CHEMICAL ENGINEERING COMMUNICATIONS
2025, VOL. 212, NO. 12, 1896–1913
https://doi.org/10.1080/00986445.2025.2509564

Taylor & Francis
Taylor & Francis Group

REVIEW ARTICLE

OPEN ACCESS Check for updates

# CO conversion to liquid fuel over a bi-functional Co/H-ZSM-5 catalyst: effect of support desilication and catalyst promotion

Tsireledzo L. Mudau[a], Olawumi O. Sadare[b], Samuel A. Iwarere[b], and Michael O. Daramola[b]

[a]School of Chemical and Metallurgical Engineering, Faculty of Engineering and the Built Environment, University of the Witwatersrand, Johannesburg, South Africa; [b]Sustainable Energy and Environment Research Group, Department of Chemical Engineering, Faculty of Engineering, Built Environment and Information Technology, University of Pretoria, Hatfield, Pretoria, South Africa

**ABSTRACT**

This study presents the performance of a bi-functional catalyst (Co/H-ZSM-5), supported on desilicated H-ZSM-5 zeolite support and promoted with calcium, during Fischer-Tropsch synthesis (FTS). Desilication of the support was *via* alkaline treatment using 0.2 M NaOH aqueous solution at varied temperature (40 °C, 55 °C, and 70 °C). Co/H-ZSM-5 catalysts were prepared *via* incipient wetness impregnation, ensuring 10 wt.% of Co in the H-ZSM-5. In total, six catalysts were synthesized and named as follows: Co/H-ZSM-5, Co/H-ZSM-5(40), Co/H-ZSM-5(55), Co/H-ZSM-5(70), Ca-Co/H-ZSM-5, and Ca-Co/H-ZSM-5(55). Textural analysis of the catalysts reveal that the BET surface area of the catalyst increased from 391.81 $m^2$/g to 419.75 $m^2$/g and the CO conversion increased from 49.7% to 84.2% upon H-ZSM-5 desilication. The Co/desilicated H-ZSM-5 catalyst (mesoporous H-ZSM-5) displayed better selectivity toward higher hydrocarbons ($C_5 - C_{6+}$) when compared to the original Co/H-ZSM-5 during FTS. Addition of calcium as a promoter (1 wt.%) to the Co/desilicated H-ZSM-5 further enhanced CO conversion and $C_{5+}$ selectivity. The hierarchical ZSM-5 obtained *via* desilication at 55 °C using 0.2 M NaOH aqueous solution was the most efficient support for the cobalt catalyst during FTS. Promotion of the hierarchical ZSM-5 catalyst (Ca-Co/H-ZSM-5(55)) enhanced both CO conversion and the selectivity toward $C_5 - C_{6+}$ to 90.9% and 57.2%, respectively. This study highlights a new approach for further improvement of $C_5 - C_{6+}$ selectivity in FT synthesis.

**KEYWORDS**

Fischer-Tropsch synthesis; desilication; H-ZSM-5; bi-functional catalyst; hydrocarbons; promotion

## Introduction

Fischer-Tropsch synthesis (FTS) is a catalytic reaction that converts syngas (predominantly CO and $H_2$), obtained from resources like coal, natural gas, and renewable biomass, to clean hydrocarbons (liquid fuels) and other chemicals (Lu et al. 2010). F-T synthesis produces several hydrocarbons, mainly paraffins and olefins arranged in a product distribution based on the type of catalyst and industrial process used (Dagle et al. 2014). The common industrially used catalysts for F-T process are cobalt (Co) and iron (Fe). These catalysts can be applied on two industrial processes: low temperature Fischer-Tropsch (LTFT) and high temperature Fischer-Tropsch (HTFT) (Sartipi, Parashar, Makkee et al. 2013; Sartipi, Parashar, Valero-Romero et al. 2013; Sartipi, Van Dijk, et al. 2013). Either cobalt (Co)-based catalyst or iron (Fe)-based catalyst can be applied on LTFT but Co-based catalysts are more preferred to the Fe-based catalysts at LTFT because they demonstrate higher performance at lower FT synthesis pressure when compared to the Fe-based catalysts (Dancuart and Steynberg 2007). In addition, at LTFT, Co-based catalysts display higher reactivity (activity and selectivity) to long-chain hydrocarbons (HCs) and they exhibit ability to produce more olefins in comparison to the Fe-based catalysts. Also, they are more stable and less prone to deactivation than the Fe-based catalysts (Jahangiri et al. 2014). The cobalt-based catalyst is employed in the F-T synthesis reaction for the production of hydrocarbons, mainly paraffins and olefins. In

CONTACT Michael O. Daramola Michael.Daramola@up.ac.za Sustainable Energy and Environment Research Group, Department of Chemical Engineering, Faculty of Engineering, Built Environment and Information Technology, University of Pretoria, Hatfield, Pretoria 0028, South Africa.

the industry, hydrocracking and isomerization are also employed as the second step for isoparaffins (gasoline) after F-T synthesis catalytic reaction.

In recent years, many studies have been dedicated to developing effective F-T catalysts that can combine both syngas reaction and hydrocracking and/or isomerization for desired products (gasoline). Interestingly, zeolite has been the most useful hydrocracking and isomerization catalyst because of its acidity (Dry 2002). However, zeolite is naturally microporous, limiting access of reactants into the catalytically active acid sites. Consequently, many studies in literature reported on the improvement of zeolite performance by synthesizing micro/mesoporous zeolite material, scientifically called hierarchical zeolite. The hierarchical zeolite is believed to increase the accessibility of reactants to active sites of these zeolites. The synthesis of this hierarchical zeolite can be done either by following non-templating or templating approaches (Zhou et al. 2011). Templating method uses templates such as carbon nanotubes, carbon nanoparticles, carbon nano-fiber, carbon aerogels, polymer aerogels, and calcium carbonate (Xing et al. 2016). For instance, Janssen et al. (2003) successfully generated mesoporous zeolites using carbon nanofibers. However, the process of synthesizing mesoporous zeolite by templating with carbon sources can be very challenging with high cost of materials particularly carbon nanotubes.

