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Effect of CO Conversion on the Product Distribution of a Co/Al_2O_3 Fischer–Tropsch Synthesis Catalyst Using a Fixed Bed Reactor

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Abstract The effect of CO conversion (35–91 %) on hydrocarbon product distribution (CH_4, C_5^+ and olefin selectivities) and CO_2 selectivity was studied in a fixed bed reactor on 15 % Co/Al_2O_3 catalyst at conditions of industrial relevance. Selectivity to CH_4 decreased, whereas those of C_5^+ and CO_2 increased with increasing CO conversion (and consequently, partial pressure of water produced during the Fischer–Tropsch synthesis). 1-Olefin content of C_2–C_5 olefins decreased and 2-olefin content of C_4 hydrocarbon increased with increasing CO conversion.

Keywords Fischer–Tropsch synthesis · Cobalt on alumina catalyst · Product distribution · Fixed-bed and slurry-bed reactors · Catalyst deactivation

1 Introduction

Supported cobalt catalysts are used for natural gas conversion to transportation fuels due to their high activity, selectivity to long chain products, long term stability and low water–gas-shift activity. In addition to hydrocarbons, water is the main product of Fischer–Tropsch synthesis (FTS).

Some of the beneficial effects (e.g., increased C_5^+ selectivity and lower CH_4 selectivity) of indigenous water produced during FTS and/or water added with the H_2/CO feed have been reported in the patent literature [1–3] and later in the open literature [4–9]. Also, it has been reported that reaction rate on some catalysts increases with an increase in the partial pressure of water [4–6, 10], whereas some researchers have observed an increase in olefinicity of hydrocarbon products [5, 6, 8–10]. Water induced selectivity changes have been attributed to inhibition of secondary hydrogenation of 1-olefins [2, 5, 10] and chain termination reactions [5]. Additional explanations for the water effect on activity and selectivity of supported cobalt FTS catalysts have been proposed [5, 6, 11, 12] but as of yet, there is no unifying explanation to account for the variations observed amongst different investigators.

Operation at high single pass conversion coupled with improvements in hydrocarbon selectivity would provide an attractive alternative to low single pass conversion with recycle. However, data illustrating the effect of high CO conversion on hydrocarbon and CO_2 selectivities, and on catalyst stability, are scarce. Previously cited studies examining the effect of water on activity and product distributions were conducted at low to moderate CO conversions (10–60 %), and the highest level of conversion achieved was 72 % [7]. This study was conducted in a fixed-bed reactor with Re promoted Co/Al_2O_3 catalyst. Recently, Ma et al. [13] studied the effect of CO conversion (12–94 %) on CH_4 and C_5^+ selectivities, CO_2 selectivity, H_2/CO usage ratio, olefin-to-paraffin ratio (OPR) and catalyst stability in a 1 L stirred tank slurry reactor (STSR) with a Ru promoted Co/Al_2O_3 catalyst.

The purpose of the present work is to study the effect of CO conversion (including high conversions above 80 %) on product distribution and catalyst activity of unpromoted

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alumina supported cobalt catalyst. This complements our STSR study and provides a comparison between the two reactor configurations. Also, we report new results from the STSR with $Co–Ru/Al_2O_3$ catalyst to illustrate the impact of operation at high CO conversion (>90 %) on the catalyst stability and CH_4 selectivity.

2 Experimental

2.1 Catalyst Preparation

Cobalt supported on alumina catalyst (Co/Al_2O_3) with a loading of 15 wt% was prepared by the incipient wetness impregnation (IWI) method. γ-Al_2O_3 (Puralox SCCa 150/200 from Sasol) was calcined at 973 K for 10 h prior to impregnation with an aqueous solution of cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$, Sigma-Aldrich, 99.0 %). The mixture was dried in air flow of 0.11 NL/g-cat/h at 373 K for 1 h and then calcined in an air flow of 0.56 NL/g-cat/h at 573 K for 10 h.

2.2 Characterization

Brunauer–Emmett–Teller (BET) measurements were carried out at 77 K with N_2 (Micromeritics Tri-Star II 3020). Samples of about 0.2 g were heated at 523 K for 4 h in flow of helium prior to measurements. Surface area was calculated from the BET equation, whereas total pore volume, average pore radius and pore size distribution were obtained using the Barrett–Joyner–Halenda (BJH) method. The nitrogen desorption branch was selected for pore size analysis.

