

B. Group II Alkali Metal Promoted Iron Fischer-Tropsch Synthesis Catalysts

Abstract

The effects of group II alkali metals (barium, beryllium, calcium and magnesium) and potassium promoted iron catalysts on Fischer-Tropsch Synthesis (FTS) product selectivity, reaction conversions and productivity was investigated. Iron FTS catalysts promoted with group II alkali metals produced lower CO conversions, less diesel and heavier fraction products than potassium promoted catalysts. Slightly higher alpha value was observed for potassium promoted catalysts than group II alkalis promoted catalysts. Beryllium and barium promoted iron catalysts, however, showed the best stability among all alkali metal promoted catalysts based on the results of over 500 hours of FTS.

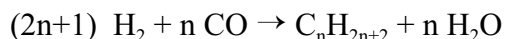
It is also found that a potassium promoted iron catalyst produced higher water gas shift and FTS activities than group II alkali promoted catalysts. Among the group II alkalis, barium showed the highest water gas shift activity. All group II alkalis generated similar hydrocarbon, CO₂ and methane rates. It was also shown that group II alkali promoted catalysts produced similar oxygenates, except that Ba yielded more ethanol and Mg and more normal propanol than other group II alkali metals. Olefin ratio, however, did not reveal any difference among group II alkalis and potassium. Higher WGS activity for potassium promoted catalysts may cause a lower carbon utilization rate than group II alkalis because a significant amount of CO is consumed in the water gas shift reaction.

Introduction

Fischer-Tropsch synthesis process converts CO and H₂ to liquid fuels, and the feedstock, a mixture of CO and H₂, can be produced from coal gasification. As a cleaner raw material source than coal, natural gas can also be used for Fischer-Tropsch synthesis. One of the advantages of FTS

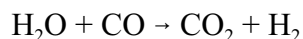
is that the process can be designed to produce either gasoline, diesel and/or chemicals. There are two types of operational modes: the low temperature FTS, which produces mostly wax, and the high temperature FTS, which is designed for production of gasoline and alkenes.

In an FTS process, the hydrocarbon is produced from CO and H₂, which can be expressed as



where n is defined as $n = 1/(1-\alpha)$ or it can be rearranged as $\alpha = 1 - (1/n)$ (1).

When an iron catalyst is used for FTS reactions, the water gas shift (WGS) reaction can also occur. This side reaction consumes CO and water produced in the FTS process to produce additional hydrogen.



Potassium has long been used as a promoter for iron catalysts to increase the alkene yield and to decrease the CH₄ selectivity (2). It is believed that potassium can also increase FTS and water gas shift reaction activity (3).

Iron FTS catalysts promoted with 1.44 atomic % Ggroup II alkali (beryllium, magnesium, calcium and barium) were used in this study. A simulated synthesis gas of 40% hydrogen and 60% carbon monoxide was fed to a one-liter continuous stirred tank reactor (CSTR). Liquid oil, water, heavy wax and gas samples from the FTS reaction were collected and analyzed with gas chromatographs (GC). Reaction conversion, product selectivity and other results were calculated using a database system. The influence of alkali on product selectivity, productivity, water gas shift and FTS activity are compared with results obtained from FTS reactions using a potassium promoted iron catalyst.

Experimental

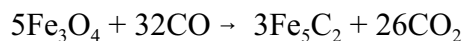
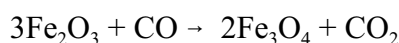
Preparation of alkali metal promoted catalysts

Four iron catalysts promoted with Be, Ba, Ca and Mg and one with potassium were prepared and tested in this study. The promoter was added at a 1.44:100 of promoter to iron atomic ratio. Precipitated iron catalysts were prepared with tetraethyl orthosilicate, iron nitrate, potassium carbonate and copper nitrate. Ferric nitrate solution was first prepared by dissolving $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in distilled and deionized water, and the amount of orthosilicate needed to make Si:Fe of 4.6:100 atomic ratio was added. The mixture was stirred vigorously until the tetraethyl orthosilicate has hydrolyzed. The tetraethyl orthosilicate and iron nitrate mixture was then added to a CSTR precipitation vessel together with ammonium hydroxide. By maintaining the slurry pH at 9 and an average residence time of 6 minutes, a base catalyst material with an iron to silicon molar ratio of 100:4.6 was obtained. The slurry exiting the CSTR was filtered using a vacuum drum filter and then washed twice with deionized water. The final filter cake was dried in an oven with flowing air at 110°C for 24 hours. The catalyst was crushed to approximately $60\ \mu\text{m}$ and calcined in a 350°C oven under an air flow for 4 hours.

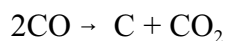
In this study, the iron catalyst was impregnated with an aqueous nitrate solutions of barium, beryllium, calcium or magnesium for alkali metal promoted catalysts, and K_2CO_3 solution for the potassium promoted catalyst. The alkali metal or potassium solution was added to obtain a promoter to iron atomic ratio of 1.44:100. The catalysts was dried at 110°C overnight with good mixing following the impregnation. Thus, catalysts promoted with four group II alkali metals and one with potassium were prepared for FTS studies.

In-situ catalysts activation

The iron catalyst needs to be activated with either H₂, CO or synthesis gas. Activation procedures can have a significant effect on the selectivity and activity of iron catalysts (6, 7). It was reported that catalysts activated with CO yielded higher long-chain hydrocarbons than syngas and H₂ activated catalysts. In addition, activation conditions may also influence the performance of the iron catalyst. In this study, the promoted iron catalysts were pretreated with CO at 270°C and 1.2 MPa for 24 hours. The reduction of Fe₂O₃ with CO occurs in two steps:



In addition, CO₂ may be formed by the Boudouard reaction:



Previous work in our lab showed that approximately 50 % to 75% more carbon was present in the catalyst mass after 24 hrs than was needed to form Fe₅C₂ (8). Gradual oxidation of Fe₅C₂ to Fe₃O₄ was observed when iron catalyst was used in FTS. The results showed that at the end of the run an unpromoted iron catalysts had been completely oxidized to Fe₃O₄.

Reactor system

A one-liter continuous stirred tank reactor (CSTR) was used in this study (Figure 1). A sintered metal filter was installed to allow the removal of the wax from the catalyst slurry. The wax sample was extracted through the internal filter and collected in the hot trap (200°C). The vapor products and unconverted reactants passed continuously to a warm trap (100°C) and cold trap (0°C) that were used to collect oil, light wax and water samples. Tail gas from the cold trap was analyzed with an HP quick GC.

A gas mixer equipped with a CO and an H₂ mass controller was used to provide a simulated synthesis gas. After the catalysts was activated with CO, syngas was introduced at a rate of 10 NL/hr/gram-catalyst. Then the gas space velocity was varied in the range of 3 to 60 sl/hr/g-Fe to collect kinetic data. Other reaction conditions were maintained at 270°C, 1.2 MPa and a stirrer speed of 750 rpm.

Product sampling and analysis

Daily gas, water, oil, light and heavy wax samples were collected and analyzed. Table 1 gives the summary of the instruments for gas and liquid product analysis. A heavy wax sample was taken from the 200°C hot trap connected to the filter. Vapor phase above the slurry phase passed to the warm (100°C) and the cold (0°C) traps outside the reactor. The light wax and water mixture was collected from the warm trap and an oil plus water sample from the cold trap. Tail gas from the cold trap was analyzed with an online HP Quad Series Micro GC. Molar compositions of C₁-C₇ olefins and paraffins were thus obtained. Hydrogen and carbon monoxide conversions were calculated based on the gas product GC analysis results and the gas flow measured at reactor outlet. Hydrogen, carbon monoxide and syngas conversion were obtained using the following formula:

$$\text{Conversion} = \frac{(N_{\text{in}} - N_{\text{out}})}{N_{\text{in}}} \times 100\%$$

The oil and light wax samples were mixed before being analyzed with an HP 5790A GC. The heavy wax was analyzed with an HP5890 Series II Plus GC while the water sample was analyzed with an HP5890 GC.

