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## Efficient utilization of bimetallic catalyst in low H<sub>2</sub>/CO environment syngas for liquid fuel production

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**Abstract.** Application of Fischer-Tropsch synthesis (FTS) in the utilization of low H<sub>2</sub>/CO ratio (0.5–1.5) gas obtained from coal and biomass gasification can be done by selecting a catalyst system active for both FTS and WGS reaction. The enhancement of H<sub>2</sub> content depends on the extent of water gas shift (WGS) reaction and can be quantified by measuring usage ratio define as a mole of H<sub>2</sub> to CO converted. With an attempt to utilize low H<sub>2</sub>/CO ratio syngas bimetallic (Fe/Co/SiO<sub>2</sub>) were prepared and compared with monometallic (Fe/SiO<sub>2</sub> and Co/SiO<sub>2</sub>) catalysts. The catalysts were tested in fixed bed reactor at industrial relevant FTS conditions (T: 220–260 °C, P: 2.0 MPa, GHSV-1.2 SL/gcat-h, H<sub>2</sub>/CO: 1–1.5). The incorporation of Fe-Co bimetallic catalyst facilitates both FT and WGS reaction because of the presence of iron and cobalt phases. Compared to monometallic catalyst there is a significant increase in CO conversion over the bimetallic catalyst. Also, the yield of C<sub>5+</sub> was significantly higher over bimetallic catalyst compared to iron catalyst, where olefin was the major product. Selected catalyst (Fe/Co/SiO<sub>2</sub>) was tested for their activity toward WGS reaction. Effects of temperature, pressure, and feed composition on WGS reaction over bimetallic catalyst were studied. Lower value usage ratio (1.62 and 1.58) reveals the occurrence WGS reaction Fe-Co bimetallic catalyst at 240 °C and 260 °C. At 240 °C, 72% CO conversion, and 60% C<sub>5+</sub> selectivity show that the catalyst efficiently utilizes the increased H<sub>2</sub>/CO ratio in the production of liquid hydrocarbon.

**Keywords.** H<sub>2</sub>/CO usage ratio; bimetallic catalyst; Fischer-Tropsch synthesis; WGS reaction.

### 1. Introduction

In the search of cleaner fuel production via economic resources which may able to uphold the environmental norms, the research is diverted towards Fisher Tropsch synthesis route. Conversion of biomass and coal-derived syngas into liquid fuel via Fischer-Tropsch route is gaining interest in the recent years as the derived fuel (gasoline and diesel) are clean and environment-friendly which can satisfy strict environmental norms.<sup>1</sup> Syngas produced from coal and biomass have different H<sub>2</sub>/CO ratio based on gasification process and feedstock.<sup>2</sup> The stoichiometric demand of H<sub>2</sub>/CO ratio in Fischer-Tropsch synthesis reaction can be fulfilled using the water-gas shift reaction. This might result in a loss of carbon in the form of CO<sub>2</sub> which affects the yield of liquid fuel. Henceforth, catalysts which are active in the syngas conversion reaction, as well as the syngas ratio adjustment for maximizing fuel range products need to be developed.

Fischer-Tropsch synthesis is the catalytic conversion of syngas into feasible gaseous, liquid hydrocarbons and wax.<sup>3</sup> These can further be transformed into hydrocarbons of lower molecular mass at elevated temperature and pressures in the presence of a catalyst. Several catalysts have been analyzed to produce fruitful results and among them, cobalt (Co) and iron (Fe) based catalyst exhibit good activity and are used industrially.<sup>4–7</sup> It has been observed that cobalt catalysts exhibit high selectivity and activity towards long-chain paraffin and reluctance to WGS reaction, whereas, Fe catalysts promote WGS reaction.<sup>8</sup> Supported bimetallic Fe/Co catalyst is considered to be a feasible option for conversion of low H<sub>2</sub>/CO syngas ratio.<sup>9</sup> WGS reaction is an important reaction for the efficient utilization of coal and biomass-derived syngas. The measure of WGS reaction over the catalyst is the measure of formed CO<sub>2</sub>. The usage ratio, which is a ratio of moles of H<sub>2</sub> converted per mole of CO converted is also important when the catalyst is active for both FTS and WGS. The usage ratio is approximately 2 in absence of WGS reaction. And the value decreases to 0.5 when all the water from FTS

