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# Methane homologation and reactivity of carbon species on supported Co catalysts

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## Abstract

The effect of catalyst support on the activity of Co catalysts has been investigated for the two-step $CH_4$ homologation reaction. The total amount of $CH_4$ per mole of surface Co decomposed at 450°C, in a reaction time of 1 or 3 min, was greater on the $Co/Al_2O_3$ catalyst than the $Co/SiO_2$ catalyst. In the subsequent hydrogenation step at 100°C, more of the carbonaceous deposit was hydrogenated on the $Co/SiO_2$ than the $Co/Al_2O_3$. The selectivity to $C_2^+$ hydrocarbons was also higher on the $Co/SiO_2$ catalyst. These results are discussed in terms of the effect of migration of the carbonaceous deposit from the metal to the support, that apparently occurs more readily on the $Co/Al_2O_3$ catalyst than on the $Co/SiO_2$ catalyst.

*Keywords:* Methane; Homologation; Catalyst; Cobalt; Carbon deposit

## 1. Introduction

Methane homologation refers to the two-stage conversion of $CH_4$ to higher hydrocarbons over Group VIII metal catalysts. In the first stage, $CH_4$ is decomposed at temperatures above 350°C. In the second stage, the resulting carbonaceous surface deposits are hydrogenated at low temperature (<200°C) to yield higher hydrocarbons [1,2]. Interest in this approach stems from the fact that as compared to methane partial oxidation or oxidative coupling, the reaction temperatures are low and the undesired oxidation products CO and $CO_2$ are avoided since $O_2$ is not present in the reaction system.

Temperature-Programmed-Surface-Reaction (TPSR) in $H_2$ has been used in previous studies to characterize the reactivity of carbonaceous deposits on catalysts [1–4]. Using this technique, decomposition of $CH_4$ on supported metal catalysts has been shown to yield three types of deposit [1]. $C_2^+$ hydrocarbons (hydrocarbons with carbon number $\geq 2$) are formed primarily from the most reactive species, referred to as $C_\alpha$ by Koerts et al. [1] and identified as a $CH_x$ species [2,5,6]. Two less reactive forms of carbon (referred to as $C_\beta$ and $C_\gamma$) 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 [1,6]. In general, as the deposit ages at elevated temperature it becomes less reactive because of transformations that occur from the $C_\alpha$ form to the less reactive $C_\beta$ and $C_\gamma$ forms. Examination of these surface species on Ru single crystals by high resolution electron energy-loss spectroscopy has shown them to be associated with hydrogen and that surface vinylidene is likely the key intermediate for $C_2^+$ production [5,7].

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The catalyst support also influences $CH_4$ homologation. Solymosi et al. [6] reported that the turnover number for $CH_4$ decomposition over Pd catalysts decreased with the type of support in the order $TiO_2>Al_2O_3>SiO_2>MgO$. These differences were either due to differences in Pd particle size or the ease with which carbon migration occurred from the metal to the support [6]. In their study, the amount of carbon deposited was greater than the amount needed for monolayer coverage of the exposed metal catalysts. The $CH_4$ decomposition procedure of Koerts et al. [1] 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 the observation by Koerts et al. that the $C_2^+$ selectivity was not influenced by acidic or basic supports [1]. With Pd, the $C_\alpha$, $C_\beta$ and $C_\gamma$ carbonaceous species were identified on the $SiO_2$ supported catalyst, whereas only the $C_\beta$ and $C_\gamma$ deposits were present with $Al_2O_3$, $TiO_2$ and MgO supports [6]. 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 [6].

Previous studies have shown that Co supported catalysts have high activity for $CH_4$ decomposition and high selectivities toward higher hydrocarbons during the low temperature hydrogenation stage [1]. In the present paper, we report on a study of $CH_4$ homologation over Co catalysts and compare $Al_2O_3$ and $SiO_2$ supports. Both the $CH_4$ decomposition stage and the subsequent hydrogenation stage have been investigated. In addition, the effect of support on the reactivity of the carbonaceous deposit generated during $CH_4$ decomposition has been examined by TPSR in both $H_2$ and $O_2$.

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## 2. Experimental methods

### 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 dried overnight at 100°C and calcined in air at 500°C for 5 h. Temperature-Programmed-Reduction (TPR) of the catalysts was achieved 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 X-ray diffraction (XRD) to determine the bulk compounds present in the catalysts.

