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Enhanced formation of ethane in the conversion of methane over Cu–Rh/SiO_2

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We report on the enhanced formation of ethane in the non-oxidative conversion of methane, and on the increase of the higher hydrocarbons in the hydrogenation of surface carbon over copper-promoted Rh/SiO_2 catalyst.

Keywords: decomposition of methane under non-oxidative conditions; formation of ethane; hydrogenation of surface carbon; effects of copper promoter on the catalytic behaviour of Rh/SiO_2

1. Introduction

In recent studies it was explored that methane decomposes readily at high space velocity on dispersed Pt metal at 573–773 K, but it decays soon to low activities due to the deposition of carbon [1–10]. In a comparative study for the specific activity of silica supported Pt metals we found that supported Rh is one of the most active Pt metals for this reaction [3]. The main products of the decomposition were H_2 and $\underline{C}$ with a very small amount of C_2H_6. This led us to assume that the primary step in the dehydrogenation of CH_4 is the formation of CH_3 which decomposes rapidly to carbon, but a small fraction of it recombines to C_2H_6.

This is in harmony with the behavior of adsorbed CH_3 species (produced by thermal or photodissociation of CH_3I) on Rh(111) surfaces where its recombination to C_2H_6 was found to be very limited [11]. A similar feature was observed on Pd(100) [12] and on other Pt metals [13]. The propensity for coupling was somewhat larger for CH_2 to C_2H_4, particularly on Pd(100) surfaces [14,15]. A completely different result was obtained for CH_3 on Ag(111) surfaces: CH_3 species generated by the dissociation of CH_3I gave only C_2H_6 with a negligible decomposition to carbon [16]. The same was observed for Cu(111) [17] and Cu(110) [18]. Another result of

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surface science studies worth mentioning is that the reaction pathways of C_xH_y fragments on Rh(111) and Pd(100) surfaces are strongly affected by additives and coadsorbed species; Zn adatoms promote the coupling of C_2H_5 to butane and butene [19,20], whereas adsorbed O atoms react with CH_2 to give formaldehyde [21,22].

Taking into account all these findings the combination of a good dehydrogenating catalyst with one which promotes only the C–C coupling seemed promising to enhance the production of C_2 compounds in the dehydrogenation of CH_4. In the present paper we report on the behavior of Cu–Rh/SiO_2 catalyst.

2. Experimental

2.1. MATERIALS

The catalysts were prepared by impregnating the SiO_2 (Cab-O-Sil) support with a solution of $Rh(NO_3)_3$ and $Cu(NO_3)_2$ salts to yield a nominal 3 wt% metal with 2 : 1, 1 : 1 and 0.5 : 1 Cu/Rh ratios. The amount of catalyst was 0.1 g. For catalytic studies small fragments of slightly compressed pellets were used. Before the measurements the catalysts were oxidized for 30 min and reduced for 60 min at 673 K in situ. After oxidation and reduction the sample was flushed with He or N_2 at 673 K for 15 min. After such a treatment, the Cu–Rh catalyst can be considered as bimetallic cluster which exhibits some miscibility in the bulk [23].

The gases used were of commercial purity. The purity of CH_4 (Linde) was 99.996%. Ethane impurity was not detectable by gas chromatography. He (99.996), and N_2 (99.995) were deoxygenated with an oxytrap. The other impurities were observed by a 5A molecular sieve at the temperature of liquid nitrogen.

2.2. METHODS

The decomposition of CH_4 was investigated in a flow reactor [8,9]. The carrier gas was N_2 which contained 12.5 vol% of CH_4. The flow rate was 40 ml/min. The exit gases were analyzed gas chromatographically (Hewlett-Packard 5890) on a Porapack QS column.

The dispersion of the supported metal was determined by H_2–O_2 titration at 298 K using the pulse technique [8]. Data obtained for catalyst samples studied in this work are listed in table 1.

3. Results and discussion

3.1. DEHYDROGENATION OF METHANE

First we examined the interaction of CH_4 with pure 2 wt% Cu/SiO_2. We found no decomposition in the temperature range 473–773 K.

