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Decomposition of propane and its reactions with CO_2 over alumina-supported Pt metals

Frigyes Solymosi * and Péter Tolmacsov

Institute of Solid State and Radiochemistry, University of Szeged, Reaction Kinetics Research Group of the Hungarian Academy of Sciences†,
P.O. Box 168, H-6701 Szeged, Hungary

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Propane underwent dehydrogenation and cracking on alumina-supported Pt metals at 823–923 K. Propylene formed with highest selectivity (50–80%) on Pt/Al_2O_3. The deposition of carbonaceous species was observed on every sample, the hydrogenation of which occurred only above 700–750 K with a peak temperature of 900–950 K. The presence of CO_2 basically altered the reaction pathway of propane, and the formation of CO and H_2 came into prominence. The highest specific rates for the production of H_2 and CO were measured for the Ru and Rh catalysts.

KEY WORDS: propane; carbonaceous species; Ru and Rh catalysts.

1. Introduction

The dry reforming of methane to produce synthesis gas has been the subject of extensive research in the last decade [1–4]. Less attention has been paid to the catalytic reaction of ethane with CO_2 [5], and we found only one work dealing with CO_2-reforming of propane [6]. The aim of the present work is to make a comparative study on the catalytic efficiencies of Pt metals in the dry-reforming of propane. In addition, an account is given on the decomposition of propane over the same catalysts in the temperature range of the above reaction. Afterwards, we plan to perform detailed kinetic measurements on the most effective metal.

2. Experimental

The catalysts were prepared by impregnating the alumina support (Degussa, P 110 C1) with solutions of metal salts to yield a nominal 1 wt% metal. The following salts of Pt metals were used: $H_2PtC_6{\cdot}6H_2O$, $PdCl_2$, $RhCl_3{\cdot}3H_2O$, H_2IrCl_6 and $RuCl_3{\cdot}3H_2O$. The impregnated powders were dried at 383 K. The fragments of catalyst pellets were oxidized at 523 K for 30 min and reduced at 773 K in the catalytic reactor for 1 h. The dispersity of the supported metals was determined by hydrogen adsorption at 300 K.

Catalytic measurements were carried out in a fixed-bed continuous-flow reactor made of quartz (100 mm × 7 mm i.d.). The amount of catalysts used was 0.3 g. Analyses of the exit gases were performed with a Hewlett-Packard 5780 gas chromatograph using a Porapack QS column. The system was operated at a total pressure of 1 atm. The flow rate of the reactant was 60 ml/min. The absence of diffusional limitation was confirmed [7]. The conversions of propane and carbon dioxide were calculated, taking into account their amounts consumed in the reaction. The selectivity for reaction products, S_i, was defined as

$$S_i = \frac{x_i n_i}{\sum_i x_i n_i}$$

where x_i is the mole fraction of product i, and n_i is the number of carbon atoms in each molecule of gaseous products.

3. Results and discussion

3.1. Decomposition of propane

First we examined the decomposition of propane on supported Pt metals. The reaction occurred with a well-measurable rate at and above 823 K. The dominant process was the dehydrogenation of propane to propylene and hydrogen:

$$C_3H_8 = C_3H_6 + H_2. \tag{1}$$

The appearance of ethylene and methane in the product suggests the occurrence of the reaction

$$C_3H_8 = C_2H_4 + CH_4. \tag{2}$$

Ethane, butane and benzene were also formed in minor amounts. Results obtained for Pt/Al_2O_3 at 923 K are

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* To whom correspondence should be addressed.

† This laboratory is a part of the Center for Catalysis, Surface and Material Science at the University of Szeged.