Results and Discussion

Effect of Promoter on Fischer-Tropsch synthesis activity

In this study, all FTS reactions were first conducted using base reaction conditions of 270°C, 1.2 MPA and at a space velocity of 10 sl/h/g-Fe. Following this period, the space velocity was changed at intervals from 3 to 50 sl/h/g-Fe. Simulated synthesis gas was prepared from a mixture of CO and H₂ with a molecular ratio of 1:0.7. Figure 2 shows the results of FTS reactions using catalysts promoted with group II alkali metals (Ba, Be, Ca and Mg) and potassium. It is shown from Figure 2 that the potassium promoted catalyst yielded the highest overall CO conversion of 70%. Calcium promoted FTS catalyst yielded the lowest initial conversion of 47% while all other group II alkali metal promoted catalysts produced a initial CO conversions over 50%.

The deactivation rates (%/day) for these five catalysts were obtained from the CO conversion results of over 500 hours of FTS reaction. As indicated in Figure 3, beryllium and barium yielded a low deactivation rate of 0.07 and 0.15% CO conversion per day, respectively, while the values for potassium and calcium were 0.91 and 0.88, respectively. Magnesium promoted catalysts showed the poorest stability (2.24%/day CO conversion) among all five catalysts tested.

After the CO conversion reached a stable level under the initial base conditions, syngas space velocity was varied from 3 to 50 sl/h/g-Fe. Figure 4 shows the results of CO conversions at various space velocity (SL/g-Fe/h) or space time (h•g-Fe/SL). The data indicate that at low space times, all group II alkali metal promoted catalysts produced a CO conversion that is similar to the potassium promoted catalyst. At a high or mid-range space time, however, different catalysts showed different CO conversions. The potassium promoted catalyst yielded the highest overall CO conversion at both a high and a medium space time. At a high space time,

magnesium promoted iron catalyst yielded a conversion similar to the potassium promoted catalyst. Both beryllium and barium promoted catalysts showed nearly the same CO conversions over the full range of the space time of 3 to 50 h•g-Fe/sl. Calcium promoted iron produced the lowest CO conversion at a space time of over 0.1 h•g-Fe/SL.

Effect on Fischer-Tropsch synthesis selectivity

Figure 5 shows the rates of CO₂, hydrocarbon, methane and water obtained from FTS reactions for the iron catalysts promoted with Group II alkali metals and potassium under the base conditions. All five catalysts produced the same methane rate of 0.1 g/h/g-Fe, suggesting that the nature of different alkali metals did not affect methane yield of Fischer-Tropsch synthesis. Potassium produced the highest CO₂ and hydrocarbon rates but the lowest water production rate; therefore, higher FTS and water gas shift activities were obtained from potassium promoted iron catalyst than those from any Group II alkali metal promoted catalysts. All Group II alkali metals produced similar CO₂, hydrocarbon and methane rates. Both calcium and magnesium produced a water rate of 1.1 g/h/g-Fe while both beryllium and barium yielded a water rate of 0.4 g/h/g-Fe.

Oxygenate results were obtained from water phase products analyzed with an HP 5890 GC. Figure 6 gives the oxygenates data from FTS reactions catalyzed with four Group II alkali metal (Ba, Ba, Ca and Mg) promoters. It shows that all catalysts produced similar aldehyde, i-propanol and acetone rates. The barium promoted catalyst yielded the highest methanol and ethanol content while magnesium promoted catalyst produced the most normal propanol. The principal products from the water phase were ethanol (~2%), methanol (~1%) and normal propanol (~0.5%). Less than 0.08% of aldehyde, 0.03% of iso-propanol and 0.25% of acetone were present in the water phase products.

The olefin ratio was calculated using the following equation:

$$\text{Olefin ratio} = \frac{\text{Olefin}}{(\text{Olefin} + \text{Paraffin})} \times 100\%$$

Figure 7 shows that all Group II alkali metal and potassium promoted catalysts yielded a similar C₃ and C₄ olefin ratios of 0.83-0.85.

The distribution of different liquid fractions are given in Figure 8. It is shown that potassium produced more C₅₊, C₁₂₊, C₁₉₊ and C₁₂-C₁₈ fractions and therefore less gas (methane and C₂-C₄) and gasoline (C₅-C₁₁) products than any Group II alkali metal promoted catalyst. Among the Group II alkali metal promoters, magnesium produced the largest gasoline fraction (44.9%) and the smallest C₁₉₊ fraction. For Mg, Ca and Ba promoted catalysts, similar gas (C₁ and C₂-C₄) and diesel fractions were obtained. The gasoline fraction (C₅-C₁₁) decreased and both C₁₂₊ and C₁₉₊ fractions increased as the atomic weight of the promoter metal increased. However, the potassium promoted catalyst produced the largest heavy fractions (C₁₉₊), and the C₁₉₊ yields and these decreased in the order of Ba>Be>Ca>Mg among the Group II alkali metal promoters.

Figure 9 shows the CO₂ selectivity obtained from FTS reactions catalyzed by Group II alkali metal promoted catalysts. In this study, space time was varied in the range of 0.02 to 0.33 hr-g(Fe)/l, i.e., space velocity in the range of 3 to 50 l/h/g(Fe). Potassium produced more CO₂ than any alkali metals over the range of space times although the CO₂ selectivity lines converged at a space time of 0.1. Both magnesium and calcium promoted catalysts produced a lower CO₂ yield than beryllium and barium promoted catalysts. At a low space velocity, the barium promoted catalyst generated the most CO₂ while all the other group II alkali metal promoted catalysts produced similar CO₂ selectivities of 40-42%. Therefore, calcium and magnesium provided a better carbon utilization than beryllium and barium promoted catalysts. The potassium promoted catalyst produced a lower carbon utilization rate than any Group II alkali metal

promoter. The higher CO₂ production from potassium promoted catalyst also shows that potassium yielded a better water gas shift activity.

As another measurement of carbon utilization and FTS activity, methane selectivity is shown in Figure 10. Although the potassium promoted catalyst produced the most CO₂, it generated the least methane at high space velocity among the five catalysts tested. Except at a low space velocity, all Group II alkali metal promoted catalysts generated similar amounts of methane.

Effect on product partial pressure and water gas shift activity

Figures 11 and 12 give the water vapor and CO₂ partial pressure results obtained from the FTS reactions. Both Group II alkali metal and potassium promoted catalysts showed a peak water partial pressure at a space time of about 0.05 h. The potassium promoted catalyst generated a lower water and higher CO₂ partial pressures than all Group II alkali metal promoted catalysts showing that the potassium promoter yielded the catalyst with highest water gas shift activity. Among the Group II metal promoters, barium shows the lowest water and the highest CO₂ partial pressures while beryllium shows the opposite results. This indicates that the beryllium promoted catalyst possesses the lowest water gas shift activity while the highest WGS activity was obtained when the barium promoter was used.

Figure 13 shows the result of water gas shift quotient, which is calculated from the following equation:

$$\text{Water gas shift quotient} = \frac{P_{[CO_2]} \cdot P_{[H_2]}}{P_{[CO]} \cdot P_{[H_2O]}}$$

which defines the extent of the water gas shift reaction. At CO conversions lower than about 40%, all promoters yielded a similar water gas shift quotient. The differences in water gas shift

quotient between the Group II metal and potassium promoted catalyst become greater as the CO conversion increases.

Effect on Fischer-Tropsch synthesis productivity

Figure 14 shows the results of hydrocarbon production rate for the FTS reactions obtained with the potassium and Group II alkali metal promoted catalyst. As shown in this figure, all Group II alkali metal promoted catalysts yielded a similar hydrocarbon rate. Only barium showed a slightly higher and calcium slightly lower, hydrocarbon rate than other Group II metal promoted catalyst. Potassium promoted iron produced a significantly higher hydrocarbon rate only at a medium space time of 0.1 hour. FTS rates are similar results to those from Figure 14.

Figure 15 gives the results of carbon utilization rate, which was calculated from the following equation:

$$\text{Carbon usage} = \frac{\text{Rate}_{[\text{Hydrocarbon}]}}{\text{Rate}_{[\text{hydrocarbon}]} + \text{Rate}_{[\text{CO}_2]}}$$

Potassium promoted catalysts generated an overall carbon usage that was 5-10% lower than Group II alkali metal promoted catalysts, although it had higher FTS and water gas shift activities. Little difference in carbon usage and alpha values were found among the Group II alkali metal promoted catalysts, as shown in Figures 15 and 16, respectively.

