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Reactions of ethane with CO_2 over supported Au

Anita Tóth, Gyula Halasi, Frigyes Solymosi *

MTA-SZTE Reaction Kinetics and Surface Chemistry Research Group, Rerrich Béla tér 1, H-6720 Szeged, Hungary

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ABSTRACT

The dehydrogenation of C_2H_6 and its reaction with CO_2 have been investigated on Au deposited on various oxides. Both reactions occurred at relatively high temperatures, above 650 K. Ethylene formed in the dehydrogenation process with high selectivity, 94–98%, on most of the catalysts. The conversion of C_2H_6 varied with the nature of support and fell in the range of 3–19%. Adding CO_2 to C_2H_6 only slightly influenced the reaction of C_2H_6 on Au/MgO and Au/Al_2O_3, but markedly increased the conversion of C_2H_6 and changed its reaction pathways on Au deposited on *n*-type TiO_2, CeO_2 and ZnO. Taking into account the properties of these oxides, we came to the conclusion that their electric behavior and not their defect structure play a dominant role in the enhanced activity of Au deposited on these supports. Based on the different work functions, an electronic interaction between Au particles and these oxides is proposed, which facilitates the formation of reactive negatively charged CO_2.

1. Introduction

The conversion of hydrocarbons, particularly CH_4 and C_2H_6, into more valuable compounds is an important project for heterogeneous catalysis. A surprising reaction of CH_4 is its transformation into benzene, which is catalyzed by a new type of catalyst, Mo_2C/ZSM-5 [1–7]. The technological importance of the initial findings is indicated by a large number of publications and patents [8]. Several new catalyst combinations have been tested, but neither of them were better than Mo_2C/ZSM-5. Aromatization of C_2H_6 also occurs on Mo_2C/ZSM-5 [9,10], but it proceeds on several other catalysts, too. An alternative way of the conversion C_2H_6 is its dehydrogenation into C_2H_4, which is one of the most important petrochemicals. On the most active catalysts, however, the decomposition of C_xH_y, formed during the reaction cannot be avoided. Adding O_2 or N_2O lowers the reaction temperatures and opens a new route for the formation of olefins. In this case, however, we may count with the undesired oxidation of C_xH_y species. This side reaction can be minimized by using CO_2 as a mild oxidant [11–17]. Pt metals are active catalysts for $C_2H_6 + CO_2$ reaction, but at higher temperatures instead of dehydrogenation of ethane its dry-reforming becomes the dominant process. Rh/ZSM-5 presents a good example for this feature [13]. On the less reactive Mo_2C/SiO_2 [14], the selectivity of ethylene formation was 90–95% at an ethane conversion of 30%. More attractive results were obtained on the combination of various oxides [11,12,15–17]. On Ni–Nb–O mixed oxides the yield for ethylene was 46% at 673 K [15]. A series of chromium catalysts supported on titanosilicates effectively dehydrogenated ethane with CO_2 with a selectivity of 90.0% at 923 K [16].

In the present work the influence of CO_2 on the reaction of C_2H_6 is investigated over Au nanoparticles deposited on various oxidic supports. It is expected that due to the less reactivity of Au particles compared to transitional metals we can avoid the side reactions. One of the aims of this study was to test the effect of defect structure of various oxides, and the possible role of the electronic interaction between Au and oxides. As was demonstrated several decades ago the electronic interaction between metal and oxides due to their different work functions plays an important role in the support effect [18,19]. This was well demonstrated by using *n*-type TiO_2. After the first use of TiO_2 as a support [20,21] a dramatic increase in its application occurred [22]. Recently a greater attention is paid to the role of O vacancy in the catalytic and support effect of TiO_2 [23–25]. As the *n*-type character of TiO_2 is due to the O vacancy [26], it is not easy to differentiate between the role of O vacancy and the electric property. The importance of the latter in the catalytic and support effect of TiO_2 may be established by the comparison of its influence with that of ZnO, which is also an *n*-type oxide. However, its semiconducting behavior is due to the excess of Zn in the interstitial position and not due to the O vacancy.

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* Corresponding author. Fax: +36 62 544 106.
E-mail address: fsolym@chem.u-szeged.hu (F. Solymosi).

