A comparative study on the activation and reactions of CH_4 on supported metals

Frigyes Solymosi, András Erdöhelyi and József Cserényi

Reaction Kinetics Research Group and Institute of Solid State and Radiochemistry [1],
University of Szeged, PO Box 168, H-6701 Szeged, Hungary

Received 21 July 1992; accepted 23 September 1992

The catalytic effects of silica-supported Pt metals were tested and compared in the decomposition of methane and its conversion into higher hydrocarbons. The dissociation of methane is readily measurable at 473–673 K. The rate of initial decomposition at 523 K was the highest on Rh, but it dropped to a low value within a short contact time. The gaseous products were hydrogen and ethane in small, variable amounts. Hydrogen of the carbonaceous species formed in the decomposition led to the production of aliphatic hydrocarbons.

Keywords: Activation of methane; decomposition of methane; formation of ethane from methane; formation of hydrogen from methane; formation of surface carbon; TPR study of the reaction of surface carbon; silica-supported Pt metals

1. Introduction

A considerable effort has been made in the past decade to convert the cheap raw materials CH_4 and CO_2 into more valuable compounds [1–4]. Both substances are thermodynamically stable and their activation and transformation pose a great challenge to homogeneous and heterogeneous catalysis [5,6].

The present paper reports a comparative study on the interaction of CH_4 with silica-supported Pt metals. In recent studies of the reactions of CH_4 with CO_2 on supported Pt metals, we observed that CH_4 undergoes dissociation at the reaction temperature of the CH_4–CO_2 mixture (773 K) to produce CH_3 and H. A small fraction of the CH_3 dimerizes to C_2H_6, while most of it decomposes to surface carbon [7]. A similar reaction was observed on the Pd(100) surface under UHV conditions, when adsorbed CH_3 was generated by the photodissociation of CH_3Cl [8,9] or the thermal dissociation of CH_3I [10,11]. The dimeriza-

---

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

© J.C. Baltzer A.G. Scientific Publishing Company

tion of adsorbed CH_3 in these cases occurred at temperatures as low as 120–150 K. More recently, Amariglio and co-workers [12] reported the conversion of CH_4 into higher hydrocarbons on Pt/SiO_2 (EUROPT-1).

2. Experimental

The catalysts were prepared by impregnating the silica support (Cabosil) with solutions of Pt metals to yield a nominal 5 wt% metal. The following salts of Pt metals were used: $H_2PtCl_5 \cdot 6H_2O$, $PdCl_2$, $RhCl_3 \cdot 3H_2O$, 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 673 K for 30 min and reduced at 673 K in the catalytic reactor for 1 h.

Catalytic measurements were carried out in a fixed bed continuous-flow reactor made of quartz (100 × 27 mm) o.d.). The amount of catalysts used was 0.1 g. Analyses of the exit gases were performed with a Hewlett–Packard 5890 gas chromatograph using Parapack QS column. The system was operated at a total pressure of 1 atm.

Infrared spectroscopic studies were made in a vacuum IR cell using self-supporting wafers of catalyst powders (30 × 10 mm, ≈ 20 mg/cm^2) which underwent the same pretreatments as before catalytic measurements. The IR cell used made it possible to register the spectra between 100–300 K. Spectra were recorded with a Biorad (Digilab. Div.) Fourier transform IR spectrometer (FTS 7).

The dispersity of the supported metals was determined by hydrogen adsorption.