Hydrogen chemisorption (H_2-TPD) measurements were performed using a Micromeritics AutoChem II 2920 unit. The catalyst (~0.1 g) was reduced at 648 K for 12 h by flowing 50 mL/min of ultra-high purity hydrogen and then cooling under flowing hydrogen to 353 K. At this temperature, the catalyst was held under 50 mL/min of flowing argon to desorb weakly bound hydrogen species. Then the temperature was increased from 353 to 648 K at a heating rate of 10 K/min and held at 648 K for 2 h to desorb the remaining chemisorbed hydrogen.

After TPD of hydrogen, the gas was switched from argon to helium at 648 K and then the sample was reoxidized at the activation temperature (648 K) by injecting pulses of 10 % O_2/He in helium referenced to helium gas. After oxidation of the cobalt metal clusters, the number of moles of oxygen consumed was determined, and the percentage reduction was calculated assuming that the Co^0 reoxidized to Co_3O_4. While the uncorrected dispersions (uc) are based on the assumption of complete reduction, the corrected dispersion (c), which is reported in this work, include the percentage of reduced cobalt as follows.

D_{uc} (%) = (# of Co^0 atoms on surface × 100 %)/(total # Co atoms)

D_c (%) = (# of Co^0 atoms on surface × 100 %)/[(total # Co atoms) × (fraction reduced)]

Average crystallite size was calculated from the corrected dispersion as d_c (nm) = $96/D_c$ (%)

2.3 Fischer–Tropsch Synthesis

Fischer–Tropsch synthesis (FTS) test was performed in a downflow fixed-bed reactor (1.1 cm ID and effective volume of 30 cm^3). A detailed description of our reactor system is provided elsewhere [14, 15].

Briefly, reductant or feed gas flow rates were adjusted with mass flow controllers and passed through a series of oxygen removal (BASF R3-11G catalyst), sulfur removal (Actisorb Süd-Chemie G-1) and carbonyl removal (BASF E-315 catalyst) traps to remove trace impurities. The feed stream was preheated. After leaving the reactor, the exit gas passed through a series of high and low (ambient) pressure traps to condense out liquid products. Uncondensed reactants and products (CO, H_2, CO_2 and C_1–C_5 hydrocarbons) were analyzed by online gas chromatography (Agilent 7890A) using two thermal conductivity detectors (TCD) and a flame ionization detector (FID).

Calcined catalyst (2.5 g, 150–250 μm) was diluted with quartz sand (average dilution ratio of quartz sand: catalyst = 7:1 (v/v) with a non-uniform catalyst distribution). A non-uniform catalyst distribution (i.e., smaller amount of catalyst at the top and larger amount at the bottom) was employed to minimize temperature gradients in the axial direction. The catalyst was activated with hydrogen at a gas space velocity (SV) of 12.4 NL/g-cat/h at atmospheric pressure. Temperature was increased to 453 K at a heating rate of 5 K/min and then to 648 K at a heating rate of 1 K/min and held at 648 K for 12 h. Then, the catalyst bed was cooled down to 453 K in flow of N_2 of 7.5 NL/g-cat/h, and then syngas (H_2/CO = 2/1 containing 5 % of Ar) was introduced at a SV of 2.8 NL/g-cat/h. The reactor was pressurized to 2.0 MPa with syngas, and then the temperature was raised to 493 K at a heating rate of 1 K/min. During the test, gas space velocity was varied from 2.8 to 6 NL/g-cat/h in order to achieve a wide range of CO conversions.