Conclusion

Iron FTS catalysts promoted with Group II alkali metals produced lower CO conversions than potassium promoted iron catalysts. Among the four Group II alkalis, magnesium provided the highest and calcium the lowest conversions. Beryllium and barium promoted iron catalysts, however, showed better stability than other Group II alkali and the potassium promoted catalysts, based on these results of over 500 hours of FTS reactions.

Potassium also generated the highest CO₂ and hydrocarbon rates but the lowest water rate, as potassium promoted catalysts possess both higher water gas shift and FTS activities than Group II alkali metal promoted catalysts. Among the group II alkalis, barium produced the lowest water yield. Group II alkali metal promoted catalysts generated similar hydrocarbon, CO₂ and methane rates. It was also found that Group II alkali metal catalysts produced a similar oxygenate rate, except that Ba yielded higher ethanol and Mg higher normal propanol than other Group II alkali metal promoted catalysts; olefin ratios, however, did not reveal any difference among Group II alkali and potassium promoted catalysts.

FTS production distributions indicate that potassium generated a higher diesel (C₁₂-C₁₈) and heavier (C₁₉₊) fraction and lower gaseous (C₁-C₄) and gasoline (C₅-C₁₁) fractions than Group II alkali metal promoted catalysts. All alkali metal promoted catalysts produced the same hydrocarbon rate with potassium promoted catalyst showing a higher hydrocarbon rate than the Group II alkali metal promoted catalysts at a medium space time.

Among the Group II alkalis, beryllium produced the highest methane (C₂-C₄) fraction as well as the highest gasoline fractions. All Group II alkali promoted catalysts yielded a similar diesel fraction but magnesium and calcium produced lower heavy fractions (C₁₉₊) than beryllium and barium. At a low space time, potassium produced a lower methane selectivity than Group II alkali metal promoted catalysts. At a relatively high space time, potassium produced a similar methane selectivity as calcium, magnesium and beryllium. Barium yielded the higher methane selectivity than the other alkali metals at a high space time. Potassium generated a slightly higher alpha value than the Group II alkali metal promoted catalysts but made little difference in alpha values.

Carbon dioxide selectivity, water and CO₂ partial pressure results indicate that potassium possesses a better water gas shift activity than any Group II alkali metal promoters. Barium generated the highest WGS activity among the Group II alkali metals while magnesium showed the lowest.

Acknowledgment

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References

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Table 1. Analyzers for FTS Products

Analyzer	Sample	GC Detector
HP Quad Series Micro GC	Gas	TCD
HP5890 GC	Water	FID
HP 5790A GC	Oil+light Wax	TCD
HP5890 Series II Plus	Heavy Wax	FID