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reaction consumed in WGS reaction. So, the two extreme value of usage ratio (2 and 0.5) suggest the minimum and maximum extent of WGS reaction over the catalyst. Some previous literature showed the utilization of iron-based catalyst in the low  $H_2/CO$  environment.<sup>10–15</sup> Bukur *et al.*,<sup>15</sup> employed commercial precipitated iron catalyst to utilize coal-based syngas with feed ratio 0.67 ( $H_2/CO$ ) at pressure 1.5 MPa and temperature 220–260 °C. At 260 °C, the observed usage ratio was 0.62 at % CO conversion of 87%. However, the carbon loss in term of  $CO_2$  product was 45%. While investigating the activity of iron–manganese based catalyst in a varied range of inlet  $H_2/CO$  ratio, Ding and coworker<sup>12</sup> observed that at lower range of  $H_2/CO$  ratio (0.25–1), hydrogen becomes limiting reactant. Although, the selectivity to long chained hydrocarbon was high due to decreased chain termination probability with low surface concentration of hydrogen, yet the low per pass CO conversion decreased the catalyst performance. At 260 °C, 1.50 MPa and  $H_2/CO = 1$ , the observed CO conversion was 42% with 50%  $C_{5+}$  selectivity. The value of usage ratio 1.03 reveals the occurrence of WGS reaction and maximum possible carbon loss in the form of the  $CO_2$  formation. While investigating the effect of alkali promotion over Fe/AC catalyst in low  $H_2/CO$  (0.9) environment Ma *et al.*,<sup>16</sup> observed that, in the temperature range of 260–280 °C, % CO conversion increases from 50% to 85.7% with almost constant  $CO_2$  selectivity 47%. This is due to the increased WGS activity with alkali promotion. Todici *et al.*, reported that at with an inlet  $H_2/CO$  ratio of 0.67, 84% CO conversion can be achieved with 50%  $C_{5+}$  selectivity. The observed usage ratio was 0.64 with %  $CO_2$  selectivity of 30%. In all the above case, due to their high WGS activity carbon loss was high which affect the yield of desired liquid product. Hence a catalyst system with optimum WGS activity with good FTS activity is desired to maximize the liquid yield in a low  $H_2/CO$  environment with minimum carbon loss. Here, it is hypothesized that the Fe-Co bimetallic catalyst can work synergistically to achieve high activity towards FTS as well as WGS reaction. Some earlier work<sup>9,17,18</sup> have reported the use of bimetallic in FTS reaction, however, the WGS activity of the catalysts have not been taken into the consideration. Tavasoli *et al.*,<sup>17</sup> reported an increase CO conversion up to an addition of 0.5 wt % of Fe into Co-Fe supported on carbon nanotubes. Further increase in Fe loadings decreased the activity. Selectivity did not change at the lower end of iron addition whereas the higher amounts of Fe shift the selectivity to low chained hydrocarbon. Logdberg *et al.*,<sup>9</sup> reported that at a low  $H_2/CO$  ratio ( $\sim 1$ ), iron cobalt bimetallic catalyst with small amounts of iron improved the FTS activ-

ity of monometallic catalyst  $Co/Al_2O_3$ . They did not observe any synergistic effect bimetallic catalysts with respect to hydrocarbon selectivities. The active phases that form during the pre-treatment/reduction stages in the catalyst is an issue as the product distribution is highly dependent on that. Depending on the calcination and reduction condition, the two metals may remain in separate phases or form alloy on the support, or react separately with the support to form mixed oxides. Some authors have reported that at sufficiently high loading FeCo alloy formation takes place on  $TiO_2$  and  $SiO_2$ .<sup>9,19</sup> While investigating the CO adsorption theoretically on Fe-Co bimetallic surface, Rochana *et al.*,<sup>20</sup> used density functional theory to prove that the presence of iron around the cobalt facilitates the CO adsorption on cobalt surface. CO adsorption energy also increases in case of bimetallic Fe-Co phase in comparison to only iron or cobalt phases due to which probability of formation of long-chain hydrocarbon increases and the amount of methane decreases. In a study on silica-supported bimetallic catalyst it was shown that calcined samples consist of separate  $Co_3O_4$  and  $Fe_2O_3$  phases, however, after hydrogen reduction at 500 °C, Fe-Co bimetallic phases was observed with a major portion of  $Co^0$  phase of reduced cobalt which increases FTS activity of catalyst.<sup>21</sup>

In the present study, the bimetallic catalyst was compared with the monometallic catalyst. The extent of WGS reaction can be calculated using usage ratio and  $CO_2$  selectivity. Effect of reaction conditions on the activity of WGS reaction was also investigated to select an optimum condition.

## 2. Experimental

### 2.1 Catalyst preparation

Silica supported iron, cobalt, and bimetallic catalysts were prepared using co-precipitation method. Cobalt nitrate and ferric nitrate were taken as the precursor for cobalt and iron respectively. Tetra ethyl orthosilicate (TEOS) was taken as a precursor for silica. The nitrates were precipitated using liquid  $NH_3$ . The catalyst was characterized using techniques such as BET surface area analyzer, XRD, TPR, HR-TEM, etc. The detailed description of the catalyst preparation method and characterization is mentioned elsewhere.<sup>22</sup> Based on previous research<sup>22</sup> it was observed that 10Fe/20Co/ $SiO_2$  is an appropriate catalyst for further studies. Therefore, in the present studies, the activity of bimetallic (10Fe/20Co/ $SiO_2$ ) and monometallic catalyst (30Co/ $SiO_2$  and 30Fe/ $SiO_2$ ) for FTS and WGS reaction were tested at different reaction condition.

## 2.2 Catalyst performance evaluation

All the catalysts were tested in a continuous fixed bed reactor. The tubular reactor of ID 12.5 mm and length 30 cm was loaded with 3 g of calcined catalyst. The catalyst was mixed with silicon carbide in order to maintain uniform heat distribution. Quartz wool was used to fix the catalyst bed in the center of the tubular reactor. Separate gas cylinders for the gasses hydrogen, carbon monoxide, and nitrogen with 99.99% purity were attached with separate mass flow controller for the controlled flow. At the exit of the reactor, a hot trap at  $100 \pm 2^\circ\text{C}$  and a cold trap at  $0 \pm 1^\circ\text{C}$  were placed to collect the wax and the condensed liquid content of the product. A detailed description of reactor set up is mentioned elsewhere.<sup>22,23</sup> Analysis of exit gas was done in a gas chromatograph equipped with TCD and FID detectors. In the GC-TCD, Carbosieve column was used to analyze H<sub>2</sub>, CO, CO<sub>2</sub>, and CH<sub>4</sub> gasses. Porapak-Q column was used in GC-FID for the analysis of uncondensed gaseous hydrocarbon in exit gas. Qualitative analysis of collected liquid hydrocarbon was done in GCMS and quantitative analysis was done using simulative distillation taking ASTM D2887 method.