Recently, a few studies have focused on synthesizing mesoporous zeolite by non-templating method particularly dealumination or desilication. Ogura et al. (Ogura et al. 2001), reported that dealumination treatment in acidic medium generates meso-porosity in zeolite and enhances the catalytic activity, but leads to zeolite framework structural change. The removal of Al ions from zeolite framework deforms the structure of zeolite since aluminum is a more reactive acid medium compared to silicon. Alternatively, desilication method using alkaline medium can help preserve the structure and meso-porosity of zeolite (Müller et al. 2000; Yoo et al. 2012). In order to prove the preservation of zeolite framework, Ogura et al. (Ogura et al. 2001) investigated and found that treating ZSM-5 zeolite with NaOH does not deform the structure of zeolite, but preserves both structural shape and the catalytic activity of the zeolite. In the same vein, Groen et al. (Groen et al. 2004), further investigated optimization of desilication of ZSM-5 using NaOH and considered influence of temperature and time on the treatment. The authors concluded that the best optimal treatment conditions (NaOH concentration, desilication time, and desilication temperature) were NaOH concentration of 0.2 M at treatment time of 30 min at temperature of 65 °C. Major emphasis of their work was mainly on optimizing the mesoporosity and structure of ZSM-5. Abelló et al. (Abelló et al. 2009) compared the performance of ZSM-5 prepared *via* desilication using tetra-alkylammoniumhydroxide (TPAOH) with ZSM-5 prepared *via* desilication using sodium hydroxide (NaOH) aqueous solutions. The desilication was done at the optimal conditions reported by Groen et al. (Groen et al. 2004). Abelló et al. (Abelló et al. 2009) reported that organic hydroxides have low reactivity compared to inorganic sodium hydroxide with a faster desilication by NaOH compared to TPAOH. Based on previous studies, Sartipi, Parashar,Valero-Romero et al. (2013) investigated the performance of Co/hierarchical H-ZSM-5 during FTS. The authors reported that the introduction of hierarchical ZSM-5 as a support for cobalt FT catalyst prepared *via* incipient wetness impregnation (IWI) method, enhanced its catalytic performance in term of CO conversion and selectivity to gasoline ($C_5 - C_{11}$) from syngas during FT synthesis.

In the same vein, Yusuf et al. (2023) reported the application of desilication to enhance the activity of a Zr-modified desilicated ZSM-5 catalysts during transesterification of soya bean oil into biodiesel. The authors reported an optimal conversion of 97.84%; and also attributed this performance to the desilication of the catalyst. Furthermore, Daramola et al. (Daramola et al. 2017) investigated the catalytic activity of a bi-functional Co/H-ZSM-5 catalyst (without desilicating the support) at low pressure and temperature. The authors reported a decrease in CO conversion and more production of methane and $C_2$ hydrocarbon at both pressure and temperature.

As far as could be ascertained, there are limited or no reports from previous researchers on the effect of desilication temperature on

desilication of zeolite support and the effect of catalyst promotion on the hierarchical catalyst. Against this background, this study investigated the performance of a bi-functional catalyst (Co/H-ZSM-5), specifically considering the effect of desilication of H-ZSM-5 zeolite and its promotion, on the performance of Co-based catalyst supported on H-ZSM-5 zeolite. The study used desilication method at different temperatures to remove silica from the original ZSM-5 zeolite, which has an initial Si/Al of 47. In addition, the study investigated the influence of a promoter, in this case, calcium on the cobalt-based catalyst toward the production of hydrocarbons. This study offers a new perspective to further enhance the activity and selectivity of Co/H-ZSM-5 catalyst during FT synthesis for the production of higher hydrocarbon chains ($C_5$ to $C_{6+}$).

## Experimental

### Material

The ammonium form of Zeolite Socony-Mobil-5 (ZSM-5) (with Si/Al = 48) used in this study was purchased from Zeolyst in the USA. Sodium hydroxide (NaOH) and ammonium nitrate ($NH_4NO_3$) were purchased from Sigma-Aldrich (Pty) South Africa. Deionized water, with resistivity of 18.2 MΩ, was prepared in house. Cobalt (II) nitrate hexahydrate (Co $(NO_3)_2.6H_2O$) used as a cobalt source in this study was purchased from Sigma-Aldrich (Pty) South Africa. Syngas (composition: 20% CO, 50% $H_2$, and 30% $N_2$) used for the Fischer-Tropsch synthesis reaction, Argon (Ar), Hydrogen ($H_2$), Nitrogen ($N_2$), Air and calibration gas (consists of $N_2$, $H_2$, CO, $CO_2$, $CH_4$, $C_2H_6$ & $C_2H_4$) were purchased from Afrox (Pty) SA.

### Catalyst preparation

#### Synthesis of un-desilicated catalyst

Ammonium form of Zeolite Socony-Mobil-5 (ZSM-5) was calcined at 550 °C for 5 h and then dried overnight at 120 °C for 2 h to form H-ZSM-5. Thereafter, the Co supported on HZSM-5 catalyst, containing 10 wt% of Co, was prepared using H-ZSM-5 as the support and cobalt nitrate solution as the cobalt source. The synthesis was done by using incipient wetness impregnation (IWI) method. The prepared catalyst was kept at room temperature in an oven overnight, at 120 °C for 12 h, to remove moisture; and then calcined at 400 °C for 2 h. The final product obtained thereof is referred to Co/H-ZSM-5 catalyst.