The Co dispersion was measured on 0.2 g of catalyst using a $O_2$–$H_2$ titration procedure similar to that described by Erdöhelyi et al. [8]. 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 $O_2$ until adsorption was complete. The subsequent $H_2$ titration of the absorbed $O_2$ was performed in the same manner at a temperature of 200°C.

### 2.2. Activity and selectivity measurement

The activity and selectivity measurements were made in the same quartz, fixed-bed microreactor used for reduction and with the same catalyst loading of 0.5 g. Following reduction, the gas flow was switched to Ar and the reactor temperature was adjusted to 450°C. After the temperature stabilized the catalyst was exposed to a mixture of 7.4 mol% $CH_4$ in Ar at a flow of 55 ml(STP)/min for a reaction period of 1 or 3 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 absorbed $CH_4$. The remaining carbonaceous deposit was then hydrogenated isothermally at 100°C in pure $H_2$ at a flowrate of 11 ml(STP)/min. The products of both the first-stage $CH_4$ decomposition and the second-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 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. TPSR was also used to examine the hydrogenation and oxidation of the carbonaceous deposit generated during the $CH_4$ decomposition stage. In the case of TPSR in $H_2$, the temperature was increased at a ramp rate of 10°C/min to 600°C in a 20% $H_2$ in Ar gas mixture at a flowrate of 25 ml(STP)/min. The same ramp rate was used for TPSR in $O_2$ but the feed gas contained 3.5% $O_2$ in Ar and the gas feed rate was 58 ml(STP)/min.

## 3. Results and discussion

### 3.1. Catalyst characterization

The TPR profiles of the calcined $Co/SiO_2$ and $Co/Al_2O_3$ were characterized by two peaks due to the bulk reduction of $Co_3O_4$ to Co [9]. 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. 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 catalyst than the $Al_2O_3$ supported catalyst 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 based on the amount of Co reduced during the TPR. The Co dispersion was lower on the $Al_2O_3$ supported catalyst than the $SiO_2$ supported catalyst and this trend was consistent with XPS surface composition data reported elsewhere [9].

Table 1
Catalyst properties

| Catalyst | Degree of reduction (%) | Co dispersion (%) |
|---|---|---|
| $Co/SiO_2$ | 83 | 8.4 |
| $Co/Al_2O_3$ | 77 | 4.7 |

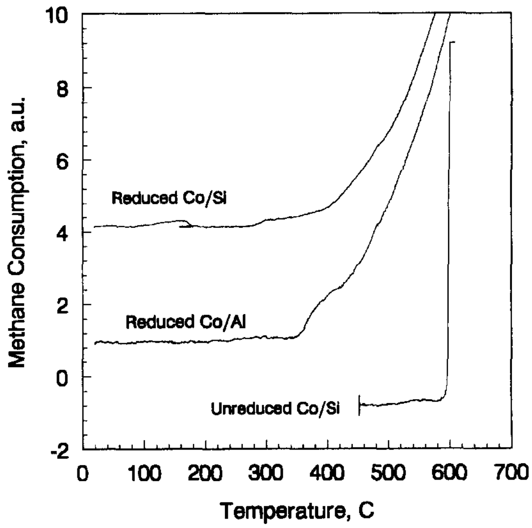

Fig. 1. TPSR in $CH_4$ of various Co catalysts.

### 3.2. Methane decomposition

The temperature at which $CH_4$ decomposition occurred over the Co catalysts was determined by TPSR. Fig. 1 compares the TPSR profiles measured on reduced $Co/Al_2O_3$, $Co/SiO_2$ and unreduced $Co/SiO_2$. $CH_4$ decomposition was initiated at 280°C on the reduced $Co/SiO_2$ compared to 350°C on the reduced $Co/Al_2O_3$. On the unreduced $Co/SiO_2$, no $CH_4$ conversion occurred until the temperature reached 600°C, corresponding to the thermal decomposition of $CH_4$ and/or the reduction of $Co_3O_4$ by $CH_4$. Clearly, below 600°C, $CH_4$ decomposition occurred on the reduced metal only. Control experiments with the $Al_2O_3$ and $SiO_2$ support alone showed no $CH_4$ decomposition below 600°C.

