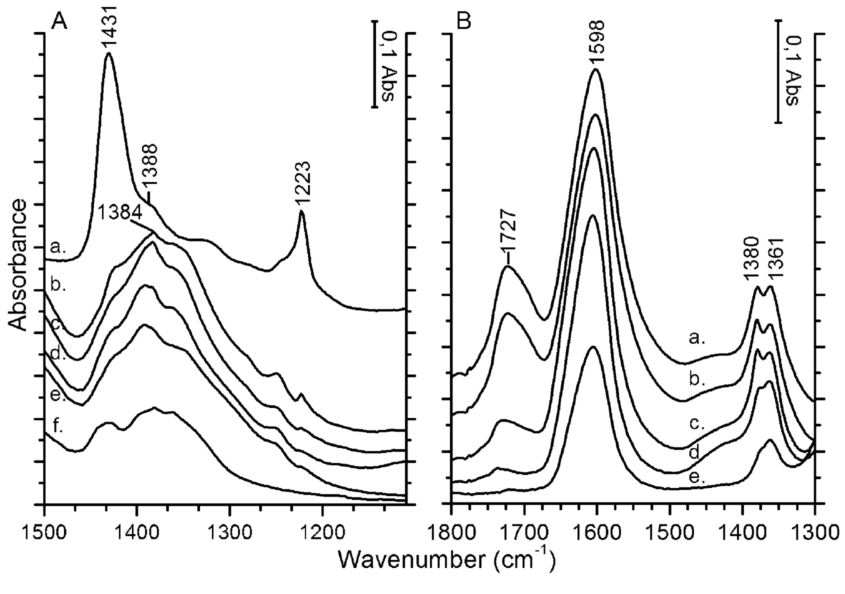

**Fig. 2.** Selected IR spectra observed at room temperature after $H_2 + CO_2$ (4:1) reaction at different temperature on $Au/TiO_2$ (A) a, 300 K (15 m); b, 373 K (30 m); c, 423 K (30 m); d, 523 K (30 m); e, 573 K (30 m); f, after evacuation at 300 K; and following 0.5 Torr HCOOH adsorption on $Au/SiO_2$ (B) a, adsorption at 300 K (5 m); b, 300 K (10 m); c, 373 K (10 m); d, 473 K (10 m); e, 573 K (10 m).

## 2. Experimental

### 2.1. Materials

Supported Au catalysts with a gold loading of 1 and 5 wt% was prepared by a deposition-precipitation method. Chloroauric acid ($HAuCl_4 \times$ aq p.a. 49% Au, Fluka AG) was first dissolved in triply distilled water. After the pH of the $HAuCl_4$ aqueous solution was adjusted to 7.5 pH by adding 25% ammonia solution, the fine powder of oxidic support was suspended and kept at 343 K for 1 h with continuous stirring. The suspension was aged for 24 h at room temperature and washed with distilled water repeatedly, dried at 353 K, calcined in air and reduced at 673 K for 4 h. The following supports were used: $Al_2O_3$ (Degussa); $SiO_2$ (Aerosil 380); $CeO_2$ (ALFA AESAR) and MgO (DAB). In addition, we used commercial 1% Au/$TiO_2$ and 1% Au/ZnO (AUROlite) samples purchased by Strem Chem.

### 2.2. Methods and characterization techniques

X-ray photoelectron spectra (XPS) were taken with a Kratos XSAM 800 instruments, using non-monochromatic Al K$\alpha$ radiation ($h\nu = 1486.6$ eV) and a 180° hemispherical analyser at a base pressure of $1 \times 10^{-9}$ mbar. Binding energies were referenced to the C 1s binding energy (BE) (285.1 eV), with the exception of Au/$SiO_2$, where the Si 2p core level at 103.4 eV was used as reference. Transmission electron microscopy (TEM) images were taken with a Philips CM 20 and a Morgagni 268 D electron microscope at 300 K. Approximately 1 mg of catalyst was placed on a TEM grid.

Infrared spectra were recorded with a Biorad (Digilab. Div. FTS 155) with a wave number accuracy $\pm 4$ cm$^{-1}$. Typically, 128 scans were collected. All substractions of the spectra were taken without the use of a scaling factor ($f = 1.0$). The sample can be heated and cooled in situ. The chamber can be evacuated to $10^{-6}$ mbar.

