Effects of H2O on the thermal and photocatalytic reactions of ethane on supported Au

Anita Tóth, Tamás Bánsági, Frigyes Solymosi*

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

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The effect of illumination on the H2O + C2H4 reaction was investigated on Au deposited on TiO2, ZnO and CeO2 samples. Whereas the photocatalytic decomposition of ethane is very limited even on the most active pure TiO2, the conversion was only ~4% at 300 K in 210 min, the deposition of Au metal onto TiO2 markedly enhanced the rate of photo-induced decomposition of C2H4. Addition of H2O to ethane further enhanced the conversion and led to the production of H2. The highest conversion of ethane, 23.5% was measured for Au/TiO2. Ethylene was not detected even in traces, indicating the complete degradation of C2H4 to H2 and carbon containing deposit. Temperature programmed reaction (TPR) measurements revealed that the carbonaceous deposit on the catalysts is very stable. On Au/TiO2 it reacted with H2 to give CH4 at Tp~453 and 604 K and C2H6 and C3H8 with Tp~602 K. The promoting effect of metals was explained by a better separation of charge carriers induced by illumination and by the enhanced electronic interaction between metals and TiO2.

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1. Introduction

A great attempt is being made to obtain hydrogen in economical ways. Besides the water-gas shift process, the catalytic decomposition of C–H compounds is the most suitable source of H2 production [1–8]. Although dispersed metals are effective catalysts for the decomposition of methane and ethane, their reactions need high temperature, and we can count with the deposition of carbon leading to the deactivation of the catalysts. As in other cases the reaction can be accelerated by illumination [8–19]. The rate of the photocatalytic reaction can be further increased by using another reaction partner, CO2 or H2O, which may react with the hydrocarbons and/or with the carbon deposition, thereby enhancing the production of H2 [20].

There is a growing interest in establishing how the defect structure and electric properties of oxidic supports influence the catalytic performance of deposited metals [21,22]. This interest can be led back to the early findings, namely that changing the electric conductivity of n-type TiO2 markedly influences the catalytic efficiency of metals deposited on its surface [23–27]. The electric structure of the support was found to be decisive in the different types of reactions, such as photocatalytic decomposition of dimethyl ether [16], in the reaction of ethane with CO2 [7], in the hydrogenation of CO2 [20], and in the production of H2 in the photocatalytic reactions of ethane [15].

In the present work an account is given on the H2O-promoted thermal and photocatalytic decomposition of ethane at 300 K. The catalyst chosen is supported Au, which was deposited on various semiconductor oxides, such as TiO2, ZnO and CeO2.

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 analysed 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 H2O + C2H4 reaction we applied a gas mixture of 1:1 mol ratio.

The photocatalytic reaction was followed in the same way as described in our previous paper [7]. The reactor was equipped with a 500 W medium pressure mercury vapor lamp (TQ 718, Heraeus Noble light, Germany) as a light source. The approximate light intensity at the catalyst films is 59.4 mW/cm². The photoreactor (volume: 670 ml) consists of two concentric quartz glass tubes fitted one into the other and a centrally positioned lamp. It is connected to a gas-mixing unit serving for the adjustment of
2.2. Other pump. dissolved under NaOH heating as derived spectra.

Fig. 20 In chromatograph the temperature, supports 330 at 353. The lamp and K oxidic supported Au/TiO2 and The chromatograph based on the temperature, washed 155) programmed with PORAPAK 1/2Q+PORAPAK 1/2S packed and Equity-1 capillary columns. The volume of the sampling loop of the GC was 500 µL. The amount of all products was related to this loop. The conversion of C2H6 was calculated taking into account the amount of C2H6 consumed. This value agreed well with that based on the H2 basis, e.g., taking into account the H content of the C2H6 and the amount of H2 formed.

For FTIR studies a mobile IR cell housed in a metal cell was used [15]. Infrared spectra were recorded with a Biorad (Digilab, Div. FTIS 155) instrument. Samples were illuminated by the full arc of a Hg lamp (100 W LPS-220, PTI) outside the IR sample compartment. The filtered light passed through a high-purity CaF2 window into the cell. All the spectra presented in this study are difference spectra.

In the temperature programmed desorption (TPD) studies the heating rate was 5 K/ml and the flow rate of Ar was 20 ml/min.