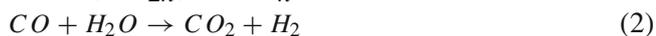
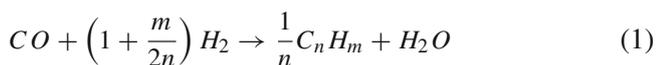
Initially, the catalyst was reduced in-situ in the flow of pure hydrogen (60 mL/min) at  $400^\circ\text{C}$  and 0.1 MPa. After that, the temperature and pressure condition was brought to the reaction conditions. At each reaction condition, initial 12 h was taken to reach steady state conditions and the data was collected for next 60 h of the experimental run. The average of the value of 60 h run was reported in every reaction condition, wherein,  $100 \pm 5\%$  carbon balance was achieved. The percentage CO conversion and hydrocarbon selectivity were using following equations.

$$\text{CO conversion(\%)} = \frac{(\text{moles of CO})_{\text{in}} - (\text{moles of CO})_{\text{out}}}{(\text{moles of CO})_{\text{in}}} \times 100$$

$$\text{Selectivity of product Ci (\%)} = \frac{(\text{moles of carbon in product Ci})}{(\text{moles of carbon in CO reacted})} \times 100$$

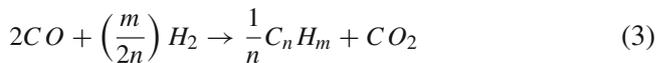
## 2.3 Measurement of WGS activity

WGS activity of the catalyst can be measured by calculating usage ratio. Usage ratio (U) is defined as the mole of H<sub>2</sub> converted per mole of CO conversion.<sup>9,24</sup> The calculation of the U is important when both FT and WGS reactions are occurring simultaneously over catalyst surface. FT and WGS can be written as a parallel reaction (equation 1 and equation 2).



Where m and n are the average number of carbon and hydrogen per molecule of hydrocarbon. If there is no WGS reaction the usage ratio will be  $1 + m/2n$ . However, if we take extreme case wherein, all the water produced from FTS is consumed

in WGS then the overall reaction can be written as



The usage ratio for the reaction will be  $m/4n$ . the value of  $m/n$  in the typical product of FTS varied between 2.12–2.2 therefore if an average value of  $m/n$  is taken i.e., 2.15, the two extreme value of usage ratio will be 2.07 (at no WGS reaction) and 0.53.

WGS reaction is reversible and therefore the comparison between usage ratio at equilibrium conversion and at experimentally achieved conversion is desired. The usage ratio at equilibrium is calculated as explained in the literature.<sup>14,24,25</sup> Equation 4, 5 and 6 were derived using a stoichiometric relation in equation 1, 2 and 3. Here  $a$  and  $b$  in the equation 4, 5 and 6 are moles of H<sub>2</sub>O and moles of CO<sub>2</sub> respectively. For a given value of syngas conversion, H/C ratio of the liquid i.e.  $\gamma$  and inlet molar feed ratio  $F$ , the value of  $a$  can be calculated from equation 5. The value of  $b$  can be calculated from equation 6 where the value of equilibrium constant  $K_{\text{WGS}}$  for a given temperature can be calculated from equation 7. Hence the value of usage ratio at equilibrium can be calculated using equation 4 and value of  $a$  and  $b$ .

$$U = \frac{[(1 + \gamma/2)a - b]}{(a + b)} \quad (4)$$

$$X_{\text{CO}+\text{H}_2} = \frac{(2 + \gamma/2)a}{(1 + F)} \quad (5)$$

$$K_{\text{WGS}} = \left(\frac{P_{\text{CO}_2} P_{\text{H}_2}}{P_{\text{CO}} P_{\text{H}_2\text{O}}}\right)_{\text{eq}} = \frac{b[F + b - (1 + \gamma/2)a]}{(a - b)(1 - a - b)} \quad (6)$$

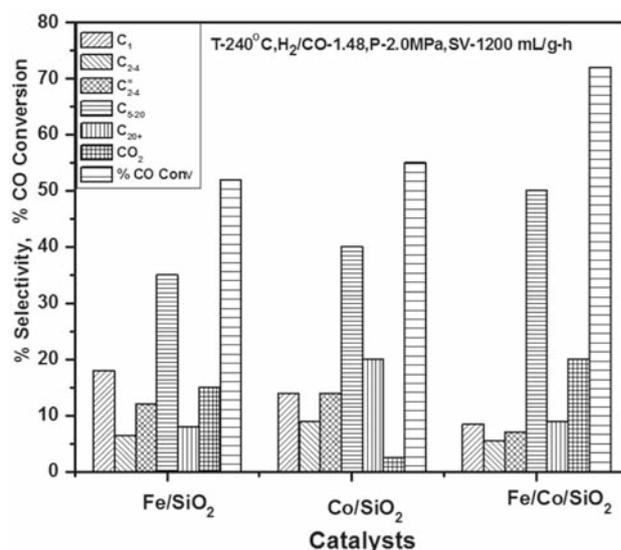
$$K_{\text{WGS}} = 0.0132 \exp\left(\frac{4578}{T}\right) \quad (7)$$