### 2.3. Catalytic test

The reaction of $H_2 + CO_2$ was investigated in a flow microreactor at atmospheric pressure. The inner diameter of the reactor was 8 mm, and its length was 250 mm. The reactor was heated by an external oven. The weight of the catalyst was 0.3 g. The space velocities were 3000–6000 h$^{-1}$. In the kinetic measurements the conversion of $CO_2$ was kept less than 10–15%. Experiments at 9.5 bar pressure were carried out in stainless steel tube. Analyses of the gases were performed with an Agilent 4890D gas chromatograph. A 2 m long 0.25 in diameter column packed with Porapak QS allowed complete separation and determination of reactants and products.

The photocatalytic reaction was followed in a thermally controllable photoreactor (volume: 1650 cm$^{-1}$) equipped with a 500 W medium pressure mercury vapor lamp (TQ 718, Heraeus Noble light, Germany) as a light source. This lamp emits predominantly in the wavelength range of 250–440 nm. Its maximum intensity is at 254 nm.

## 3. Results

### 3.1. Characterization of the catalysts

As shown in Fig. 1A, the particle size distribution depended on the nature of the support. In the case of Au/$TiO_2$ and Au/ZnO the main size of the Au particles is small, 1.5–2.5 nm, and uniform. This value for Au/$SiO_2$ and Au/$Al_2O_3$ fells in the range of 2–10 nm. The average sizes of Au particles on different oxidic supports are given in Table 1. The XPS spectra of some selected Au samples are shown in Fig. 1B. In the analysis of XPS spectra, we accepted the BEs of three Au states: 84.0 eV for $Au^0$, 84.6 eV for $Au^{1+}$ and 85.9 eV for $Au^{3+}$ [31–33]. Binding energies are also given in Table 1. Accordingly, the Au in the reduced samples is in the form of $Au^0$. However, we cannot exclude the presence of $Au^{1+}$ in the Au/$TiO_2$ and Au/$CeO_2$ in a very small concentration.

### 3.2. FTIR studies

The primary aim of the IR spectroscopic measurements is the detection of formate species formed in the surface interaction between $H_2$ and $CO_2$. This surface group was very easily identified in the case of supported Pt metals [6–9,27–30]. As was established before the asymmetric stretch of adsorbed formate is at 155–1591 cm$^{-1}$ and the symmetric one at 1351–1390 cm$^{-1}$ [6–9,27–30]. As $CO_2$ forming different carbonate species on $TiO_2$ and other oxides gave similar spectral features, it is not easy to establish the presence of a very small amount of formate generated in the $H_2 + CO_2$ interaction on supported Au catalysts. In Fig. 2A, we presented the selected region of the spectra following the coadsorption of $H_2 + CO_2$ over Au/$TiO_2$ sample. It shows that no absorption band is developed at 1384 cm$^{-1}$ at 300 K, but it clearly appeared at 373 K. Its intensity slightly increased up to 423 K, then started attenuating at higher temperature. In order to establish the location formate species, HCOOH was adsorbed on Au/$SiO_2$ sample. As seen in Fig. 2B, intense absorption bands appeared at 1727, 1598, 1380 and 1361 cm$^{-1}$. Their intensities gradually decreased with the raising of the adsorption temperature.

### 3.3. Catalytic study

On the most active 1% Au/$TiO_2$ catalyst the reaction of $H_2$+$CO_2$ was measurable even around 450 K. The conversion of $CO_2$ reached 50% at 773 K. This value was ~35% on the 1% Au/$CeO_2$ and 28% on Au/ZnO. Much less activity was exhibited by Au/$SiO_2$ and Au/MgO. All the catalysts exhibited a remarkable stability at 773 K. The main product of the reaction was CO and $H_2O$. Methane and methanol formed only in trace quantities even on the active samples. Increasing the amount of Au from 1% to 5% did not lead to higher catalytic performance. Note that the pure oxides exhibited no or very little activity even at 773 K. The catalytic behavior of $CeO_2$ nanowire and nanotube was also tested without any positive results. Some important data are presented in Fig. 3A.

The effect of potassium promotor was examined in the case of Au/$CeO_2$. As shown in Fig. 3B, adding 1% $K_2O$ to Au/$CeO_2$ appreciably enhanced its catalytic performance. The conversion of $CO_2$ increased from 38 to 50% and a slight formation of $CH_4$ also occurred. Note that potassium exerted no promotor effect in the case of pure $CeO_2$ support.

