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Catalysis Today 77 (2002) 257–268

CATALYSIS TODAY

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CH_4 decomposition on Co catalysts: effect of temperature, dispersion, and the presence of H_2 or CO in the feed

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Abstract

The effect of Co dispersion, reaction temperature and the presence of CO or H_2 on the kinetics of CH_4 decomposition over 5–30 wt.% Co/SiO_2 catalysts is reported. The initial CH_4 decomposition activity increased and the catalyst deactivation rate decreased as Co dispersion decreased in the range 13–5%. The deactivation rate increased with reaction temperature because of rapid ageing of the deposited carbon. Indirect evidence for CH_x migration from the metal to the support is presented. The migration is much less important than filamentous carbon formation in removing carbon from the metal surface and thereby maintaining catalyst activity during CH_4 decomposition. The presence of H_2 or CO reduced the net rate of carbon deposition and increased the net rate of carbon removal by diffusion through the Co, respectively. Thus, under the appropriate reaction conditions and in the presence of H_2 or CO, stable CH_4 decomposition activity and filamentous carbon formation were observed on supported Co catalysts with low metal loading.

Keywords: CH_4 decomposition; Hydrogen production; Metal particle size; Filamentous carbon; Catalyst deactivation; Cobalt catalyst

1. Introduction

Methane decomposition is important in a number of reactions that aim to convert natural gas to more valuable products using supported metal catalysts [1]. Methane decomposition under low temperature conditions is of interest in methane homologation to higher hydrocarbons [2–4], in methane decomposition to produce hydrogen and in stepwise methane reforming for low temperature hydrogen production [5]. In previous work reported by Zadeh and Smith [4], the initial high rate of CH_4 decomposition on supported Co catalysts at 723 K and 101 kPa decreased rapidly but continued despite the fact that the nominal coverage of surface Co by CH_x was greater than 1. A semi-empirical model that was developed to describe this observation assumed that the dissociation of CH_4 on a Co site was followed by the migration of the resulting CH_x surface species from the metal to the support. This CH_x migration/site regeneration step during CH_4 decomposition was a necessary part of the model used to describe the observed deactivation profile [4].

Migration of carbon species from the metal to the support has been proposed in a number of previous studies [6–10]. For example, Ferreira-Aparicio et al. [8] proposed carbon species diffusion from active metal sites, where CH_4 is dehydrogenated, to silica and alumina supports during CH_4 decomposition over Co, Ni, Ru, Rh, Pt, Ir catalysts. Spillover was invoked based on the observation that CH_4 was consumed in quantities greater than expected if one assumed a 1:1 CH_x:metal adsorption stoichiometry. In addition,

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PII: S0920-5861(02)00251-1

during the decomposition reaction, a simultaneous release of CO and H_2 occurred in the temperature range 550–873 K as a result of the consumption of the hydroxyl groups of the support by CH_x.

An alternative explanation for active site regeneration during CH_4 decomposition is through the formation of filamentous carbon. The mechanism of filamentous carbon formation from CO, CH_4 and other hydrocarbons has been studied extensively on Ni catalysts. Studies on supported Co catalysts are far fewer [3,4,11,12] due to the lower activity and lower capacity for carbon deposition of Co compared to Ni [13]. However, data presented recently by Avdeeva et al. [14] demonstrated that co-precipitated 60–75 wt.% Co–alumina catalysts showed a high capacity for filamentous carbon formation during CH_4 decomposition at 773 K. Filamentous carbon formation is influenced by carbon diffusivity in the metal which depends on temperature [15–18], and metal particle size. Ni particles with diameters of 10–50 nm are known to initiate the growth of filamentous carbon, but the formation of filamentous carbon reportedly does not occur if the metal particle size is less than 7 nm [19]. The effect of Co metal particle size on filamentous carbon formation has not been reported. Hence it remains unclear as to whether filamentous carbon formation during CH_4 decomposition under the mild reaction conditions employed during CH_4 homologation can indeed explain the observed kinetics [4] on supported Co catalysts with low metal loading.

Bartholomew [20] reported that carbon formation and carbon gasification rates are influenced differently by modifications in metal crystallite surface chemistry, which are in turn a function of catalyst size. Also the formation of coke and filamentous carbon involves the formation of C–C bonds on multi-atom sites, and hence, one might expect coke or carbon formation on metals to be structure sensitive. The carbon formation activity and the rate of deactivation is strongly dependent on metal particle size during the reforming of CH_4 with CO_2 [21,22]. Solymosi et al. [23] reported that the turnover frequency (TOF) for CH_4 decomposition over Pd catalysts decreased with the type of support in the order $TiO_2 > Al_2O_3 > SiO_2 > MgO$ and this trend was interpreted as being due either to differences in Pd particle size (dispersion decreased in the same order), or the ease with which carbon migration occurred from the metal to the support. However, to date the effects of metal particle size on CH_4 decomposition kinetics have not been distinguished from support effects. Also, the effect of Co dispersion on catalyst deactivation during CH_4 decomposition has not been reported.

The influence of H_2 on activity is also important during methane decomposition. H_2 evolution parallels CH_4 decomposition and adsorption of H_2 onto the metal catalyst can promote gasification of deposited carbon species. The presence of H_2 can also affect the carbon morphology [24]. Similarly, according to Rodriguez et al. [25] CO promoted the adsorption and decomposition of ethylene towards the growth of carbon filaments, pointing to a strong influence of gas phase components on filamentous carbon formation.