## 3. Results and Discussion

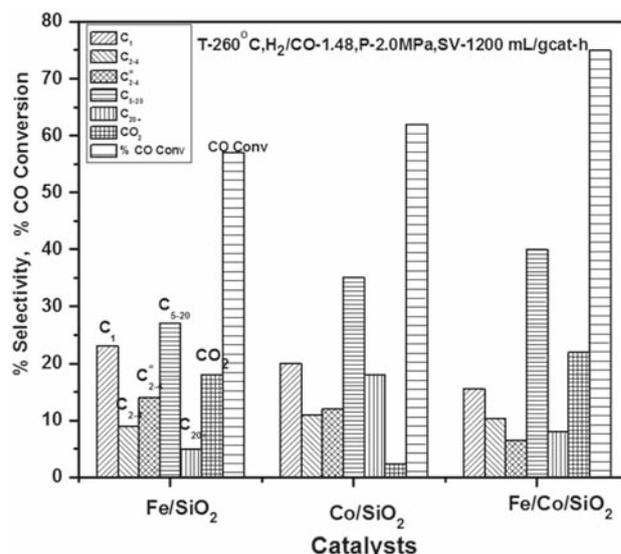
The activity of bimetallic catalyst (10Fe/20Co/SiO<sub>2</sub>) was compared with the monometallic catalysts (30Fe/SiO<sub>2</sub> and 30Co/SiO<sub>2</sub>) at similar reaction conditions. Catalysts were tested at T: 240–260 °C, P-2.0 MPa, H<sub>2</sub>/CO: 1.48 and space velocity 1200 mL/gcat-h. In our previous work it was observed that, at 220 °C, the activity of Fe-Co bimetallic catalyst towards WGS reaction was low with H<sub>2</sub>/CO usage ratio of 2.06. At 280 °C, WGS activity was high with the usage ratio of 1.55, however, the loss of carbon in form of CO<sub>2</sub> was high.<sup>22</sup> Henceforth, the temperatures 240 °C and 260 °C were taken for the further investigation of the performance of mono and bimetallic catalysts.

### 3.1 Catalyst activity test

Figure 1 and 2 show the product distribution and % CO conversion over all the three catalysts at temperature 240 °C and 260 °C. The results reveal that the % CO conversion was higher in the case of the bimetallic catalyst at both the temperatures. At 240 °C, % CO conversion was 52, 55 and 72 for the catalysts Fe/SiO<sub>2</sub>, Co/SiO<sub>2</sub> and Fe/Co/SiO<sub>2</sub> respectively. The selectivity to the C<sub>5+</sub> was highest 70% over the monometallic cobalt catalyst. However, the catalyst also Cobalt catalyst showed highest C<sub>5+</sub> selectivity with maximum (20%) wax formation. Selectivity to C<sub>5+</sub> over iron and Fe-Co bimetallic catalyst was 47% and 60% respectively. However, the desired product range i.e., C<sub>5</sub>–C<sub>20</sub> was maximum (50%) in the case of the bimetallic catalyst. This can be attributed to the formation of some bimetallic phases which also facilitates CO adsorption and hydrogenation. Product distributions in the gaseous phase show selectivities of paraffin and olefin in the range of C<sub>2</sub>–C<sub>4</sub>. The olefin+paraffin selectivity in C<sub>2</sub>–C<sub>4</sub> were 14.7%, 22% and 12.5% over the catalysts Fe/SiO<sub>2</sub>, Co/SiO<sub>2</sub> and Fe/Co/SiO<sub>2</sub> respectively. Olefin to paraffin ratio is an important parameter for the identification of hydrogenation tendency of lower hydrocarbon. Olefin to paraffin ratio was maximum (1.84) over Fe/SiO<sub>2</sub> catalyst and was observed to be 1.27 over the bimetallic catalyst. The formation of methane is a loss of carbon, so it is an undesired product of FTS reaction. Highest methane selectivity (18%) was observed over the monometallic iron catalyst whereas it was lower (8.5%) over Fe-Co bimetallic catalyst. Over cobalt catalyst Co/SiO<sub>2</sub>, methane selectivity was 14%. The WGS activity can be examined by calculating CO<sub>2</sub> selectivity and the usage ratio U. At 240 °C, the selectivity to CO<sub>2</sub> was very low (2.5%) over Co/SiO<sub>2</sub> catalyst due to its low WGS reaction activity and also the usage ratio was 2.19. On the other hand, Fe/SiO<sub>2</sub> catalyst showed high activity to the WGS reaction with the usage ratio of 1.64. The usage ratio over Fe-Co bimetallic catalyst was 1.61. Also, the selectivity to the CO<sub>2</sub> over the catalysts Fe/SiO<sub>2</sub> and Fe-Co/SiO<sub>2</sub> were 15% and 20% respectively. Henceforth, the carbon loss in the form of CO<sub>2</sub> was high in case of the bimetallic catalyst. At 260 °C, the WGS shift activity increases as the rate of WGS reaction increases with the temperature. The H<sub>2</sub>/CO usage ratio decreased from 1.64 to 1.5 and selectivity to CO<sub>2</sub> increased from 15% to 18% over Fe/SiO<sub>2</sub> catalyst as temperature increases from 240 to 260 °C. Similarly, the H<sub>2</sub>/CO usage ratio decreased from 1.61 to 1.57 and selectivity to CO<sub>2</sub> increased from 20% to 22% over Fe/Co/SiO<sub>2</sub> catalyst as temperature increases. CO conversion was observed to be 57% and 75% with %



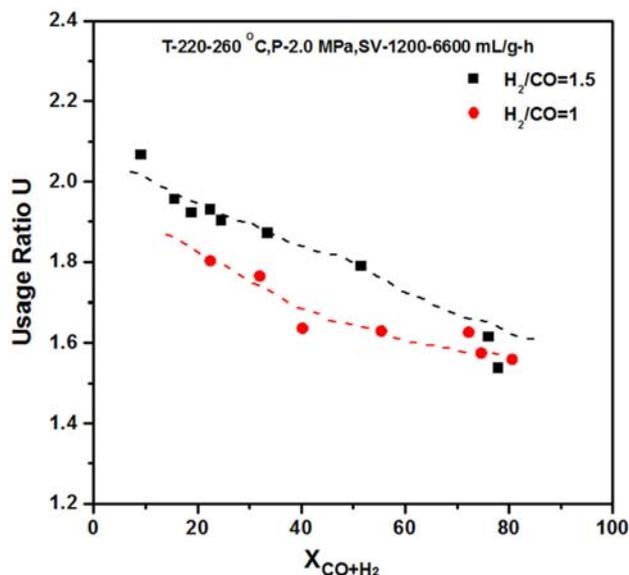
**Figure 1.** % CO conversion and product distribution at T-240 °C, H<sub>2</sub>/CO-1.48, P-2.0MPa, SV-1200 mL/g-h.