The dependence of the rate of CO formation on the partial pressures of $H_2$ and $CO_2$ was determined on Au/$TiO_2$ from the slopes of log–log plots of the rate against the reactant partial pressures (Fig. 3C). It was found that the kinetic order for $CO_2$ was 0.62 and that for $H_2$ 0.57. The activation energy of the reaction was determined from the temperature dependence of the rate of CO formation in the steady state. The Arrhenius plot is shown in Fig. 3D. We obtained a value of 64.8 kJ/mol.

Some measurement were carried out at higher pressure, 9.5 bar. On Au/$TiO_2$, beside CO a significant amount of methane and methanol also formed. Less amount of these compounds were produced on Au/$CeO_2$ and Au/ZnO. Important results are presented in Fig. 4.

### 3.4. Effect of illumination

Illumination of the active catalysts initiated the reaction even at room temperature. The most efficient sample was Au/$TiO_2$ followed by Au/ZnO and Au/$CeO_2$. Results are plotted in Fig. 5. The major

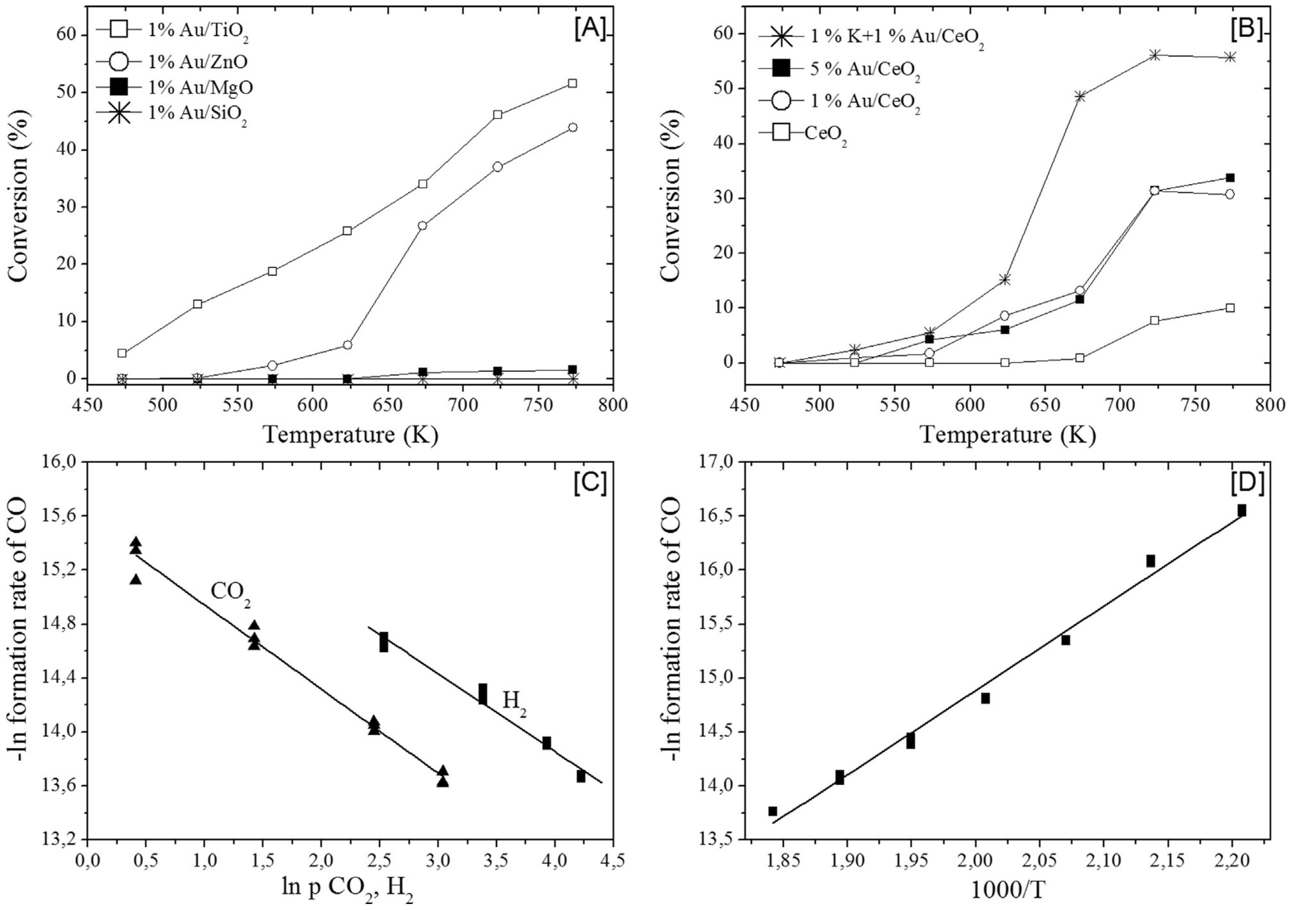

**Fig. 3.** Conversion of $CO_2$ in the $H_2 + CO_2$ (4:1) reaction on various Au catalysts at different temperatures (A) and (B). Dependence of rate of CO formation on the partial pressure of $CO_2$ and $H_2$ on $Au/TiO_2$ catalyst (C). Arrhenius plot of $H_2 + CO_2$ reaction for $Au/TiO_2$ (D).

product in this case was $CH_4$, CO formed only in a trace amount. The conversion of $CO_2$ on $Au/TiO_2$ reached 3.5% in 220 m.

## 4. Discussion

### *4.1. IR studies*

Before discussing the results of IR spectroscopic measurements, we mention that in the interaction of $H_2 + CO_2$ on supported Pt metals, the formation of adsorbed CO and formate species was detected [6,7,26–29]. As the number of formate groups on $Rh/Al_2O_3$ and Rh/MgO was 5–7 times higher than that of surface Rh atoms, it was concluded that