The present work is aimed at clarifying the relative importance of migration of surface carbon species and filamentous carbon formation during methane decomposition. The influence of reaction temperature, metal dispersion and the effect of the presence of CO or H_2 on the deactivation rate during CH_4 decomposition on Co/SiO_2 catalysts has also been investigated. The results of the study add to the understanding of the mechanism of CH_4 decomposition and catalyst deactivation on Co catalysts.

2. Experimental

2.1. Catalyst preparation

Co catalysts were prepared by incipient wetness impregnation of the support using an aqueous solution of $Co(NO_3)_2 \cdot 6H_2O$ (>98% Aldrich). Precalcined (25 h at 773 K) silica gel (Grade 62, Aldrich) with a BET surface area of 300 m^2/g and pore volume of 1.15 ml/g was used as the support. After impregnation, the catalysts were vacuum-dried at 383 K for 37 h and then calcined for 10 min at 723 K. The catalysts were then reduced by temperature-programmed reduction (TPR) in a 100 ml/min of 40% H_2/Ar to the desired reduction temperature.

2.2. Catalyst characterization

Catalyst surface areas and pore volumes were measured by nitrogen adsorption–desorption at 77 K using a FlowSorb II 2300 analyzer. A 30% N_2/He mixture fed at 15 ml/min was used for surface area measurement and a 95% N_2/He mixture fed at 20 ml/min was used for pore volume measurements. Samples were degassed at 398 K for approximately 3 h prior to measurement.

The catalyst metal dispersion was determined by CO chemisorption. The CO uptake was measured gravimetrically (Perkin-Elmer TGS-2 thermogravimetric analyzer with a sensitivity of ±1 μg). About 10 mg of sample was dried at 523 K for 8 h in He. The drying temperature was chosen to avoid the transformation of Co_3O_4 to CoO, which was shown by in situ XRD and EXAFS measurements to occur in the temperature range 623–673 K under inert atmospheres [26]. After drying, the catalyst was cooled to 323 K, then reduced by TPR from 323 K to the desired temperature (Table 1) in 1 h in a 40% H_2/He gas mixture flowing at 400 ml/min, followed by cooling to 323 K. The degree of reduction was calculated from the catalyst weight change during TPR. Following a 5 min He purge after cooling, CO adsorption was initiated using a 12% CO/He gas mixture flowing at 400 ml/min and 101 kPa total pressure. After the sample weight stabilized, the sample was flushed in pure He. No CO desorption was detected during this purge and hence the measured weight gain was attributed to CO chemisorption at 323 K. The catalyst dispersion was calculated from the CO uptake assuming a 1:1 adsorption stoichiometry and is reported as a mol% of reduced Co. The Co particle size was estimated from the equation $d\ (\text{nm}) = 0.962/\Phi$, where Φ is the metal dispersion [27].

The formation of filamentous carbon was detected by TEM (Hitachi H-800 electron microscope) examination of the used catalysts. TEM specimens were prepared by dispersing the used catalysts in ethanol and applying a drop of this dispersion onto a carbon coated copper grid, followed by drying. The microscope was operated at an acceleration voltage of 100–150 kV, with magnification in the range of 10,000–100,000×. The average metal particle size was estimated directly from the number average diameter of the filaments observed by TEM, knowing that the metal particle size equals the filament diameter [33].

2.3. Methane decomposition

The methane decomposition rate on the catalysts of interest was measured in a fixed-bed reactor operated isothermally in a differential mode. A flow diagram of the reactor and the on-line analytical equipment used are shown in Fig. 1. Gas flow rates were controlled by calibrated Brooks 5878 mass flow controllers. The stainless steel reactor ($l = 60$ cm, o.d. $= 0.95$ cm) was loaded with 0.2 g catalyst (average particle size 0.17 mm) that was supported on a quartz wool plug. A thermocouple was placed at the top of the catalyst bed to control the reaction temperature. A Varian Star 3400CX gas chromatograph, fitted with flame ionization and thermal conductivity detectors connected in series, and equipped with a 60/80 Carbosieve G column was used for the product and feed gas analyses. UHP grade H_2, CH_4, He, Ar (99.999%, Praxair) and a 5% CH_4/Ar calibrated gas (Praxair) and CP

Table 1
Properties of Co/SiO_2 catalysts of the present study

Co loading (wt.%)	BET surface area (m^2/g)	Pore volume (cm^3/g)	Reduction temperature (K)	Reduction degree (mol%)	CO uptake (mmol/g)	Co dispersion (%)	d_p (CO uptake) (nm)[a]	d_p (TEM) (nm)
5	239	0.971	923	100	0.084	9.2	10.4	
8	230	1.080	923	100	0.103	7.1	13.5	
10	217	0.989	723	96.9	0.208	12.6	7.6	
			923	100	0.094	5.4	17.8	
12	210	0.889	723	96.5	0.166	8.4	11.4	10[b]
			923	100	0.102	5.0	19.4	25[c]
30	–	–	723	76.5	0.240	6.2	15.6	

[a] Estimated Co particle size.
[b] Estimated from TEM image of catalyst after reaction at 723 K.
[c] Measured from TEM image of catalyst after reaction at 773 K.