3. Results and discussion

In the first series of measurements the reaction of methane on supported Pt metals was investigated. Results obtained are shown in fig. 1. Hydrogen and ethane formation, indicative of the decomposition of methane, was observed immediately in every case. The activity of the catalysts, however, quickly dropped to a low value, and after 15–25 min only traces of hydrogen and ethane were detected. The rate of the ethane evolution passed through a maximum. On Pd/SiO_2 ethylene also appeared among the reaction products. Its concentration was commensurable with that of ethane. The largest initial amount of ethane was formed on Pt/SiO_2. This value was about 40% of the data calculated from the equilibrium constant of the reaction ($2CH_4 \rightleftharpoons C_2H_6 + H_2$) taking into account the actual pressure of the H_2. The initial amount of hydrogen was the highest also on Rh/SiO_2. The amount of hydrogen greatly exceeded that of ethane on all catalyst samples. This suggests the accumulation of a carbonaceous

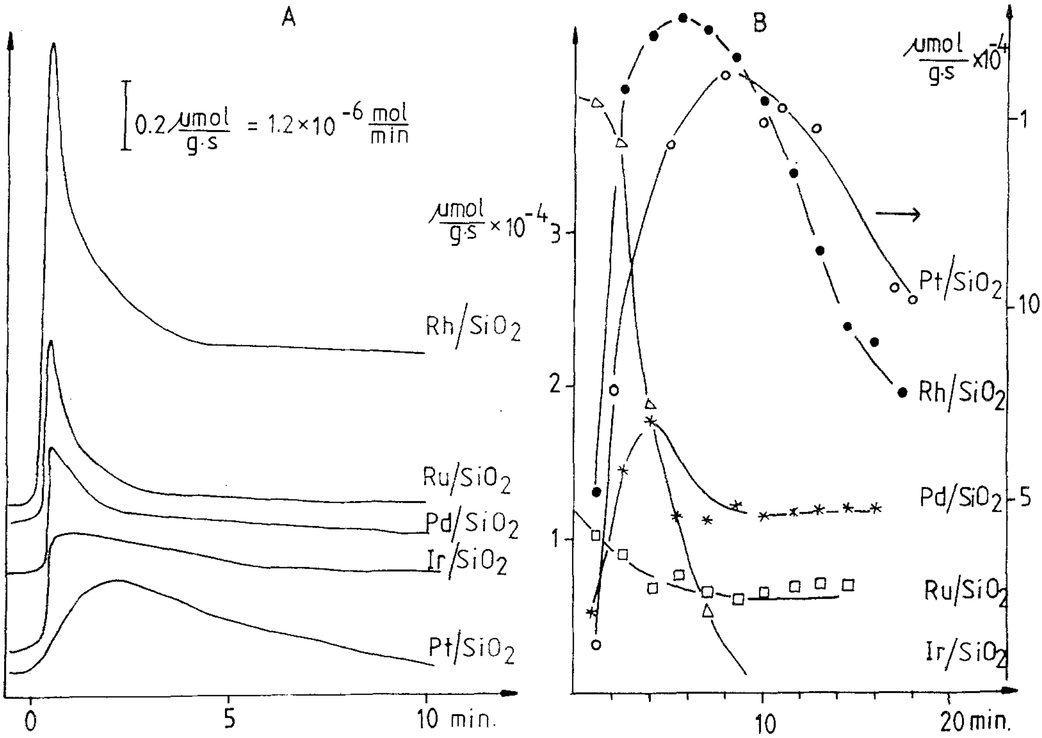

Fig. 1. Rates of H_2 (A) and C_2H_6 (B) formation in the decomposition of CH_4 on silica supported Pt metals at 523 K. Flow rate of $N_2 + CH_4$ (12.5%): 40 ml/min. Sample mass: 100 mg.

residue on the catalysts during methane exposure, which is very probably responsible for the activity decay.

More detailed measurements were performed on Pd/SiO_2. The decomposition of methane was observed even at 473 K. An increase in the methane content from 10 to 100% led to a well observable increase in the rate of hydrogen and ethane formation. Variation of the flow rate had a much greater effect: the higher the flow rate, the higher was the production of ethane and ethylene, as experienced by Belgued et al. [12] on EUROPT-1 catalyst. This supports the idea that the removal of hydrogen formed in the dissociation of methane is a key factor in the accumulation of CH_x species on the surface, and hence in the formation of ethane.