E-mail: fsolym@chem.u-szeged.hu

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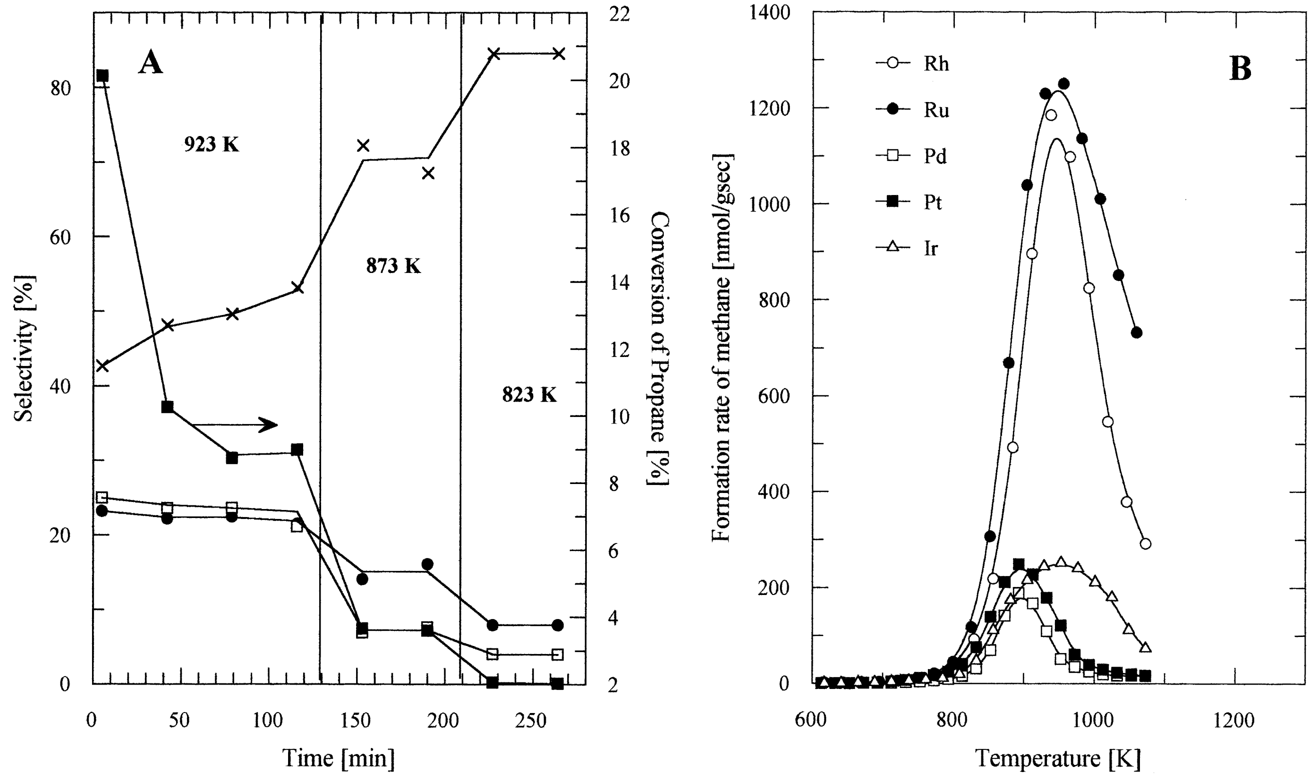

Figure 1. (A) Reaction of propane over Pt/Al_2O_3 at different temperatures. ●, methane; □, ethylene; ×, propylene; ■, conversion of propane. (B) TPR spectra for the hydrogenation of carbon species deposited on alumina-supported Pt metals during the reaction of propane at 923 K for 150 min.

shown in figure 1. The activity of the catalyst continuously decayed in time on stream. The selectivity of the propylene formation depended on the temperature. At 823 K it was 80–85%, while at 923 K, 48–53%. From the comparison of data obtained for Pt metals (table 1), we can say that propylene was formed with the highest selectivity on Rh and Pt, and with less selectivity on Pd and Ir catalysts. The specific activities of the Pt metals in terms of turnover numbers (NC_3H_6, rates per unit surface area of metal) at 923 K are also given in table 1. Accordingly, the rate of the production of C_3H_6 was the highest for Rh and Pd; the dispersity of them was relatively low.

As the amount of hydrogen always exceeded that of propylene we assumed that the cracking of propane (or that of its products) led to the deposition of some kind

Table 1
Decomposition of propane and its reactions with CO_2 over alumina-supported Pt metals at 923 K.

	Decomposition of C_3H_8					Reaction between C_3H_8 and CO_2			
Metals dispersity (%)	Conversion of propane (%)	NC_3H_6 (s^{-1})	Selectivity of C_3H_6 (%)	Selectivity of C_2H_4 (%)	C_s (nmol)	Conversion of propane (%)	H_2/CO ratio	NH_2 (s^{-1})	NCO (s^{-1})
Rh	5.59	0.0082	55.1	21.8	4.30×10^5	63.5	0.54	0.849	1.592
31.0	5.01	0.0071	48.1	30.6					
Ru	6.85	0.0542	47.2	31.8	7.28×10^5	45.3	0.62	6.67	10.76
4.5									
Ir	7.11	0.0076	42.3	36.1	1.36×10^5	7.6	0.50	0.076	0.153
87.0									
Pt	8.98	0.0057	53.2	21.1	1.07×10^5	5.4	0.25	0.047	0.187
48.0	4.77	0.0098	45.1	32.8	1.13×10^5				
Pd	6.38	0.0154	42.8	33.8	1.07×10^5	4.3	0.53	0.117	0.219
16.0									

Data were taken at 110 min on stream.