formate resides on the support and not on the Rh [6–9]. This conclusion was supported by the finding that no formate was detected on $SiO_2$-supported Pt metals above 300 K [6–9]. As CO adsorbs weakly on Au particles at and above 300 K [17–19], it is not surprising that we found no absorption bands due to CO bonded to Au metal. It is an open question, whether adsorbed formate is being formed in the catalytic reaction of $H_2$ and $CO_2$

$$H_2 + CO_2 = HCOO_{(a)} + H_{(a)} (1)$$

on supported Au catalyst. The difficulty of the detection of a very small amount of formate in the presence of large amount of $CO_2$ is described in chapter 1. After several unsuccessful attempts, we identified the symmetric stretch of formate species at 1384 $cm^{-1}$ generated by the $H_2$ and $CO_2$ reaction on $Au/TiO_2$ catalyst (Fig. 2A). The finding that adsorption HCOOH on $Au/SiO_2$ gave intense absorption bands at 1598 $cm^{-1}$ (asymmetric stretch) and 1380 $cm^{-1}$ (symmetric stretch) suggests that the formate group exists on Au particles (Fig. 2B). These absorption features were detected even after heating the adsorbed layer to 573 K indicating the high stability of formate species on Au metal, and the less reactivity of Au particles compared to that of Pt metals. The intense

**Table 1**
Some characteristic data for the supported Au catalysts.

| Catalyst | Surface area of the support ($m^2$/g) | Average size of the Au particles (nm) | Calculated surface area of Au particles ($nm^2$) | D (%) | Binding energy of the Au on different supports (eV) |
|---|---|---|---|---|---|
| 1% $Au/TiO_2$ | 50 | 2 | 12 | 70 | 84.2 |
| 1% $Au/Al_2O_3$ | 100 | 5,5 | 35 | 26 | – |
| 1% Au/ZnO | 40–50 | 2 | 12 | 70 | – |
| 1% Au/MgO | 170 | 2,1 | 13 | 67 | 84.1 |
| 1% $Au/SiO_2$ | 380 | 6,5 | 133 | 21 | 84.0 |
| 1% $Au/CeO_2$ | 50 | 1,9 | 11 | 74 | 84.2 |

