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Catalytic reaction of CH_4 with CO_2 over alumina-supported Pt metals

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The dissociation of CH_4 and CO_2, as well as the reaction between CH_4 and CO_2 at 723–823 K have been studied over alumina supported Pt metals. In the high temperature interaction of CH_4 with catalyst surface small amounts of C_2H_6 were detected. In the reaction of $CH_4 + CO_2$, CO and H_2 were produced with different ratios. The specific activities of the catalysts decreased in the order: Ru, Pd, Rh, Pt and Ir, which agreed with their activity order towards the dissociation of CO_2.

Keywords: Formation of C_2H_6 from CH_4; reactions of methane; supported Pt metal catalysts; formation of surface carbon; alumina supports

1. Introduction

Great attention is being paid to the conversion of methane and carbon dioxide, the cheapest carbon-containing materials, into more valuable compounds in catalytic reactions [1,2]. Methane can be partially oxidized into methanol and formaldehyde at high temperature with low conversion and selectivity, or can be dimerized into ethane in an oxidative dehydrogenation process. The simplest way to convert CO_2 into other compounds is its catalytic hydrogenation. In this respect, the formation of methanol represents a useful route.

An attractive and challenging problem for catalysis is to react the two compounds, CO_2 and CH_4, with each other and to produce useful gases (e.g. synthesis gas) or even more valuable compounds. Relatively few papers are available on the catalytic reaction between CH_4 and CO_2 [3–7], which is commercialised as the "Calcor Process" [3], and only little is known of the

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mechanism of the reaction. Supported Ni and Rh have been found to be the most effective catalysts [4–7], although a comparison on a turnover basis has not yet been made.

We recently studied the activation and reactions of CO_2 on supported Pt metals [8–12], and also examined the reactivity of adsorbed CH_3 on some of these metal surfaces [13–17]. The present paper reports on the catalytic efficiencies of alumina-supported Pt metals in the $CH_4 + CO_2$ reaction. In order to obtain a reliable basis for comparison of the catalytic activities of the metals, rates per unit surface area of the metals were determined by using a differential reactor.

2. Experimental

The catalysts were prepared by impregnating the alumina support (Degussa. P 110 Cl) with solutions of Pt metals to yield a nominal 1 wt% metal. The following salts of Pt metals were used: $H_2PtCl_6 \cdot 6H_2O$, $PdCl_2$, $RhCl_3 \cdot 3H_2O$, 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 773 K for 30 min and reduced at 773 K in the catalytic reactor for 1 hr. After reduction, the sample was flushed with helium and cooled down or heated to the reaction temperature.

Catalytic measurements were carried out in a flow reactor. The amount of catalysts used was 0.3 g. The ratio of CH_4/CO_2 in the reacting gas mixture was 1 : 1. Analyses of the exit gases were performed with a Hewlett-Packard 5750 gas chromatograph using Parapack QS column. The system was operated at a total pressure of 1 atm. High space velocities of 3000–6000 h^{-1} were used. The absence of diffusional limitation was confirmed [18]. The pulse reactor was an 8-mm-i.d. quartz tube, it was incorporated between the sample inlet and the column of the gas chromatograph. One pulse contained 32.6 μmol of gases.

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 dispersity of the supported metals was determined by hydrogen and oxygen titration by use of dynamic impulse method [19].

3. Results and discussion

Before kinetic measurements, we investigated the high-temperature interaction of CH_4 and CO_2 with a catalyst surface by the pulse method. On exposure of the reduced surface to CH_4 pulses, we detected the formation of ethane and

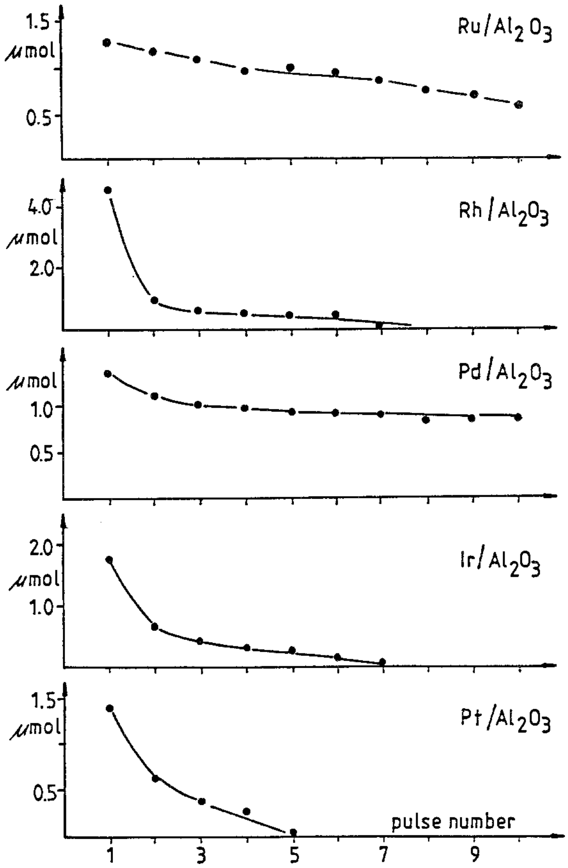

Fig. 1. The amount of ethane formed treating the catalyst samples (0.3 g) with CH_4 pulses (1 pulse contains 32.6 μmol CH_4) at 773 K.

