K promotion of Co catalysts for the two-step methane homologation reaction

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The promotion of Co catalysts with K has been examined for the two-step CH_4 homologation reaction. The effect of K was strongly influenced by the catalyst support. In the case of the SiO_2 supported catalyst, addition of K increased the CH_4 decomposition activity and decreased the second-stage hydrogenation activity while the C_{2+} selectivity increased from 14 C at% to 36 C at%. With the Al_2O_3 support, addition of K increased CH_4 decomposition activity but the C_{2+} selectivity increased only marginally. These results are discussed in terms of Co dispersion, support effects and the effect of K on the reactivity of the carbon species deposited during CH_4 decomposition.

Keywords: K promotion of Co catalysts; methane homologation reaction; Co dispersion; support effects

1. Introduction

In recent years there have been many studies aimed at the direct conversion of CH_4 to more valuable products such as synthesis gas, oxygenates and higher hydrocarbons [1–3]. Methane homologation is a two-stage approach recently proposed whereby CH_4 is decomposed over Group VIII metal catalysts at elevated temperature (about 450°C) in the first stage. The resulting carbonaceous surface deposits are hydrogenated at low temperature ($< 200°C$) in the second stage, to yield higher hydrocarbons [4]. Interest in this approach stems from the fact that compared to methane partial oxidation or oxidative coupling, the reaction temperatures are low and undesired CO_x products are avoided since O_2 is not present in the reaction system.

Based on initial activities, Rh has been identified as the most active CH_4 decomposition catalyst among Ru, Rh, Pd, Pt and Ir supported on SiO_2 [5]. The CH_4 decomposition activities of a number of supported metal catalysts have also been ranked according to the decreasing activity sequence Co, Ru, Ni, Rh>Pt, Re, Ir>Pd, Cu, W, Fe, Mo by Koerts et al. [4]. Temperature-programmed surface reaction (TPSR) with H_2 has been used to identify three different types of carbonaceous deposit that result from CH_4 decomposition [4]. C_{2+} hydrocarbons (hydrocarbons with carbon number $\geqslant 2$) are formed primarily from the most reactive species, referred to as C_α by Koerts et al. [4] and identified as a CH_x species [4,6–8]. Two less reactive forms of carbon (referred to as C_β and C_γ) yield primarily CH_4 during TPSR. The relative amount of each of these species depends on the conditions of the decomposition and the temperature history and age of the carbonaceous deposit [4,9]. In general, as the deposit ages at elevated temperature it becomes less reactive because of transformations that occur from the C_α form to the less reactive C_β and C_γ forms. Examination of these surface species on Ru single crystals by high resolution electron energy-loss spectroscopy (HREELS) has shown them to be associated with hydrogen and that surface vinylidene is likely the key intermediate for C_{2+} production [8,10].

The maximum C_{2+} yield of Group VIII metal catalysts reported by Koerts et al. [4] in the hydrogenation stage of the CH_4 homologation process was 13%, with the CH_4 decomposition conditions chosen to obtain 100% CH_4 conversion. Recently, much higher yields (> 40%) were reported for Pt catalysts using a batch reactor in which the CH_4 supply was limited and H_2 was removed from the reactor system [11]. The mechanism of C_{2+} formation is thought to be similar to the polymerization of CH_x surface species that occurs in the Fischer–Tropsch synthesis (FTS). Hence the product distribution can be described by the α value of the Anderson–Schulz–Flory (ASF) distribution [4,12]. Koerts et al. [4] used the time-integrated selectivities measured during the hydrogenation period to calculate α values and showed these to depend on the metal–carbon (M–C) bond strength of the catalyst. Values of zero reported for Cu and Fe were due to very weak and very strong M–C bond strengths, respectively. Optimum M–C bond strengths occurred for Co and Ru, corresponding to the maximum α values of about 0.25 and C_{2+} selectivities of 20 mol%.

The catalyst support is also known to influence CH_4 homologation. Solymosi et al. [9] have shown that the turnover number (TON) for CH_4 decomposition over

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Pd catalysts decreased with the type of support in the order $TiO_2 > Al_2O_3 > SiO_2 > MgO$. These differences were attributed to differences in Pd particle size as well as the ease with which carbon migration occurred from the metal to the support [9]. In their study the amount of carbon deposited was greater than the amount needed for monolayer coverage of the exposed metal catalysts whereas the CH_4 decomposition procedure of Koerts et al. [4] resulted in less than a monolayer coverage of carbon. In the latter case the effect of support is expected to be less important, in agreement with their observation that the C_{2+} selectivity was not influenced by acidic or basic supports [4]. With Pd, the C_α, C_β, and C_γ carbonaceous species were identified on the SiO_2 supported catalyst, whereas only the C_β and C_γ deposits were present with Al_2O_3, TiO_2 and MgO supports [9]. Furthermore, the amount of CH_4 obtained during subsequent hydrogenation varied with the support, in part due to the different amounts of carbon deposited during the CH_4 decomposition stage [9]. The fact that the support can influence the chemical nature of the carbonaceous deposit has also been reported for the FTS [13].