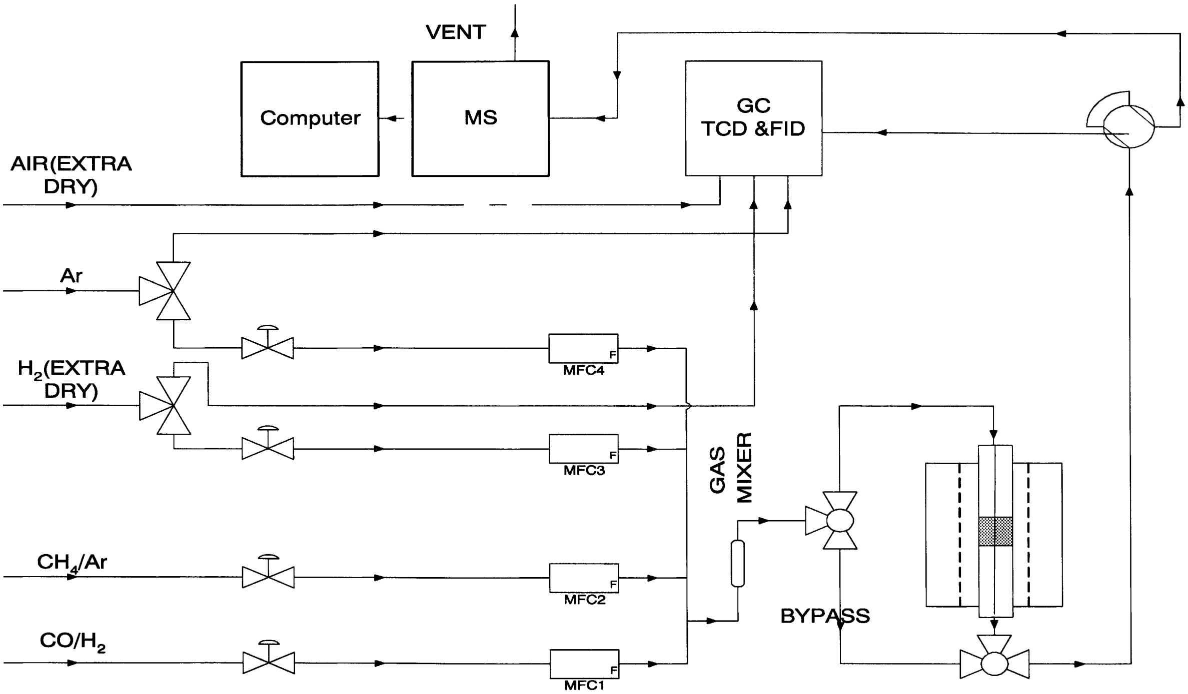

Fig. 1. Block diagram of the experimental set-up used for CH_4 decomposition catalyst tests.

grade CO (purity 99.5%, Praxair) were used in the experiments.

Tests to determine the significance of external and internal diffusional effects were done following the guidelines given by Froment and Bischoff [28]. For the range of experimental conditions used in the present study, internal and external gradients in concentration and temperature were insignificant.

3. Results

3.1. Catalyst characterization

A series of catalysts with estimated metal dispersion in the range 5–13% were obtained by reducing 5–30 wt.% Co/SiO_2 at 723 and 923 K. The data of Table 1 shows that reduction of the Co_3O_4 precursor was almost complete for all catalysts except the 30 wt.% Co/SiO_2 catalyst. The average Co particle size, estimated from the metal dispersion assuming pure Co particles, increased with increased Co loading (Table 1). The metal particle size of 11.4 nm estimated by CO chemisorption on the 12 wt.% Co/SiO_2 reduced at 723 K was in good agreement with the metal particle size (9.6 nm) estimated previously by XRD line-broadening [4], and with the 10 nm estimated from the TEM micrograph of the same catalyst after reaction (Fig. 6).

3.2. Catalyst activity and deactivation rate—r^* and k_d

The kinetics of methane decomposition on the catalysts investigated herein are conveniently described by a kinetic equation of the type $r = r^*a$, where r^* is the initial decomposition rate and a the catalyst activity factor. According to Demicheli et al. [29], if the rate is first-order with respect to the activity factor, i.e. $da/dt = -k_d a^d$, where $d = 1$ and k_d is the decay constant, then $r = r^* e^{-k_d t}$. Curve fitting of the measured CH_4 decomposition rate versus time data

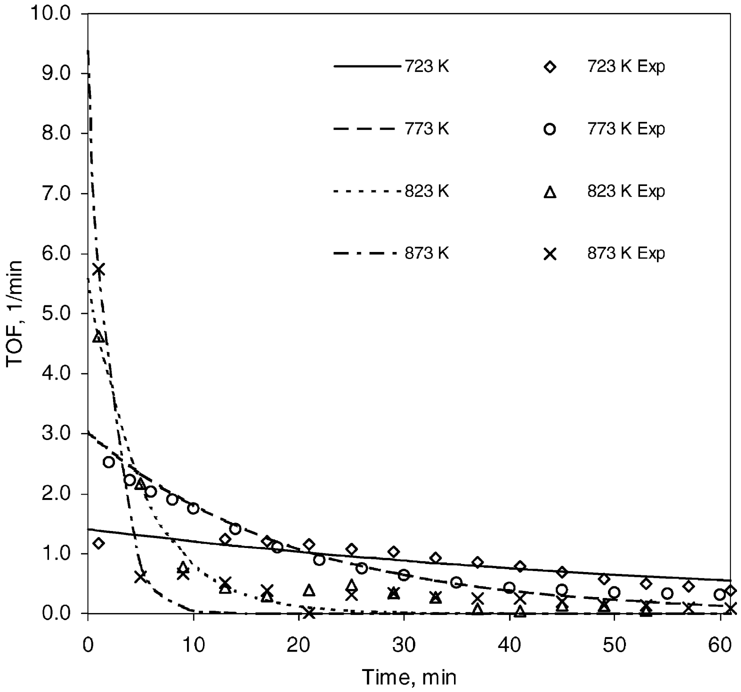

Fig. 2. Effect of temperature on the activity of 12 wt.% Co/SiO_2 catalysts, reduced at 923 K and reacted with 5% CH_4/Ar at 140 ml/min (lines are first-order decay model fit to the experimental data points).