Table 1
Formation of hydrocarbons (in µmol/g) in the reaction at five hydrogen pulses with carbon produced in the decomposition of CH_4 at 523 K and for 1.5 and 10 min

Catalyst	Disp. (%)	t (min)	C_1 $\times 10^{-1}$	C_2 $\times 10^{-3}$	C_3 $\times 10^{-4}$	C_4 $\times 10^{-4}$	C_5 $\times 10^{-3}$	C_6 $\times 10^{-3}$	C_s[a]
2%Rh/SiO$_2$	40.6	1.5	10.73	2.11	4.02	3.01	9.12	–	3.01
3%(Cu–Rh)/SiO$_2$ Cu : Rh = 0.5 : 1	30.8	1.5	7.75	1.02	1.82	1.14	3.28	2.55	0.466
3%(Cu–Rh)/SiO$_2$ Cu : Rh = 1 : 1	24.8	1.5	9.41	1.96	4.24	3.20	7.46	0.0055	0.234
2%Rh/SiO$_2$	40.6	10	12.14	2.33	3.95	3.29	7.14	–	27.67
3%(Cu–Rh)/SiO$_2$ Cu : Rh = 0.5 : 1	30.8	10	10.38	4.28	1.48	18.85	8.49	1.69	5.05
3%(Cu–Rh)/SiO$_2$ Cu : Rh = 1 : 1	24.8	10	12.25	4.05	8.21	12.81	18.33	1.39	3.54

[a] C_s is the total amount of surface carbon formed in the decomposition of CH_4. It was determined by TPR measurements from the amount of CH_4 formed in the hydrogenation of carbon up to 700 K.

Fig. 1 displays data for the decomposition of CH_4 on Cu–Rh/SiO$_2$ (1 : 1 Cu/Rh ratio) at different temperatures. Product formation occurred at a temperature as low as 523 K. The gaseous products identified were H_2 and C_2H_6. At 773 K, a small amount of ethylene (6.0–10.5% of ethane) was also detected. The amount of

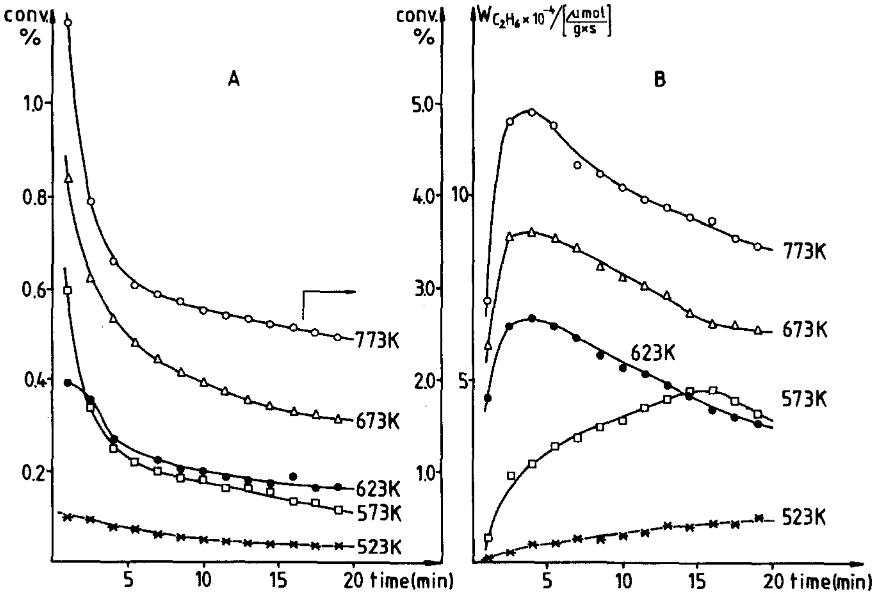

Fig. 1. Effects of temperature on the conversion of CH_4 (A) and on the rate of C_2H_6 formation (B) on a 3 wt% (Cu + Rh)/SiO$_2$ catalyst. Cu : Rh ratio 1 : 1.

H_2 was higher by more than three orders of magnitude than that of C_2H_6. With increasing temperature, the rate of decomposition significantly increased. Independently of the temperature the initial CH_4 conversion drastically decayed in a short reaction time to low values, nevertheless gas evolution was observed even after several hours.

The formation of C_2H_6 showed a complex picture. At 523–573 K the rate of C_2H_6 formation increased with time, but above 573 K it exhibited a maximum. Similarly to H_2, ethane formation did not cease even after 5 h at 523–773 K. When the Cu–Rh ratio was decreased to 1 : 1, we obtained a similar picture. At a 2 : 1 Cu : Rh ratio, however, the copper blocked the Rh as we found very little decomposition even at 773 K.