In the present paper we report on the influence of K promoter on the two-stage homologation of CH_4 over Co catalysts supported on Al_2O_3 and SiO_2. Previous studies have not reported on the effect of basic promoters in CH_4 homologation. However, K is expected to alter the M–C bond strength and increase the C_{2+} selectivity, in the same way as this promoter acts in FTS. The catalysts have been characterized by various techniques and the activities determined during hydrogenation are interpreted taking account of both the amount of carbonaceous species on the surface following CH_4 decomposition and the Co dispersion.

2. Experimental

2.1. Catalyst preparation

Catalysts containing 10 wt% of Co were prepared by wetness impregnation of SiO_2 (Aldrich Chemicals, grade 951) or Al_2O_3 (Activated alumina F-200, Alcoa Chemicals) with an appropriate amount of $Co(NO_3)_2$ solution. The catalysts were then dried overnight at 110°C and calcined in air at 500°C for 5 h. After calcination, 1 wt% K was added as promoter to the supported catalyst from a solution of KNO_3, followed by drying overnight at 110°C. Both promoted and unpromoted catalysts were reduced according to the temperature-programmed reduction (TPR) procedures described below with the final temperatures being held for 1 h.

2.2. Catalyst characterization

The TPR profiles were measured by placing 0.5 g of the calcined catalyst in a fixed-bed quartz reactor and increasing the reactor temperature from 30 to 600°C (for the Al_2O_3 support) or 500°C (for the SiO_2 support), at a ramp rate of 10°C/min while flowing 60 ml(STP)/min of a 20 mol% H_2 in Ar gas mixture (Linde, UHP grade). Trace O_2 was removed from the H_2 by placing a Mn/SiO_2 trap in the feed line. The extent of catalyst reduction was monitored by passing the reactor feed and effluent through opposite sides of a thermal conductivity cell that responded proportionately to a decreased effluent H_2 concentration as the catalyst was reduced. Both the calcined and reduced catalysts were examined by XRD to determine the bulk compounds present in the catalysts.

The Co dispersion was measured on 0.2 g of catalyst using an O_2–H_2 titration procedure similar to that described by Erdöhelyi et al. [14]. Following TPR the reactor temperature was increased by 50°C and the catalyst was maintained at this temperature for 15 min in an Ar flow. The catalyst was then cooled to room temperature and exposed to several pulses of 4.09 μmol of O_2 until adsorption was complete. The subsequent H_2 titration of the adsorbed O_2 was performed in the same manner at a temperature of 200°C.

The surface compositions of the catalysts were determined by X-ray photoelectron spectroscopy (XPS). The spectrometer was a Leybold-Heraeus MAX-200 with dual magnesium and aluminum sources and the aluminum source was used for the analysis. The catalyst samples were transferred from the reactor to the spectrometer preparation chamber in an Ar atmosphere using a glove bag to minimize exposure to air. Samples were examined after TPR or following the standard CH_4 activation sequence which preceded the hydrogenation step in the activity and selectivity measurements described below. The samples were degassed at room temperature over-night to a pressure of 3×10^{-8} kPa. Subsequently, the samples were transferred to the analysis chamber where the base pressure was 4×10^{-9} kPa. The spectral resolution was 0.75 eV for each scan. Charge effects were minimized by secondary electrons generated by the X-ray source close to the sample.

2.3. Activity and selectivity measurement

The activity and selectivity measurements were made in the same quartz, fixed-bed microreactor used for the TPR measurements and with the same catalyst loading of 0.5 g. Following TPR the gas flow was switched to Ar and the reactor temperature was adjusted to 450°C. After the temperature stabilized the catalyst was exposed for 1 min to a mixture of 7.4 mol% CH_4 in Ar at a flow of 55 ml(STP)/min. After cooling to 100°C within 30 s, the sample was purged for 15 min in Ar at a flowrate of 50 ml(STP)/min to remove weakly adsorbed CH_4. The activity was then measured isothermally at 100°C in 11 ml(STP)/min of pure H_2. The products of both the first-stage CH_4 decomposition and the second-

