Reactions of ethane with CO2 over supported Au

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Abstract

The dehydrogenation of C2H6 and its reaction with CO2 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 C2H6 varied with the nature of support and fell in the range of 3–19%. Adding CO2 to C2H6 only slightly influenced the reaction of C2H6 on Au/MgO and Au/Al2O3, but markedly increased the conversion of C2H6 and changed its reaction pathways on Au deposited on n-type TiO2, CeO2 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 CO2.

1. Introduction

The conversion of hydrocarbons, particularly CH4 and C2H6, into more valuable compounds is an important project for heterogeneous catalysis. A surprising reaction of CH4 is its transformation into benzene, which is catalyzed by a new type of catalyst, Mo2C/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 Mo2C/ZSM-5. Aromatization of C2H6 also occurs on Mo2C/ZSM-5 [9,10], but it proceeds on several other catalysts, too. An alternative way of the conversion C2H6 is its dehydrogenation into C2H4, which is one of the most important petrochemicals. On the most active catalysts, however, the decomposition of C2H6, formed during the reaction cannot be avoided. Adding O2 or N2O 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 C2H6 species. This side reaction can be minimized by using CO2 as a mild oxidant [11–17]. Pt metals are active catalysts for C2H6 + CO2 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 Mo2C/SlO2 [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 CO2 with a selectivity of 90.0% at 923 K [16].

In the present work the influence of CO2 on the reaction of C2H6 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 TiO2. After the first use of TiO2 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 TiO2 [23–25]. As the n-type character of TiO2 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 TiO2 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.
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 C2H6. In the study of CO2 + C2H6 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 H2 was 20 ml/min. The selectivity for C2H4 was calculated as follows:

\[ \text{C}_2\text{H}_4 \text{ selectivity} = \frac{2 \times n_{\text{C}_2\text{H}_4}}{(2 \times n_{\text{C}_2\text{H}_4} + n_{\text{C}_2\text{H}_6})} \]

2.2. Materials

1% Au/TiO2 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. HAuCl4·aq (p.a., 49% Au, Fluka AG) was first dissolved in triply distilled water. After the pH of the aqueous HAuCl4 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: Al2O3 (Degussa C), MgO (Reanal) and CeO2 (Alfa Aesar). The average gold crystallite size in these samples is 5–8 nm.

3. Results

3.1. Dehydrogenation of C2H6

The reaction of C2H6 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/TiO2, Au/CeO2, Au/MgO and Au/Al2O3. The major product was C2H4 with a small amount of CH4. 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 CO2 + C2H6

The effect of CO2 depended on the nature of the support. The conversion of C2H6 was only slightly higher on Au/MgO and Au/Al2O3 compared to the values obtained in the absence of CO2 (Table 2). In contrast, CO2 markedly enhanced the catalytic performance of Au deposited on TiO2, CeO2, and ZnO. An appreciable reaction occurred even at 650 K. The conversion of C2H6 as a function of temperature is shown in Fig. 2A. Nearly the same values were calculated from the consumption of CO2. The decomposition of CO2 was also examined in the absence of C2H6 on all catalysts under similar conditions. No sign of the formation of CO was observed even at 923 K. Produdct distribution obtained on Au/TiO2 is presented in Fig. 2B. The major product is CO. H2 and C2H4 formed almost in same quantity. A small amount of CH4 was also produced. The selectivity of C2H4 production at 923 K was 85.8% neglecting the production of CO from CO2. This catalyst exhibited a remarkable stability at 923 K. This is shown in Fig. 3A.

Different results were obtained on the more active Au/CeO2 catalyst (Fig. 2C). In this case, the amount of C2H4 was much less than that of H2. Whereas on Au/TiO2 the H2/C2H6 ratio was almost 1, on Au/CeO2 this ratio reached a factor of 4. The (maximum) selectivity value of C2H4 formation is about 88.1%. An interesting feature of the reaction is the more extended formation of CO. Similarly to Au/TiO2 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 CH4 was formed. This is well reflected in the selectivity and yield of CH4 production (Table 2). In harmony with this feature, we obtained the lowest values for both the selectivity and the yield of C2H4 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 CO2 + C2H6 reaction on different catalysts are presented in Table 2.

Some experiments have been performed concerning the effect of the CO2 content added to the C2H6. Results obtained are given in Fig. 3B. It appears that with the increase of the CO2/C2H6 ratio the amounts of C2H4 and H2 are increased up to CO2/C2H6 = 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/TiO2 in the temperature range of 773–840 K, where the conversion of C2H6 was below 12%. The rate of formation of H2 and C2H4 in steady state was plotted according to the Arrhenius equation. We obtained 74.0 ± 2 kJ/mol for the formation of C2H4 and 97.7 ± 2 kJ/mol for the production of CO.

The amount of carbon deposit formed in the CO2 + C2H6 reaction and its reactivity was determined by TPR measurements. On Au/ZnO a small amount of CH4 formed with a Tp ≈ 710 K, a significant quantity of CH4 was produced with Tp = 915 K. A very small amount of C2H4 was also detected with Tp = 875 K (Fig. 4A). In the case of Au/TiO2 the CH4 peaks appeared at 775 and 1055 K (Fig. 4B). Formation of C2H4 was not detected. Similar measurements with Au/CeO2 catalyst gave no products formed.