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2. Experimental

2.1. Methods

Catalytic measurements were carried out in a fixed bed continuous flow reactor made of a quartz tube. The flow rate of reactant gases was 12 ml/min. The exit gas was analyzed by gas chromatograph (Hewlett–Packard 5890) on a Porapak QS column. The carrier gas was Ar which contained 12.5% of C_2H_6. In the study of $CO_2 + C_2H_6$ reaction we applied a gas mixture of 1:1 mol ratio. In the temperature programmed reduction (TPR), the heating rate was 5 K/min and the flow of H_2 was 20 ml/min. The selectivity for C_2H_4 was calculated as follows:

$$C_2H_4\ \text{selectivity} = 2 \times n_{C_2H_4}/(2 \times n_{C_2H_4} + n_{C_2H_4})$$

2.2. Materials

1% Au/TiO_2 and 1% Au/ZnO catalysts were purchased from STREM Chem. Inc. Average gold crystallite size is ~2–3 nm. The other supported Au catalysts were prepared by a deposition–precipitation method. $HAuCl_4$·aq (p.a., 49% Au, Fluka AG) was first dissolved in triply distilled water. After the pH of the aqueous $HAuCl_4$ solution had been adjusted to 7.5 by the addition of 1 M NaOH solution, a suspension was prepared with the finely powdered oxidic support, and the system was kept at 343 K for 1 h under continuous stirring. The suspension was then aged for 24 h at room temperature, washed repeatedly with distilled water, dried at 353 K and calcined in air at 573 K for 4 h. The following oxides were used as supports: Al_2O_3 (Degussa C), MgO (Reanal) and CeO_2 (Alfa Aesar). The average gold crystallite size in these samples is 5–8 nm.

3. Results

3.1. Dehydrogenation of C_2H_6

The reaction of C_2H_6 started on most of the catalysts at high temperature, above 650–700 K (Fig. 1A). The conversion was relatively low even at 923 K. Largest value was obtained for Au/ZnO (~19%) followed by Au/TiO_2, Au/CeO_2, Au/MgO and Au/Al_2O_3. The major product was C_2H_4 with a small amount of CH_4. High selectivity, more than 90%, was measured for all samples, which altered only little with the temperature (Fig. 1B). All the catalysts exhibited a remarkable stability. To establish the contribution of the Au similar experiments were performed with the supports alone. Oxides also catalyzed the dehydrogenation reaction, their effect was somewhat less than that of Au-containing catalysts. Some characteristic data are presented in Table 1.

3.2. Reaction of $CO_2 + C_2H_6$

The effect of CO_2 depended on the nature of the support. The conversion of C_2H_6 was only slightly higher on Au/MgO and Au/Al_2O_3 compared to the values obtained in the absence of CO_2 (Table 2). In contrast, CO_2 markedly enhanced the catalytic performance of Au deposited on TiO_2, CeO_2 and ZnO. An appreciable reaction occurred even at 650 K. The conversion of C_2H_6 as a function of temperature is shown in Fig. 2A. Nearly the same values were calculated from the consumption of CO_2. The decomposition of CO_2 was also examined in the absence of C_2H_6 on all catalysts under similar conditions. No sign of the formation of CO was observed even at 923 K.

Product distribution obtained on Au/TiO_2 is presented in Fig. 2B. The major product is CO. H_2 and C_2H_4 formed almost in same quantity. A small amount of CH_4 was also produced. The selectivity of C_2H_4 production at 923 K was 85.8% neglecting the production of CO from CO_2. This catalyst exhibited a remarkable stability at 923 K. This is shown in Fig. 3A.

Different results were obtained on the more active Au/CeO_2 catalyst (Fig. 2C). In this case, the amount of C_2H_4 was much less than that of H_2. Whereas on Au/TiO_2 the H_2/C_2H_4 ratio was almost 1, on Au/CeO_2 this ratio reached a factor of 4. The (maximum) selectivity value of C_2H_4 formation is about 88.1%. An interesting feature of the reaction is the more extended formation of CO. Similarly to Au/TiO_2 catalyst only slight deactivation was experienced (Fig. 3A).