using Table 2D Curve software, as shown in Fig. 2, provided estimates of r^* and k_d. For all of the data reported herein, the fits to the first-order decay model had regression coefficients $R^2 > 0.90$.

3.3. Dependence of activity on CH_4 decomposition temperature

Fig. 2 shows the catalytic activity of the 12 wt.% Co/SiO_2 catalyst at different decomposition temperatures. Generally, the initial CH_4 decomposition rate was high but the catalyst deactivated rapidly. At 823 K, for example, the CH_4 decomposition rate decreased to only 2.3% of its initial value after 30 min reaction. The influence of decomposition temperature on r^* and k_d is shown in Fig. 3. The initial CH_4 decomposition TOF (r^*, min^{-1}) increased from 1.4 to 9.4 min^{-1} over the temperature range 723–873 K with an apparent activation energy of 66.3 kJ/mol. The catalyst deactivation rate also increased with increasing temperature with an apparent activation energy of 122.7 kJ/mol.

3.4. Dependence of activity on metal dispersion

The influence of metal dispersion (or particle size) on CH_4 decomposition activity over the Co/SiO_2 catalysts was measured at two different operating conditions, using catalysts with varying metal dispersion as given in Table 1. At each operating condition, the initial TOF (r^*) and the decay constant (k_d) were estimated by fitting the experimental data to the first-order decay model and the values obtained are plotted in Fig. 4a and b, respectively.

The data of Fig. 4a shows the general trend of increasing initial TOF with decreased Co dispersion, indicative of the structure sensitivity of the CH_4 decomposition reaction [12]. Note that the effect of dispersion on TOF was small under the low temperature, low CH_4 partial pressure conditions of Fig. 4a (5% CH_4 in Ar at 101 kPa and 723 K); however at higher temperatures and CH_4 partial pressure (23% CH_4/12% H_2 in Ar at 101 kPa and 773 K), the Co dispersion effect is much more significant. The two sets of data in Fig. 4b shows the

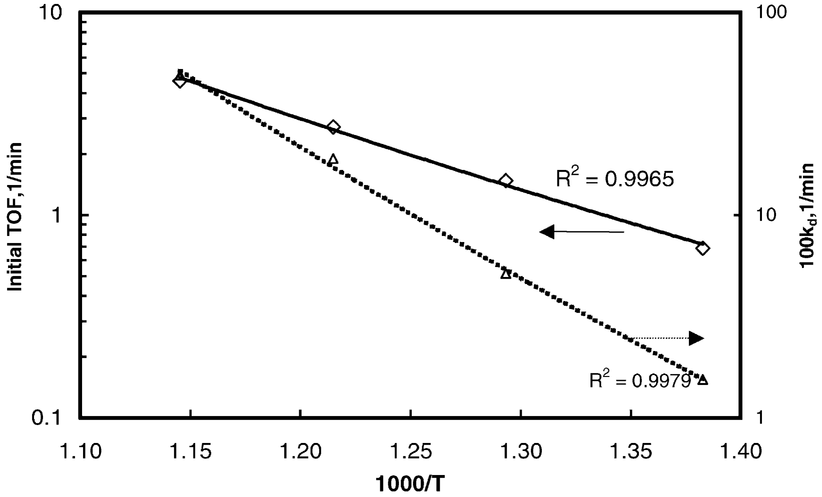

Fig. 3. Arrhenius plot of initial CH_4 decomposition rate (TOF, min^{-1}) and 100k_d versus 1000/T.

general trend of decreased k_d with decreased Co dispersion.

3.5. Catalyst deactivation, carbon species migration and filamentous carbon formation

To detect the migration of carbon species from the Co metal to the SiO_2 support, where interaction with hydroxyl groups produces CO [8], mass spectroscopy was used to measure the production of CO during CH_4 decomposition. Data of Fig. 5 shows that minimal amounts of CO were detected when SiO_2 alone was exposed to 5% CH_4/Ar. However, CO production during CH_4 decomposition on the 12 wt.% Co/SiO_2 was significant, especially within the first few minutes of reaction. In accordance with the arguments presented by Ferreira-Aparicio et al. [8] we assume that the source of CO is carbon species (CH_x) that migrate from the metal onto the support where they react with hydroxyl groups to produce CO. The possibility of CO production due to CH_x and OH interaction localized near the metal particle perimeter cannot be ruled out, but the continued CO production after the initial rapid decline suggests that CH_x migration to the support occurs, albeit to a small extent. Also note that the possibility of CO being produced from CH_4 interacting with the unreduced metal oxide is small, since it is highly unlikely that the unreduced cobalt would react with methane following a 1 h reduction in 40% hydrogen at the same temperature. Furthermore, for the 12 wt.% Co/SiO_2 catalyst of Fig. 5, the degree of reduction was 96.5 mol%, so that approximately 12 μmol of oxygen would be available for reaction with CH_4 to produce an equivalent number of moles of CO. This is much less than the 77 μmol of CO produced during the reaction period shown in Fig. 5.