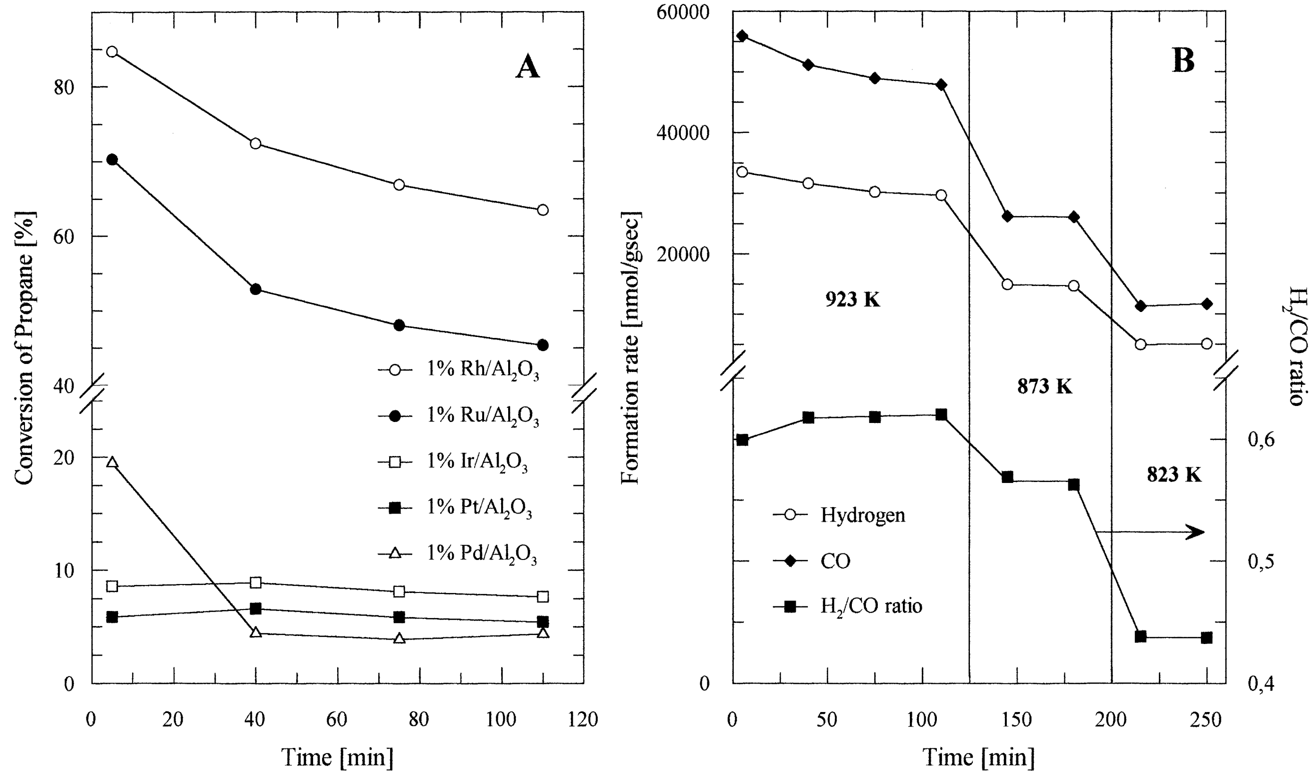

Figure 2. (A) Conversion of propane in the $C_3H_8 + CO_2$ reaction over alumina-supported Pt metals at 923 K in time on stream. (B) Rate of formation of H_2 and CO in the $C_3H_8 + CO_2$ reaction over Pt/Al_2O_3 at different temperatures.

of carbonaceous species on the catalysts. This is probably responsible for the deactivation of the catalysts. Treating the used catalyst with hydrogen produced methane and a small amount of ethane. The amount and the reactivity of this surface carbon was also determined by TPR measurements. Some TPR spectra are shown in figure 1(B). Interestingly, evolution of methane started in most cases above 700–750 K and produced only one high-temperature peak between 900 and 950 K. This is in contrast to our previous studies, when we detected at least three TPR peaks, suggesting that different carbon species exist on the surface [4,8–11]. The reason for the divergent result is that in the present case the carbon was produced at high temperature, when the most reactive carbon transformed at once into the less reactive graphitic form. The amount of carbon calculated is given in table 1. The largest amount was found over Rh/Al_2O_3 and the least amount on Ir-Al_2O_3 catalyst.