3. Results and discussion

3.1. IR spectroscopic studies

In a previous paper we demonstrated that deposition of Pt metals onto TiO2 only slightly influenced the absorption spectra of C2H6 at the room temperature [15]. In the case of Au/TiO2 the adsorption of H2O+C2H6 produced absorption bands at 3001, 2963, 2952, 2928, 2890, 2870 and 1636 cm⁻¹, which agreed well with those obtained for pure TiO2 [15]. Illumination only slightly affected the positions of the above absorption bands. After flushing the C2H6+H2O mixture absorption bands at 2972, 2935 and 2868 cm⁻¹ remained in the high frequency region. New spectral features were detected at 1662, 1533, 1442, 1380 and 1344 cm⁻¹ in the low frequency range, which we attribute to the different vibrations of adsorbed C2H6 and C2H4 fragments formed in the photocatalytic reaction (Fig. 1A). As these absorption bands were seen only after evacuating the gas phase, in order to see the development of these bands the cell was evacuated at various times. Spectra obtained are shown in Fig. 1B. Accordingly, the above bands developed at very early stage of the photoreaction and they became somewhat larger with the increase of illumination time.

3.2. TPD measurements

Following the adsorption of C2H6 on Au/TiO2 a very small amount of C2H4 desorbed first with Tp ∼ 363 K, followed by C2H6 (Tp = 753 K) and CH4 (Tp = 723 K). A larger amount of H2 was released above 600 K with a peak of 663 and 993 K (Fig. 2). Adsorbing H2O+C2H6 gas mixture over Au/TiO2 gave CH4 (Tp = 753 and 903 K) and a smaller amount of C2H4 (Tp = 753 K). H2 desorbed with
The fact that the amount of \( \text{H}_2 \) desorbed is incomparably larger than that of \( \text{C}_2\text{H}_4 \) suggests the occurrence of the following reactions:

\[
\begin{align*}
\text{C}_2\text{H}_6 &= \text{C}_2\text{H}_4 + \text{H}_2 \\
\text{C}_2\text{H}_4 &= \text{CH}_4 + \text{C} \\
\text{C}_2\text{H}_4 &= 2\text{C} + 2\text{H}_2
\end{align*}
\]

The decomposition of \( \text{C}_2\text{H}_6 \) starts around 550 K. The desorption of weakly bonded \( \text{C}_2\text{H}_6 \) and \( \text{C}_2\text{H}_4 \) occurs slightly above 300 K. The main feature of TPD curves remain the same when \( \text{H}_2\text{O} \) was added to \( \text{C}_2\text{H}_6 \). Qualitatively similar TPD curves were obtained for \( \text{Au/ZnO} \).

3.3. Thermal catalytic reaction

Fig. 3 shows the results obtained for the thermal decomposition of ethane as a function of temperature on various Au catalysts. \( \text{Au/ZnO} \) proved to be the most active: the conversion of ethane reached 10% at 773 K, whereas on other samples this value required higher temperatures to be reached. The product distribution depends on the nature of the supports. On \( \text{Au/TiO}_2 \) the same amount of \( \text{H}_2 \) and \( \text{C}_2\text{H}_4 \) was formed in the whole temperature range, on another Au sample the \( \text{H}_2/\text{C}_2\text{H}_4 \) ratio was larger than 1, and a well measurable amount of \( \text{CH}_4 \) was also produced. Adding \( \text{H}_2\text{O} \) to \( \text{C}_2\text{H}_6 \) (\( \text{H}_2\text{O}/\text{C}_2\text{H}_6 \sim 1 \)) markedly increased the conversion of \( \text{C}_2\text{H}_6 \) on all samples (Fig. 4). Its effect was more explicit in the formation of \( \text{H}_2 \). On \( \text{Au/TiO}_2 \) the amount of \( \text{H}_2 \) increased by a factor of 5 at 950 K. Interestingly, much less enhancement occurred in the production of \( \text{C}_2\text{H}_4 \).