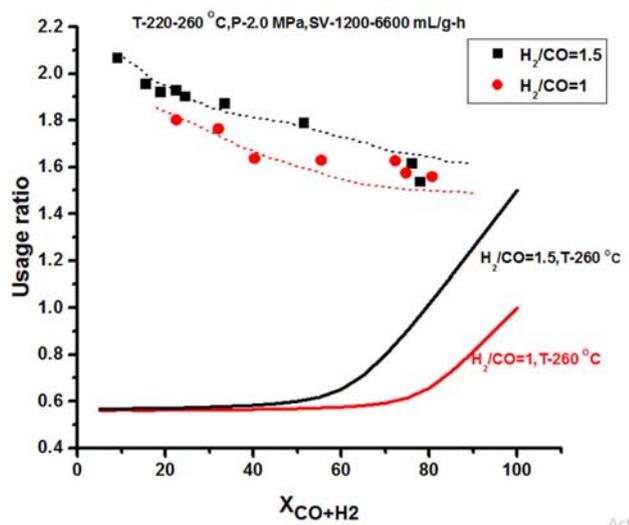
**Figure 2.** % CO conversion and product distribution at 260 °C T-260 °C, H<sub>2</sub>/CO-1.48, P-2.0MPa, SV-1200 mL/g-h.

C<sub>5</sub>–C<sub>20</sub> selectivities of 28% and 40% over Fe/SiO<sub>2</sub> and Fe-Co/SiO<sub>2</sub> catalysts. Above discussion reveals that the bimetallic Fe-Co/SiO<sub>2</sub> catalyst is an appropriate catalyst for maximum liquid yield with optimum WGS activity. Although, the carbon loss in the form of CO<sub>2</sub> was 4 % higher than the monometallic catalyst, yet the loss can be compensated by lower methane formation with a comparison of the same catalyst. Henceforth, the catalyst was selected for further investigations.

In the next section, the WGS shift activity was tested at varying reaction conditions over Fe-Co/SiO<sub>2</sub> catalyst. The value of usage ratio was calculated to examine the extent of WGS reaction various conditions.



**Figure 3.** Effect of syngas conversion level and feed  $H_2/CO$  ratios on usage ratios over  $10Fe/20Co/SiO_2$  catalyst.

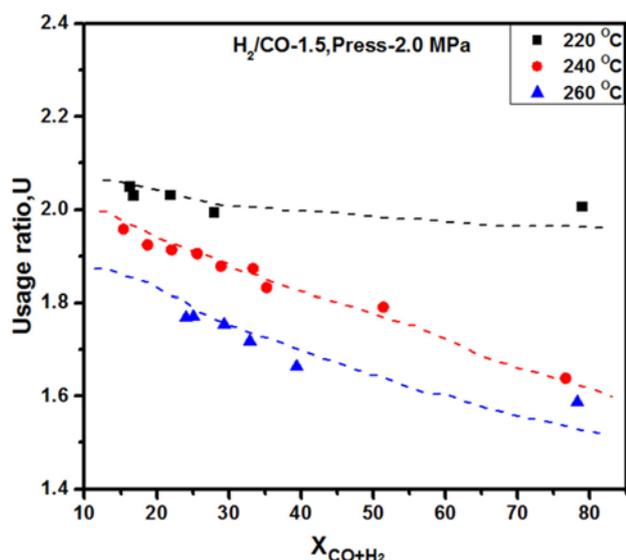


**Figure 4.** Comparison of experimental data with equilibrium predicted data for usage ratios at different syngas conversion level.

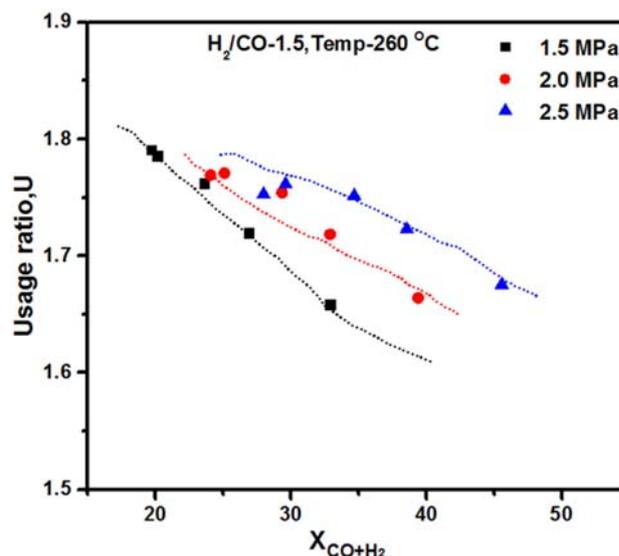
### 3.2 Effect of composition on WGS activity