#### Synthesis of desilicated catalyst

The hierarchical mesoporous H-ZSM-5 was prepared using 0.2 M NaOH aqueous solution as desilication solution analogous reports of Sartipi, Parashar, Valero-Romero et al. (2013) and Groen et al. (Groen et al. 2004). The H-ZSM-5 was added into three separate vessels containing 0.2 M NaOH aqueous solutions (volume $_{\text{base solution}}$/weight $_{\text{H-ZSM-5}} = 8.0\,\text{cm}^3\,\text{g}^{-1}$). The vessel was heated in an oil bath under vigorous stirring for 1 h. The desilication was carried out at varied temperature (40 °C; to 55 °C; and to 70 °C). Thereafter, the suspensions were cooled down to room temperature, then the solid fine particles were filtered by centrifuge followed by washing with deionized water until the pH was neutral. The subsequent solid samples were dried at 373 K, and then dissolved in 1 M $NH_4NO_3$ aqueous solution to convert it into H-form of zeolite. Then, the samples were filtered to remove $Na^+$ ions, and then followed by calcination at 550 °C for 5 h. The samples obtained after calcination are referred to as hierarchical mesoporous H-ZSM-5. Incipient wetness impregnation (IWI), described in Synthesis of un-desilicated catalyst section, was followed to produce additional three catalysts named: Co/H-ZSM-5 (40) (desilicated at 40 °C), Co/H-ZSM-5 (55) (desilicated at 55 °C), and Co/H-ZSM-5 (70) (desilicated at 70 °C).

#### Promotion of catalyst

The Co/H-ZSM-5 catalyst (from the synthesis of desilicated catalyst section) that displayed the best F-T performance in terms of conversion and selectivity was subsequently promoted with calcium metal. The promoter was added during IWI method. Calcium nitrate solution, Ca $(NO_3)_2$, was used as the source of Ca for the promotion. Eventually the composition of the promoter in the catalyst was about 2 wt.%. Thereafter, the promoted catalysts were dried and calcined at the

same conditions as in synthesis of un-desilicated catalyst section.

### Catalyst characterization

All the synthesized catalysts were characterized and tested for FTS. The following analytical techniques were employed for characterization of the prepared catalysts. X-ray diffraction (XRD) for crystalline structure of ZSM-5; nitrogen physisorption at 77 K for textural properties; and scanning electron microscopy (SEM) coupled with energy dispersive spectroscopy (EDS) for morphology and elemental composition of the catalyst. Fourier transform infrared (FTIR) spectroscopy was used to study the surface chemistry of the catalyst. The pore size distributions of the materials were calculated using the Barrett–Joyner–Halenda (BJH) model with cylindrical pore geometry assumed.

### F-T synthesis experiments

All the prepared catalysts were tested for F-T synthesis under same conditions indicated in Performance evaluation of the catalysts section. The F-T synthesis was carried out in a fixed-bed reactor (inner diameter of 16 mm) operated as a plug flow reactor (PFR) (see Figure 1). A 0.5 g catalyst was loaded in the reactor and reduced in $H_2$ gas flow (30 $cm^3$ STP/min) at 330 °C and 8 bar for 17 to 20 h before reaction according to Sartipi, Parashar, Makkee et al. (2013). After the reduction of the catalyst, the reactor was allowed to cool down to room temperature at a cooling rate of 2 °C/min. A syngas of $H_2$-to-CO ratio of 2.5 was introduced into the reactor while heating it up to the desired temperature (250 °C) at a heating rate of 2 °C/min. The feed and the reaction products were analyzed by two pre-calibrated on-line gas chromatographs (GCs) equipped with thermal conductivity detector (TCD) and flame ionization detector (FID). Inorganics such as CO, $H_2$, $N_2$, and $CO_2$ were analyzed by the online GC equipped with a TCD using argon as the carrier gas while the hydrocarbons $C_1$ – $C_{6+}$ were analyzed using the GC equipped with an FID using nitrogen as the carrier gas. The experimental set-up was equipped with two traps (tr-1 and tr-2, see Figure 1) to collect the heavy hydrocarbons and the water-oil mixture. The heavy hydrocarbons (wax) were collected in tr-1 while water-oil mixture was collected in trap (tr-2) and they were analyzed using an offline GC-MS. The data from the analysis of the products were received by the PC transmission box detected on the computer screen using DataApex chromatograph software called Clarity® (v.2.5). All the catalyst testing was conducted in the experimental setup in Figure 1 for a period of 73 h. After attaining a steady state at 25 h, each experimental data was collected.

The CO conversion was calculated using Equation (1), a modified version of the equation used by Yao (2011). In addition, it is the modified version of the equation used by Su et al. (2019) in their work on syngas to light olefins conversion with high olefin/paraffin ratio using ZnCrOx/AlPO-18 bi-functional catalysts (see the supplementary information), by Santos et al. (2017), Sartipi, Parashar, Makkee et al. (2013), though Sartipi et al. considered only $C_6$ hydrocarbon.

$$\%\ CO\ Conversion = \frac{F_{CO,in} - F_{CO,out}\left(\frac{F_{N2,in}}{F_{N2,out}}\right)}{F_{CO,in}} \times 100 \quad (1)$$

Where $\left(\frac{F_{N_2,in}}{F_{N_2,out}}\right)$ is the nitrogen gas correction factor. This value should be approx. 1 since nitrogen does not react during the reaction, its amount in the feed stream is equal to that in the outlet stream. The molar fraction of nitrogen in the reactor outlet $(X_{N_2,out})$ was obtained from nitrogen balance around the reactor using Equation (2):

$$F_{in} \cdot X_{N_2,in} = F_{out} \cdot X_{N_2,out} \quad (2)$$

Where:

$F_{in}$ = total molar flow rate (mol/min) of the reactor;

$F_{out}$ = total molar flow rate (mol/min) of the outlet gas stream, calculated from measured volumetric flowrate using standard volume flow of a gas.