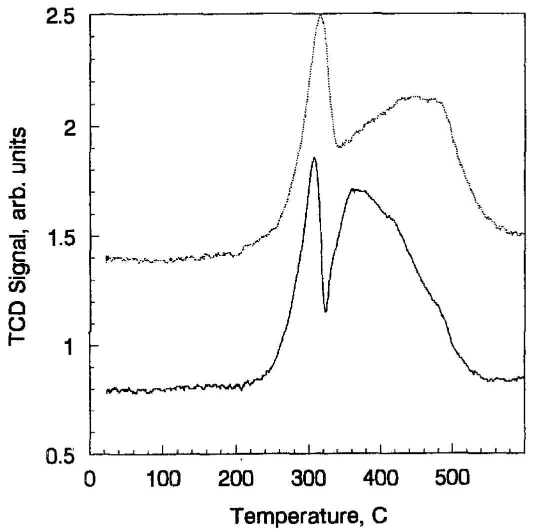

Fig. 1. TPR profiles of Co/SiO_2 (——) and $K–Co/SiO_2$ (...) catalysts.

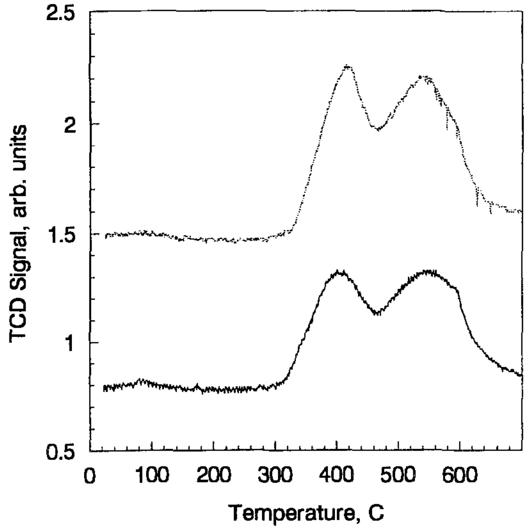

Fig. 2. TPR profiles of Co/Al_2O_3 (——) and $K–Co/Al_2O_3$(...) catalysts.

stage hydrogenation were analyzed continuously using a Spectramass DAQ100/DXM quadrupole mass spectrometer. The product composition determined from the mass spectrometer was confirmed periodically by gas chromatography using a flame ionization detector.

CH_4 decomposition was also examined under temperature-programmed surface reaction (TPSR) conditions with a feed gas of 7.4 mol% CH_4 diluted with Ar. The reactor temperature was increased at a ramp rate of 10°C/min to 600°C. CH_4 consumption was monitored by mass spectrometer.

3. Results and discussion

3.1. Catalyst characterization

The TPR profiles of the calcined catalysts (Co/SiO_2, $K–Co/SiO_2$, Co/Al_2O_3 and $K–Co/Al_2O_3$) are presented in figs. 1 and 2. All the profiles were characterized by two peaks, reflecting the bulk reduction of Co_3O_4 to Co. XRD confirmed that cobalt was present as Co_3O_4 before reduction and as Co after reduction. No other cobalt-containing phases were detectable by XRD in either the calcined or reduced catalysts.

The addition of K to the Al_2O_3 and SiO_2 supported catalysts marginally increased the reduction temperatures. However, a much more significant difference in reduction temperature was observed between the Al_2O_3 and SiO_2 supported catalysts. The TPR peak temperatures of the Al_2O_3 supported catalysts were approximately 100°C above that of the SiO_2 supported catalysts. Similar differences in reduction temperature of Group VIII metal catalysts supported on Al_2O_3 and SiO_2 have been reported in the literature [15,16]. Based on a reduction stoichiometry of $Co_3O_4 + 4H_2 \rightarrow 3Co + 4H_2O$, the percent reduction was calculated from the H_2 consumption measured during TPR. In agreement with previous studies, the degree of reduction was higher on the SiO_2 supported catalysts than the Al_2O_3 supported catalysts as shown by the data of table 1.

The data of table 1 also summarize the Co dispersions, as determined by H_2–O_2 titration and calculated with respect to the total amount of reduced Co determined from the TPR measurements. The nominal and surface compositions of the reduced catalysts, the latter determined by XPS, are also included in table 1. The Co dispersions were lower on the Al_2O_3 supported catalysts than the SiO_2 supported catalysts and this trend is consistent with the XPS surface composition data. With

Table 1
Properties of reduced Co catalysts

Catalyst	Reduction (%)	Co dispersion (%)	Nominal composition		Surface composition	
			Co/Al or Co/Si atom ratio	K/Co atom ratio	Co/Al or Co/Si atom ratio	K/Co atom ratio
Co/SiO_2	83	8.4	0.113	–	0.060	–
$K–Co/SiO_2$	84	5.2	0.115	0.151	0.058	0.326
Co/Al_2O_3	77	4.7	0.096	–	–	–
$K–Co/Al_2O_3$	67	4.0	0.097	0.151	0.033	0.644