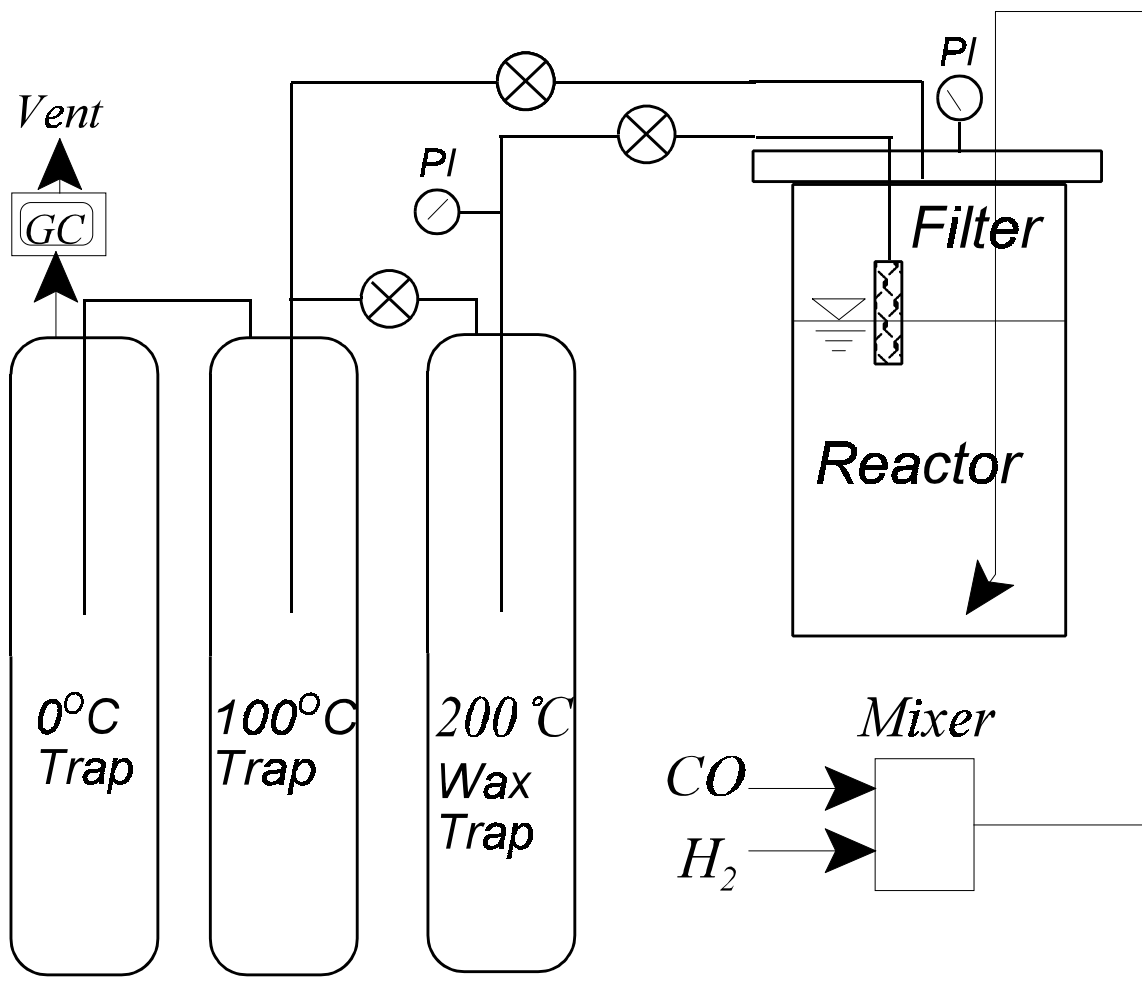


Figure 1. Schematic of CSTR FTS Reactor System

Figure 2. Alkali Effect on Iron Catalyst Stability

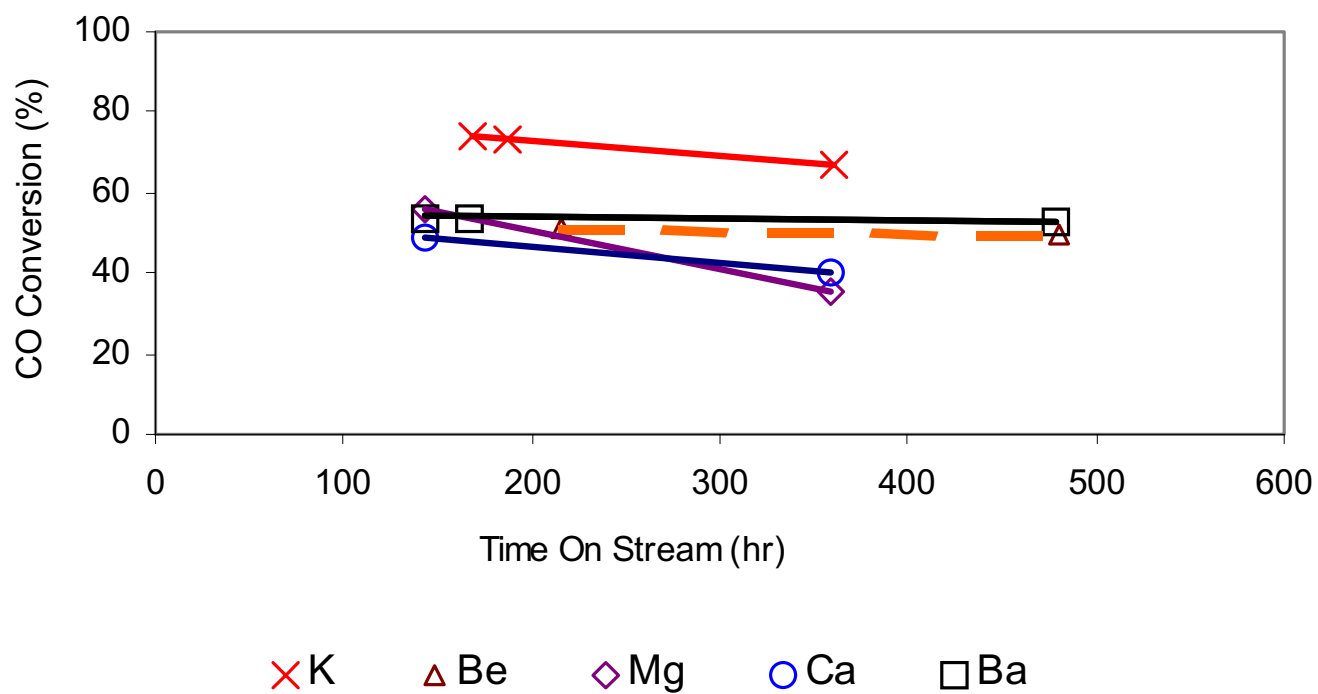


Figure 3. Deactivation Rate

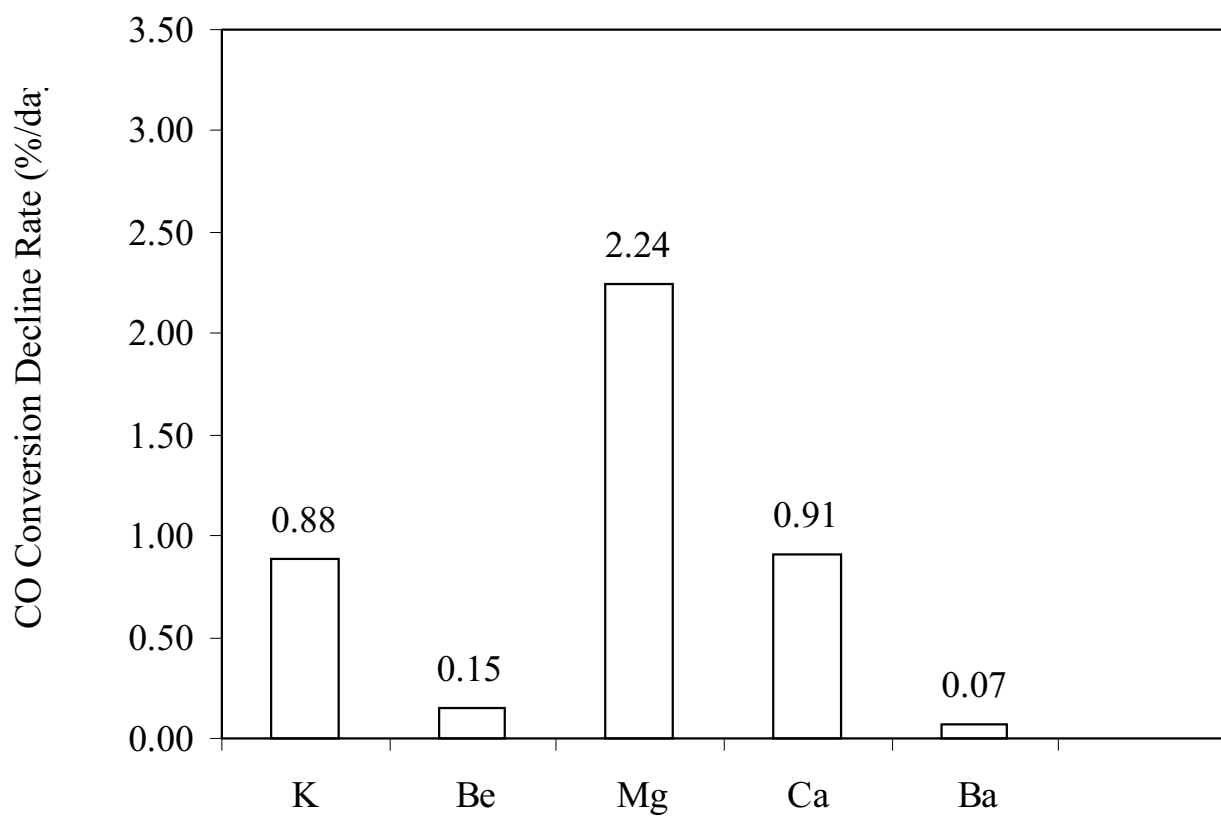


Figure 4. Effect of alkali promoter on CO conversion