As the course of the reaction of CH_4 is very sensitive to the pretreatment of the catalyst, to the metal content and to the experimental conditions, measurements were carried out with Cu-free Rh/SiO$_2$ of different Rh contents. Samples were prepared and treated in an exactly similar way as for the Cu + Rh/SiO$_2$ catalyst. Some data are presented in fig. 2. Whereas the conversion of CH_4 slightly increased, the rate and the selectivity of C_2H_6 formation decreased with increasing Rh content, at least in the initial phase of the reaction. From the comparison of the Cu-free and Cu-containing samples it appears that conversion of CH_4 is reduced by copper. This is very likely due to the decreasing number of Rh sites available for the reaction. The determination of the dispersion of Rh by H_2 adsorption clearly showed that the uptake of H_2 is reduced by the presence of Cu (table 1), which probably covers a certain fraction of Rh metal. The most important feature

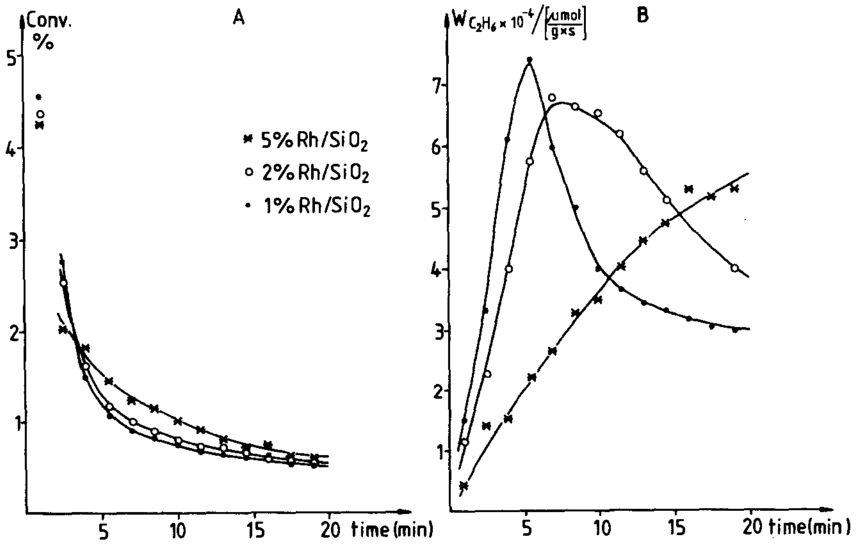

Fig. 2. Effects of the Rh content on the conversion of CH_4 (A) and on the rate of C_2H_6 formation (B) at 673 K.

of the effect of Cu is the significant increase in the C_2H_6/H_2 ratio. This is shown in fig. 3, where we plotted the selectivity of C_2H_6 formation at different temperatures as a function of reaction time. The effect of Cu is particularly exhibited at lower reaction temperatures. At 773 K, where the selectivity for C_2H_6 production is generally very low, there is no difference between the two catalyst systems. Variation of the Cu/Rh ratio also showed that the 1 : 1 Cu : Rh ratio is the optimum composition, not only for the conversion of CH_4, but also for the selectivity of C_2H_6 formation.

In the explanation of these results we assume that CH_3 species formed in the primary dissociation step of CH_4 over Rh may migrate onto Cu, where, instead of decomposition, they are dimerized into C_2H_6. We cannot rule out the occurrence of coupling between CH_3 and CH_2 on Cu to yield ethyl species which are hydrogenated into ethane:

$$CH_3(a) + CH_2(a) \rightleftharpoons C_2H_5(a)$$

$$C_2H_5(a) + H(a) \rightleftharpoons C_2H_6$$

The fact that ethylene was also detected among the products suggests that CH_2 species formed in the stepwise dehydrogenation of CH_4 also migrate onto the Cu, where they are dimerized into ethylene. The recombination of CH_2 is a favoured process on Cu(110) surfaces [17,18].

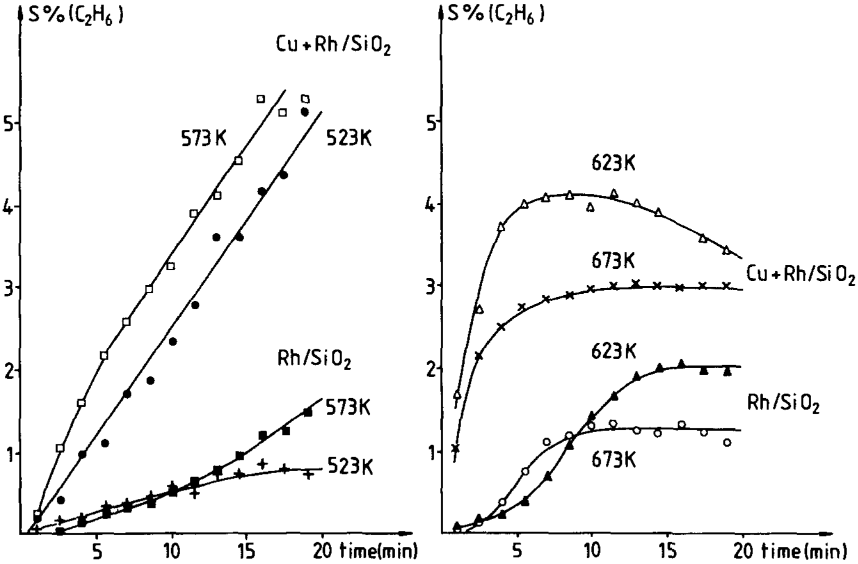

Fig. 3. Selectivity values for C_2H_6 production as a function of reaction time at different temperatures for Cu-free and Cu-containing Rh/SiO$_2$ catalysts. Cu : Rh ratio 1 : 1.