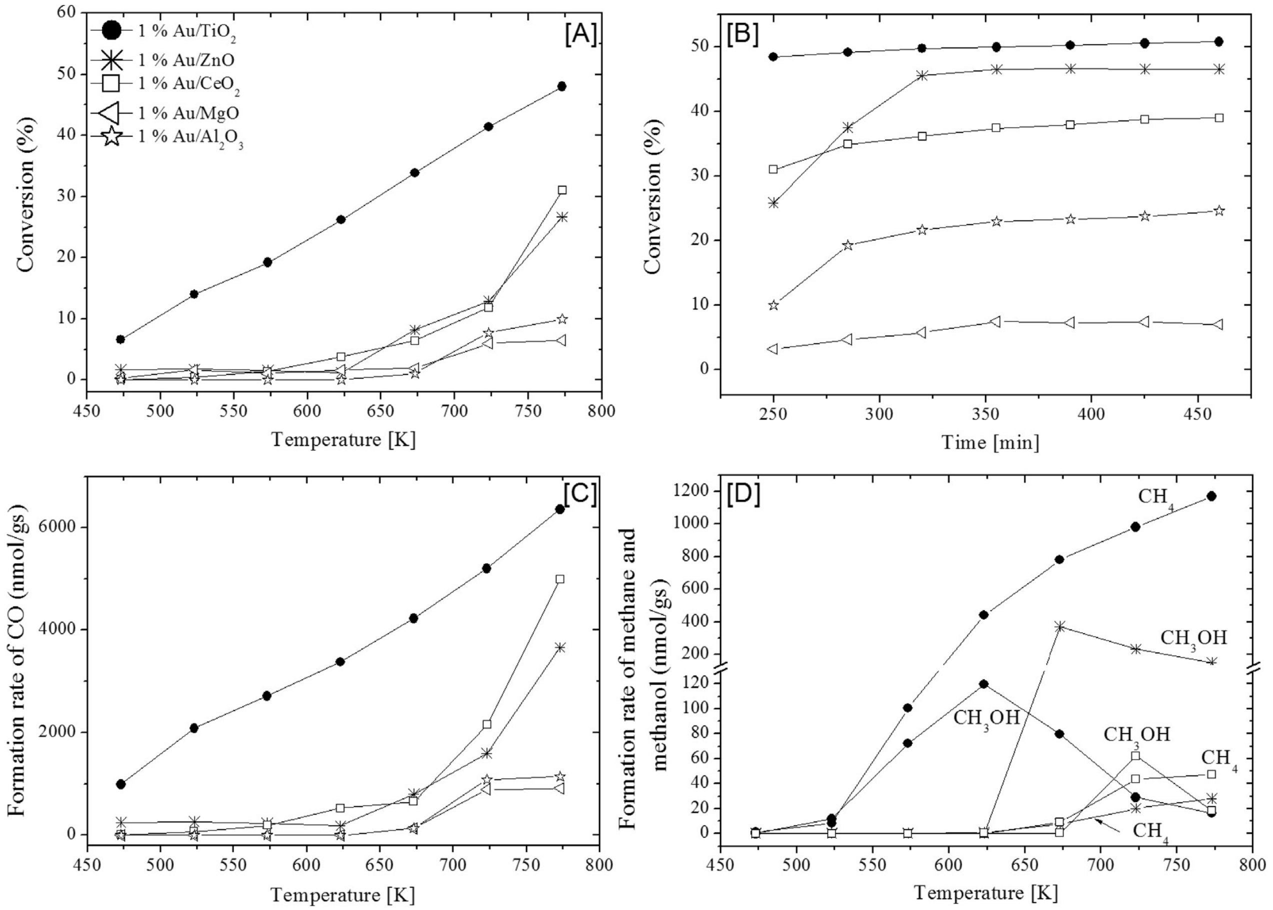

**Fig. 4.** Conversion of $CO_2$ in the $H_2 + CO_2$ (4:1) reaction over $Au/TiO_2$ at 9.5 bar as a function of temperature (A) and in time at 773 K (B). Formation of CO (C) and $CH_4$ and $CH_3OH$ (D).