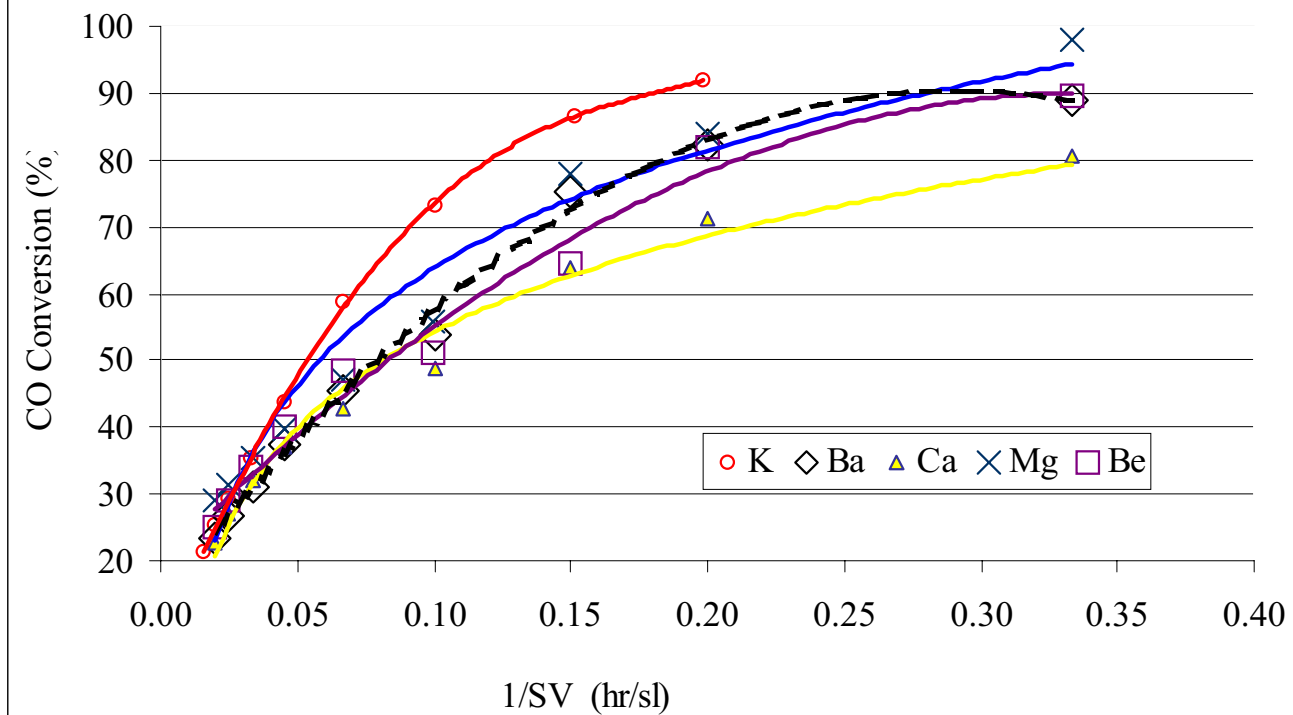


Figure 5. Gas and liquid product distributions

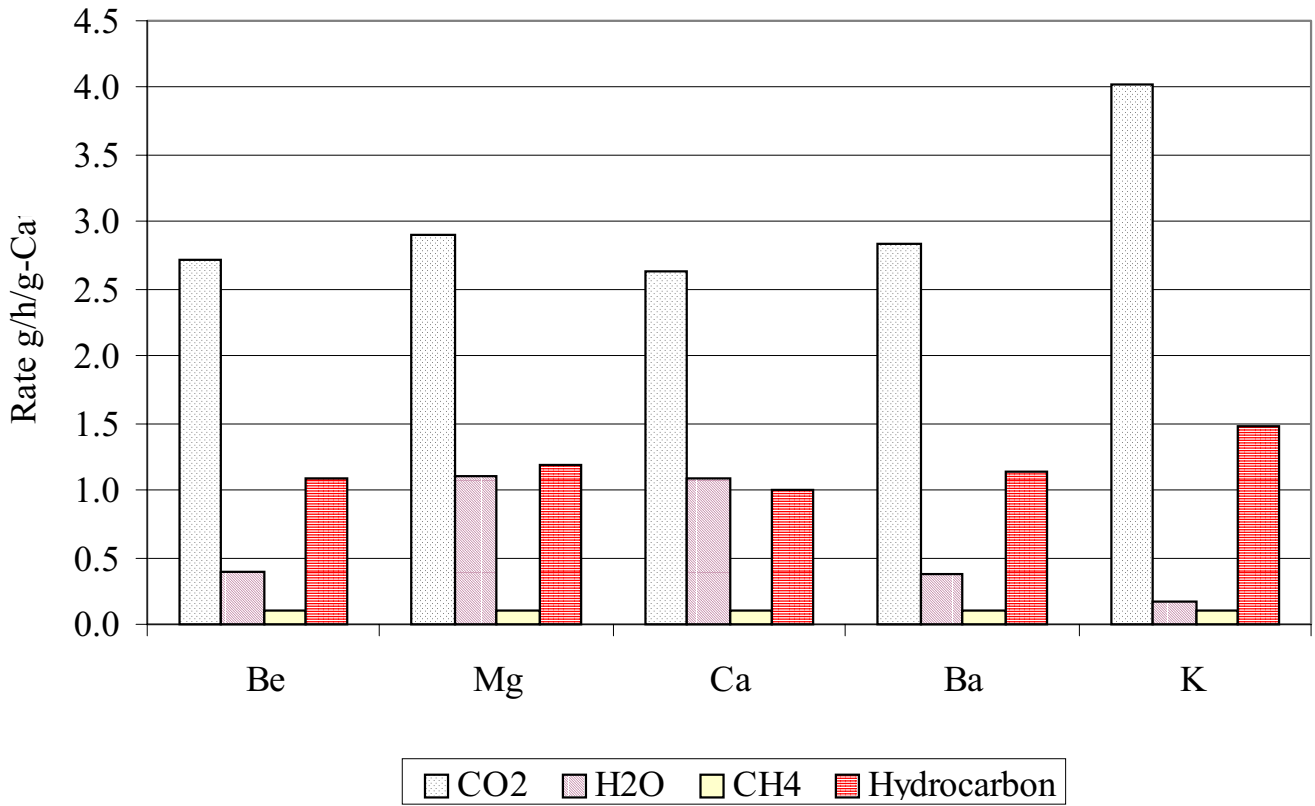


Figure 6. Effect of alkali metals on oxygenates

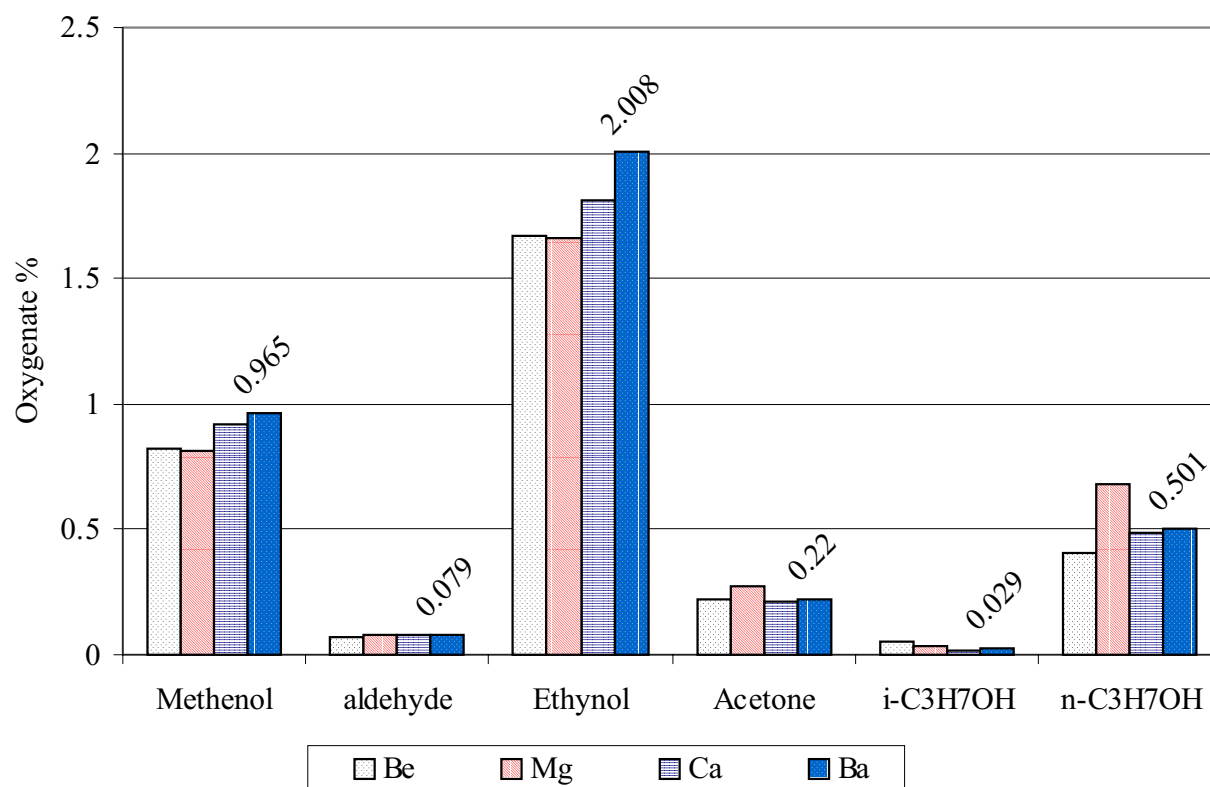


Figure 7. Effect of alkali nature on olefin ratios