One test was conducted at CAER using a 1 L stirred tank slurry reactor (STSR) and a 0.27 % Ru/25 % Co/Al_2O_3 catalyst. Catalyst preparation procedure was provided in Ref. [13]. The catalyst was ground and sieved to 44–90 μm before loading into a fixed-bed reactor for 10 h of ex-situ reduction at 623 K and atmospheric pressure using a gas mixture of H_2/He (60 NL/h) with a molar ratio of 1:3. The reduced catalyst was then transferred to the STSR containing 315 g of melted Polywax 3000, under the protection of N_2 inert gas. The transferred catalyst was further reduced in situ at 503 K at atmospheric pressure using pure hydrogen (30 NL/h) for another 10 h before starting the FT reaction. In this study, the FTS conditions that were used are 493 K, 1.5 MPa, $H_2/CO = 2.1$, and 1.2 NL/g-cat/h.

Conversions and selectivities reported here were calculated from analysis of gas products as follows:

CO conversion $(\%) = 100 \times ((n_{CO})_{in} - (n_{CO})_{out})/(n_{CO})_{in}$

CO_2 selectivity $(\%) = 100 \times \frac{(n_{CO_2})_{out}}{(n_{CO})_{in} - (n_{CO})_{out}}$

Hydrocarbon selectivities (C_1–C_5):

$$S_{ij}(\%) = \frac{100 \times (in_{ij})}{(n_{CO})_{in} - (n_{CO})_{out} - (n_{CO_2})_{out}}$$

where S_{ij} is the selectivity of hydrocarbon species j containing i carbon atoms, n_{ij} is molar flow of compound j in the gas phase, $(n_{CO})_{in}$ and $(n_{CO})_{out}$ are molar flow rates of CO in and out of the reactor, and $(n_{CO_2})_{out}$ is the molar flow rate of carbon dioxide out of the reactor.

Selectivity of C_5^+ ($S_{C_5^+}$) hydrocarbons was calculated from C_1–C_4 selectivities as:

$$S_{C_5^+}(\%) = 100 - (S_{C_1} + S_{C_2} + S_{C_3} + S_{C_4})$$

Olefin and paraffin selectivities (contents), based on molar flow rates of the corresponding hydrocarbons of the same carbon number, are calculated as:

1-olefin content (%) = 100 × (1-olefin)/(1-olefin + 2-olefin + *n*-paraffin)

2-olefin content (%) = 100 × (2-olefin)/(1-olefin + 2-olefin + *n*-paraffin)

3 Results and Discussion

Results from BET and chemisorption measurements are summarized in Table 1. BET surface area, pore volume and average diameter decreased after impregnation of Puralox γ-Al_2O_3 support. The average pore diameter of the catalyst is slightly lower than that of the support (8.8 vs. 9.2 nm) indicating that no significant pore blocking occurred upon introduction of cobalt.

The degree of reduction, from O_2 pulse reoxidation, was high (92.7 %) and the corrected Co dispersion was 8.6 %. The crystallite size from chemisorption measurements was 11.2 nm which is comparable to the average pore diameter (8.8 nm) of the catalyst.

Table 1 Results of BET surface area, porosity, and hydrogen chemisorption with pulse reoxidation

Description	N_2 physisorption			Chemisorption with pulse reoxidation		
	BET surface area (m^2/g)	Pore volume[a] (cm^3/g)	Average pore diameter[a] (nm)	DR[b] (%)	D_c[c] (%)	d_c[d] (nm)
Puralox SCCa 150/200 γ-Al_2O_3	180	0.60	9.2			
15 % Co/γ-Al_2O_3	153	0.42	8.8	92.7	8.6	11.2

[a] Calculation by BJH desorption method

[b] Degree of reduction (DR%) was calculated from O_2 consumption during pulse reoxidation (TPO)

[c] Corrected cobalt dispersion (D_c%) was calculated from the amount of H_2 desorbed during H_2-TPD from 353 to 648 K and DR

[d] Average Co crystallite size was calculated from the corrected dispersion as d_c (nm) = $96/D_c$ (%)

Effects of gas space velocity and time on stream (TOS) on CO conversion and methane selectivity are shown in Fig. 1. During testing at SV = 2.8 NL/g-cat/h, the average catalyst bed temperature was initially 498 K resulting in a CO conversion of 91 %, but the latter decreased to 82.4 % when the bed temperature was adjusted to 496 K. This drop in conversion was not only the result of a temperature decrease, but was also affected by pore filling with wax and initial catalyst deactivation. Methane selectivity increased slightly during this time period, even though one would expect it to decrease while operating at lower temperature. As the space velocity was increased to higher values (3, 3.75 and 6 NL/g-cat/h), the CO conversion decreased, as expected, whereas methane selectivity increased. The average catalyst bed temperature at SV = 6 NL/g-cat/h was 495 K.