4. Discussion

Deposition of Au on various oxidic supports enhanced only moderately the dehydrogenation of C2H6

\[ \text{C}_2\text{H}_6(a) = \text{C}_2\text{H}_4(a) + 2\text{H}_2(a) \]  

measured on pure oxides. The high selectivity of C2H4 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 C2H4 or CH4 to carbon

\[ \text{C}_2\text{H}_4(a) = \text{CH}_4(g) + \text{C} \]  

As regards the efficiency of the catalysts Au/MgO and Au/Al2O3 exhibited the lowest activity (Table 1). Adding CO2 to C2H6 only slightly increased the catalytic performance of these two samples, which suggests that Au particles on these oxides cannot activate the CO2 molecule to a greater extent. The situation is completely different in the case of Au/TiO2, Au/CeO2 and Au/ZnO, when the reaction between CO2 and C2H6 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 (TiO2, CeO2, ZnO) belong to the n-type semiconductors, while Al2O3 and MgO are insulating materials. In light of this
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 TiO₂ (~4.6 eV), CeO₂ (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 CO₂ is a very stable molecule. In previous studies performed on TiO₂-supported metals [27] and metal single crystals including Au(111) [28–31], it was revealed that the donation of electrons from the catalyst to the antibonding \( \pi \) level of CO₂ leads to the formation of reactive negatively charged \( \text{CO}_2^{-} \). Based on this consideration we propose the occurrence of following steps for the reaction of CO₂ and C₂H₆.

\[
\begin{align*}
\text{CO}_2(a) + - = \text{CO}_2^{-} & \quad (3) \\
\text{CO}_2^{+} + \text{C}_2\text{H}_6(a) = \text{C}_2\text{H}_5(a) + \text{CO} + \text{OH}^{+} & \quad (4) \\
\text{C}_2\text{H}_5(a) = \text{C}_2\text{H}_5(g) + \text{H}(a) & \quad (5) \\
2\text{OH}^{+} = \text{H}_2\text{O}(g) + \text{O}^{2-} & \quad (6) \\
2\text{H}(a) = \text{H}_2(g) & \quad (7)
\end{align*}
\]

The slow, rate determining step is very likely the reaction of C₂H₆ with \( \text{CO}_2^{-} \) (Eq. (4)).

As there was no indication of the formation of CO in the absence of C₂H₆, we can exclude the decomposition of activated CO₂ alone

\[
\begin{align*}
\text{CO}_2^{+} = \text{CO}_2 + \text{O}^{+} & \quad (8)
\end{align*}
\]

The product distribution obtained on the active catalysts indicates that CO₂ exerts different influences on the reaction of C₂H₆. The enhanced of formation of C₂H₄, in other words the oxidative dehydrogenation of C₂H₆ is mainly occurred on Au/TiO₂. The more extended formation of CO and H₂ on Au/CeO₂ and on Au/ZnO suggests the occurrence of the dry reforming of C₂H₆

\[
\begin{align*}
\text{C}_2\text{H}_6 + \text{CO}_2 = 4\text{CO} + 3\text{H}_2 & \quad (9)
\end{align*}
\]

which probably consists of the reactions of C₂H₆ formed in the oxidative dehydrogenation of C₂H₆ with the activated CO₂ and \( \text{O}^{+} \). Furthermore, the catalytic behavior of Au/ZnO basically differs from the previous ones as a very large amount of CH₄ is also formed in the CO₂ + C₂H₆ reaction above 823 K and a significant deactivation of the catalyst also proceeds (Fig. 3D). Accordingly, we can count with the cracking of C₂H₆ and C₂H₄

\[
\begin{align*}
\text{C}_2\text{H}_6 + \text{H}_2 = 2\text{CH}_4 & \quad (11)
\end{align*}
\]
Fig. 2. Reaction of C₂H₆ + CO₂. Conversion of C₂H₆ (A); Formation of various products: Au/TiO₂ (B); Au/CeO₂ (C); Au/ZnO (D).

Fig. 3. Conversion of C₂H₆ in the CO₂ + C₂H₆ reaction in time at 923 K (A). Effects of CO₂/C₂H₆ ratio on the formation of various products on Au/TiO₂ at 823 K (B).
C\textsubscript{2}H\textsubscript{4} = CH\textsubscript{4} + C \tag{12}

The hydrogenation of CO\textsubscript{2} as a source of CH\textsubscript{4}
CO\textsubscript{2} + 4H\textsubscript{2} = CH\textsubscript{4} + 2H\textsubscript{2}O \tag{13}

can contribute only very little to the formation of CH\textsubscript{4}. According to our control experiments this reaction on supported Au samples at atmospheric pressure gives mainly CO and H\textsubscript{2}O. 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 position of carbon. TPR studies clearly indicated the presence of a large defect structure. As mentioned in the introduction, in the supporting oxides is more important than the nature of their electronic property of that of ZnO (with excess Zn the interstitial position) is comparable, that of TiO\textsubscript{2} increased attention is paid to the role of its oxygen vacancy [24–26]. As the carrier effect of TiO\textsubscript{2} defective structure.

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\textsubscript{2} as a support an increased attention is paid to the role of its oxygen vacancy [23–25]. As the carrier effect of TiO\textsubscript{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\textsubscript{2}H\textsubscript{6} and its reaction with CO\textsubscript{2} are moderately catalyzed by Au/MgO and Au/Al\textsubscript{2}O\textsubscript{3}.
(ii) Deposition of Au on the n-type TiO\textsubscript{2}, CeO\textsubscript{2} and ZnO exhibited a much higher catalytic effect, particularly in the reaction of C\textsubscript{2}H\textsubscript{6} with CO\textsubscript{2}. This was attributed to the occurrence of an electronic interaction between Au and the n-type oxides leading to the formation of reactive negatively charged CO\textsubscript{2}.
(iii) While Au/TiO\textsubscript{2} catalyzes mainly the oxidative dehydrogenation of C\textsubscript{2}H\textsubscript{6} on Au/CeO\textsubscript{2} and Au/ZnO the dry reforming of C\textsubscript{2}H\textsubscript{6} is the dominant reaction pathway.

References