The $CH_4$ decomposition activity of the reduced catalysts was measured isothermally at 450 and 600°C for a period of 1 or 3 min, whereupon, the reactor was cooled to 100°C within about 30 s. The $CH_4$ flow was continued during the cool down period. Figs. 2 and 3 show the cumulative $CH_4$ consumption per mole of surface Co plotted against reaction time for the $Co/Al_2O_3$ and the $Co/SiO_2$ catalysts operated at 450°C. The reported $CH_4$ consumption is based on the exposed surface Co determined by chemisorption

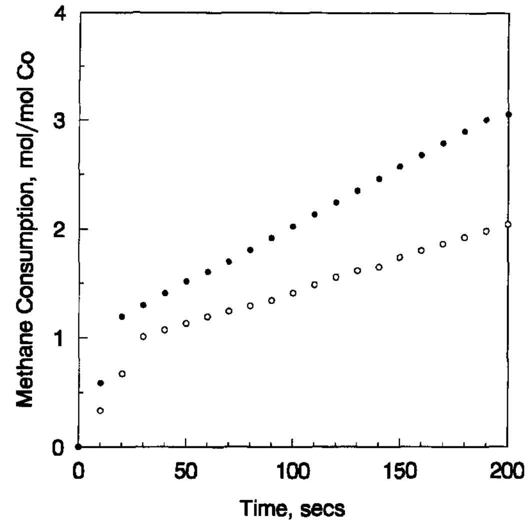

Fig. 2. Cumulative $CH_4$ consumption at 450°C and a reaction period of 3 min for the $Co/Al_2O_3$ (●) and $Co/SiO_2$ (○) catalysts.

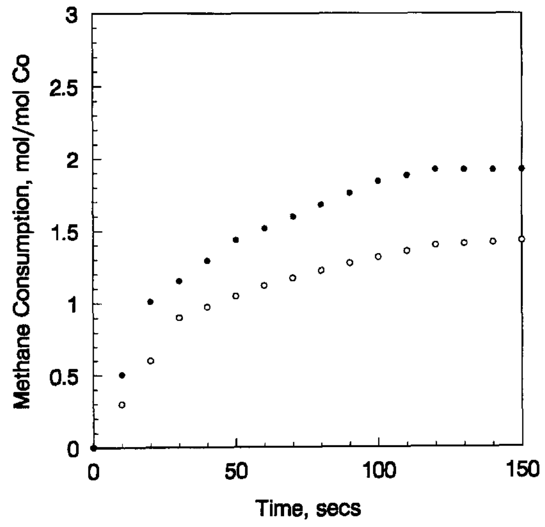

Fig. 3. Cumulative $CH_4$ consumption at 450°C and a reaction period of 1 min for the $Co/Al_2O_3$ (●) and $Co/SiO_2$ (○) catalysts.

prior to reaction. The shape of the plots suggests that the initial $CH_4$ decomposition rate decreased most significantly after about 30 s, as indicated by the distinct decrease in the slope of the cumulative $CH_4$ consumption vs. time plots. Since the decrease in rate occurred within about 30 s, the rate change was clearly not related to the decrease in reactor temperature from 450 to 100°C that followed the 1 or 3 min $CH_4$ decomposition period.

The data of Figs. 2 and 3 show that the moles of $CH_4$ consumed per mole of surface Co on the $Al_2O_3$ supported catalyst was much greater than that on the $SiO_2$ supported catalyst. Solymosi et al. [6] invoked the mobility of surface carbon species to explain the differences in $CH_4$ decomposition activity of Pd catalysts dispersed on different supports. Accordingly, as the carbonaceous species migrate from the metal to the support, metal sites are regenerated and further reaction can occur. Hence, the moles of $CH_4$ decomposed per mole of surface Co may be >1, i.e. greater than a monolayer coverage of Co by $CH_x$ ($x$=0, 1, 2 or 3). The total amount of $CH_4$ decomposed at the conditions of the present study corresponded to more than that needed for a monolayer coverage of Co. Hence, the mobility of the carbonaceous deposit from the metal to the support must be an important factor. In accord with the $CH_4$ decomposition data on Pd [6], we conclude that the carbonaceous deposit migrates onto the $Al_2O_3$ support more readily than onto the $SiO_2$ support and the cumulative $CH_4$ decomposition is therefore greater on the $Al_2O_3$ than the $SiO_2$ supported catalyst.