Figure 2 illustrates the effect of CO conversion on selectivities (CH_4, C_5^+, 2-olefin content of C_4 hydrocarbons and CO_2 selectivity). Figure 2a shows that methane selectivity decreased (11.8–9.1 %) as CO conversion increased (35–91 %), whereas C_5^+ and CO_2 selectivities increased with increasing CO conversion (Fig. 2b, c). 2-olefin content of C_4 hydrocarbons increased with increase in CO conversion (Fig. 2d), due to secondary isomerization of 1-olefins, which are the primary products of FTS [16–19].

The effect of gas space velocity (i.e., CO conversion) on 1-olefin content of gaseous hydrocarbons (C_2–C_5) is shown in Fig. 3. 1-olefin content for all carbon numbers decreased with increase in CO conversion, which is the result of secondary reactions of 1-olefins: hydrogenation, isomerization, readsorption and/or reincorporation in growing chains [16–19]. Ethylene is the most reactive, and its selectivity is lower than that of C_3–C_5 hydrocarbons,

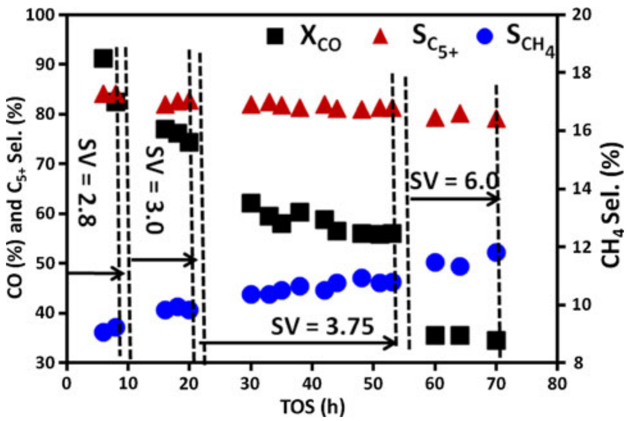


Fig. 1 Effect of gas space velocity and time on CO conversion, CH$_4$ and C$_5^+$ selectivity (Fixed bed reactor: 15 % Co/Al$_2$O$_3$ catalyst, T = 495–498 K, 2 MPa, H$_2$/CO = 2)

whereas a decrease in 1-olefin content with increasing carbon number (for C$_3^+$ hydrocarbons) is caused by differences in reactivity, intraparticle diffusional effects and solubility variation with molecular weight [16–21]. Diffusivity decreases with increases in molecular weights of species, and higher molecular weight 1-olefins have longer residence times within the catalyst pores, thus increasing the probability for secondary reactions [16–18]. Increase in solubility with increase in carbon number also results in increased residence time of higher molecular weight hydrocarbons in the reactor as well as their higher liquid phase concentrations, resulting in a greater extent of secondary reactions. [18–21].