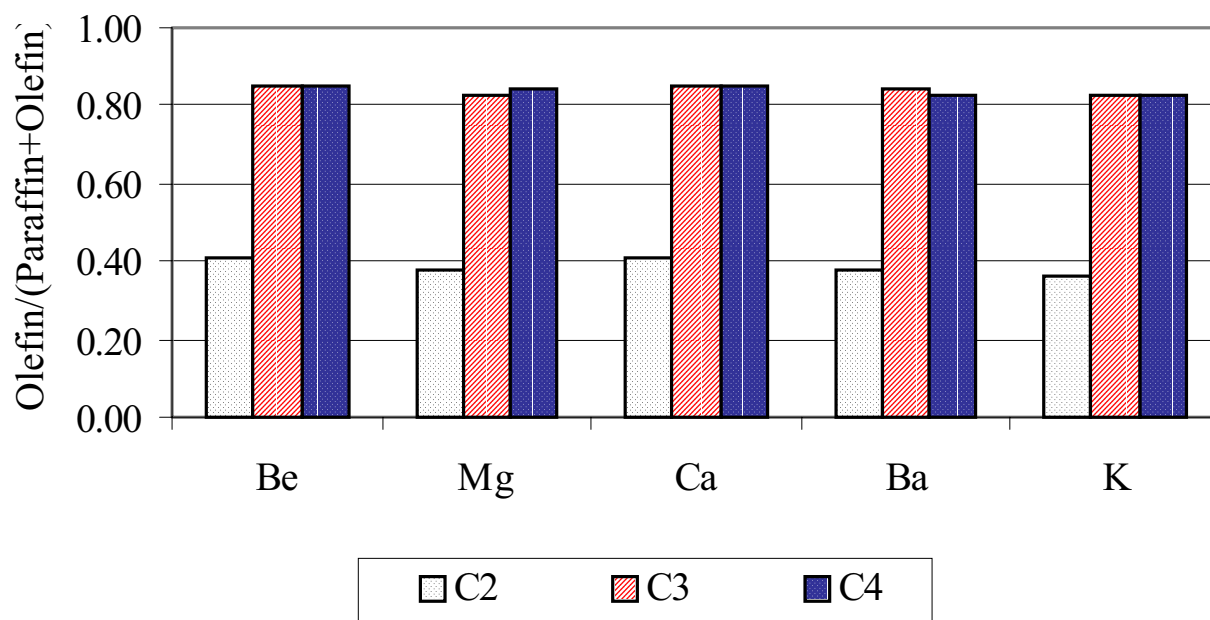


Figure 8. Liquid Production Distribution

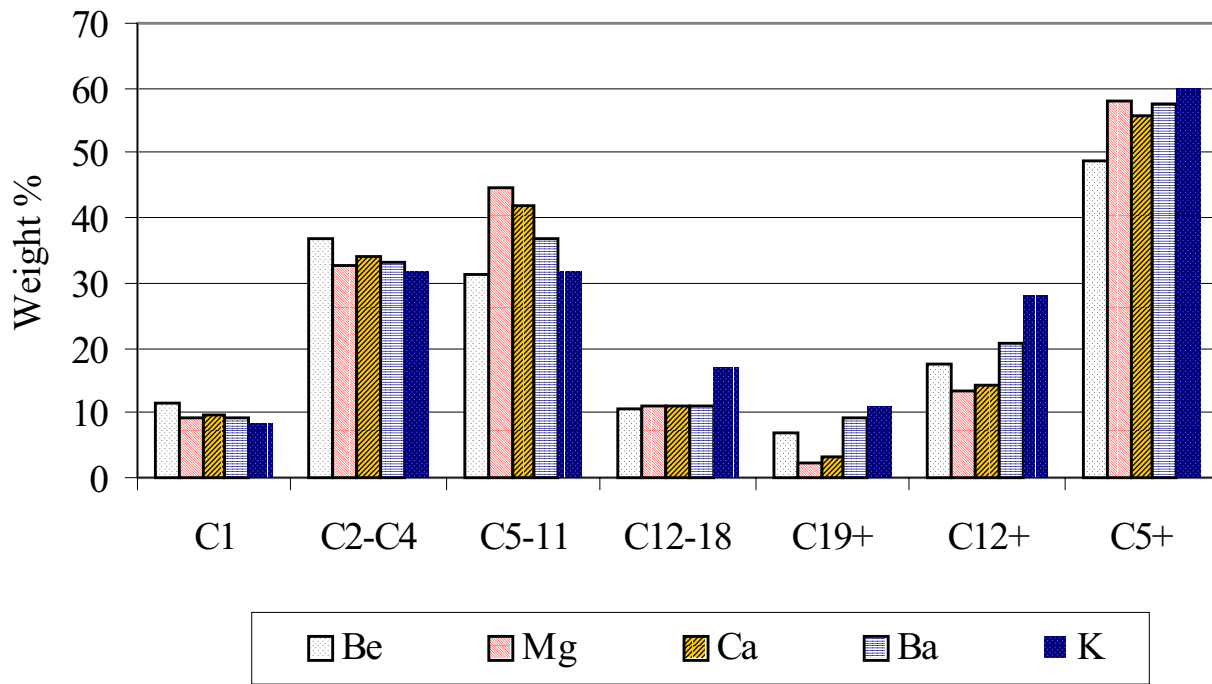


Figure 9. Influence of alkali nature on CO₂ selectivity

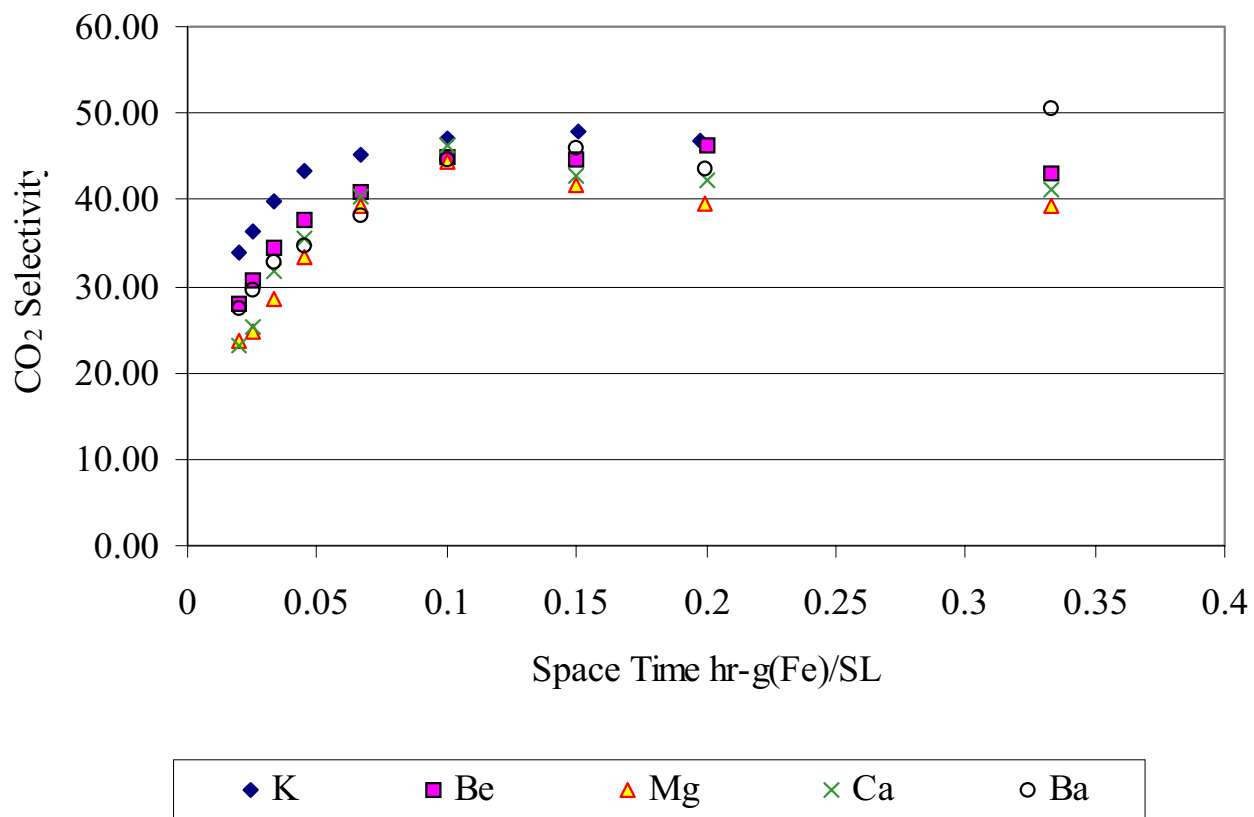


Figure 10. Alkali nature on methane selectivity