$X_{N_2,in}$ = molar fraction of nitrogen in the reactor feed;

$X_{N_2,out}$ = molar fraction of nitrogen in the reactor outlet;

$X_{CO,in}$ = molar fraction of carbon monoxide in the reactor feed;

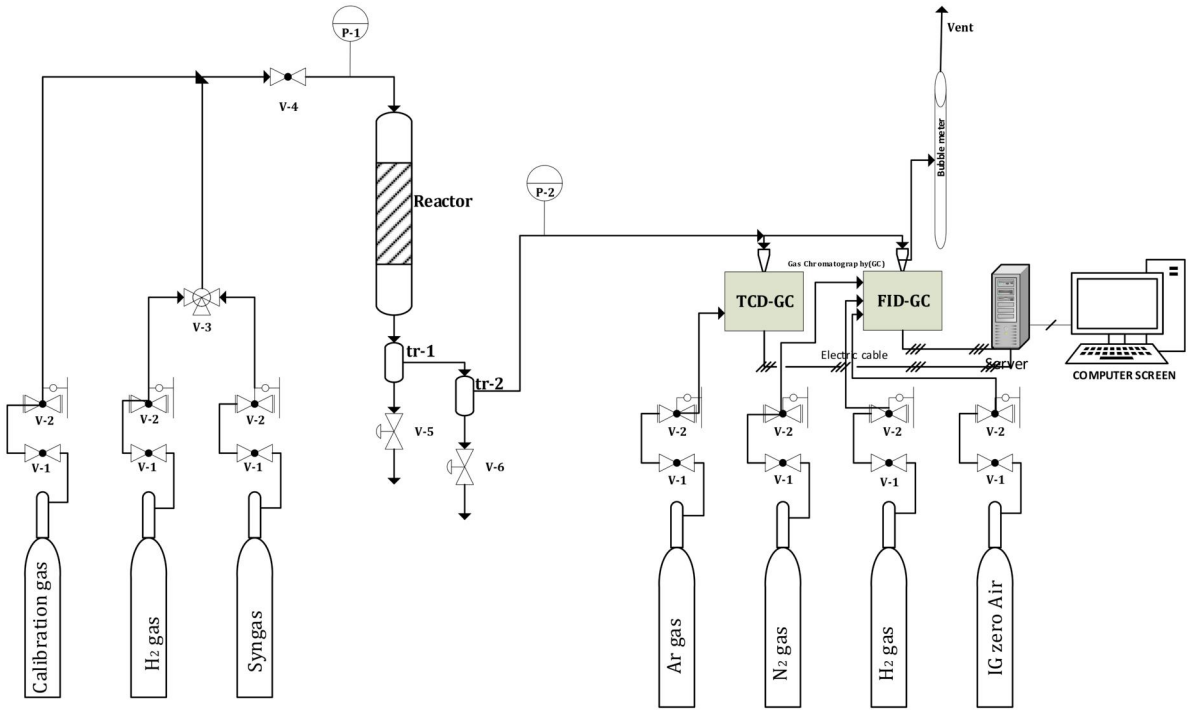


**Figure 1.** Experimental setup for catalyst testing.

$X_{CO,out}$ = molar fraction of carbon monoxide in the reactor outlet.

For the calculation of the selectivity, Equation (3) was used. Equation (3) is the modified version of the equation used by Yao (2011) and also used by Matamela (2016).

$$Selectivity\ (S_{HC,i}) = \left(\frac{N_{HC,i}}{\Delta W}\right)\left(\frac{1}{-r_{co}\ \times t_{rxn}}\right)\left[\frac{mol}{g}\times\frac{g\times h}{mol\times h}\right] \quad (3)$$

Then, Equation (4) was used in calculating the percentage selectivity.

$$\%\ Selectivity = \frac{S_{HC,i}}{\sum S_{HC,i}}\times 100 \quad (4)$$

$S_{HC,i}$ = selectivity of paraffin $i$;

$\sum S_{HC,i}$ = sum of all selectivity of paraffin $i$

$N_{HC,i}$ = the number of moles of product for each component in a gas;

$\Delta W$ = weight of a catalyst (g);

$t_{rxn}$ = total reaction time (h);

$r_{co}$ = rate of CO conversion (mol.g$^{-1}$.h$^{-1}$)

Where $F_{CO,in}$ indicates molar flow of carbon monoxide before reaction, $F_{CO,out}$ represents molar flow of carbon monoxide after reaction, $F_{N2}$ stands for molar flow of nitrogen, "n" is the carbon number, $N_{HC,i}$ represents moles of hydrocarbons containing $i$ carbon atom, $\Delta W$ is catalyst weight, $t_{rxn}$ is the reaction time and $r_{co}$ is the rate of CO conversion.