In order to detect filamentous carbon by TEM on the 12 wt.% Co/SiO_2 after reaction with 5% CH_4/Ar at 723 K, the reaction time was extended to 120 min. Evidence of filamentous carbon growing from metal particles, corresponding to a low but stable CH_4 decomposition activity is shown in Fig. 6. The micrograph shows that the diameter of the filamentous carbon was about 10 nm, close to the initial metal particle size of 11.4 nm measured by CO chemisorption on the unused Co catalyst.

3.6. Influence of reactants on activity: effect of H_2 and CO

To determine the effect of adding small quantities of H_2 or CO to the CH_4 feed, a series of experiments were done to compare changes in the CH_4 decomposition activity due to the presence of 1.2% H_2 or 0.4% CO added to the 5% CH_4 in Ar feed. By fitting the experimental data to the first-order decay model,

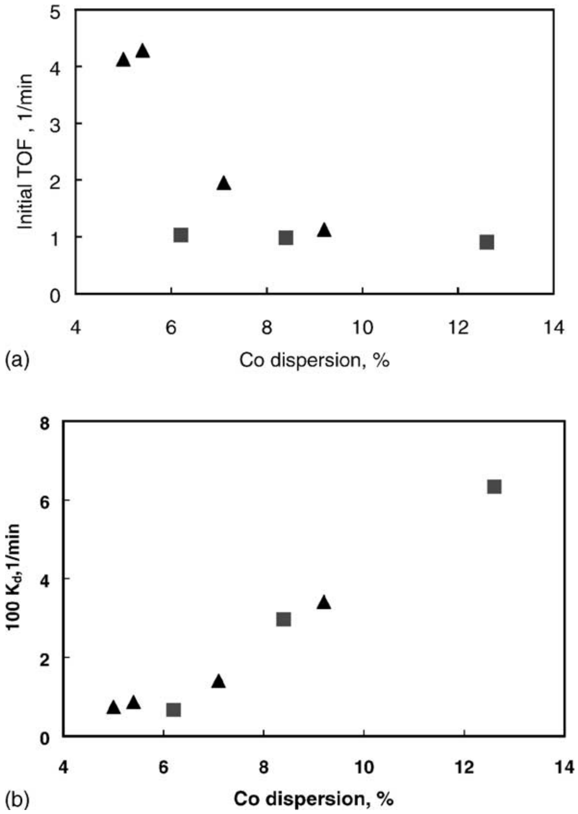

Fig. 4. Dependence of (a) initial activity (TOF, r^*) and (b) deactivation rate (k_d) on Co dispersion, measured at 140 ml/min 5% CH_4/Ar at 723 K (■), and 185 ml/min 23% CH_4/12% H_2/Ar at 773 K (▲).

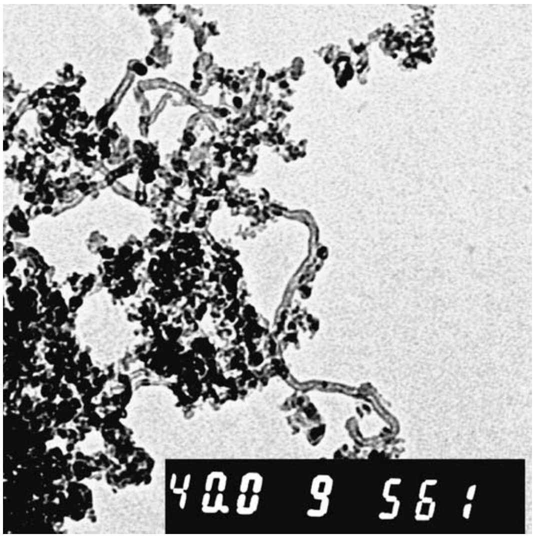

Fig. 6. TEM image (40,000×) of 12 wt.% Co/SiO_2 catalyst after 120 min reaction in 5% CH_4/Ar at 723 K, showing the presence of filamentous carbon, diameter ∼10 nm.

the initial TOF and k_d were obtained and these values are plotted in Fig. 7. Data of Fig. 7 shows that H_2 not only decreased the deactivation rate of the catalyst but also reduced the initial decomposition TOF. TEM of the used catalyst after 1 h reaction (Fig. 8) showed filamentous carbon formation during CH_4 decomposition in the presence of 1.4% H_2 in the feed at 500 °C.

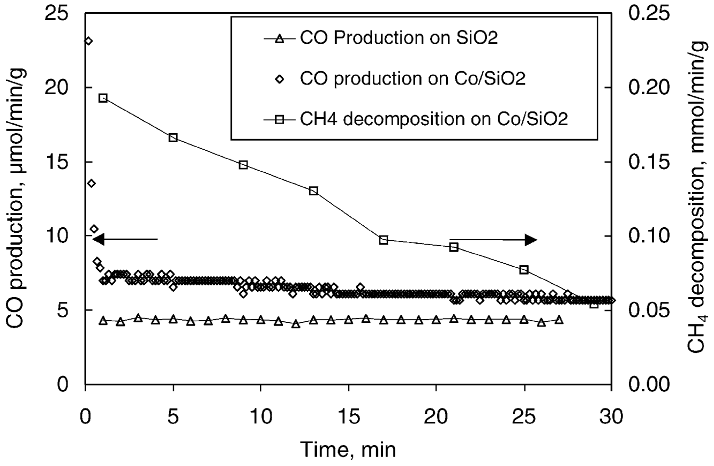

Fig. 5. CO production over SiO_2 and 12 wt.% Co/SiO_2 at 723 K in 140 ml/min of 5% CH_4 in Ar feed.