All these results suggest that the methane molecule dissociates on reduced Pt metals to give adsorbed H and CH_3 species,

$$CH_4(g) \rightleftharpoons CH_3(a) + H(a).$$

The latter undergoes fast decomposition,

$$CH_3(a) \rightleftharpoons CH_2(a) + H(a),$$
$$CH_2(a) \rightleftharpoons CH(a) + H(a),$$
$$CH(a) \rightleftharpoons C(a) + H(a).$$

At the same time, however, the recombination of CH_3

$$2CH_3(a) \rightleftharpoons C_2H_6(g)$$

competes with the decomposition process. Moreover, on Pd/SiO_2 the recombination of CH_2,

$$2CH_2(a) \rightleftharpoons C_2H_4(g),$$

also proceeds. Alternatively, ethylene could be formed in the dehydrogenation of ethane. We suppose that ethane could be formed in the hydrogenation of ethylene on the catalysts. This step is less likely under the conditions employed.

A great effort was made to detect adsorbed CH_x fragments formed in the decomposition of methane by means of sensitive FTIR spectroscopy. However, no absorption bands attributable to any of the vibration modes of CH_x were identified either by in situ measurements or after sudden cooling of the sample in a continuous $CH_4 + N_2$ flow to 200 K. This means that all the above CH_x fragments react or decompose quickly at high temperature, or their surface concentrations are below the detection limit.

However, the presence of surface carbon was well manifested by its reaction with hydrogen. After flushing of the reactor with pure argon (following CH_4 dissociation at 523 K for 20 min) and changing to a H_2 flow, methane was initially produced at high rates on almost all catalysts. Under these conditions ethane was detected only on Pt/SiO_2, but even in this case only in traces. Methane evolution did not cease even after one to two hours.

The hydrogenation of the surface carbon formed in the dissociation of CH_4 was also investigated by TPR spectroscopy, which revealed a large variance of carbon reactivity with the conditions of its formation and with the nature of the metal (fig. 2). When the surface carbon was produced at low temperatures (473–523 K) and in a short time on Pd, Rh and Pt, a fraction of this form (designated α) was hydrogenated to CH_4 even below or at 400 K. In the case of Rh, a significant fraction of the surface carbon, β form, reacted at 400–500 K. This stage was small or absent for the other metals. The majority of the surface carbon was hydrogenated at 530–650 K (γ form). When the supported metals were exposed to CH_4 at 573–673 K, the reactivity of the surface carbon produced was greatly reduced. This is particularly true for Rh. In this case the highly reactive α form was missing, and a significant proportion of the β carbon was transformed into the less reactive γ form.

Furthermore, in the case of silica-supported Pt and Pd it appeared that not only the temperature, but also the duration of carbon formation (i.e. the length of the time the carbon is kept at high temperature) influenced its reactivity. This was manifested in the product distribution of the hydrocarbons formed. If these catalysts were exposed to CH_4 at 523 K for only a short time (1–2 min), C_2–C_5 hydrocarbons were also produced in addition to CH_4 (table 1). The same behavior was previously observed for EUROPT-I catalyst by Belgued et al. [12]