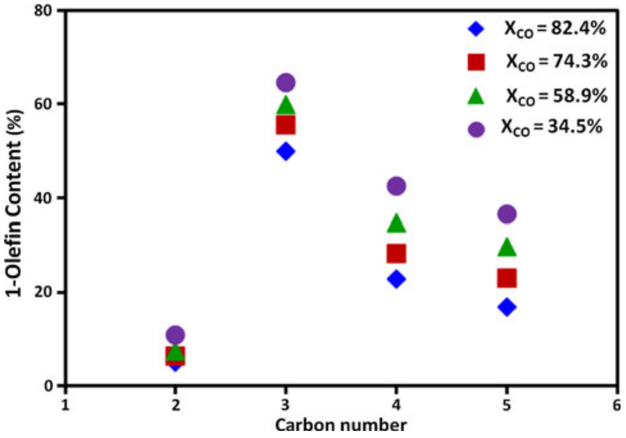
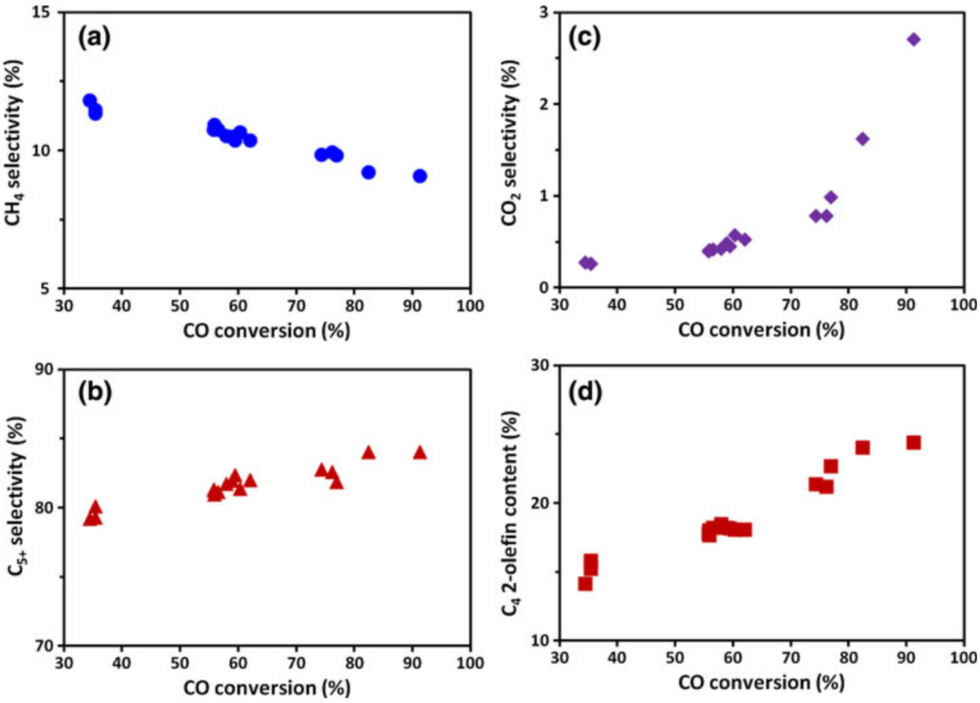


Fig. 3 Effect of CO conversion on 1-olefin content of C$_2$–C$_5$ hydrocarbons (Fixed bed reactor: 15 % Co/Al$_2$O$_3$ catalyst, T = 495–498 K, 2 MPa, H$_2$/CO = 2, SV = 2.8–6 NL/g-cat/h)

The observed trend of decreasing methane selectivity with increasing CO conversion is consistent with previous studies on supported cobalt catalysts using either a fixed-bed reactor [4, 5, 7, 8, 10] or a stirred tank slurry reactor [9, 22].

We found that 1-olefin content (Fig. 4) and OPR (not shown) decreased with increase in CO conversion, even though increased water concentration was reported to inhibit secondary reactions of 1-olefins [2, 5, 8, 9]. Krishnamoorthy et al. [6] also found that the residence time effect is dominant, leading to decrease in OPR in spite of concomitant increase in water concentration, whereas they observed increase in OPR in experiments with external

Fig. 2 Change of **a** CH$_4$ selectivity, **b** C$_5^+$ selectivity, **c** CO$_2$ selectivity, and **d** 2-olefin content of C$_4$ hydrocarbons with CO conversion (Fixed bed reactor: 15 % Co/Al$_2$O$_3$ catalyst, T = 495–498 K, 2 MPa, H$_2$/CO = 2, SV = 2.8–6 NL/g-cat/h)