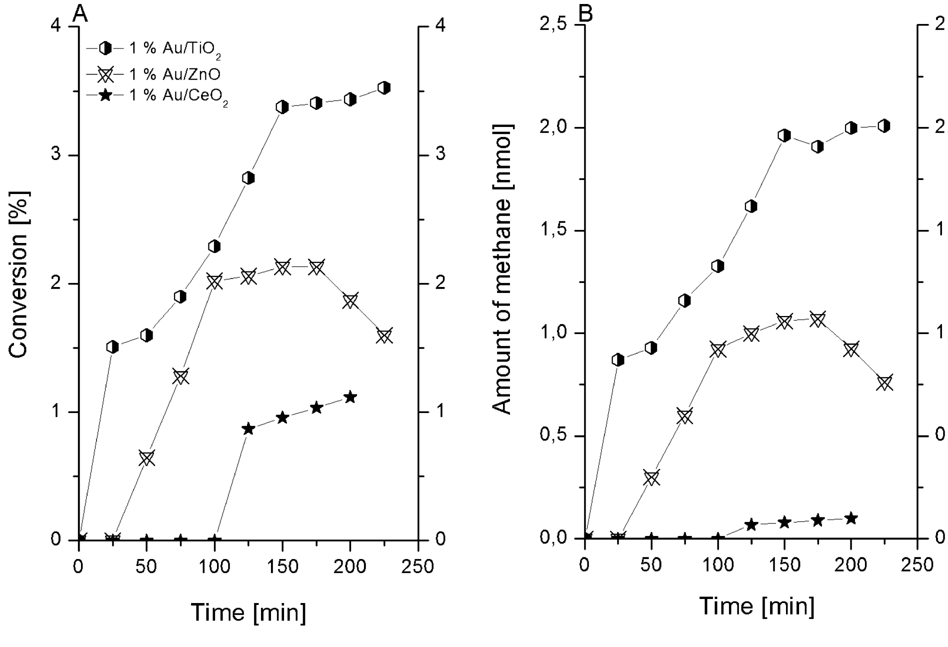

**Fig. 5.** Effect of illumination on the photocatalytic reaction of $H_2 + CO_2$ (4:1) on different catalysts at 300 K.

absorption band at 1727 $cm^{-1}$ is very likely due to the vibration of molecularly adsorbed HCOOH on silica surface.

### 4.2. Catalytic studies

As the methanation of $CO_2$ on supported Pt metals also involves the dissociation of CO and the hydrogenation of surface carbon [7–9], it is not surprising the absence of methane in the catalytic reaction of $H_2 + CO_2$ on supported Au (see Fig. 3). The weak bonding between CO and Au metal is probably the reason that $H_2 + CO_2$ reaction did not produce $CH_4$ even at high temperatures.

According to our previous results, $CO_2$ alone does not dissociate on either Au(1 1 1) or supported Au [25]. In harmony with this finding, the reaction between $H_2$ and $CO_2$ is very limited on Au deposited on insulating $SiO_2$, $Al_2O_3$ and MgO. However, when Au is deposited on n-type semiconducting oxides, $TiO_2$, ZnO and $CeO_2$, a partial activation of $CO_2$ occurred at the Au/oxide interface, which reacted with hydrogen leading to the production of CO. As the work function of Au (5.31 eV) is higher than that of $TiO_2$ (4.6 eV), ZnO (3.9–4.2 eV) and $CeO_2$ (2.5–2.7 eV), we expect an electron transfer from these oxides to the deposited Au particles. This assists the activation of $CO_2$ on Au, e.g. the formation of negatively charged $CO_2^-$, which reacts more easily with hydrogen to give CO

$$CO_2 + e^- = CO_2^{\delta-} \quad (2)$$

$$CO_{2(a)}^{\delta-} + H_2 = CO + H_2O + e^- \quad (3)$$

In the explanation of the high efficiency of $TiO_2$ as a support recently, a great attention is paid to the role of its oxygen vacancy [34–36]. As the ZnO, which contains excess Zn in the interstitial position, was also an effective support, we believe that in the electric properties of the supporting oxides in this reaction are more important than the nature of their defect structure.

The positive effect of potassium addition on $Au/CeO_2$ (Fig. 3B) can be also attributed to the donation of an electron to the Au particles, which contributes to the activation of $CO_2$ [25]. It is to be mentioned that Praliaud et al. [37] disclosed that an electron donation can also occur from $K^+–O^{2-}$ overlayers to the metal. The electron donating character of this overlayer was also considered by others as well [38,39].

As regards the effect of illumination, we may assume the generation of an electron in a photoexcitation process,

$$TiO_2 + h\nu = h^+ + e^- \quad (4)$$

which enhances the charge transfer between n-type oxides and Au particles leading also to the activation of CO (adsorbed molecules) and to the slight formation of $CH_4$

$$CO + 3H_2 = CH_4 + H_2O \quad (5)$$

At higher pressure (9.5 atm) a small amount of methanol was also produced,

$$3H_2 + CO_2 = CH_3OH + H_2O \quad (6)$$

but the dominant pathway of the $H_2 + CO_2$ reaction was still the formation of CO.

## 5. Conclusions

(i) Infrared spectroscopic measurements revealed a slight formation of formate species in the $H_2 + CO_2$ reaction on $Au/TiO_2$.
(ii) Au particles deposited on n-type semiconducting oxides (ZnO, $TiO_2$, $CeO_2$) catalyses the $H_2 + CO_2$ reaction to give CO above 500 K, which was explained by the occurrence of an electronic interaction between Au and the oxides.
(iii) At higher pressure, 9.5 bar a small amount of methanol also formed.
(iv) Illumination of $Au/TiO_2$ induced the $H_2 + CO_2$ reaction even at room temperature.

## Acknowledgements

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