3.4. Photocatalytic reactions

The photoactivity of previously studied Au samples was investigated at 300 K. In the absence of \( \text{H}_2\text{O} \) the illumination over supported metals led only to a very little, less than 1% decomposition of ethane. Adding \( \text{H}_2\text{O} \) to the \( \text{C}_2\text{H}_6 \) (\( \text{H}_2\text{O}/\text{C}_2\text{H}_6 \sim 1:1 \)) induced only a slight photoreaction either on \( \text{Au/ZnO}, \text{Au/MgO} \) or on \( \text{Au/CoO} \). The situation was completely different over \( \text{Au/TiO}_2 \). A significant amount of \( \text{H}_2 \) evolved and also a smaller amount of \( \text{CO}_2 \). This is shown in Fig. 5A. The slight formation of methane also occurred. On the basis of \( \text{H}_2 \) formed the conversion of ethane approached 25% in 200 min. The consumption of ethane gave somewhat lower values. For comparison we mention that illumination exerted only very slight effect on the decomposition of \( \text{H}_2\text{O} \) and \( \text{C}_2\text{H}_6 \) alone. In the case of \( \text{H}_2\text{O} \) we registered only 1–2% decomposition in 200 min, whereas a larger photoeffect was found for \( \text{C}_2\text{H}_6 \): in 200 min the conversion reached ~5%.

In the explanation of the high photoactivity of \( \text{Au/TiO}_2 \) we have to take into account that \( \text{TiO}_2 \) is a semiconducting oxide. The fact that on pure \( \text{TiO}_2 \) the illumination caused only a slight increase in the conversion is probably due to the recombination of the charges induced by illumination.

\[
\begin{align*}
\text{TiO}_2 + hv &= h^+ + e^- \\
\text{h}^+ + e^- &= hv
\end{align*}
\]

is very fast on \( \text{TiO}_2 \). The deposition of Au metal onto \( \text{TiO}_2 \), however, markedly enhanced the extent of photo-effect of \( \text{TiO}_2 \). This promoting effect of metals in photocatalytic processes is generally explained by the better separation of the charge carriers generated in the primary process [8,9], which provides a greater possibility for the activation of \( \text{C}_2\text{H}_6 \).

\[
\begin{align*}
\text{C}_2\text{H}_6 + e^- &= \text{C}_2\text{H}_5^{\text{H}^-} \\
\text{C}_2\text{H}_5^{\text{H}^-} &= \text{C}_2\text{H}_4^{\text{H}^-} + \text{H}_2
\end{align*}
\]
Fig. 3. Effect of support on the thermal decomposition of C₂H₆ from Au/ZnO, Au/CeO₂, and Au/TiO₂.

Fig. 4. Effect of H₂O on the decomposition of C₂H₆ catalyzed by supported Au catalysts.
enhanced activation of adsorbed molecules. The role of the electron transfer in the enhanced catalytic effect of TiO₂ supported metals catalysts has been assumed and confirmed long time ago [24–27] and this idea has been generally used since then.

As regards the further steps we could assume the decomposition of C₂H₅ radical to C₂H₄

\[ \text{C}_2\text{H}_5(a) = \text{C}_2\text{H}_4(g) + \text{H}(a) \] (8)

or as was found on many metal surfaces [29,30], its recombination

\[ 2\text{C}_2\text{H}_5(a) = \text{C}_4\text{H}_{10}(a) \] (9)

The fact that neither C₂H₄ nor C₄H₁₀ was detectable in the products suggests that the lifetime of transiently formed C₂H₅ or C₄H₁₀ is very short, and instead of their coupling reactions they underwent fast photo-generated degradation resulting in some kind of carbonaceous deposit onto the catalyst.

\[ \text{C}_2\text{H}_5(a) = \text{C}(s) + 2.5\text{H}_2 \] (10)

It is an open question how the H₂O participates in the photocatalytic process. A separate study on the photolysis of H₂O on the same Au/TiO₂ catalyst indicated that illumination induces only a very slight decomposition of H₂O, less than 2%. The possible reason is that the product of dissociation of H₂O, very likely O atoms formed in the recombination of OH groups

\[ 2\text{OH} = \text{H}_2\text{O} + \text{O} \] (11)

remain the surface occupying the active center. We assume that in the case of TiO₂-containing sample the oxygen vacancies are the active centers for this process. The fact that ZnO does not contain O vacancy, but Zn excess occupies interstitial position in the lattice may be one of the reasons of the less activity of Au/ZnO compared to Au/TiO₂.

5. Conclusions

(i) n-type oxides (TiO₂, ZnO, CeO₂) only slightly catalyses the thermal and the photoreaction of H₂O + C₂H₅.

(ii) Deposition of Au on the above oxides enhances the thermal reaction of H₂O + C₂H₅ at very high temperature; the conversion exceeds 40% on the most active catalyst at 900 K

(iii) Illumination, however, induces the H₂O + C₂H₅ reaction over Au/TiO₂ even at room temperature resulting in 20% conversion of C₂H₆ in 200 min yielding H₂ and some CH₄ fragments.

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References