Figure 3 shows the effect of feed composition on the water gas shift reaction over Fe-Co bimetallic catalyst. The variation of usage ratio with syngas  $X_{H_2+CO}$  conversion at different initial feed gas composition was shown. Also, Figure 4 shows the comparison of usage ratio predicted from equilibrium calculation. The continuous line in Figure 4 shows the value of usage ratio at various syngas conversion when the WGS reaction was at its equilibrium at the particular temperature. The values were calculated using equation 4 to 7 as described in

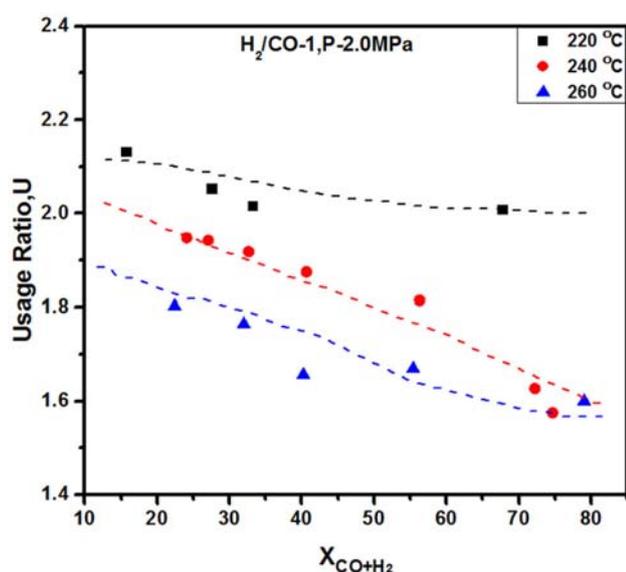
section 3. The equilibrium constant of WGS reaction changes from 51.9 to 142.3 as temperature decreases from 280 to 220 °C. Also, the value of  $\gamma$  merely changes as temperature changes from 280 to 220 °C. Henceforth, the equilibrium calculation was done at 260 °C wherein the value of the equilibrium constant for WGS reaction was 70.9. The experimental data shown in Figure 3 and 4 were taken from our previous work<sup>22,26</sup> in a range of experimental condition (T-220–260 °C, P-2.0 MPa, SV-1200–6600 mL/g-h). Results reveal that the at lower syngas conversion (up to 45%) the usage ratio is independent of feed ratio. However, on further increase in conversion, usage ratio increases rapidly. However, the experimental trends suggest that the usage ratio is significantly different from equilibrium predicted value at low conversion. At low conversion, the partial pressure of water remains so the rate of WGS reaction remains low and a higher value of usage value ( $\sim 2$ ) was observed. The decrease in usage ratio is attributed to the increasing rate of WGS reaction. The trend shown in Figure 4 is consistent with trend suggested by Bukur *et al.*,<sup>27</sup> and Satterfield *et al.*<sup>25</sup> In the present experimental data over a bimetallic catalyst, usage ratio decreases from 2 to 1.53 as syngas conversion reaches up to 78%. In the case of precipitated iron catalyst ( $100Fe/5Cu/4.2K/25SiO_2$ , wt %) with an initial feed ratio of 0.67, Bukur *et al.*,<sup>15</sup> observed a decrease in usage ratio from 1.33 to 0.6 which almost equal to the equilibrium value. With initial feed ratio of 2.0, they reported the same trend of usage ratio which increased after reaching the equilibrium value, at 55% conversion. This is because at higher conversion WGS reaction approaches towards equilibrium<sup>8</sup>. The conversion at which this transition takes place depends on reaction condition and initial feed ratio. With initial feed ratio of 0.65 to 0.67 and temperature of 250 to 265 °C, Zimmerman *et al.*,<sup>28</sup> observed the same trend of decreasing usage ratio over the  $100Fe/0.3Cu/0.2K$  catalyst. The experimental value of usage ratio reaches the equilibrium value at 60% conversion. In Figure 4 the experimental data suggest that the value of usage ratio will reach the equilibrium value at about 90% conversion of syngas with feed ratio 1.5. The decreasing trend of usage ratio was similar at both feed ratios (1 and 1.5) whereas the extent of WGS reaction was high at low in let feed ratio i.e., 1. In the case of feed ratio of 1 the data predict that the value of usage ratio will meet the equilibrium at much higher conversion level. However, at this feed ratio, it is difficult to achieve higher per pass conversion as the hydrogen becomes limiting reagent. Hence, at the lower range of feed ratio (1–1.5), WGS reaction remains far from equilibrium over Fe-Co bimetallic catalyst. This is because only a part of the bimetallic catalyst is active for WGS reaction whereas



**Figure 5.** Effect of temperature on usage ratio over Fe-Co/SiO<sub>2</sub> catalyst at H<sub>2</sub>/CO -1.5, P-2.0 MPa.



**Figure 7.** Effect of pressure on the usage ratio over Fe-Co/SiO<sub>2</sub> catalyst at H<sub>2</sub>/CO -1.5, T = 260 °C.



**Figure 6.** Effect of temperature on usage ratio over Fe-Co/SiO<sub>2</sub> catalyst at H<sub>2</sub>/CO -1, P-2.0 MPa.

the precipitated catalysts are equally active for FT as well as WGS reaction.