The decrease in the observed rate of $CH_4$ decomposition shown in Figs. 2 and 3 for both the $Al_2O_3$ and $SiO_2$ supported catalysts was most significant when the $CH_4$ consumed per surface Co approached unity, i.e. when the $CH_4$ consumption corresponded approximately to a monolayer coverage of Co. This observation can be explained in terms of the relative magnitudes of the rate of $CH_4$ decomposition and the rate of migration of the deposit from the metal to the support, assuming that the rate of $CH_4$ decomposition decreases with increasing coverage while the rate of migration of the deposit from the metal to the support increases with coverage. Initially, the observed rate will be determined by the rate of $CH_4$ decomposition since all metal sites are vacant. However, as coverage of the active metal by the carbonaceous deposit increases, the rate of migration of the deposit from the metal to the support will increase whereas the $CH_4$ decomposition rate will decrease. When monolayer coverage is achieved, the observed rate will be controlled by the rate of migration of the carbonaceous deposit from the metal to the support. Since the slopes of Figs. 2 and 3 decrease, we con-

Table 2
Intial rate of $CH_4$ decomposition on Co catalysts

| Decomposition conditions | | Initial decomposition rate (μmol $CH_4$/μmol Co per min) | |
|---|---|---|---|
| Reaction temperature (°C) | Reaction time (min) | $Co/Al_2O_3$ | $Co/SiO_2$ |
| 450 | 1 | 3.73 | 1.81 |
| 450 | 3 | 3.63 | 2.01 |

clude that the rate of migration at monolayer coverage is lower than the initial rate of decomposition and as coverage of the metal increases, the rate controlling step changes from decomposition of $CH_4$ to migration of the deposit from the metal to the support.

Table 2 reports the initial $CH_4$ decomposition rate estimated from the cumulative $CH_4$ decomposition data obtained within the first 20 s of reaction. These data should be relatively free of deactivation effects due to blocking of active sites by the decomposition products. The initial rate was higher on the $Co/Al_2O_3$ catalyst than the $Co/SiO_2$ catalyst. From the data of Table 1, this higher rate corresponded to the catalyst with lower Co dispersion, suggesting that $CH_4$ decomposition is structure-sensitive on Co.

Fig. 4 compares the cumulative $CH_4$ decomposition determined at 450 and 600°C for a reaction time of 3 min. Initially, the rate of decomposition was lower at 600°C than 450°C and the data at 600°C do not show the characteristic decrease in rate observed at 450°C. Presumably the Co was deactivated by thermal sintering at 600°C. In agreement with the TPSR data of Fig. 1, the data suggest that at 600°C, the decomposition reaction was dominated by a non-catalytic reaction that continued at approximately the same rate throughout the reaction period.

### 3.3. Hydrogenation of the carbonaceous deposit

Following exposure to $CH_4$ the catalysts were rapidly cooled to ambient and the reactant gas switched to $H_2$. The reactor temperature was then ramped to 600°C at 10°C/min in a flow of $H_2$. Fig. 5 presents the resulting TPSR profile for the $Co/SiO_2$ catalyst. The TPSR profiles are presented in terms of $CH_4$ production since above 100°C the

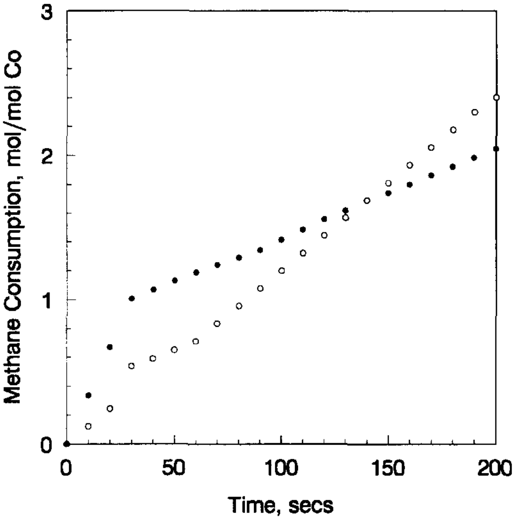

Fig. 4. Cumulative $CH_4$ consumption at 450°C (●) and 600°C (○) for a reaction period of 3 min on the $Co/Al_2O_3$ catalyst.

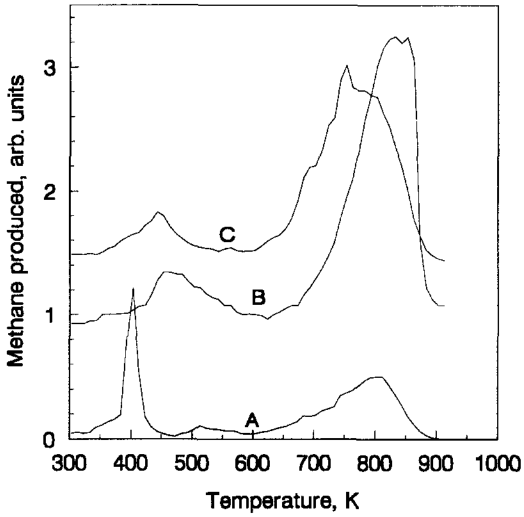

Fig. 5. TPSR in $H_2$ of the $Co/SiO_2$ catalyst following $CH_4$ decomposition at: (A) 450°C for 1 min; (B) 600°C for 3 min and (C) 450°C for 3 min.