3.2. Reaction of C_3H_8 with CO_2

The supported Pt metals exhibited a marked catalytic activity in the CO_2-reforming of C_3H_8. The presence of CO_2 basically altered the reaction pathway of propane, and the dehydrogenation and cracking reactions were suppressed. The reaction proceeded at the highest rate on Rh and Ru followed by Ir, Pt and Pd. As demonstrated in figure 2, only a slight deactivation of the catalyst occurred during the reaction at 923 K. Propylene and methane were still formed particularly at higher temperatures. In harmony with this, the conversion of C_3H_8 exceeded that of CO_2 for every catalyst sample. The H_2/CO ratio was somewhat less than that corresponding to the reaction (0.66):

$$C_3H_8 + 3CO_2 = 6CO + 4H_2. \tag{3}$$

It varied during the conditioning period and with the temperature. The highest value 0.62 was measured for Ru, and the lowest one for Pt.

Examination of the catalyst surface after the reaction revealed again the presence of carbonaceous deposition. Its amount, however, was less than that measured in the case of the decomposition of pure propane. The largest amount of carbon was formed on Rh and Ru, which were the most active catalysts. The specific activities of the Pt metals in the production of CO and H_2 decrease in the sequence Ru > Rh > Pd > Pt = Ir (table 1).

Although the complexity of the reaction and the occurrence of several secondary processes make it difficult to determine the mechanism of the $C_3H_8 + CO_2$ reaction, some conclusions can be drawn on the basis of our supplementary studies on the reaction of CO_2 and C_XH_Y fragments on metal surfaces. It is expected that the primary step of both the dehydrogenation and dry-reforming of propane is its dissociation to propyl species, C_3H_7:

$$C_3H_{8(a)} = C_3H_{7(a)} + H_{(a)} \tag{4}$$

followed by its dehydrogenation

$$C_3H_{7(a)} = C_3H_6 + 1/2H_2 \tag{5}$$

to propylene and hydrogen.

On the single-crystal surfaces of Pt metals under UHV conditions, the coupling of C_3H_7 species was not observed [12–14]. It occurred, however, over Ag [15], Au [16], Cu [17] and Mo_2C [18] surfaces. The latter, with the combination of ZSM-5, is able to convert methane into aromatics [19,20]. It is an interesting result that we detected a slight formation of benzene in the reaction of pure propane on some supported Pt metals, suggesting that under the present experimental conditions the reductive coupling of C_3H_7 also proceeds into C_6 compounds. A significant fraction of propyl species or its cracking products, however, decompose on the active sites of the catalysts to yield a very unreactive carbon species.

The presence of CO_2 dramatically influenced the reaction pathway of C_3H_6, and, instead of the dehydrogenation and cracking, the formation of H_2 and CO came into prominence. We may assume that the adsorbed O atoms formed in the dissociation of CO_2:

$$CO_{2(a)} = CO_{(a)} + O_{(a)} \tag{6}$$

promoted the activation of propane, and it opened a new route for the formation of C_3H_7 and C_3H_6:

$$C_3H_{8(a)} + O_{(a)} = C_3H_{7(a)} + OH_{(a)} \tag{7}$$

$$C_3H_{7(a)} = C_3H_{6(g)} + \tfrac{1}{2}H_{2(g)}. \tag{8}$$

The reaction, however, does not stop at the formation of propylene, which may also be activated by adsorbed O atoms to give further reactive species

$$C_3H_{6(a)} + O_{(a)} = C_3H_{5(a)} + OH_{(a)} \tag{9}$$

$$C_3H_{5(a)} = C_3H_{4(a)} + \tfrac{1}{2}H_{2(g)}. \tag{10}$$

Control measurements showed that the cracking of propylene proceeds at a high rate on alumina-supported Pt metals, and it also reacts with CO_2 to give CO and H_2.

In our previous study on the dry reforming of methane over Rh and Pd catalysts we found that the carbon species formed or treated at high temperature is very unreactive towards CO_2 [21,22]. Therefore, the lack of the deposition of a significant amount of carbon, which also leads to the deactivation, was explained by the direct reaction of CH_3 or CH_2 with CO_2:

$$CH_{3(a)} + CO_{2(g)} = 2CO_{(g)} + 1.5H_{2(g)} \tag{11}$$

which does not involve the formation of any kind of carbon. Experiments with CH_3 produced by the pyrolysis of azomethane confirmed this assumption, as adsorbed CH_3 reacted readily with gaseous CO_2 [23]. We may assume that the reaction of C_xH_y fragments with CO_2 proceeds in the present case, too.

4. Conclusions

(i) The dehydrogenation of propane occurred with selectivities of 40–55% over alumina-supported Pt metals. (ii) The carbon species deposited was very unreactive towards H_2: the peak temperature of its dehydrogenation fell in the range of 900–950 K. (iii) Supported Pt metals are effective catalysts for the dry reforming of propane to produce synthesis gas. (iv) The highest rates were measured for Ru and Rh.

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