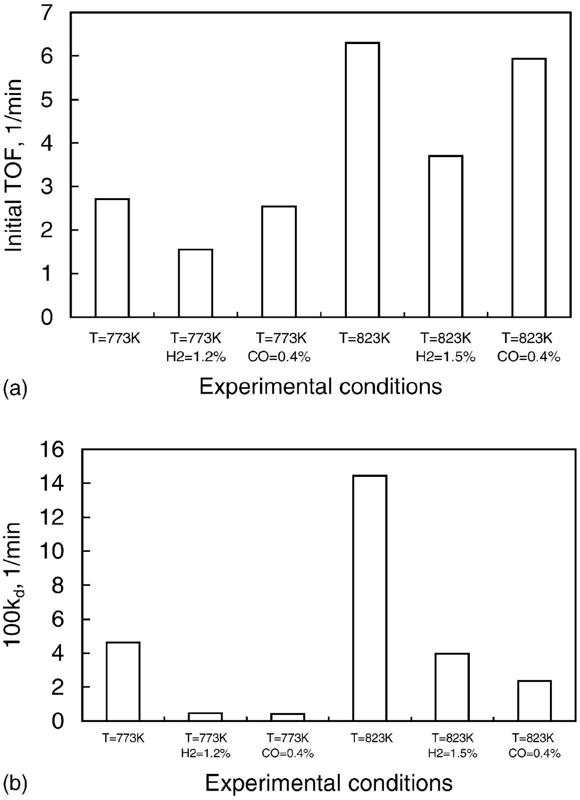

Fig. 7. Effect of the presence of H_2 or CO on (a) the initial activity (TOF, r^*) and (b) the deactivation rate (k_d) on the 12 wt.% Co/SiO_2 catalyst, exposed to 5% CH_4/Ar at the reaction temperature indicated.

The data of Fig. 7 also shows that CO addition decreased the rate of catalyst deactivation, similar to the effect of adding H_2. However, an important difference between the effects of H_2 and CO is that the high initial CH_4 decomposition TOF was maintained upon the introduction of CO, whereas H_2 addition reduced the initial TOF. No higher hydrocarbons were detected upon CO addition, suggesting that no FTS type reaction occurred at the reaction conditions. Hence, the CO promotional effect could not be explained by assuming that FTS type reactions removed H and thereby enhanced CH_4 decomposition.

Fig. 9 presents a TEM micrograph that showed filamentous carbon formation after the catalyst was exposed to 5% CH_4 at 773 K with 0.4% CO in the feed, corresponding to the stable CH_4 decomposition shown in Fig. 10. Although CO is known to form filamentous carbon at higher temperature on supported metal catalysts, no filamentous carbon was detected by TEM when the Co catalyst was exposed to a 2 vol.% CO in Ar. Consequently, we conclude that CH_4 decomposition was the main source of the

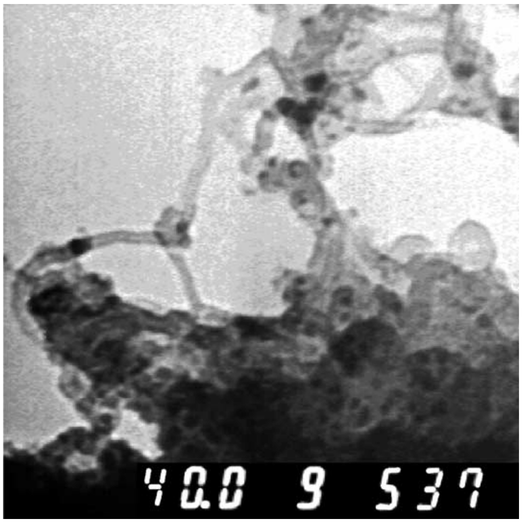

Fig. 8. TEM image (40,000×) of 12 wt.% Co/SiO_2 catalyst after reaction in 5% CH_4/1.4% H_2/Ar at 500 °C for 60 min showing presence of filamentous carbon with diameter ∼25 nm.

Fig. 9. TEM image (50,000×) of 12 wt.% Co/SiO_2 after reaction in 5% CH_4/0.4% CO/Ar at 773 K for 60 min showing presence of filamentous carbon with diameter ∼25 nm.

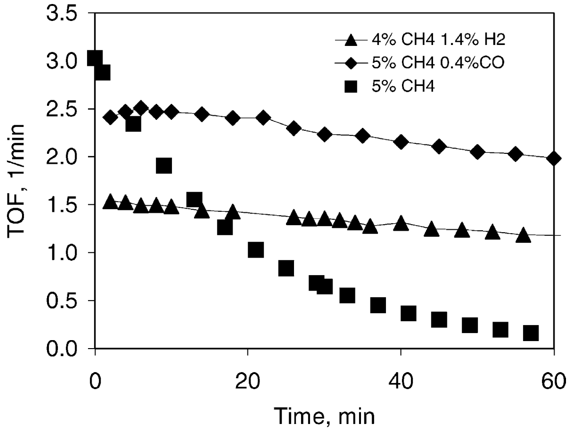

Fig. 10. Comparison of CH_4 decomposition TOFs in the presence of CO or H_2 at the reaction conditions shown. Reaction temperature 773 K, total gas flow 140 ml/min.

filamentous carbon shown in Fig. 9, corresponding to the stable CH_4 decomposition activity shown in Fig. 10.