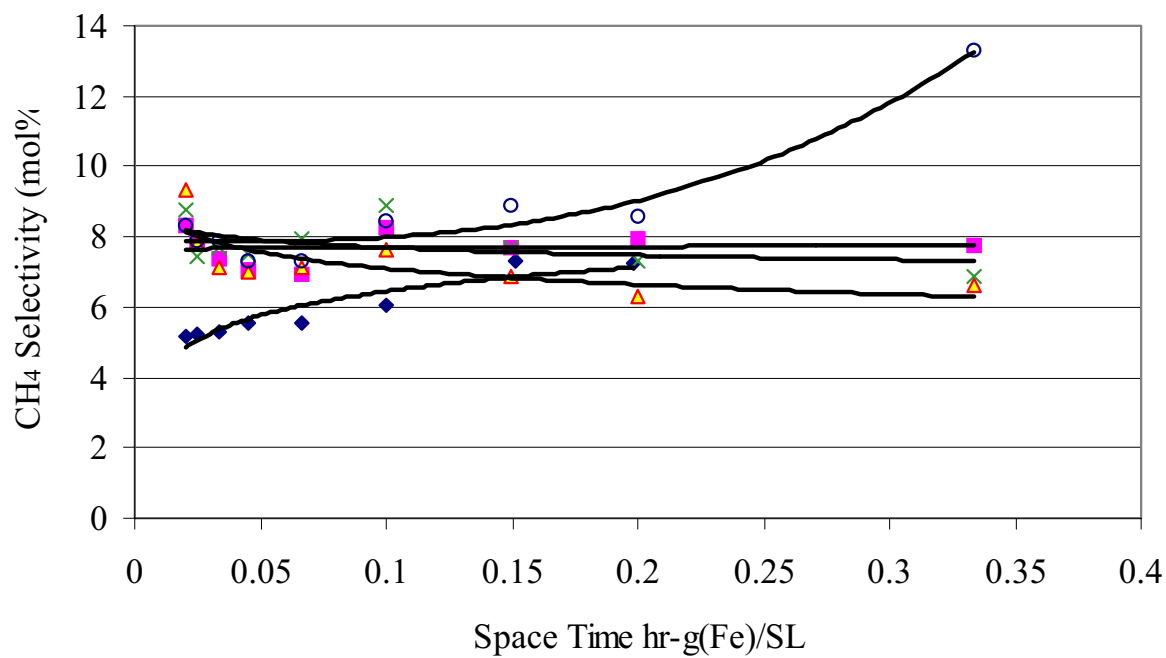


Figure 11. Effect of alkali nature on water partial pressure

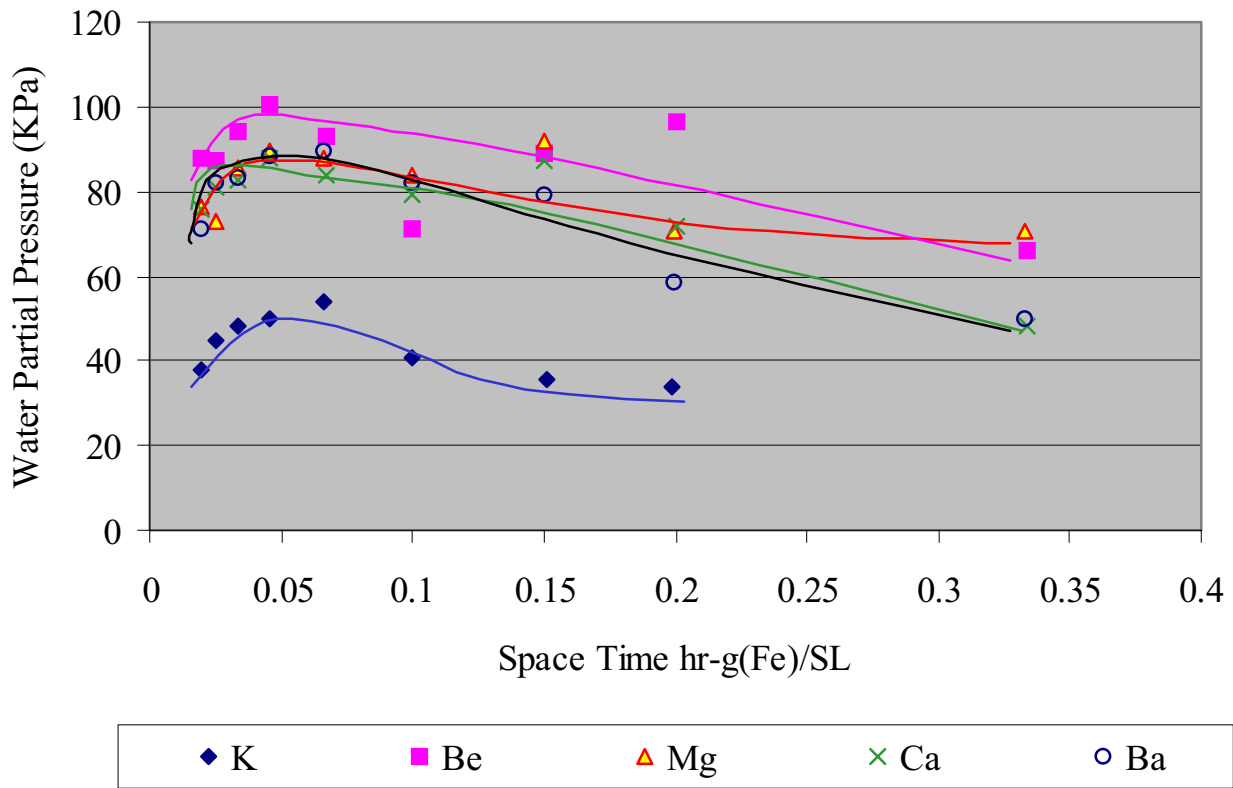


Figure 12. Effect of alkali nature on CO₂ partial pressure

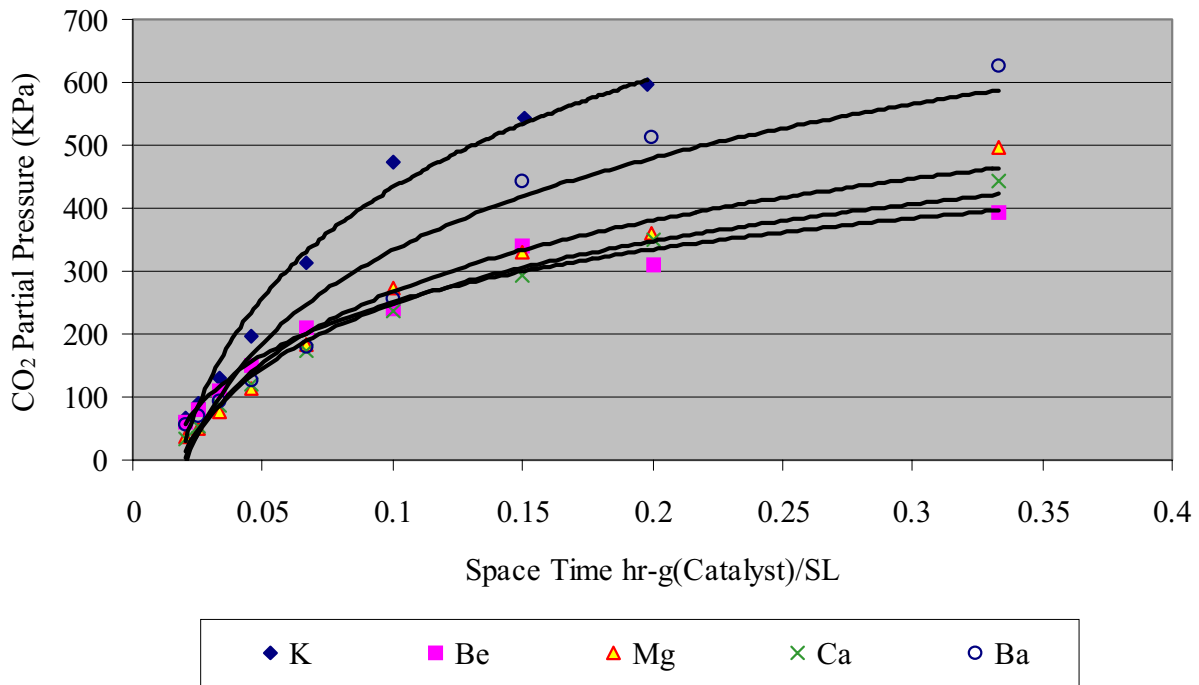


Figure 13. Effect of alkali nature on water gas shift activity