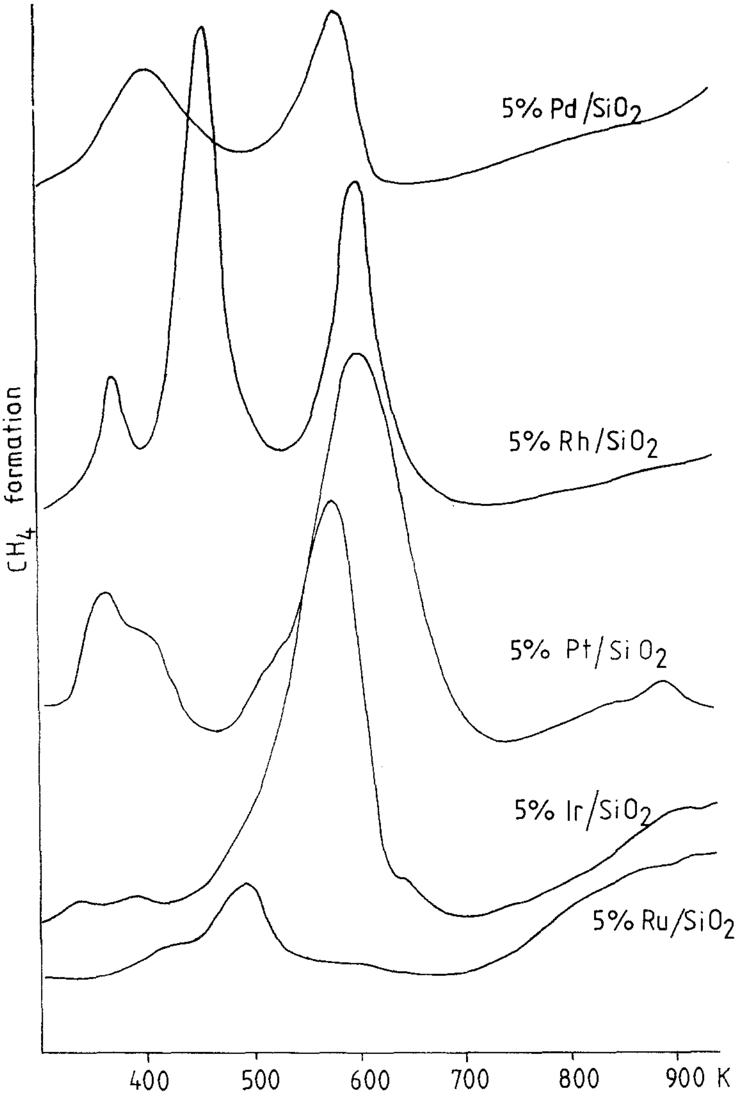

Fig. 2. Temperature-programmed hydrogenation of surface carbon produced by CH_4 decomposition on silica supported Pt metals at 523 K for 10 min. Flow rate of $N_2 + CH_4$ (12.5%) was 200 ml/min. Sample mass: 300 mg. Flow rate of H_2: 40 ml/min.

and for Ru/SiO_2 by Koerts and van Santen [13]. When the exposure time was extended to 10 min, the absolute and relative amounts of CH_4 were greatly increased and higher hydrocarbons were detected only in traces. On the other Pt metals, hydrogenation of the surface carbon, independently of the conditions of its formation, gave mostly only methane.

Similar features have been observed following hydrogenation of the surface carbon formed in the dissociation of CO on supported Rh [14,15], when the α

Table 1
The amount of C_2H_6 and H_2 formed in the decomposition of CH_4 on supported Pt metals at 523 K in 10 min [a]

Catalysts	D (%)	C_2H_6 (μmol/g)	C_2H_6/M [b] ($\times10^{-3}$)	H_2 (μmol/g)	H_2/M [b]
5% Ru/SiO_2	3.1	0.051	3.3	72.2	4.7
5% Rh/SiO_2	23.3	0.22	1.94	340	3.05
5% Pd/SiO_2	10.7	0.083 [c]	1.64	73.3	1.45
5% Pt/SiO_2	23.4	0.69	11.5	83.3	1.38
5% Ir/SiO_2	22.9	0.105	1.76	165	2.76

[a] 12.5% CH_4 in N_2 was used as reactant; the flow rate was 40 ml/min.
[b] The amounts of C_2H_6 or H_2 are related to the number of surface metal atoms.
[c] Sum of ethane and ethylene.

form was attributed to carbidic, the β form to amorphous and the γ form to graphitic carbon. This similarity suggests that adsorbed O (also produced in the dissociation of CO) hardly exerts a great influence on the chemistry of surface carbon under these conditions.