amount of higher hydrocarbons produced during TPSR was negligible. In agreement with previous studies, three TPSR peaks were identified and these occurred at approximately 400, 450–520 and 800 K, each peak being associated with carbon deposits of different reactivity. The TPSR profiles also show that as the severity of the $CH_4$ decomposition reaction increased (i.e. the reaction time and temperature increased), the reactivity of the carbonaceous deposit in $H_2$ decreased. The most reactive carbonaceous deposit, referred to as $C_\alpha$ by Koerts et al. [1], was most abundant when the decomposition was carried out at 450°C for 1 min. By contrast, at 600°C and a reaction time of 3 min, no $C_\alpha$ was present and most of the deposit reacted at 800 K.

The synthesis of higher hydrocarbons by $CH_4$ homologation requires that the second-stage hydrogenation be carried out at low temperatures [1] or low hydrogen concentrations [10] to limit the production of $CH_4$. Table 3 compares the results of isothermal hydrogenation at 100°C, carried out over the $Co/SiO_2$ and $Co/Al_2O_3$ catalysts following $CH_4$ decomposition at 450°C for 1 and 3 min. The products from the hydrogenation, reported in terms of $C_2^+$ carbon atom % selectivities, were mainly paraffinic and followed the Anderson–Schulz–Flory carbon number distribution [9]. In all cases the $C_2^+$ selectivities were <15% with the $Co/SiO_2$ catalyst having marginally greater $C_2^+$ selectivities than the $Co/Al_2O_3$ catalyst. Furthermore, $C_2^+$ selectivity was higher and more of the deposit was hydrogenated for the $CH_4$ decomposition time of 1 min compared to 3 min. This observation is consistent with the TPSR data of Fig. 5 showing that the decomposition time of 1 min gave more of the reactive $C_\alpha$ carbonaceous deposit than the 3 min decomposition time.

The data of Table 3 also show that the percent of carbonaceous deposit hydrogenated at 100°C was very low. Performing TPSR in $H_2$ at 600°C, following the isothermal hydrogenation, removed the less reactive carbon but still this did not account for the amount of $CH_4$ decomposed at 450°C. Chemical analysis of the catalyst following TPSR confirmed that a large amount of carbon remained on the catalyst following TPSR. These data are consistent with the hypothesis that much of the $CH_4$ decomposed at the conditions of the present study yielded a carbonaceous deposit that migrated to the support and was unreactive to $H_2$ even at 600°C. Based on the total moles of $CH_4$ decomposed per mole of surface Co, the amount of the deposit that migrated to the support was greater on the $Co/Al_2O_3$ than the $Co/SiO_2$ catalyst. Hence, more hydrocarbons would be produced on the $Co/SiO_2$ catalyst than the $Co/Al_2O_3$ during hydrogenation, in agreement with the experimental observations.

### 3.4. *Oxidation of the carbonaceous deposit*

The reactivity of the carbonaceous deposit to $O_2$ was also examined by TPSR. Fig. 6 shows the TPSR profiles in $O_2$ for the Co catalysts following $CH_4$ decomposition at 450°C for 1 and 3 min. At the conditions of the present study, $CO_2$ was the only component detected in the product from TPSR in $O_2$. These data show that the oxidation of the carbonaceous deposit occurred at approximately 600–650 K and unlike the TPSR in $H_2$, the profile had only one peak. Furthermore, no detectable difference in the profiles was apparent between the 1 and 3 min $CH_4$ decomposition reaction times. The carbonaceous deposit was therefore very reactive to $O_2$ and the reactivity was not dependent upon the age and location of the deposit as it was in the case of $H_2$.