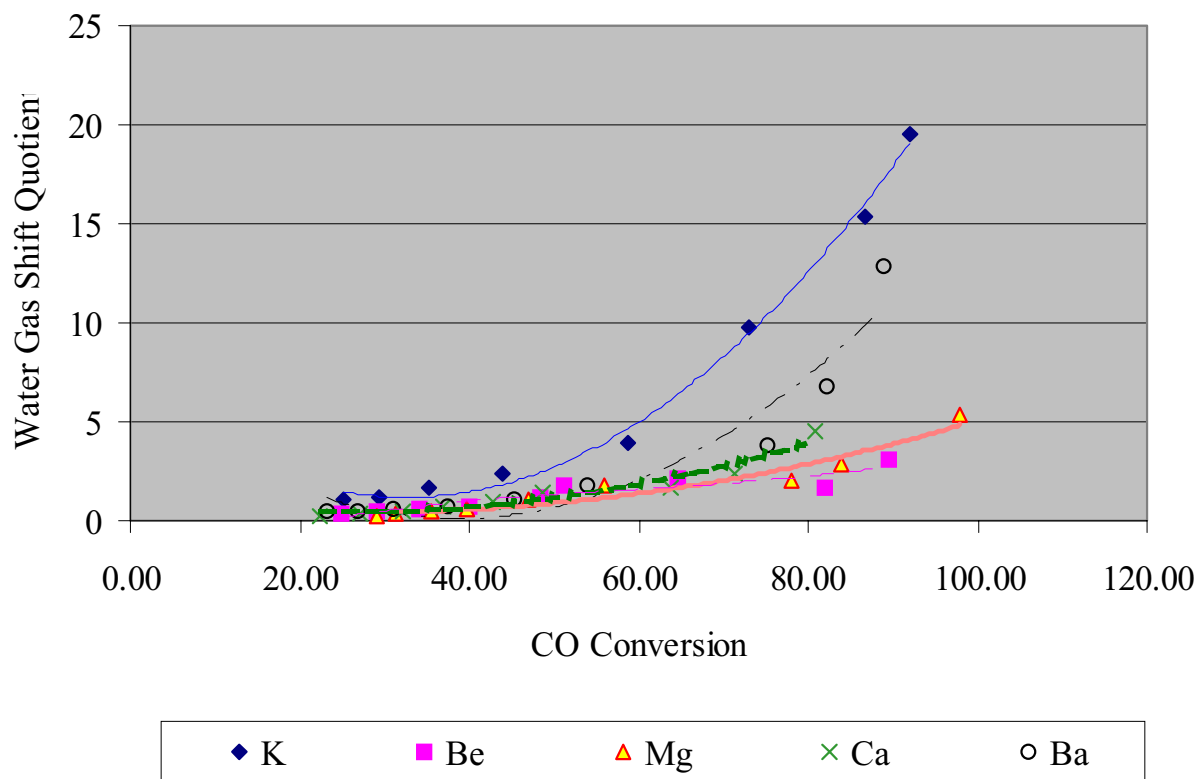


Figure 14. Effect of alkali nature on hydrocarbon rate

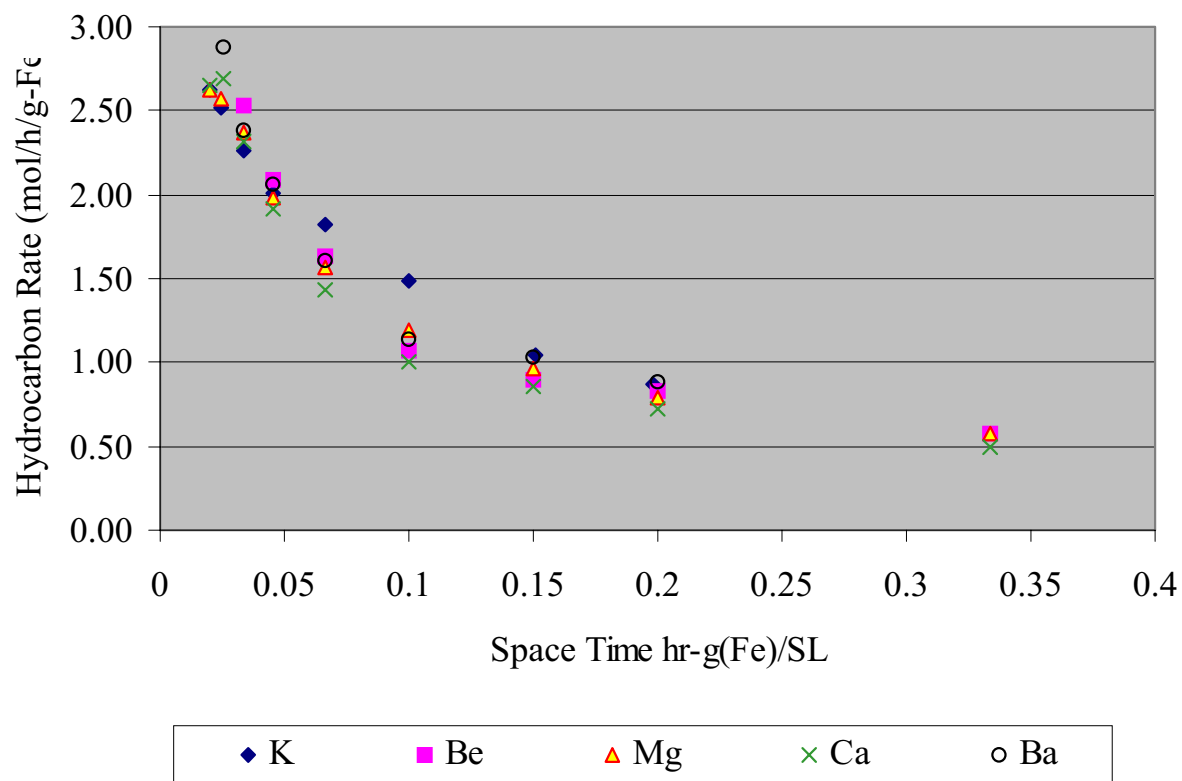


Figure 15. Effect of alkali nature on carbon utilization

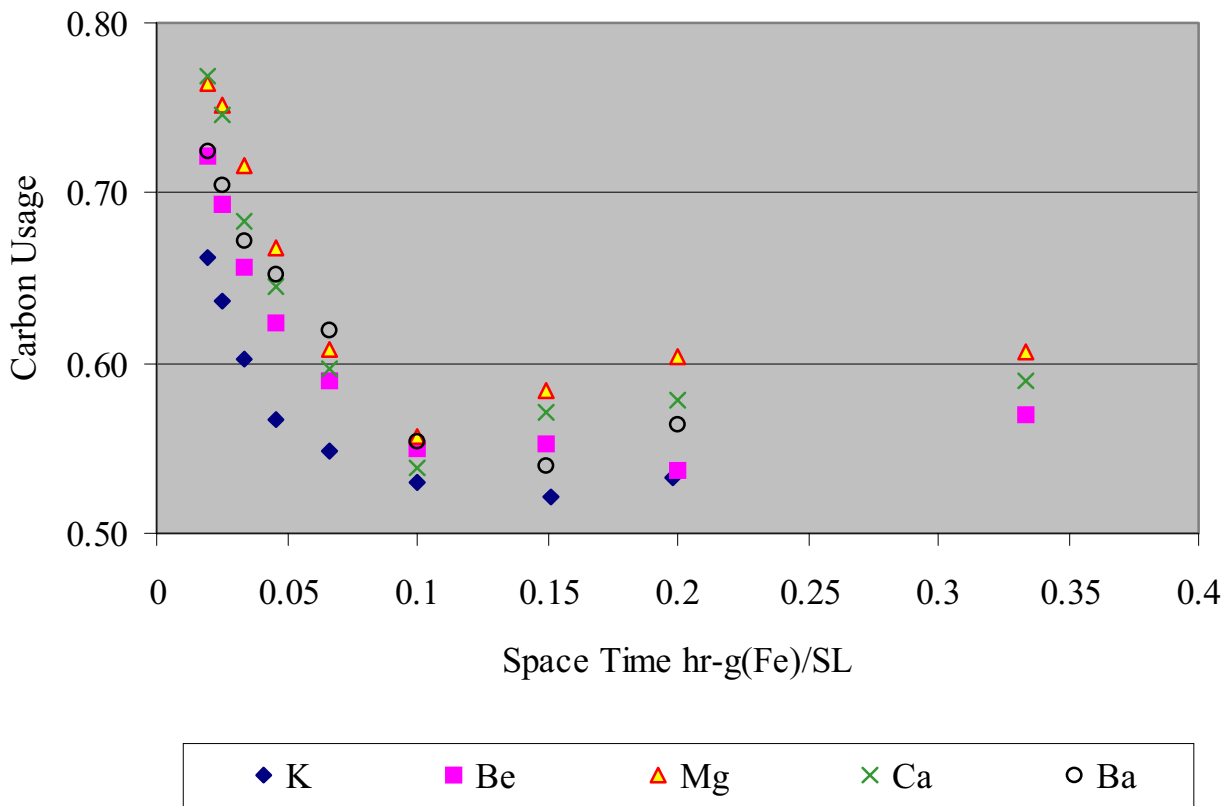


Figure 16. Alpha values of alkalis promoted catalysts