Table 2
Surface composition of Co catalysts following CH_4 exposure at 450°C for 1 min

Catalyst	Surface composition	
	Co/Al or Co/Si atom ratio	K/Co atom ratio
Co/SiO_2	0.041	–
$K–Co/SiO_2$	0.049	0.307
Co/Al_2O_3	0.031	–
$K–Co/Al_2O_3$	0.026	0.419

both supports, addition of K resulted in decreased Co dispersions. The surface K/Co atom ratios were significantly greater than the nominal atom ratios, indicating a catalyst surface enriched with K, likely a result of the sequential method of adding K to the supported catalyst. The surface concentration of K was also significantly higher on the Al_2O_3 supported catalyst than the SiO_2 supported catalyst. Interactions between promoter and support are known to occur when promoting Group VIII metal catalysts [17] and in the present study the difference in surface concentration of K on Al_2O_3 and SiO_2 is likely due to different acid–base interactions between support and promoter.

The chemical compositions of the reduced catalysts determined by XPS after 1 min exposure to CH_4 at 450°C (i.e. after the first stage of the homologation sequence) are presented in table 2. The decreased Co/Si and Co/Al atomic ratios upon CH_4 exposure, observed by comparing the surface composition data of tables 1 and 2, suggest that more carbon was deposited on the Co than on the support. However, these data do not exclude the possibility of migration of the carbon deposit from the metal to the support as suggested by Solymosi et al. [9]. The decrease in the K/Co ratio following CH_4 exposure for both the Al_2O_3 and SiO_2 supports suggests that the carbonaceous deposit covered more of the K than the Co and this was particularly significant on the $K/Co/Al_2O_3$ catalyst.

3.2. Methane decomposition

TPSR showed that CH_4 decomposition was initiated at 280°C on the Co/SiO_2 catalyst compared to 350°C on the Co/Al_2O_3. The same experiment performed with unreduced Co/SiO_2 catalyst showed no CH_4 conversion until the temperature reached 600°C. We conclude therefore that below 600°C, CH_4 decomposition occurred on the reduced metal phase of the catalyst.

Previous studies have shown that the reactivity of the carbonaceous deposit resulting from CH_4 decomposition over Group VIII metals is a strong function of the temperature of the activation and the age of the deposit [4,9]. In the present study the CH_4 decomposition activity was measured isothermally at 450°C with exposure to CH_4 for 1 min following the procedure of Koerts et al. [4]. The CH_4 consumption versus time data measured during this period was integrated to obtain the total CH_4 consumption. Table 3 reports the total CH_4 consumption per gram of catalyst as well as the CH_4 consumption per μmole of surface Co. The CH_4 conversions reported in table 3 were well below the 100% reported by Koerts et al. [4] due to the relatively high CH_4 concentration used in the feed of the present study.

The data of table 3 indicate that the total moles of CH_4 consumed per mole of surface Co on the Al_2O_3 supported catalysts was much greater than that on the SiO_2 supported catalysts, in agreement with the trend reported for Pd catalysts [9]. This difference may be due to differences in migration of the carbonaceous deposit from the metal to the support or may reflect the structure sensitivity of the CH_4 decomposition reaction [9]. The amount of CH_4 decomposed at the conditions of the present study corresponded to more than that needed for a monolayer coverage of Co by CH_x ($x = 0$, 1, 2 or 3). Hence the mobility of the carbonaceous deposit on the support must be an important factor in determining the amount of CH_4 decomposed on these catalysts. However, structure sensitivity cannot be excluded since the moles of CH_4 decomposed per mole of surface Co also increased with decreased Co dispersion.

Addition of K increased the total CH_4 consumption per surface Co atom over the SiO_2 and Al_2O_3 supported catalysts. The effect of K was more pronounced on the Al_2O_3 than the SiO_2 support. As before these observations may be due to mobility of the carbonaceous deposit or an effect of metal dispersion. Furthermore, as discussed previously, the K/Co surface composition data measured before and after CH_4 exposure show that the carbonaceous deposits interact differently with K on the two supports.