traces of ethylene, which indicates the occurrence of the dissociation of CH_4 and the recombination of CH_3 and CH_2 species:

$$CH_4 = CH_3 + H \tag{1}$$

$$CH_3 = CH_2 + H \tag{2}$$

$$2\,CH_3 = C_2H_6 \tag{3}$$

$$2\,CH_2 = C_2H_4. \tag{4}$$

The amount of C_2 compounds produced, however, gradually decreased for most of the catalysts. A much slower decay was observed for Pd and Ru, which exhibited the highest affinity toward the dimerization of CH_4 (fig. 1). Another fraction of CH_4 was dehydrogenated completely to carbon: on reacting the catalyst surface with O_2 pulses after treatment with CH_4 pulses and a He flush, we obtained CO_2 evolution. We cannot exclude completely that CH_x species also remained on the surface, but, due to the high temperature, this is very

Table 1
Decomposition of CH_4 and CO_2 on supported Pt metals at 773 K

Catalysts	CH_4 pulses							CO_2 pulses	
	Dispersion (%)	CH_4 reacted		C_2H_6 formed		C surface formed		CO formed	
		μmol	μmol / metals	μmol	μmol / metals	μmol	μmol / metals	μmol	μmol / metals
1% Ru/Al_2O_3	5.5	19.55	11.98	9.53	5.83	0.49	0.3	0.28	0.17
1% Rh/Al_2O_3	46.2	17.28	1.28	7.66	0.56	1.96	0.14	0.78	0.058
1% Pd/Al_2O_3	23.2	19.90	3.04	9.95	1.52	–	–	0.20	0.03
1% Ir/Al_2O_3	75.5	10.55	0.90	3.8	0.32	2.95	0.25	0.09	0.007
2% Pt/Al_2O_3	41.3	7.23	0.57	2.72	0.21	1.79	0.13	0.1	0.008

The data are the total amount of the values obtained in 10 CH_4 and 10 CO_2 pulses, respectively. The amount of catalyst was 0.3 g. One pulse contained 32.6 μmol CH_4 or CO_2.
Dispersion = amount of the surface metal atoms.

unlikely. The amount of surface carbon formed in the decomposition of CH_4 is shown in table 1. The behavior of Pd again differed from that of the other catalysts, as no detectable carbon formation occurred on Pd/Al_2O_3. On repetition of these measurements on oxidized catalysts, the total oxidation of CH_4 was experienced until the consumption of surface oxygen.

The dissociation of CO_2 to CO and O also occurred on reduced catalyst surfaces. Note that the study of the dissociation of CO_2 requires the complete elimination of traces of adsorbed hydrogen, as it effectively promotes this reaction [20–24]. The extent of CO_2 dissociation at 773 K was the largest for Ru and Rh, and the smallest for Pt and Ir (table 1). By means of infrared spectroscopy we obtained the same results. The formation of adsorbed CO was detected even at 423 K for Rh/Al_2O_3 and only above 523 K for the less active catalysts [25]. The experiments were performed in the presence of 50 Torr of CO_2 and the metal content in this case was 5 wt%. On oxidized surfaces, no dissociation of CO_2 was observed.

The supported Pt metals exhibited great differences in catalytic behaviour as concerns the $CH_4 + CO_2$ reaction. The reaction occurred at the highest rate on Rh, followed by Pt, Pd, Ru and Ir. As demonstrated in fig. 2, in most cases no or only a slight deactivation of the catalyst occurred during the reaction at 823 K. The main reaction products were CO, H_2 and H_2O; ethane was detected only in traces. The conversion of CO_2 exceeded that of CH_4 for every catalyst sample indicating that the reaction

$$CH_4 + CO_2 = 2\,CO + 2\,H_2 \tag{5}$$

was followed by several secondary processes, including the methanation of CO_2 and CO, reverse water gas shift reaction and the Boudouard reaction.