4. Discussion

4.1. Temperature and metal dispersion effects on catalyst activity

The apparent activation energy of 66.3 kJ/mol estimated for the initial CH_4 decomposition on the 12 wt.% Co/SiO_2 catalyst with average Co particle size of 9.5 nm was in reasonable agreement with the 56 kJ/mol reported for the initial CH_4 decomposition on Co/SiO_2 with metal particle size 10.3 nm [4]. These values were somewhat higher than the value of 42 kJ/mol reported for the decomposition of CH_4 on Co/SiO_2 catalysts at less than a monolayer coverage [30]. Also note that these values are significantly lower than the activation energies reported for Fe and Ni catalysts when carbon diffusion through the metal is rate determining [34,35].

The data of the present study clearly show the structure sensitivity of the initial CH_4 decomposition on Co/SiO_2 catalysts, since the CH_4 decomposition TOF increased with decreased Co dispersion in the range of 13–5%. The present data were obtained on the same SiO_2 support so that, unlike in previous studies, the effect of metal dispersion was not influenced by support effects.

4.2. Catalyst deactivation

CH_4 decomposition data on supported Co catalysts reported herein showed that an initial high CH_4 decomposition rate decreased rapidly to a lower but stable activity, despite the fact that the nominal Co coverage by CH_x species was greater than 1. Filamentous carbon was observed under the reaction conditions shown in Fig. 6. According to the filamentous carbon formation mechanism, carbon is removed from the metal surface by bulk diffusion through the metal particle [15–18]. In addition, evidence for the migration of carbon species from the Co metal site to the support is provided by the production of CO during the CH_4 decomposition and the previously reported kinetic model that, of necessity, included a CH_x migration step from the metal to the support [4]. These observations suggest that both carbon diffusion through the metal to form filamentous carbon, and the migration of CH_x from the metal to the support occur, and both contribute to the regeneration of active metal sites during CH_4 decomposition. However, the rapid decline in CO production (Fig. 5) suggests that migration of the CH_x from the metal to the support is only significant in the first 2–3 min of reaction.

Previous studies of catalyst deactivation by carbon deposition have shown that the catalyst deactivation rate is dependant upon the difference between the net rate of carbon formation and the rate of carbon removal by diffusion through the metal [20,34,35]. If the net formation and removal rates were equal, active metal sites would be available to activate CH_4 and hence the observed catalyst activity would remain stable. On the other hand, if the formation rate is greater than the removal rate the catalyst will deactivate. The experimental data of the present study were used to quantify the deactivation rate in terms of the decay constant k_d of a first-order decay model. In the following sections it is convenient to discuss the effect of process variables on k_d in terms of the difference (r_d) between the net rate of carbon formation ($r_{f,n}$—the net rate of formation and gasification of the carbon or coke precursor), and the rate of carbon removal from the active metal site ($r_{r,n}$—the net rate of removal by migration from metal to support or diffusion with filamentous carbon formation), i.e. $r_d = r_{f,n} - r_{r,n}$.

4.3. Temperature and metal dispersion effects on catalyst deactivation

The decay constant, k_d was observed to increase with increasing decomposition temperature, and the increase followed an Arrhenius dependence on temperature with an apparent activation energy of 122.7 kJ/mol. On Ni–Al_2O_3 catalysts, the apparent activation energy associated with k_d for carbon formation from CH_4–H_2 mixtures, has been reported as 229 kJ/mol [29].

As already discussed, the rate of catalyst deactivation is a consequence of the imbalance between the carbon formation rate and the carbon removal rate (the latter by both bulk diffusion and migration from the metal to the support). Although the net rates of carbon formation and carbon removal both increase exponentially with temperature, the difference between them varies with temperature because of differences in their respective activation energies. According to Holstein [31], the activation energy for filamentous carbon diffusion through Co is in the range of 145–162 kJ/mol and this activation energy is independent of reactant (either hydrocarbons or CO). The apparent activation energy for the migration of CH_x species from Co to SiO_2 support has been estimated at 48 kJ/mol [4], whereas values of 120 kJ/mol [32] have been estimated for hydrogen spillover. The present study has reported an activation energy for CH_4 decomposition of 66 kJ/mol. Consequently, an increase in reaction temperature would impact the rate of carbon diffusion through Co most significantly, which in turn would be expected to reduce the observed rate of catalyst deactivation. This is contrary to the observed effect of temperature on k_d. However, it is known that the more reactive, amorphous forms of carbon identified at low reaction temperatures are converted into less reactive graphitic forms at high temperatures over a period of time [20]. As the severity of the CH_4 decomposition increases (i.e. the reaction time and temperature increases), the reactivity in H_2 of the carbonaceous deposit will decrease [11,20]. Consequently, at higher temperature, less of the carbon species react with H (i.e. the extent of the reaction $CH_x + H \rightarrow CH_4$ decreases), the net rate of carbon deposition increases resulting in a higher deactivation rate. We conclude therefore that the increased deactivation rate with temperature is associated with the change in nature of the surface carbon species with increased temperature.