## Results and discussion

### Catalyst characterization

#### Textural property

The textural property, showing the surface area, the average pore volume and the average pore diameter of ZSM-5 zeolite, H-ZSM-5 zeolite, and Co/H-ZSM-5 catalyst, is presented in Table 1. The average pore size of these samples indicates the porosity nature of the materials, i.e. micropore or/and mesopore. Materials of the pore size between 0.4 and 2 nm are considered microporous while those with pore size between 4 and 50 nm are considered mesoporous. The results show that the BET surface area of the zeolite increased in this order: ZSM-5 < un-desilicated H-ZSM-5 <desilicated H-ZSM-5. The BET surface area of ZSM-5, un-desilicated H-ZSM-5 and desilicated H-ZSM-5 were 340.47 $m^2$/g, 391.08 $m^2$/g and 419.74 $m^2$/g, respectively. The increase in BET surface area of the zeolite from un-desilicated H-ZSM-5 (391.08 $m^2$/g) to desilicated H-ZSM-5 (419.74 $m^2$/g), indicates a reduction in microspore volume from 0.12 $m^3$/g to 0.09 $m^3$/g while pore

**Table 1.** Textural properties of the ZSM-5, H-ZSM-5 zeolites, and Co/H-ZSM-5 catalysts.

| Catalyst | BET surface area ($m^2$/g) | Microspore pore volume ($m^3$/g) | Pore diameter (nm) | Si/Al ratio |
|---|---|---|---|---|
| ZSM-5 | 340.47 | 0.1107 | 5.9217 | 47 |
| H-ZSM-5 (un-desil) | 391.08 | 0.1209 | 5.2705 | 48 |
| Co/H-ZSM-5(un-desil) | 289.68 | 0.0839 | 6.0706 | n/a |
| H-ZSM-5 (desilicated) | 419.74 | 0.0963 | 8.8087 | 26 |
| Co/H-ZSM-5 (desil) | 209.51 | 0.0463 | 13.3103 | n/a |

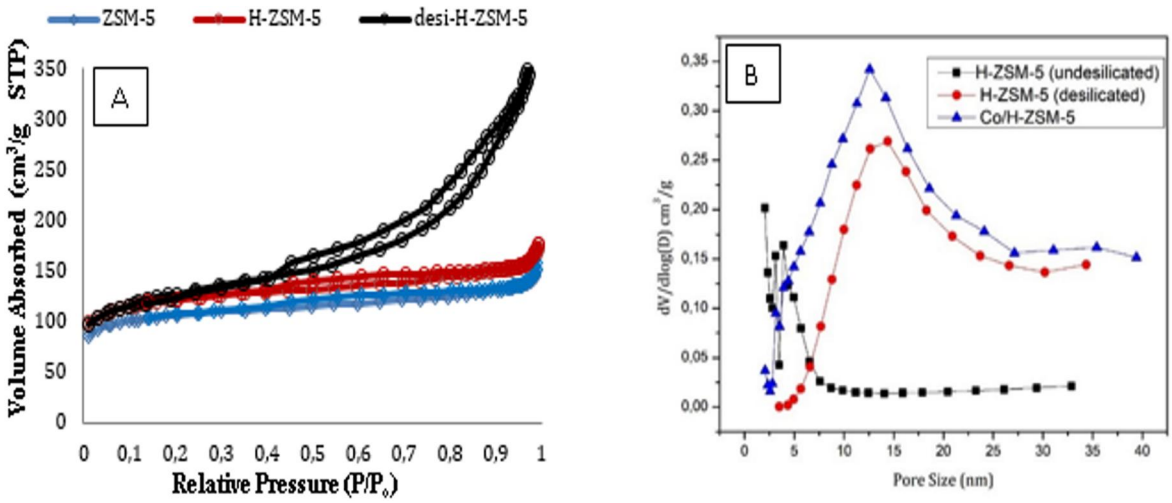


**Figure 2.** (A) $N_2$ adsorption-desorption isotherm; (B) BJH pore size distribution of H-ZSM-5 and Co/H-ZSM-5.

diameter increased from 5.27 nm to 8.81 nm. This could be attributed to the creation of mesopores on zeolite because of silica removal through desilication method. Sartipi, Parashar, Valero-Romero et al. (2013)reported an increase in BET surface area for desilicated H-ZSM-5 zeolite from 52 $m^2$/g for H-ZSM-5 to 309 $m^2$/g for desilicated H-ZSM-5 zeolite (meso-HZSM-5). In addition, the reduction in Si/Al ratio from 48 for the undesilicated H-ZSM-5 zeolite to 26 for the desilicated H-ZSM-5 zeolite shows a reduction in the silica content of the zeolite, thereby emphasizing the success of the desilication method. For the Co/H-ZSM-5 catalyst using the desilicated H-ZSM-5 zeolite, the BET surface area reduced from 419.74 $m^2$/g to 209.51 $m^2$/g, indicating that Co particles (could be in form of oxide) were successfully impregnated onto the support (desilicated H-ZSM-5) *via* IWI. Similar trend was also observed for un-desilicated -H-ZSM-5 to Co/un-desili-H-ZSM-5 (from 391.08 $m^2$/g to 289.68 $m^2$/g). The lower surface area and pore volume of Co-loaded samples (un-desilicated and desilicated) could be attributed to the cobalt compounds blocking the smaller nanopore structure of the H-ZSM-5. The total pore volume of H-ZSM-5 was expected to increase after the desilication of H-ZSM-5 zeolite with NaOH.