The highest catalytic activity was exhibited by Au/ZnO (Fig. 2A). In contrast to the previous catalysts, a much larger amount of CH_4 was formed. This is well reflected in the selectivity and yield of CH_4 production (Table 2). In harmony with this feature, we obtained the lowest values for both the selectivity and the yield of C_2H_4 production. In contrast to the previous catalysts, an extensive deactivation occurred at 923 K. Its extent was markedly smaller at lower temperatures, 873 K and 823 K. This is demonstrated in Fig 3A. Important data for the $CO_2 + C_2H_6$ reaction on different catalysts are presented in Table 2.

Some experiments have been performed concerning the effect of the CO_2 content added to the C_2H_6. Results obtained are given in Fig. 3B. It appears that with the increase of the CO_2/C_2H_6 ratio the amounts of C_2H_4 and H_2 are increased up to $CO_2/C_2H_6 = 1$. At higher ratios the formation of these compounds is declined.

The apparent activation energies for the formation of different products have been determined on Au/TiO_2 in the temperature range of 773–840 K, where the conversion of C_2H_6 was below 12%. The rate of formation of H_2 and C_2H_4 in steady state was plotted according to the Arrhenius equation. We obtained 74.0 ± 2 kJ/mol for the formation of C_2H_4 and 97.7 ± 2 kJ/mol for the production of CO.

The amount of carbon deposit formed in the $CO_2 + C_2H_6$ reaction and its reactivity was determined by TPR measurements. On Au/ZnO a small amount of CH_4 formed with a $Tp \approx 710$ K, a significant quantity of CH_4 was produced with Tp = 915 K. A very small amount of C_2H_4 was also detected with Tp = 875 K (Fig. 4A). In the case of Au/TiO_2 the CH_4 peaks appeared at 775 and 1055 K (Fig. 4B). Formation of C_2H_4 was not detected. Similar measurements with Au/CeO_2 catalyst gave no products formed.

4. Discussion

Deposition of Au on various oxidic supports enhanced only moderately the dehydrogenation of C_2H_6

$$C_2H_{6(a)} = C_2H_{4(a)} + 2H_{(a)} \tag{1}$$

measured on pure oxides. The high selectivity of C_2H_4 formation, more than 90% at 873–923 K (Table 1), indicates that we can count only with very limited side reactions, e.g. with the decomposition of C_2H_4 or C_xH_y to carbon

$$C_2H_{4(a)} = CH_{4(g)} + C \tag{2}$$

As regards the efficiency of the catalysts Au/MgO and Au/Al_2O_3 exhibited the lowest activity (Table 1). Adding CO_2 to C_2H_6 only slightly increased the catalytic performance of these two samples, which suggests that Au particles on these oxides cannot activate the CO_2 molecule to a greater extent. The situation is completely different in the case of Au/TiO_2, Au/CeO_2 and Au/ZnO, when the reaction between CO_2 and C_2H_6 is greatly enhanced compared to the activity of pure oxides. If we take into account the properties of active and inactive supporting oxides, we find that the active oxides (TiO_2, CeO_2, ZnO) belong to the *n*-type semiconductors, while Al_2O_3 and MgO are insulating materials. In light of this