Table 3
CH_4 decomposition over Co catalysts at 450°C and an exposure time of 1 min

Catalyst	CH_4 conversion (%)	CH_4 consumed (μmol CH_4/g cat)	CH_4 consumed (μmol CH_4/μmol surface Co)
Co/SiO_2	37	136	1.15
$K–Co/SiO_2$	27	99	1.33
Co/Al_2O_3	32	117	1.92
$K–Co/Al_2O_3$	31	110	2.40

3.3. Hydrogenation of the carbonaceous deposit

Following exposure to CH_4 at 450°C for 1 min and rapid cooling of the catalyst to 100°C, the reactant gas was switched to H_2. Fig. 3 presents the CH_4 and C_{2+} hydrocarbon production as a function of time-on-stream determined for the Co/SiO_2 catalyst during the hydrogenation. The total hydrocarbon production was calculated by integrating the CH_4 and C_{2+} production versus time data and the resulting values are summarized in table 4 for the four catalysts of the present study.

At the conditions of the present study, the overall C_{2+} yield based on CH_4 conversion in the decomposition step was less than 1%. The low yield was due to the low CH_4 conversion in the first stage of the process, a result of the relatively high CH_4 concentration in the feed.

The data of table 4 show that only a small fraction of the carbon deposited during CH_4 decomposition at 450°C was subsequently hydrogenated at 100°C. The percent carbon hydrogenated reflects the fraction of C_α type carbon deposited and this decreased with the addition of K to both the Co/SiO_2 and the Co/Al_2O_3 catalysts. However, the C_{2+} product selectivity increased with K addition, the highest C_{2+} selectivity of 36 C at% being obtained over the $K–Co/SiO_2$ catalyst. From the total hydrocarbon product distribution the chain growth probability parameter α of the ASF distribution was also calculated for each of the catalysts, as shown in table 4. Addition of K to the Co/SiO_2 catalyst increased α from 0.14 to 0.37, clear evidence of K promotion of C–C bond formation during hydrogenation. Hence, the effect of K on the hydrogenation stage of the homologation sequence is to reduce the hydrogenation of carbon fragments to CH_4 and increase the probability of chain growth to form higher hydrocarbons.

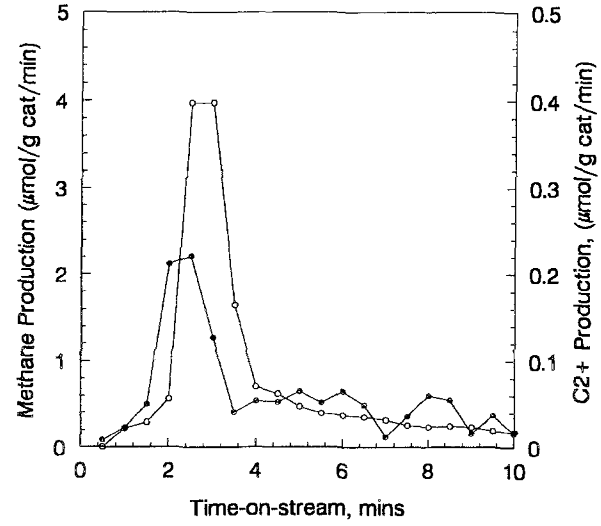

Fig. 3. CH_4 (○) and C_{2+} (●) production over Co/SiO_2 catalyst during hydrogenation at 100°C. Carbonaceous deposit generated at 450°C and 1 min exposure to CH_4.

Table 4
Hydrogenation of carbonaceous species at 100°C

Catalyst	Carbon hydrogenated (%)	C_{2+} selectivity (C at%)	α	C_{2+} yield (C at%)
Co/SiO_2	6.5	14.2	0.14	0.34
$K–Co/SiO_2$	2.4	36.0	0.37	0.23
Co/Al_2O_3	3.9	10.8	0.11	0.14
$K–Co/Al_2O_3$	2.7	11.3	0.12	0.10

Koerts et al. [4] reported that C_{2+} hydrocarbons are produced by hydrogenation of the C_α type carbon and that the amount of C_α type carbon decreases with increasing surface coverage by carbon. However, chain growth increases with surface coverage and hence maximum C_{2+} selectivity requires a compromise on surface coverage [4]. In the present study we have demonstrated that chain growth can also be increased by addition of K to Co/SiO_2. The effectiveness of the K promoter has been shown to depend on the support and in the case of Co/SiO_2, K increases the CH_4 decomposition activity and decreases the hydrogenation activity while increasing C_{2+} selectivity.

4. Conclusions

Results from the present study have shown that the C_{2+} selectivity from CH_4 homologation can be increased by K promotion. However, the effect of promoter is dependent upon the support and/or metal dispersion and the amount of C_α carbon deposited during the CH_4 decomposition cycle. In the case of Co supported on SiO_2, the increase in selectivity with K promotion is accompanied by an increase in CH_4 decomposition activity and decrease in hydrogenation activity.

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