In one experiment, TPSR in $O_2$ was performed after the TPSR in $H_2$. The presence of $CO_2$ in the reactor effluent confirmed that part of the carbonaceous

Table 3
Hydrogenation of carbonaceous species at 100°C

| | $CH_4$ decomposition | | Carbon hydrogenated | $C_2^+$ C atom selectivity |
|---|---|---|---|---|
| Catalyst | Temperature (°C) | Time (min) | (%) | (%) |
| $Co/SiO_2$ | 450 | 1 | 6.5 | 14.2 |
| $Co/SiO_2$ | 450 | 3 | 1.6 | 9.7 |
| $Co/Al_2O_3$ | 450 | 1 | 3.9 | 10.8 |
| $Co/Al_2O_3$ | 450 | 3 | 1.2 | 8.0 |

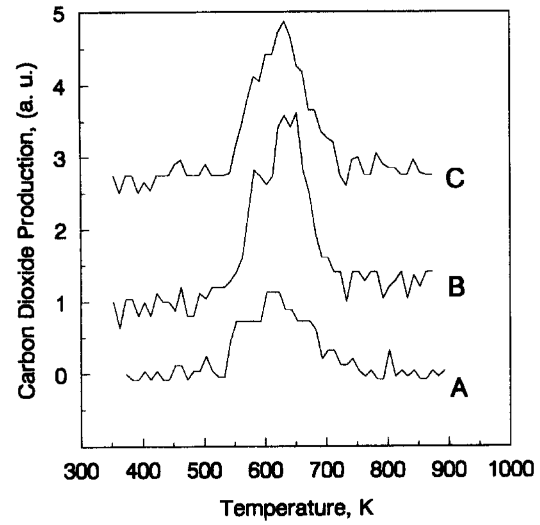

Fig. 6. TPSR in $O_2$ following $CH_4$ decomposition at: (A) 450°C for 1 min for the $Co/SiO_2$; (B) 450°C for 3 min for the $Co/Al_2O_3$; and (C) 450°C for 3 min for the $Co/SiO_2$ catalysts.

deposit was unreactive to $H_2$ even at high temperature, but that it reacted with $O_2$. Hence, it was possible to classify the types of carbonaceous deposit according to reactivity in $H_2$. The relative amounts of each type are summarized in Table 4 according to the percent reacted in $H_2$ at 100°C, the percent reacted during TPSR at 600°C in $H_2$ following the isothermal hydrogenation, and the percent that was not hydrogenated. Although the differences in the relative amounts of each type of carbonaceous deposit were small, the data show more of the reactive $C_\alpha$ type carbon on the $Co/SiO_2$ catalyst than the $Co/Al_2O_3$ catalyst. This is consistent with the $Co/SiO_2$ catalyst being more selective toward higher hydrocarbons than the $Co/Al_2O_3$ catalyst.

At the decomposition conditions of the present study, the concentration of $CH_4$ was relatively high. Hence, the percent conversion was low when compared to previous studies of $CH_4$ homologation [1]. Furthermore, the TPSR studies with $H_2$ and $O_2$ have demonstrated that at the conditions of the present study, much of the carbon deposited was unreactive at 100°C. Hence, the catalyst deactivates following numerous decomposition–hydrogenation cycles [11]. Clearly, it is important to operate the decomposition stage of the homologation reaction at conditions that maximize the deposition of the most reactive carbon and this may be achieved by limiting the amount of $CH_4$ available in the feed, as reported by Koerts et al. [1]. In addition, the selectivity toward $C_2^+$ hydrocarbons from the isothermal hydrogenation reaction can be increased by promotion of the Co catalyst with K [9].

## 4. Conclusions

At 450°C, more $CH_4$ per surface Co decomposed on the $Co/Al_2O_3$ catalyst than the $Co/SiO_2$ catalyst. In the subsequent hydrogenation step at 100°C, less than 10% of the carbon deposited from $CH_4$ was reacted and the $C_2^+$ selectivity was higher on the $Co/SiO_2$ catalyst than the $Co/Al_2O_3$ catalyst. These differences are explained in terms of migration of the carbonaceous deposit from the reduced metal to the support, that occurs more readily on the $Co/Al_2O_3$ than the $Co/SiO_2$ catalyst.

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Table 4
Reactivity of carbonaceous species deposited on Co catalysts

| | $CH_4$ decomposition | | Carbonaceous deposit reacted in $H_2$ | | |
|---|---|---|---|---|---|
| Catalyst | Temperature (°C) | Time (min) | At 100°C (%) | TPSR to 600°C (%) | Unreacted (%) |
| $Co/SiO_2$ | 450 | 1 | 7 | 20 | 73 |
| $Co/SiO_2$ | 450 | 3 | 3 | 39 | 58 |
| $Co/Al_2O_3$ | 450 | 1 | 4 | 27 | 69 |

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