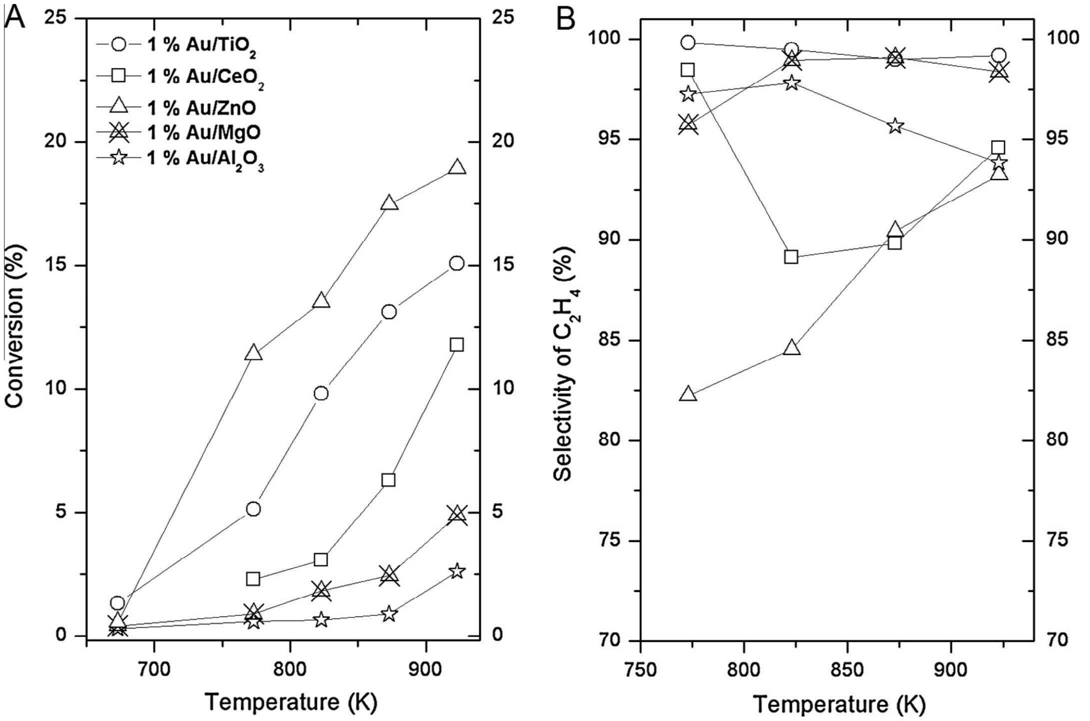

Fig. 1. Dehydrogenation of C_2H_6 (A) and selectivity of C_2H_4 formation (B) as a function of temperature and time at 923 K (C).

Table 1
Some characteristic data for dehydrogenation of C_2H_6 at 923 K.

Catalyst	Conversion of C_2H_6 (%)	Selectivity of C_2H_4 formation
TiO_2	10.5	98.0
Au/TiO_2	15.0	98.5
CeO_2	9.0	97.0
Au/CeO_2	12.0	94.6
ZnO	5.0	97.9
Au/ZnO	18.9	93.2
Au/MgO	4.9	98.3
Au/Al_2O_3	2.5	93.8

Table 2
Some characteristic data for the $CO_2 + C_2H_6$ reaction at 923 K.

Catalyst	Conversion of C_2H_6 (%)	Selectivity of C_2H_4 formation
TiO_2	17.1	98.2
Au/TiO_2	40.6	85.8
CeO_2	20.2	98.0
Au/CeO_2	52.2	88.1
ZnO	12.5	90.1
Au/ZnO	67.4	36.2
Au/MgO	7.3	98.3
Au/Al_2O_3	7.7	95.2

difference, we assume the occurrence of an electronic interaction between Au and the *n*-type oxides. As the work function of Au (5.3 eV) is higher than that of TiO_2 (~4.6 eV), CeO_2 (2.5–2.7 eV) and ZnO (3.9–4.25 eV), a charge transfer may occur at Au/oxide interface from the oxides to the Au making it more active. As known CO_2 is a very stable molecule. In previous studies performed on TiO_2-supported metals [27] and metal single crystals including Au(1 1 1) [28–31], it was revealed that the donation of electrons from the catalyst to the antibonding π level of CO_2 leads to the formation of reactive negatively charged $CO_2^{\delta-}$. Based on this consideration we propose the occurrence of following steps for the reaction of CO_2 and C_2H_6

$$CO_{2(a)} + - = CO_2^{\delta-} \tag{3}$$

$$CO_2^{\delta-} + C_2H_{6(a)} = C_2H_{5(a)} + CO + OH^{\delta-} \tag{4}$$

$$C_2H_{5(a)} = C_2H_{4(g)} + H_{(a)} \tag{5}$$

$$2OH^{\delta-} = H_2O_{(g)} + O^{2\delta-} \tag{6}$$

$$2H_{(a)} = H_{2(g)} \tag{7}$$

The slow, rate determining step is very likely the reaction of C_2H_6 with $CO_2^{\delta-}$ (Eq. (4)).