3.2. HYDROGENATION OF SURFACE CARBON FORMED IN THE DECOMPOSITION OF METHANE

Some experiments have also been conducted concerning the influence of Cu on hydrogenation of surface carbon produced by CH_4 decomposition.

TPR spectra relating to the hydrogenation of surface carbon on the catalyst samples are displayed in fig. 4. When the surface carbon was produced at 573 K for 1.5 min of reaction time, a very small proportion of it was hydrogenated slightly above room temperature. This reactive carbon is designated as the α form. A larger fraction of the surface carbon (β form) reacted above 450–550 K. The amount of surface carbon determined from the TPR curves is shown in table 1. It is clearly seen that significantly less carbon was deposited on the Cu-containing sample. In a

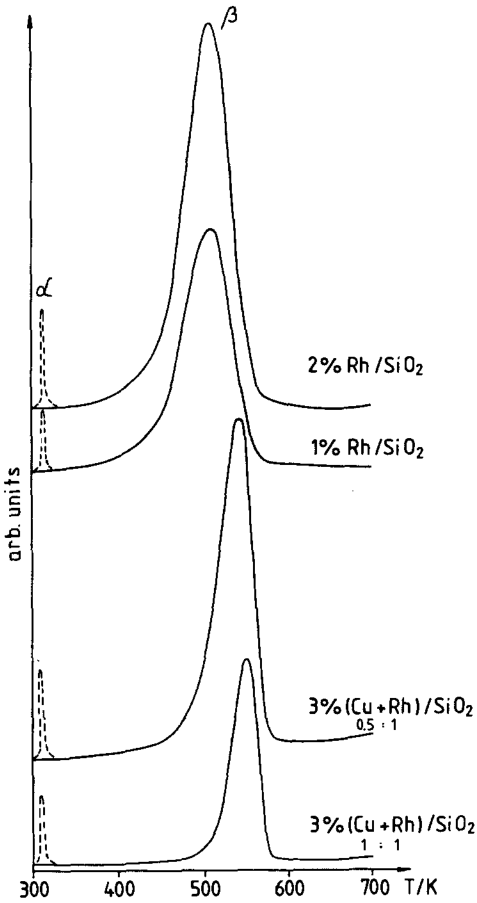

Fig. 4. Temperature programmed reaction (TPR) of surface carbon with H_2 on Cu-free and Cu-containing Rh/SiO_2 catalysts. Carbon was produced in the decomposition of CH_4 at 573 K for 1.5 min.

further TPR study it was found that an increase in the temperature of the decomposition of methane shifted the maximum rate of the hydrogenation of surface carbon to higher temperatures on both Cu-containing and Cu-free samples. This suggests a considerable aging of the carbon on the catalyst surface.

From the comparison of the reactivity of carbon on Cu–Rh/SiO$_2$ with that deposited on Rh/SiO$_2$ we can state that Cu increases the temperature of the hydrogenation of carbon (β form) at least by 40 K. A possible reason is the decrease of Rh sites available for the activation of H$_2$ molecules.

The reaction of the more reactive α form with hydrogen has been studied under isothermal conditions in greater detail. Results are listed in table 1. In harmony with previous observations [6–8] the hydrogenation of this carbon on Rh/SiO$_2$ produces not only methane, but hydrocarbons up to five C atoms, too. In the presence of Cu the amounts of hydrocarbons formed decreased, very likely due to the lower carbon content produced in the methane decomposition. Interestingly, however, benzene was also formed in the reaction, which was not detected on the Cu-free sample. When the decomposition time of methane was extended to 10 min, the amounts of C$_4$–C$_5$ hydrocarbons significantly increased on the Cu + Rh/SiO$_2$ catalyst.

4. Conclusions

(i) Addition of copper to Rh/SiO$_2$ catalysts enhances the selectivity of ethane formation in the conversion of methane under non-oxidative conditions. (ii) Copper addition also influences the hydrogenation of surface carbon by promoting the formation of C$_4$–C$_6$ hydrocarbons.

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