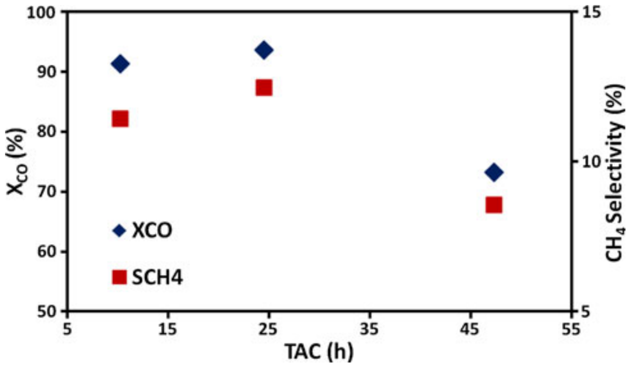


Fig. 4 Effect of time on CO conversion and CH_4 selectivity in STSR (0.27 % Ru/25 % Co/Al_2O_3 catalyst, T = 493 K, 1.5 MPa, H_2/CO = 2.1, SV = 1.2 NL/g-cat/h)

water addition. Obviously, experiments with external addition of water are better suited to study the effect of water concentration, than experiments in which water is produced indigenously. In the latter case, the bed residence time effects may cancel the water concentration effects on product selectivity and catalyst activity.

Recently, Ma et al. [13] studied the effect of CO conversion (12–94 %) on product hydrocarbon and CO_2 selectivities using a STSR at 493 K, 1.5 MPa, H_2/CO = 2.1 and gas space velocities of 0.2–15 NL/g-cat/h on a 0.27 % Ru–25 % Co/Al_2O_3 catalyst. The qualitative trends of changes in CH_4, C_5^+, CO_2 and olefin selectivities observed in the present study with unpromoted Co/Al_2O_3 catalyst in a fixed-bed reactor as displayed in Fig. 3, are consistent with those obtained in the STSR, with the exception of CH_4 selectivity at CO conversions higher than 80 %. The fact that the same trends in selectivity (hydrocarbons and CO_2) were observed on different catalysts (promoted vs. unpromoted and the use of alumina supports of having somewhat different physical properties) and in different reactor types clearly demonstrates that the CO conversion effect predominates.

Ma et al. [13] reported an increase in CH_4 selectivity and leveling off of C_5^+ selectivity for CO conversions higher than 80 %. This has been attributed to catalyst deactivation via the formation of irreducible cobalt oxide species at high partial pressures of indigenous water [23–27]. Rapid increase in CO_2 selectivity at CO conversions above 80 %, observed in the present study and in the STSR, is also consistent with this hypothesis. Furthermore, XANES studies of catalyst samples withdrawn from the STSR at different conversion levels indicated the presence of small amounts of an oxidized form of cobalt [13]. Possible reasons that this type of behavior (i.e., increases in CH_4 selectivity at high conversions) was not observed in the present study include the following. In a fixed bed reactor, only the bottom part of the catalyst bed is exposed to a high p_{H_2O}, whereas the remainder is exposed to lower p_{H_2O} and thus the detrimental effects of oxidation of metallic cobalt and/or formation of inactive surface compounds are much less severe than in the STSR where the entire catalyst is exposed to high p_{H_2O}. The average cobalt particle size of unpromoted catalyst (11.2 nm) used in the fixed-bed reactor is greater than that of Co–Ru/Al_2O_3 catalyst (5 nm) used in the STSR. It has been reported that smaller crystallites are more susceptible to oxidation and/or increased interaction with the support than the larger ones [8, 25, 27, 28] Also, the exposure of the catalyst to high p_{H_2O} was much shorter in the fixed-bed reactor than in the STSR.

Ma et al. [13] reported that the deactivation rate increased with increases in CO conversion (i.e., increases in p_{H_2O}). The same trend (loss of activity at high partial pressures of water) was observed in previous studies with co-feeding of water [8, 9, 25, 29]. Data from the present study show the same trend but were collected over a short period of time (particularly at gas space velocities of 2.8 and 3 NL/g-cat/h) and represent quasi steady state values.

Figure 4 illustrates catalyst stability at high CO conversion during one of the runs conducted at CAER in the STSR (total time on stream 152–190 h). The catalyst was initially stable (up to 25 h at conditions), but during the next 22 h CO conversion decreased significantly from about 94 to 73 %. This was accompanied with a decrease in CH_4 selectivity from 12.5 to 8.6 %. This is consistent with results in [13] where it was found that methane selectivity increases with increase in CO conversion for CO conversions higher than approximately 80 %. However, CH_4 selectivity at 73 % CO conversion was significantly higher than that obtained before exposure of the catalyst to high conversion. During the same run (TOS = 142 h), CH_4 selectivity at a CO conversion of 77 % was 5.9 % (Fig. 5). This shows that structural changes occurred in the catalyst during exposure to high partial pressure of water, thus leading to higher CH_4 selectivity.