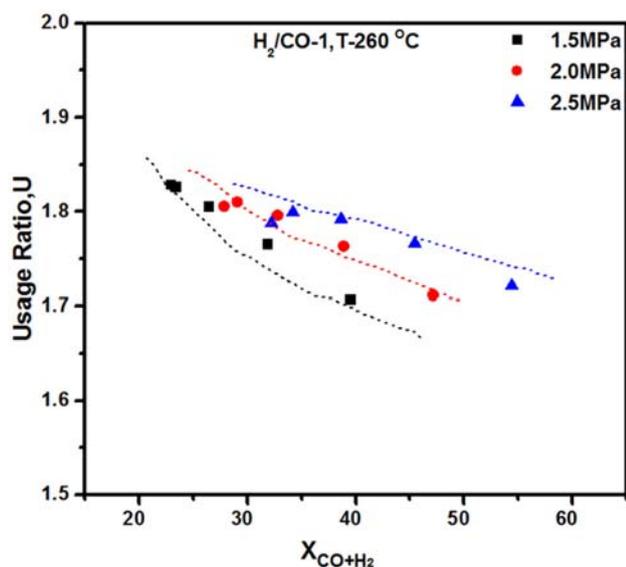
### 3.3 Effect of temperature on WGS activity

Figures 5 and 6 show the effect of temperature on water gas shift activity. The experimental data compare the results over Fe-Co/SiO<sub>2</sub> catalyst at a feed ratio of 1 and 1.5. At temperatures 220, 240 and 260 °C usage ratio decreases with increasing % syngas conversion. Also, usage ratio decreases with increasing temperature at constant conversion. The change in usage ratio

was more pronounced at 240 °C at which the usage ratio decreases from 1.91 to 1.63. At low temperature (220 °C), the change in usage ratio is not significant. This is due to the low rate of WGS reaction at this temperature. Bukur *et al.*,<sup>8</sup> observed the same trend over the precipitated iron catalyst. However, at higher syngas conversion (< 45%) they observed that the effect of temperature was not significant. They suggested that at higher conversion WGS reaction reaches an equilibrium which in turn minimizes the effect of temperature. In the present study as discussed in the earlier section, the WGS reaction is far from equilibrium, so the effect of temperature is evident at all conversion levels. Further, at low syngas conversion, catalyst showed low WGS activity at all the three temperatures wherein the value of usage ratio was almost ~ 2. As discussed earlier, this is the kinetic effect of WGS reaction. At the feed ratio of 1, the trend is almost same except at higher syngas conversion. At 240 °C, the change in H<sub>2</sub>/CO usage ratio with conversion was more pronounced at higher conversion (< 60%). However, due to less number of the data point, it is not evident at 260 °C. Therefore, the optimum range of conversion for optimum WGS activity is 70 to 80% for both the initial feed ratio.

### 3.4 Effect of pressure on WGS activity

Effect of varying pressure (1.5 to 2.5 MPa) on WGS activity of the catalyst was investigated at different inlet feed ratio 1 and 1.5 (Figure 7 and 8). Usage ratio decreases with increasing syngas conversion at each pressure. At a particular conversion, usage ratio



**Figure 8.** Effect of pressure on the usage ratio over Fe-Co/SiO<sub>2</sub> catalyst at  $H_2/CO = 1$ ,  $T = 260^\circ C$ .

decreases with decreasing pressure. Which suggest that WGS shift reaction is favored a lower pressure. Since the equilibrium of WGS reaction is independent of pressure, the increased WGS activity at decreasing pressure can be related to the FTS activity at that pressure. Both WGS and FTS reactions occur simultaneously over the catalyst surface at different active sites.<sup>29</sup> With the decreasing pressure, syngas conversion and FT rates decrease. Henceforth, the available CO will consume in WGS reaction. The similar trend of usage ratio with pressure was also observed by Donnelly and Satterfield<sup>11</sup> over commercial precipitated iron catalyst. The data suggest a lower pressure for maximum WGS activity, however, at low pressure, the FTS activity, and  $C_{5+}$  selectively will also decreased. Therefore a pressure of 2.0MPa is chosen as optimum pressure for both WGS and FTS activity.

#### 4. Conclusions

In order to utilize low  $H_2/CO$  syngas into liquid fuel production, Fe-Co bimetallic catalyst system was implied in FTS process. WGS reaction plays a crucial role to maintain the desired stoichiometric ratio of  $H_2$  and CO. FTS and WGS activity was tested over 10Fe/20Co/SiO<sub>2</sub> and monometallic catalysts (30Co/SiO<sub>2</sub> and 30Fe/SiO<sub>2</sub>). The value of usage ratio explains the extent of WGS reaction and enhancement of the  $H_2$  content. The activity of the bimetallic catalyst for FTS was higher than that of the monometallic catalyst. At 240 °C % CO conversion and  $C_{5+}$  selectivity were 72% and 60% respectively.

Further, WGS activity over 10Fe/20Co/SiO<sub>2</sub> was calculated through usage ratio which was observed to be 1.61 at 240 °C with initial feed ratio 1.5. On comparing the results with equilibrium values of WGS reaction it was observed that the over bimetallic catalyst WGS reaction is far from equilibrium. Effect of temperature pressure and feed composition on WGS activity was investigated. Results reveal that Usage ratio depends on syngas conversion. Usage ratio decreases with syngas conversion at constant temperature and pressure. Also, the value of usage ratio decreases with increasing temperature and decreasing pressure at constant syngas conversion.