As there was no indication of the formation of CO in the absence of C_2H_6, we can exclude the decomposition of activated CO_2 alone

$$CO_{2(a)}^{\delta-} = CO_{(a)} + O^{\delta-} \tag{8}$$

The product distribution obtained on the active catalysts indicates that CO_2 exerts different influences on the reaction of C_2H_6. The enhanced of formation of C_2H_4, in other words the oxidative dehydrogenation of C_2H_6

$$C_2H_6 + CO_2 = C_2H_4 + CO + H_2O \tag{9}$$

is mainly occurred on Au/TiO_2. The more extended formation of CO and H_2 on Au/CeO_2 and on Au/ZnO suggests the occurrence of the dry reforming of C_2H_6

$$C_2H_6 + 2CO_2 = 4CO + 3H_2 \tag{10}$$

which probably consists of the reactions of C_2H_4 formed in the oxidative dehydrogenation of C_2H_6 with the activated CO_2 and O^-. Furthermore, the catalytic behavior of Au/ZnO basically differs from the previous ones as a very large amount of CH_4 is also formed in the $CO_2 + C_2H_6$ reaction above 823 K and a significant deactivation of the catalyst also proceeds (Fig. 3D). Accordingly, we can count with the cracking of C_2H_6 and C_2H_4

$$C_2H_6 + H_2 = 2CH_4 \tag{11}$$

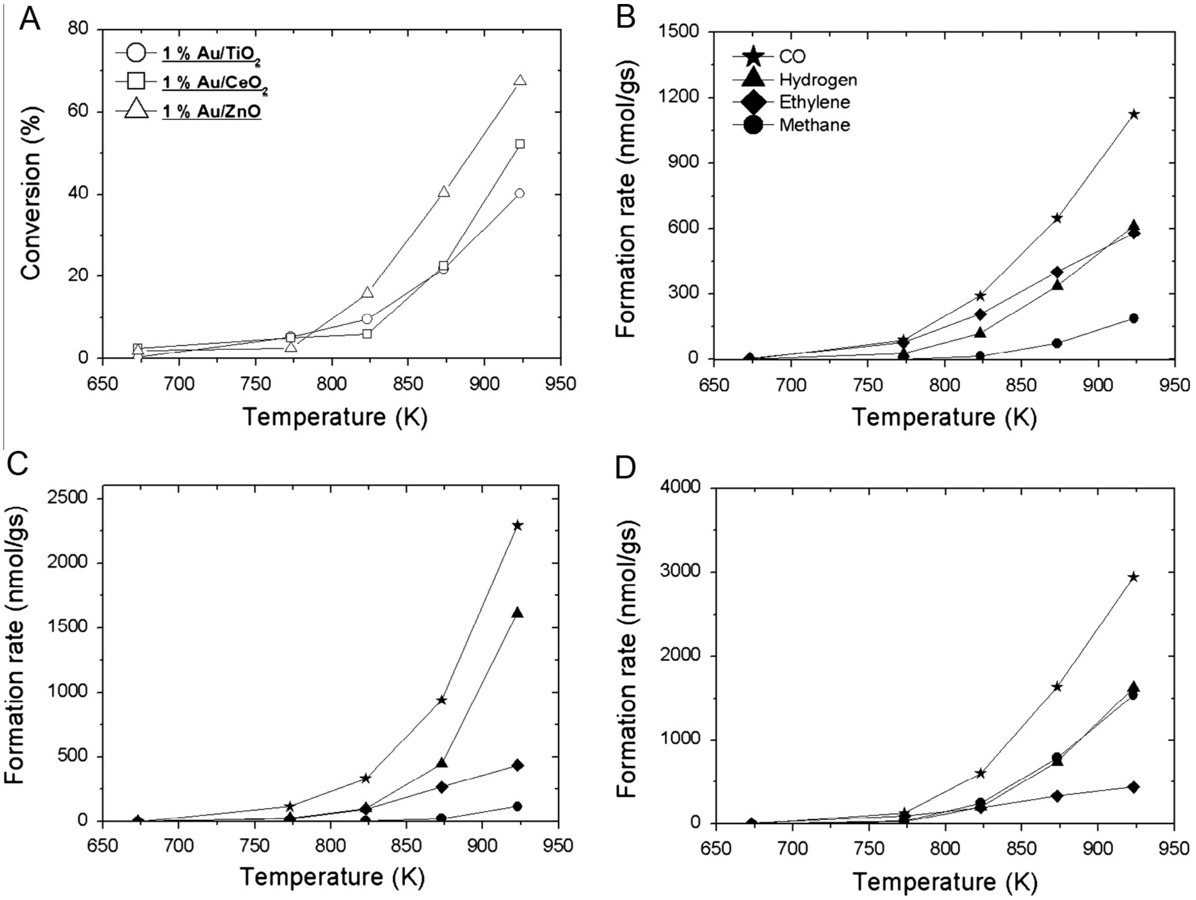

Fig. 2. Reaction of $C_2H_6 + CO_2$. Conversion of C_2H_6 (A); Formation of various products: Au/TiO_2 (B); Au/CeO_2 (C); Au/ZnO (D).

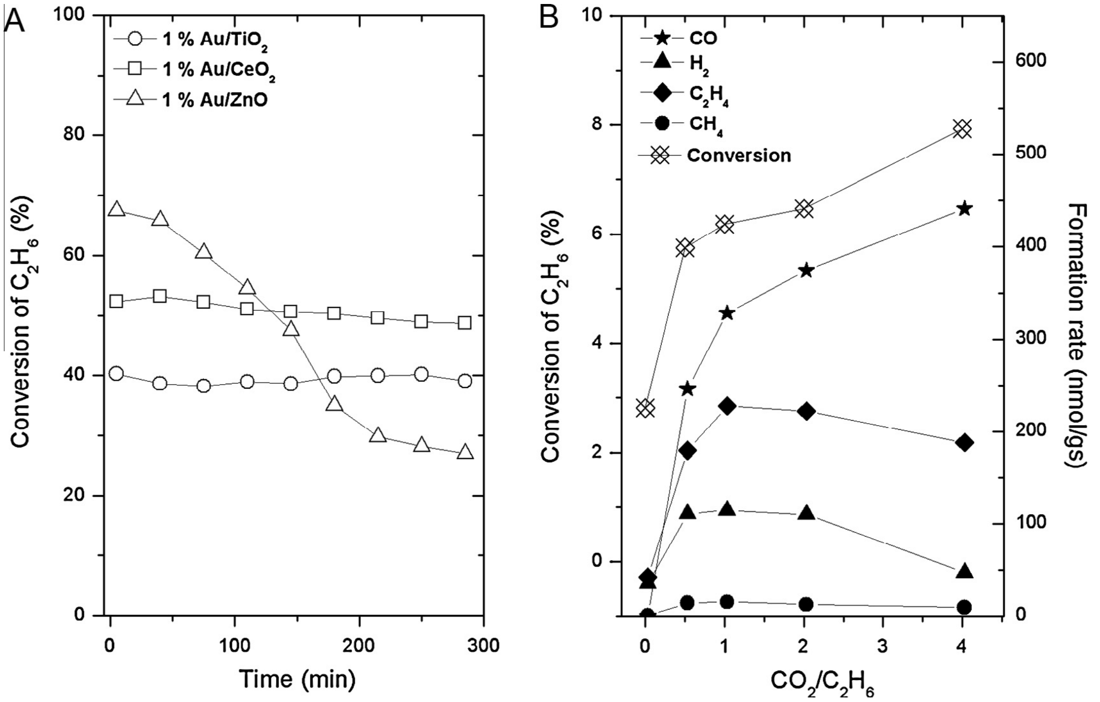

Fig. 3. Conversion of C_2H_6 in the $CO_2 + C_2H_6$ reaction in time at 923 K (A). Effects of CO_2/C_2H_6 ratio on the formation of various products on Au/TiO_2 at 823 K (B).