The effect of indigenous or externally added water on the activity and selectivity of supported cobalt catalysts is not

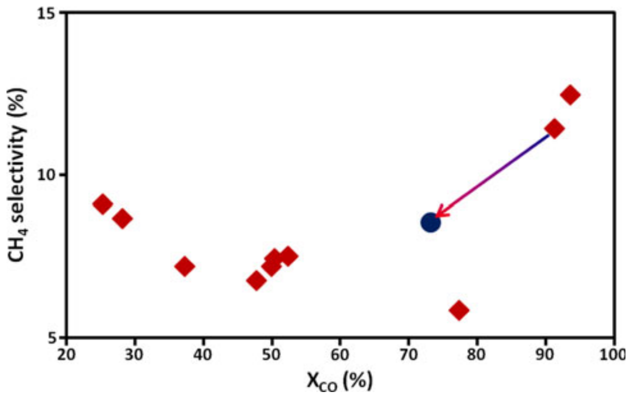


Fig. 5 Effect of CO conversion on CH_4 selectivity in STSR (0.27 % Ru/25 % Co/Al_2O_3 catalyst, T = 493 K, 1.5 MPa, H_2/CO = 2.1, SV = 1.2–10.1 NL/g-cat/h)

fully understood and is to some extent dependent on the type of support used [5, 6, 8, 12]. Reversible selectivity changes include decreased methane selectivity, higher olefin content and increased selectivity toward high molecular weight products. These changes have been attributed to inhibition of secondary hydrogenation of 1-olefins [5, 10] and chain termination reactions [5], presumably by competitive adsorption. Reduction in hydrogenation activity of primary olefins increases probability for 1-olefin readsorption and chain initiation resulting in higher C_5^+ selectivity [5, 16]. Iglesia [5] proposed that a water-rich liquid phase formed inside the catalyst pores at high water concentrations would increase the diffusion rate of CO, which in turn could increase the reaction rate and lead to higher C_5^+ selectivity (by reducing the CO concentration gradient inside the pellet). In a more recent study, Iglesia and co-workers [6] reported that water does not have a significant effect on CO transport restrictions, that it does not introduce new kinetic pathways, and that it has no cleaning effect by removing site-blocking unreactive surface intermediates. It was suggested that water may influence the relative concentrations of active and inactive carbon on the surface. Bertole et al. [11, 12] proposed that water lowers the barrier for CO dissociation (thus increasing the reaction rate) and has an effect on active carbon coverage (predominantly in the form of monomer) on the surface.

4 Conclusions

The effect of CO conversion (35–91 %) on product distribution of unpromoted alumina supported cobalt catalyst was studied in a fixed-bed reactor at 495 K, 2 MPa, H_2/CO = 2, by varying gas space velocity (2.8–6 NL/g-cat/h). CH_4 selectivity monotonically decreased, whereas C_5^+ and CO_2 selectivities increased with increases in CO conversion. Secondary reactions of 1-olefins (hydrogenation and isomerization) increased with increases in CO conversion.

The stability of a Ru promoted Co/Al_2O_3 catalyst at high CO conversion (~92 %) was studied in a STSR (493 K, 1.5 MPa, H_2/CO = 2.1, SV = 1.2 NL/g-cat/h). During the first 25 h at these conditions, the catalyst activity was stable but then decreased significantly to 73 % during the next 22 h. CH_4 selectivity (8.6 %) at a CO conversion of 73 % was significantly higher than the value obtained prior to exposure of the catalyst to high CO conversion, indicating that the catalyst had undergone structural changes after prolonged exposure to high water partial pressure. This is consistent with XANES studies, which showed oxidation of a small fraction of metallic cobalt after exposure of the catalyst to high CO conversion [13].

The underlying reasons for selectivity and activity changes with increasing partial pressure of water are not fully understood, and are the result of a complex interplay of transport processes, cobalt particle size and the effect of water on the formation of active carbon species and/or the removal of inactive carbon species from the catalyst surface.

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