The catalytic performances of the silica-supported metals in the decomposition of methane are demonstrated in fig. 1. When the amounts of C_2H_6 and H_2 formed in 10 min are related to the number of surface metal atoms, taking into account the dispersity of the supported metals, we obtain different order for activity (table 2). As regards the production of C_2 hydrocarbons, the most active catalyst is Pt followed by Ru, Rh, Ir and Pd. In the case of methane decomposition the activity sequence is Ru, Rh, Ir, Pd and Pt.

Table 2
The distribution of hydrocarbons formed during the hydrogenation of surface carbon following exposure of the supported Pt metals to CH_4 [a]

Catalyst	Products [b] (%)					
	C_2H_6	C_3H_8	n-C_4H_{10}	i-C_4H_{10}	C_5	C_6
5% Ru/SiO_2	1.16	0.65	–	–	–	–
5% Rh/SiO_2	0.14	0.03	–	–	–	–
5% Pd/SiO_2	–	–	–	–	–	–
5% Pt/SiO_2	42.9	10.4	2.18	0.79	7.8	23.7
5% Ir/SiO_2	1.2	< 0.1	0.2	–	–	–

[a] Conditions: 0.1 g of catalysts were used. Step 1: 1 min exposure of the catalysts to CH_4 flow (200 ml/min) at 523 K. Step 2: the samples were treated with H_2 pulses at 523 K.
[b] The other product was methane.

4. Conclusions

(i) The silica-supported Pt metals were found to be active in the decomposition of methane above 473 K, to give hydrogen, a small amount of ethane and different carbon species. (ii) As a result of the active metal area becoming covered with carbon, the decomposition ceases after a short contact time. (iii) As regards the dissociation of methane, the most active metal was the Rh, whereas the largest amount of ethane was measured on Pt/SiO_2. (iv) The reactivity of the surface carbon produced exhibited a large variance with the conditions of its formation. The most reactive form reacted with hydrogen to give C_2–C_5 hydrocarbons.

References

[1] D.M. Bibby, C.D. Chang, R.F. Howe and S. Yurchak, eds., *Methane Conversion*, Proc. Symp. on the Production of Fuel and Chemicals, Auckland 1987; in: Studies in Surface Science and Catalysis, Vol. 36, eds. B. Delmon and J.T. Yates Jr. (Elsevier, Amsterdam, 1988).
[2] J.S. Lee and S.T. Omaya, Catal. Rev. Sci. Eng. 30 (1988) 249.
[3] W.M. Ayers, ed., *Catalytic Activation of* CO_2, ACS Symp. Ser. (Am. Chem. Soc., Washington, 1988).
[4] R. Pichai and K. Klier, Catal. Rev. Sci. Eng. 28 (1986) 13.
[5] Q.Y. Yang, A.D. Johnson, K.J. Maynard and S.T. Ceyer, J. Am. Chem. Soc. 111 (1989) 8748.
[6] F. Solymosi, J. Mol. Catal. 65 (1991) 337.
[7] F. Solymosi, Gy. Kutsán and A. Erdöhelyi, Catal. Lett. 11 (1991) 149.
[8] F. Solymosi, J. Kiss and K. Révész, J. Phys. Chem. 94 (1990) 2224.
[9] F. Solymosi, J. Kiss and K. Révész, J. Chem. Phys. 94 (1991) 8510.
[10] F. Solymosi and K. Révész, J. Am. Chem. Soc. 113 (1991) 9145.
[11] F. Solymosi and K. Révész, Surf. Sci., in press.
[12] M. Belgued, P. Pareja, A. Ameriglio and H. Amariglio, Nature 352 (1991) 789.
[13] T. Koerts and A. van Santen, J. Chem. Soc. Chem. Commun. (1991) 1281.
[14] F. Solymosi and A. Erdöhelyi, Surf. Sci. 110 (1981) L630.
[15] A. Erdöhelyi and F. Solymosi, J. Catal. 84 (1983) 446.