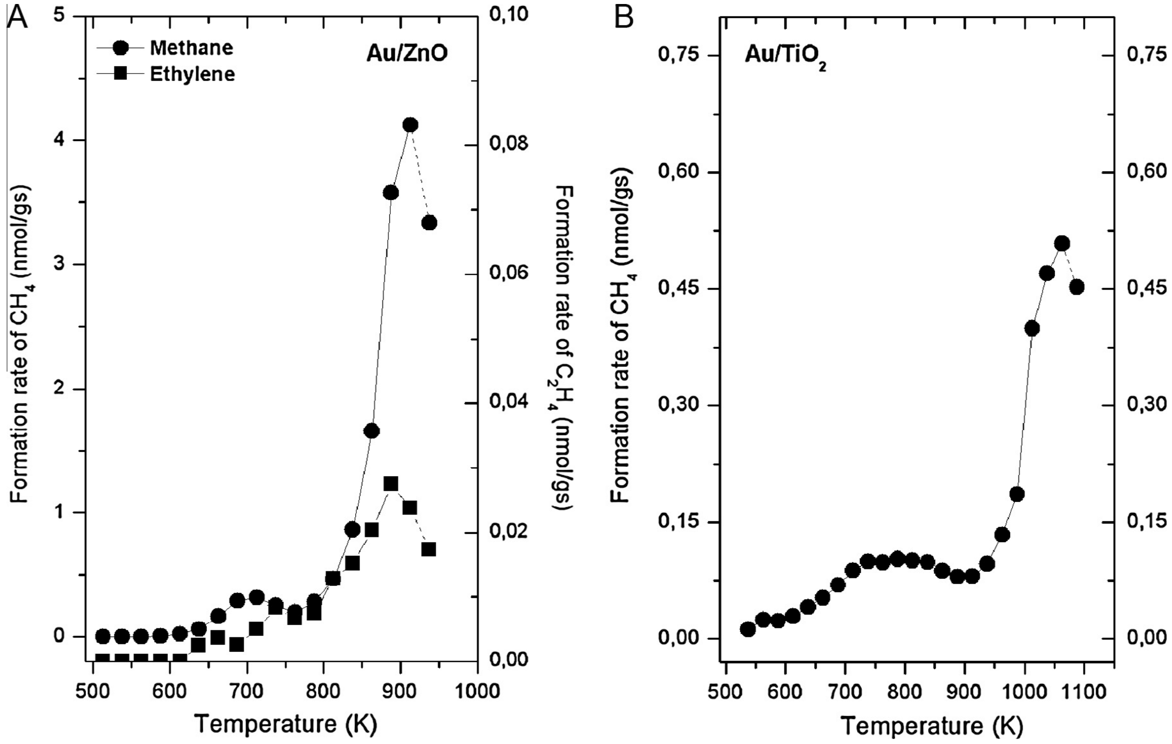

Fig. 4. TPR measurements following the $CO_2 + C_2H_6$ reaction at 923 K on Au/ZnO (A) and Au/TiO_2 (B).

$$C_2H_4 = CH_4 + C \tag{12}$$

The hydrogenation of CO_2 as a source of CH_4

$$CO_2 + 4H_2 = CH_4 + 2H_2O \tag{13}$$

can contribute only very little to the formation of CH_4. According to our control experiments this reaction on supported Au samples at atmospheric pressure gives mainly CO and H_2O. The deactivation of the Au/ZnO at higher temperatures can be attributed to the deposition of carbon. TPR studies clearly indicated the presence of a large amount of carbon deposit formed in the $CO_2 + C_2H_6$ reaction over Au/ZnO (Fig. 4).

Finally, we may deal with the possible role of the defect structure of the oxidic supports. As mentioned in the introduction, in the explanation of the effectiveness of the TiO_2 as a support an increased attention is paid to the role of its oxygen vacancy [23–25]. As the carrier effect of TiO_2 (containing O vacancy) and that of ZnO (with excess Zn the interstitial position) is comparable, we may conclude that in this reaction the electronic property of the supporting oxides is more important than the nature of their defect structure.

5. Conclusion

(i) Dehydrogenation of C_2H_6 and its reaction with CO_2 are moderately catalyzed by Au/MgO and Au/Al_2O_3.

(ii) Deposition of Au on the *n*-type TiO_2, CeO_2 and ZnO exhibited a much higher catalytic effect, particularly in the reaction of C_2H_6 with CO_2. This was attributed the occurrence of an electronic interaction between Au and the *n*-type oxides leading to the formation of reactive negatively charged CO_2.

(iii) While Au/TiO_2 catalyzes mainly the oxidative dehydrogenation of C_2H_6, on Au/CeO_2 and Au/ZnO the dry reforming of C_2H_6 is the dominant reaction pathway.

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