The data in Fig. 4b shows that the deactivation rate (k_d) decreases with decreasing Co dispersion. Since reduced k_d implies a decrease in r_d ($r_d = r_{f,n} - r_{r,n}$), and since the initial rate of carbon formation increased with decreased dispersion (Fig 4a), we can conclude that the net rate of carbon removal ($r_{r,n}$) increased with decreasing metal dispersion. Previous studies on Ni and Fe catalysts have also shown an increase in carbon filament growth rate with particle size (or decreased dispersion [33,34]).

4.4. Effect of the presence of CO or H_2 in the feed on catalyst deactivation

The data of Fig. 7 shows that the presence of either H_2 or CO in the feed reduces the deactivation rate. At 773 K addition of small amounts of H_2 or CO decreased the deactivation rate and stable activity was retained for a significant period of time during which filamentous carbon formation was detected (Fig. 10). However, addition of H_2 reduced the initial TOF compared to the case without H_2 in the feed, whereas addition of CO had no significant effect on the initial TOF.

A similar effect of H_2 during the catalytic disproportionation of CO has been reported [24] and two functions of H_2 are possible: (1) to "clean" the catalytic surface by the reaction $C+2H_2 \rightarrow CH_4$; (2) to modify the carbon/metal interaction. In the present work, the initial rate was reduced upon H_2 addition most likely because the rate of carbon gasification increases with higher hydrogen partial pressure. Hence we conclude that the net carbon formation rate ($r_{f,n}$) was reduced and consequently, the difference in net rates ($r_d = r_{f,n} - r_{r,n}$) must also decrease. This observation suggests that, for a given catalyst particle size and reaction temperature, H_2 pressure can be used to balance the net rate of decomposition which will decrease the deactivation rate and yield filamentous carbon.

With CO added to the CH_4 feed, two explanations for the reduction in k_d can be postulated: CO decreases the CH_4 decomposition rate ($r_{f,n}$ decreases) or CO adsorption changes the carbon–metal interface such that carbon diffusivity through the metal is increased ($r_{r,n}$

increases). The high initial TOF upon CO addition, shown in Fig. 10, rules out the first possibility. Hence we conclude that the reconstruction of the Co surface following CO adsorption, enhances carbon diffusivity and this is consistent with the sustained, stable CH_4 decomposition activity reported in Fig. 10. A similar promotional effect of CO on the decomposition of ethylene over Fe to form filamentous carbon has been reported [25]. The behavior was rationalized in terms of a reconstruction of the Fe surface in the presence of coadsorbed CO, which resulted in the formation of surfaces with differing activities.

Although the balance between carbon formation rate and carbon removal rate was improved by addition of either CO or H_2, and hence catalyst deactivation was reduced (Fig. 10) the mechanism of interaction of each gas is postulated to be different: CO adsorption enhances the carbon diffusion rate by surface modification, promoting filamentous carbon formation without reducing CH_4 decomposition activity whereas the presence of H_2 enhances the carbon gasification rate and thereby reduces catalyst deactivation.

Catalyst deactivation observed during CH_4 decomposition on the Co/SiO_2 catalysts has been discussed in terms of the relative net rates of carbon deposition and carbon removal from the Co surface. Another common deactivation mechanism for supported metal catalysts is by sintering. However, for the present system, this mechanism is not relevant. Initial Co particle size measured by CO chemisorption (11.4 nm, Table 1) is close to the size of the Co particle on the filamentous carbon tip, observed by TEM (∼10 nm, Fig. 6) after 120 min reaction in CH_4 at 723 K. The Co particle size measured by TEM at 773 K after reaction in the presence of H_2 or CO in the feed was ∼25 nm, somewhat larger than the 19.4 nm measured by CO chemisorption of the unused catalysts. The apparent increase in particle size in this case could be due to the fact that filamentous carbon formation favored larger metal particles and the TEM image consequently reports the larger particle size selectively, whereas CO chemisorption provides an estimate of the average metal particle size. We conclude that no significant sintering in the temperature range of 723–773 K during CH_4 decomposition occurred, in agreement with the results of Avdeeva et al. [14], who reported that the Co particle size (approximately 25 nm) did not increase at 773–823 K on 60–75 wt.% Co–alumina catalysts exposed to methane for 50 min.

5. Conclusions

The kinetics of CH_4 decomposition on supported Co catalysts has been investigated. The decomposition kinetics are well described by a first-order decay model. The apparent activation energy for the initial CH_4 decomposition rate was 66.3 kJ/mol and for the deactivation rate 122.7 kJ/mol on 12 wt.% Co/SiO_2 catalysts. The increased deactivation rate with temperature was ascribed to rapid ageing of the carbon species deposited on the catalyst surface as reaction temperature increased. The initial decomposition activity increased with decreasing metal dispersion (in the range 5–13%) and the deactivation rate decreased with decreasing metal dispersion.

The experimental observations herein suggest that the migration of CH_x from the metal to the support makes a small contribution to the regeneration of active metal sites in the first 2–3 min of reaction. In agreement with previous studies on Fe and Ni, filamentous carbon formation reduced the rate of catalyst deactivation during CH_4 decomposition by removing carbon from the metal surface. The presence of H_2 or CO reduced the net rate of carbon deposition and increased the net rate of carbon removal by diffusion through the Co, respectively. Hence, stable CH_4 decomposition activity and filamentous carbon formation were observed on supported Co catalysts with low metal loading in the presence of H_2 or CO.

Acknowledgements

Funding for the present study from the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

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