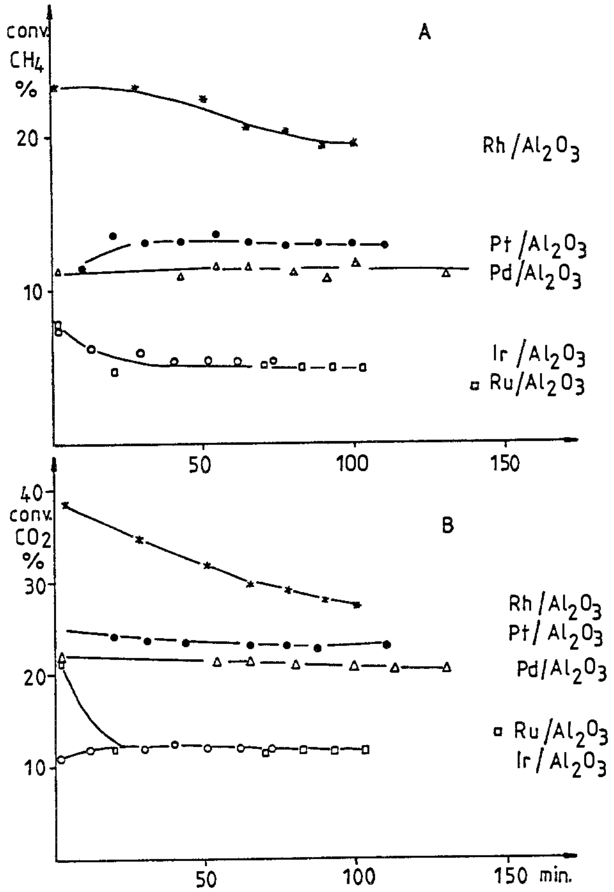

Fig. 2. Changes in the conversions of CH_4 and CO_2 in the CH_4+CO_2 reaction on different catalysts at 823 K.

The CO/H_2 ratio varied only slightly during the conditioning period. The highest value 3.8 was measured for Ru. Examination of the catalyst surface after the reaction revealed carbon deposition. The amount of surface carbon formed was determined by its oxidation to CO_2. The largest amount of carbon was formed on Rh and Pt, and the least on Pd (table 2).

From the temperature dependence of the CO_2 and CH_4 consumption, the apparent activation energies were determined. With the exception of Rh they agreed relatively well in the two cases, and lay in the range 52–131 kJ/mole (table 2).

The specific activities of the Pt metals in terms of turnover numbers (N_{CH_4}, N_{CO_2}, N_{H_2} and N_{CO}, rates per unit surface area of metal) at 823 K are shown in table 2. The specific rates for the consumption of CH_4 and CO_2, and for the production of CO and H_2, decrease in the sequence Ru, Pd, Rh, Pt, Ir. This is practically the same as the sequence for the methanation of CO [8,26].

Table 2
Some characteristic data for $CH_4 + CO_2$ reaction on alumina supported Pt metal catalysts at 823 K [a]

	N_{CH_4}	N_{CO_2}	E_{CH_4}	E_{CO_2}	N_{H_2}	N_{CO}	CO/H_2	C_s [b]
	(s^{-1})		(kJ/mol)		(s^{-1})			(μmol metals)
1% Ru/Al_2O_3	0.53	1.36	92.5 ± 1.3	131.0 ± 4.4	0.54	2.18	3.8	0.39
1% Rh/Al_2O_3	0.22	0.32	66.1 ± 1.05	52.7 ± 1.3	0.35	0.55	1.6	0.22
1% Pd/Al_2O_3	0.36	0.64	87.1 ± 1.4	90.4 ± 3.3	0.54	1.09	2.0	0.06
1% Ir/Al_2O_3	0.07	0.18	111.7 ± 5.4	131.0 ± 5.4	0.09	0.31	2.29	0.14
2% Pt/Al_2O_3	0.2	0.36	63.2 ± 1.4	52.3 ± 1.8	0.25	0.58	3.2	0.22

[a] The amount of catalysts were 0.3 g; The flow rate of the reactant was 60 ml/min.

[b] The amount of surface carbon formed in the $CH_4 + CO_2$ reaction at 773 K for 1 hour.

The activity sequence for the methanation of CO_2 differed only in that Pd/Al_2O_3 was the least active catalyst [8,11].

Although the complexity of the reaction and the occurrence of several secondary processes make it difficult to determine the mechanism of the $CH_4 + CO_2$ reaction, some conclusions can be drawn on the basis of our supplementary studies on the reaction of CO_2 and CH_3 on metal surfaces [8–17].