Figure 2A depicts the nitrogen adsorption and desorption isotherms at 77 K for ZSM-5, H-ZSM-5 and desilicated-H-ZSM-5. Both parent ZSM-5 and calcined H-ZSM-5 reveal a type I isotherm with a horizontal plateau shape at low relative pressures, no clear hysteresis loop was observed, and are considered to be of microporous characteristics (Hong and Fripiat 1995). After the removal of silicon from zeolite *via* the alkaline desilication, the $N_2$ isotherm of the desilicated H-ZSM-5 increased at ($P/P_O$) between 0.4 and 0.5. The Nitrogen adsorption isotherm of this desilicated H-ZSM-5 in Figure 2A is classified as type IV according to Hong and Fripiat (Hong and Fripiat 1995). This type IV isotherm combined with hysteresis loop is an indication of meso-porosity of the sample, with a similar observation reported by Wang et al.(Wang et al. 2013). The presence of meso-porosity in the desilicated sample is also witnessed by an increase in mesopore surface area and decrease in micropore volume given in Table 1.

The meso-porosity of desilicated-H-ZSM-5 was further confirmed by BJH pore size distribution

in Figure 2B. Prior to desilication process, H-ZSM-5 showed a narrow BJH pore size distribution. The silica removal with the 0.2 M NaOH aqueous solution altered the size of the mesopores. As shown by BJH pore size distribution, a desilicated-H-ZMS-5 zeolite formed mesopores centered at about 14.3 nm. Abelló et al. (Abelló et al. 2009) reported the formation of smaller pores (10 nm) in H-ZSM-5 zeolite subjected to NaOH (0.2 M, 338 K, and 30 min). This BJH pore size distribution of desilicated-H-ZSM-5 are in the range of 2-50 nm, indicating the meso-porosity of this sample. Che and Vedrine (Che and Védrine 2012) reported that the range of meso-porous solid samples is between 2 and 50 nm whereas that of micropores is between 0.4-2 nm. However, incipient wetness impregnation (IWI) of cobalt shifted the curve slightly to the left. In other words, the pore size of Co/desilicated-H-ZSM-5 decreased to 12.5 nm as a result of pore clogged up by the introduced cobalt particles into the desilicated H-ZSM-5. Nonetheless, the shift in the pore size distribution of Co/desilicated H-ZSM-5 is not very obvious and thus, it is an indication that the mesoporous structure of the Co loaded desilicated H-ZSM-5 is retained. Interestingly, the pore size distribution curves of both desilicated-H-ZSM-5 and Co/desilicated-H-ZSM-5 catalyst have the same shape.

### XRD patterns

Figure 3 illustrates the XRD patterns of Co/H-ZSM-5 catalyst, desilicated and un-desilicated H-ZSM-5 zeolite. Figure 3 also contains the simulated XRD patterns of H-ZSM-5 zeolite obtained from the International Zeolite Association (IZA) database and was used as the reference for comparison. The diffraction patterns of synthesized H-ZSM-5 seem to match perfectly with that of the simulated H-ZSM-5. The high intensity peaks observed at a range of $2\theta = 7 - 9^{\circ}$ and $22 - 25^{\circ}$ represent the crystallinity of H-ZSM-5 zeolite and the MFI morphology of zeolite with a high presence of silicon and aluminum elements. No structural changes in H-ZSM-5 after desilication took place; hence, the desilicated H-ZSM-5 retained the same diffraction patterns. However, the intensity of peaks particularly at $2\theta = 22 - 25^{\circ}$ reduced in size as a result of silicon removal. Upon incipient wetness impregnation of cobalt on H-ZSM-5 zeolite support, diffraction peaks emerged at 37.0 °C, 44.9 °C, 59.6 °C and 65.5 °C representing the successful impregnation of cobalt. In addition, the cobalt peaks at the stated $2\theta$ degrees, correspond with the crystal planes of $Co_3O_4$ from the American Mineralogists Crystal Structure database (Downs and Hall-Wallace 2003).

### Catalyst morphology and elemental compositions

The SEM images of calcined H-ZSM-5 and Co/H-ZSM-5 are shown in Figure 4. The surface of Figure 4A is observed to be a little rough. After adding cobalt particles, the surface in Figure 4B which is for Co/H-ZSM-5 catalyst is observed to be rougher compared to Figure 4A. Looking at Figure 4B, it can be concluded that cobalt was successfully deposited on H-ZSM-5 zeolite surface represented by the agglomerated "whitish" particles.

The EDX spectra in Figure 5 show the elemental composition of the zeolite support and the synthesized catalysts. Looking at Figure 5A, initially before desilication of zeolite, calcined ZSM-5 zeolite detected 48.14% O, 1.08% Al and 50.78% Si of elemental weight percentages. Since zeolite is mainly defined as alumino-silicate materials, it is essential to specify its silica-to-alumina molar ratio. From Figure 5A, the ratio of Si/Al was 47 (as presented in Table 1), which is almost the same as that of ammonium form of zeolite ($\sim$ 48). Same spectrum was observed for the desilicated-H-ZSM-5 as depicted in Figure 5B, but with an additional element of sodium (Na) appearing. The observed Na element could have come from the alkaline desilication using NaOH solution. The Si signal intensity of the desilicated H-ZSM-5 (Figure 5B) reduced as a result of silica extraction during the desilication process. Very interestingly, the Si/Al molar ratio dramatically decreased from 48 (for ammonium form zeolite) to 26, confirming the success of the desilication process.