#### References

1. van Steen E and Claeys M 2008 Fischer-Tropsch catalysts for the biomass-to-liquid process *Chem. Eng. Technol.* **31** 655
2. Hamelinck C N, Faaij A P C, den Uil H and Boerrigter H 2004 Production of FT transportation fuels from biomass; technical options, process analysis and optimisation, and development potential *Energy* **29** 1743
3. Davis B H 2001 Fischer-Tropsch synthesis: Current mechanism and futuristic needs *Fuel Process. Technol.* **71** 157
4. Dry M E 1996 Practical and Theoretical Aspects of the Catalytic Fischer-Tropsch Process *Appl. Catal. A Gen.* **138** 319
5. Dry M E 1999 Fischer-Tropsch reactions and the environment *Appl. Catal. A Gen.* **189** 185
6. Dry M E 1990 Fischer-Tropsch process. Commercial aspects *Catal. Today* **6** 183
7. Dry M E 2002 The Fischer-Tropsch process: 1950-2000. *Catal. Today* **71** 227
8. Bukur D B, Todic B and Elbashir N 2016 Role of water-gas-shift reaction in Fischer-Tropsch synthesis on iron catalysts: A review *Catal. Today* **275** 66
9. Lögdberg S, Tristantini D, Borg Ø, Ilver L, Gevert B, Jaras S, Blekkan E A and Holmen A 2009 Hydrocarbon production via Fischer-Tropsch synthesis from  $H_2$ -poor syngas over different Fe-Co/ $\gamma - Al_2O_3$  bimetallic catalysts *Appl. Catal. B Environ.* **89** 167
10. Bukur D B, Patel A and Lang X 1990 Fixed bed and slurry reactor studies of Fischer-Tropsch synthesis on precipitated iron catalyst *Appl. Catal.* **61** 329
11. Donnelly T J and Satterfield C N 1989 Product distributions of the Fischer-Tropsch synthesis on precipitated iron catalysts *Appl. Catal.* **52** 93
12. Ding M, Yang Y, Li Y, Wang T, Ma L and Wu C 2013 Impact of  $H_2/CO$  ratios on phase and performance of Mn-modified Fe-based Fischer Tropsch synthesis catalyst *Appl. Energy* **112** 1241
13. Kim K, Kim Y, Yang C, Moon J, Kim B, Lee J, Lee U, Lee S, Kim J and Eom W 2013 Long-term operation of biomass-to-liquid systems coupled to gasification and Fischer-Tropsch processes for biofuel production *Biorenew. Technol.* **127** 391

14. Bukur D, Lech N and Lang X 1994 Fischer-tropsch synthesis in a stirred tank slurry reactor *Chem. Eng. Sci.* **49** 4615
15. Bukur D B 2006 Kinetics of slurry phase Fischer-Tropsch synthesis *DOE Final Rep. Grant No. DE-FG26-02NT41540*
16. Ma W, Kugler E L and Dadyburjor D B 2007 Potassium effects on activated-carbon-supported iron catalysts for Fischer-Tropsch synthesis *Energy Fuels* **21** 1832
17. Tavasoli A, Trépanier M, Abbaslou M, Malek R, Dalai A K and Abatzoglou N 2009 Fischer-Tropsch synthesis on mono- and bimetallic Co and Fe catalysts supported on carbon nanotubes *Fuel Process. Technol.* **90** 1486
18. Ma X, Sun Q, Ying W and Fang D 2009 Effects of the ratio of Fe to Co over Fe-Co/SiO<sub>2</sub> bimetallic catalysts on their catalytic performance for Fischer-Tropsch synthesis *J. Nat. Gas Chem.* **18** 232
19. Duvenhage J D and Coville J N 2005 Fe:Co/TiO<sub>2</sub> bimetallic catalysts for the Fischer-Tropsch reaction part 3: The effect of Fe:Co ratio, mixing and loading on FT product selectivity *Appl. Catal. A-Gen.* **289** 231
20. Rochana P and Wilcox J A 2011 Theoretical study of CO adsorption on FeCo(100) and the effect of alloying *Surf. Sci.* **605** 681
21. de la Peña O Víctor A, Álvarez-Galván M C, Campos-Martin J M, Menéndez N N, Tornero J D and Fierro J L G 2006 Surface and structural features of Co-Fe oxide nanoparticles deposited on a silica substrate *Eur. J. Inorg. Chem.* **2006** 5057
22. Sonal, Pant K K and Upadhyayula S 2017 Synthesis of C<sub>5+</sub> hydrocarbons from low H<sub>2</sub>/CO ratio syngas over silica supported bimetallic Fe-Co catalyst *Catal. Today* **291** 133
23. Mohanty P, Pant K K, Parikh J and Sharma D K 2011 Liquid fuel production from syngas using bifunctional CuO – CoO – Cr<sub>2</sub>O<sub>3</sub> catalyst mixed with MFI zeolite. *Fuel Process. Technol.* **92** 600
24. Todic B, Nowicki L, Nikacevic N and Bukur D B 2016 Fischer-Tropsch synthesis product selectivity over an industrial iron-based catalyst: Effect of process conditions. *Catal. Today* **261** 28
25. Satterfield C N and Huff G A 1982 usefulness of a slurry/type fischer-tropsch reactor for processing synthesis gas of low hydrogen-carbon monoxide ratios *Can. J. Chem. Eng.* **60** 159
26. Sonal, Kondamudi K, Pant K K and Upadhyayula S 2017 Synergistic effect of Fe-Co bimetallic catalyst on FTS and WGS activity in the Fischer-Tropsch process: A kinetic study *Ind. Eng. Chem. Res.* **56** 4659
27. Bukur D B and Brown R F 1987 Fischer-Tropsch synthesis in a stirred tank slurry reactor and reaction rates *Can. J. Chem. Eng.* **65** 604
28. Zimmerman W H and Bukur D B 1990 Reaction kinetics over iron catalysts used for the Fischer-Tropsch synthesis *Can. J. Chem. Eng.* **68** 292
29. van der Laan G P and Beenackers A A C M 2000 Intrinsic kinetics of the gas-solid Fischer-Tropsch and water gas shift reactions over a precipitated iron catalyst *Appl. Catal. A Gen.* **193** 39