It seems almost certain that the activation of CH_4, i.e. its dissociation (eq. (1)) is very limited on reduced metal surfaces. This process is clearly promoted by the adsorbed O produced by the dissociation of CO_2:

$$CO_2 = CO + O \tag{6}$$

which occurs far below the temperature of the $CH_4 + CO_2$ reaction. Nevertheless, the dissociation of CO_2 is facilitated by adsorbed hydrogen formed in the dissociation of CH_4 molecules. In the study of the reactivity of adsorbed CH_3 (produced by the photodissociation of adsorbed CH_3Cl or the thermal dissociation of CH_3I) on Pd and Rh surfaces [13–17] we found that under UHV conditions the prevailing step is the self-hydrogenation of CH_3 into CH_4, which occurs even below 250 K. At the same time, the dimerization of CH_3 into C_2H_6 (eq. (3)) also proceeds, particularly on a Pd surface. In the present case, when adsorbed H can react with adsorbed O, the CH_3 group further decomposes:

$$CH_3 = CH_x + (3 - x)H \tag{7}$$

or is oxidized by adsorbed O to H_2O and CO (CO_2). The dimerization of CH_3 groups represents only a negligible step. The dehydrogenation of CH_3 to carbon occurs to a lesser extent on the Pd surface. At the same time, the dimerization of CH_3 species occurred more easily on this catalyst.

Taking all these features into account, we tentatively propose that the activity sequence of the Pt metals in the $CH_4 + CO_2$ reaction reflects their ability to dissociate CO_2 and to produce adsorbed O, which scavenges the hydrogen of CH_4, and hence promotes its dissociation.

Conclusions

1. Methane alone showed little reactivity towards supported Pt metals at 723–823 K. As regards the formation of ethane supported Ru and Pd exhibited the highest activity.
2. The reaction between CH_4 and CO_2 to yield CO and H_2 occurred above 700 K. The specific activities of the Pt metals in terms of turnover numbers decreased in the order Ru, Pd, Rh, Pt, Ir.
3. It is assumed that this activity order corresponds to the ability of Pt metals to dissociate CO_2 and to produce adsorbed O which scavenges the hydrogen of CH_4.

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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, eds. B. Delmon and J.T. Yates, Jr., Vol. 36 (Elsevier, 1988).

[2] W.M. Ayers (ed.), *Catalytic Activation of* CO_2 (ACS Symp. Ser. American Chemical Society, Washington D.C. 1988).

[3] S. Teuner, Hydrocarbon Processing 64 (1985) 106.

[4] J. Varga and V. Hesp, Acta Chim. Hung. 3 (1953) 209.

[5] O. Tokunaga and S. Ogasawara, React. Kinet. Catal. Lett. 39 (1989) 70.

[6] Y. Sakai, H. Saito, T. Sodesawa and F. Nozaki, React. Kinet. Catal. Lett. 24 (1984) 253;
T. Sodesawa, A. Dobashi and F. Nozaki, React. Kinet. Catal. Lett. 12 (1979) 107.

[7] M. Masai, H. Kado, A. Miyake, S. Nishiyama and S. Tsuruya, in: *Proc. Symp. on the Production of Fuels and Chemicals*, in: Studies in Surface Science and Catalysis, eds. B. Delmon and J.T. Yates, Jr., Vol. 36, p. 67.

[8] F. Solymosi and A. Erdöhelyi, J. Mol. Catal. 8 (1980) 471.

[9] F. Solymosi, A. Erdöhelyi and M. Kocsis, J. Chem. Soc., Faraday Trans. I, 77 (1981) 1003.

[10] F. Solymosi A. Erdöhelyi and T. Bánsági, J. Catal. 68 (1981) 371.

[11] A. Erdöhelyi, M. Pásztor and F. Solymosi, J. Catal. 98 (1986) 166.

[12] F. Solymosi, J. Mol. Catal. 65 (1991) 337.

[13] A. Berkó and F. Solymosi, J. Phys. Chem. 93 (1989) 12.

[14] F. Solymosi, J. Kiss and K. Révész, J. Phys. Chem. 94 (1990) 2224.

[15] F. Solymosi, A. Berkó and K. Révész, Surf. Sci. 240 (1990) 50.

[16] F. Solymosi, J. Kiss and K. Révész, J. Chem. Phys., in press.
[17] F. Solymosi and K. Révész, J. Amer. Chem. Soc., in press.
[18] R.M. Körös and E.J. Novak, J. Chem. Eng. Sci. 22 (1967) 470.
[19] J.E. Benson, H.S. Hwang and M. Boudart, J. Catal. 30 (1973) 146.
[20] F. Solymosi, A. Erdöhelyi and M. Kocsis, J. Catal. 65 (1980) 428;
F. Solymosi and J. Kiss, Surf. Sci. 135 (1983) 243.
[21] T. Iizuka and Y. Takaka, J. Catal. 70 (1981) 449.
[22] F. Solymosi and A. Erdöhelyi, J. Catal. 70 (1981) 451.
[23] S.D. Worley, G.A. Mattson and R. Candill, J. Phys. Chem. 87 (1983) 1671.
[24] M.L. McKee, C.H. Dai and S.D. Woorley, J. Phys. Chem. 92 (1988) 1056.
[25] A. Erdöhelyi, É. Novák and F. Solymosi, to be published.
[26] F. Solymosi, I. Tombácz and M. Kocsis, J. Catal. 75 (1982) 78.