**Tables**

Table 1: Comparison of steady state FT selectivites for Co/Al2O3 catalysts under various conditions (H2/CO = 2:1).

|  |  |
| --- | --- |
|  | Selectivity (mass %) at steady state a |
| Conditions | C1 | C2-4 | C5-6 | C7-9 |
| 200°C / 10 bar | 36.5 | 26.9 | 17.9 | 18.7 |
| 225°C / 10 bar | 38.9 | 22.1 | 18.5 | 20.5 |
| 250°C / 10 bar | 39.2 | 22.2 | 19.7 | 18.8 |
| 225°C / 5 bar | 32.8 | 23.0 | 21.6 | 22.6 |
| 225°C /15 bar | 40.8 | 22.2 | 16.9 | 20.1 |

a Based on average selectivities calculated between 90-360 min time on stream (4-5 data points used).

**Figures**



Figure 1: Selection of FTIR difference spectra for hydrocarbon region collected at 5, 25 60, 120, 240 and 360 min time on stream for a Co/Al2O3 catalyst under FT conditions (10 bar, H2/CO = 2:1) at 3 different reaction temperatures: (a) 200°C, (b) 225°C and (c) 250°C.



Figure 2: Estimation of chain lengths for hydrocarbon species detected for a Co/Al2O3 catalyst at 200°C, 225°C and 250°C (10 bar, H2/CO = 2:1) and 5 bar, 10 bar and 15 bar (225°C, H2/CO = 2:1) using Equation 2.



Figure 3: Estimation of chain lengths for hydrocarbon species detected for a separate disc of γ-alumina at 200°C, 225°C and 250°C (10 bar, H2/CO = 2:1) using Equation 2.



Figure 4: Top: ASF plots for a Co/Al2O3 catalyst (225°C, 10 bar, H2/CO = 2:1) at 30 and 339 min. Bottom: α value *versus* time for a Co/Al2O3 catalyst at 200, 225 and 250°C (10 bar, H2/CO = 2:1).



Figure 5: α value *versus* time for a Co/Al2O3 catalyst at 5, 10 and 15 bar (225°C, H2/CO = 2:1).



Figure 6: Average α value (based on values obtained between 90-360 min at steady state) *versus* average CH2:CH3 ratios (based on the calculated ratios between 90-360 min) for, a separate disc of γ-alumina at (a) 200°C, (b) 225°C and (c) 250°C, a Co/Al2O3 catalyst at (d) 200, (e) 225 and (f) 250°C (10 bar, H2/CO = 2:1) and for a Co/Al2O3 catalyst at (g) 5 and (h) 15 bar (225°C, H2/CO = 2:1).



Figure 7: Left: Estimation of chain lengths for hydrocarbon species detected for a Co/SiO2 catalyst at 225 and 250°C (10 bar, H2/CO = 2:1) using Equation 2. Right: Average α value (based on values obtained between 90-360 min) *versus* average CH2:CH3 ratios (based on the calculated ratios between 90-360 min) for a Co/SiO2 catalyst at 225 and 250°C.



Figure 8: Selection of FTIR difference spectra for hydrocarbon region collected for (a) Ni/Al2O3, (b) Ru/Al2O3, (c) separate disc experiment with Ni/Al2O3 and (d) separate disc experiment with Ru/Al2O3 under FT conditions (225°C, 10 bar, H2/CO = 2:1)



Figure 9: Estimation of chain lengths for hydrocarbon species detected for Ru/Al2O3, a separate disc of γ-alumina with Ru/Al2O3, Ni/Al2O3, a separate disc of γ-alumina with Ni/Al2O3 (225°C, 10 bar, H2/CO = 2:1) using Equation 2. Right: Average α value (based on values obtained between 90-360 min) versus average CH2:CH3 ratios (based on the calculated ratios between 90-360 min) and for (a) Ru/Al2O3, (b) a separate disc of γ-alumina with Ru/Al2O3, (c) Ni/Al2O3 (h) a separate disc of γ-alumina with Ni/Al2O3 (225°C, 10 bar, H2/CO = 2:1).



Figure 10: Hydrocarbon product amount (μmoles) and spectrum peak (CH2 + CH3) areas (cm-1) *versus* time (min).