The EDX results presented in Figure 5C and Figure 5D reveal an element of cobalt, which was impregnated onto the zeolite support. During the incipient wetness impregnation method, zeolite support was loaded unto 10% weight of cobalt as reported by Sartipi, Van Dijk, Gascon et al. (2013), but only 7. 98 wt% of Co was detected in

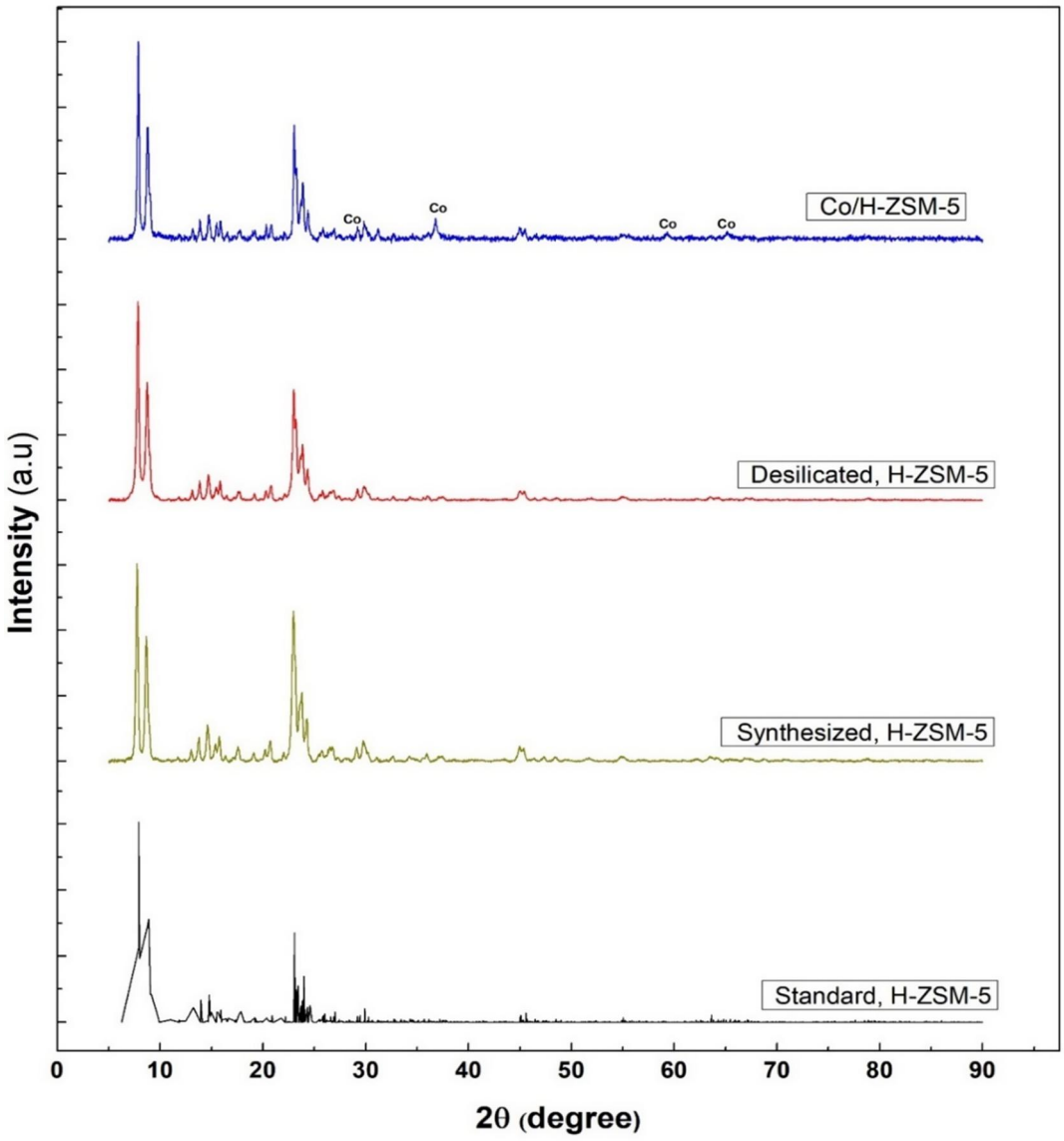


**Figure 3.** XRD patterns of synthesized H-ZSM-5, desilicated H-ZSM-5, and Co/H-ZSM-5 catalyst.

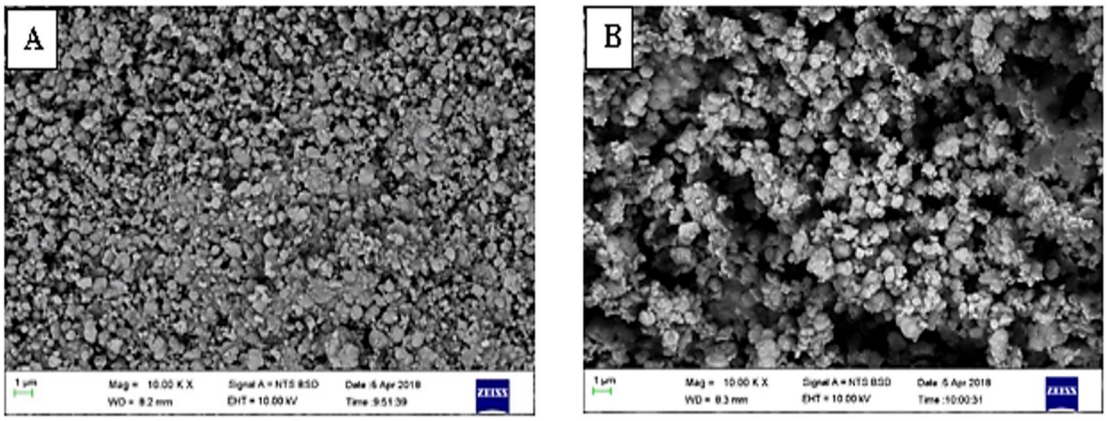


**Figure 4.** SEM images of (A) calcined H-ZSM-5, and (B) Co/H-ZSM-5, all in 10 000× magnification.

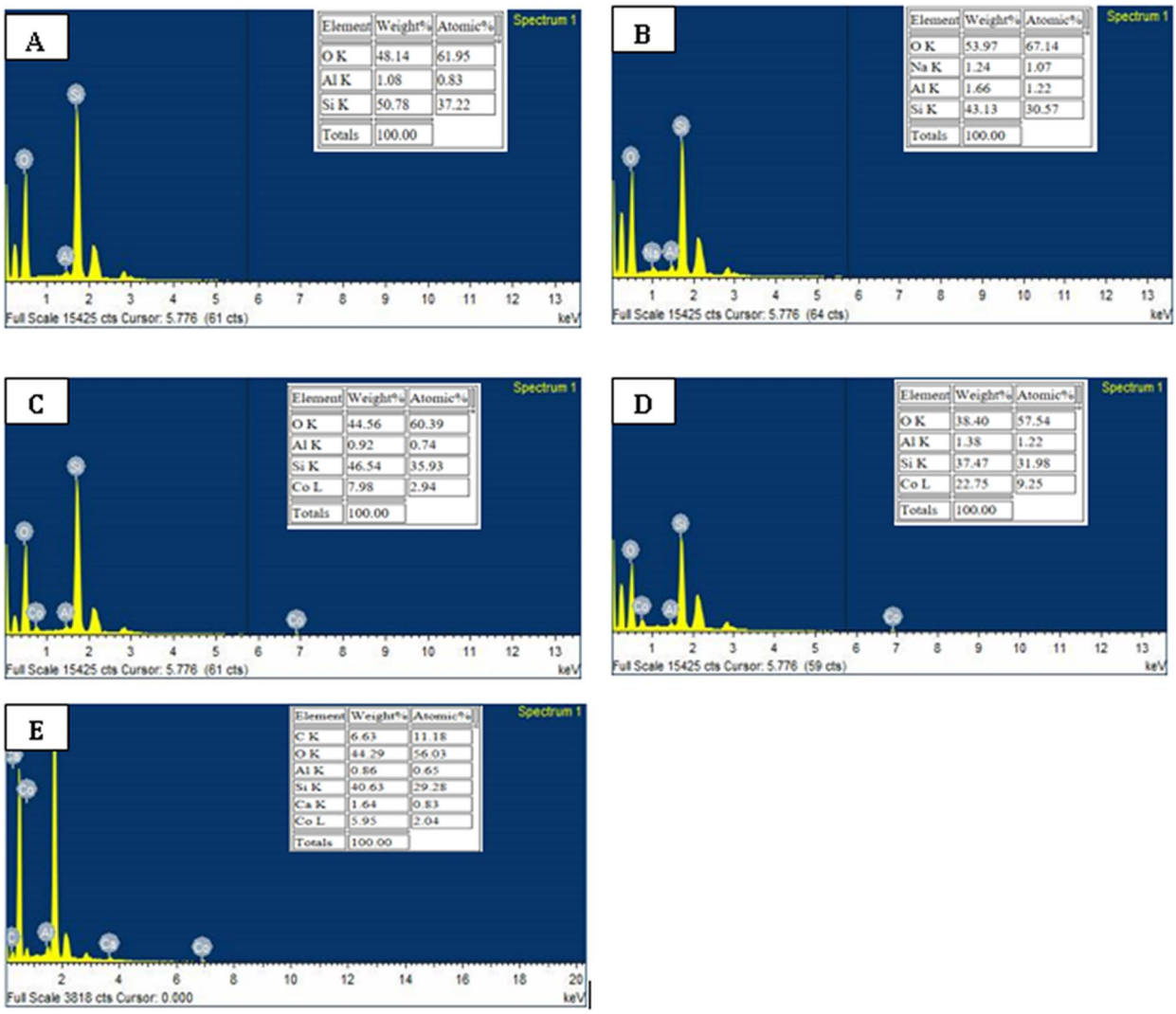


**Figure 5.** Energy dispersive spectroscopy (EDS) of (A) calcined-ZSM-5, (B) desilicated H-ZSM-5, (C) Co/H-ZSM-5, (D) Co/desilicated-H-ZSM-5, and (E) Ca-Co/H-ZSM-5.

the final Co/H-ZSM-5. It is very arguable that the possible reason for obtaining 7.98 wt. % Co loading instead of 10 wt.% loading could be that the area mapped during the EDX analysis had less of Co particles. Daramola et al. (Daramola et al. 2017) reported a 25 wt. % of Co after following the same IWI method. Sartipi et al. (Sartipi et al. 2014) reported a weight percentage of 9.3 wt. % Co loading in the $Co/SiO_2$ catalyst. A sudden increase of Cobalt wt% from 7.98% to 22.75% was observed in Figure 5D, attributable to the mesoporous surface of H-ZSM-5 that accommodate more Co particles as active sites.

It can be observed in Figure 5E that calcium, used as a promoter, was successfully added to the catalyst (1.64 wt. %). The addition of the calcium promoter resulted in a decrease of the cobalt loading from 7.98% (see Figure 5C) to 5.95% (see Figure 5E). This could be attributed to the catalyst surface being covered by Ca. This is due to the fact that $Ca(NO_3)_2$ has a higher solubility in water than Cobalt nitrate, so calcium metal may be more concentrated on catalyst surface precursor after precipitation. Tao et al. (2006) reported the reduction in content of iron carbides on the surface of their catalyst after the addition of calcium as a promoter.

### *Surface chemistry of the catalysts*

The spectra of the FTIR analysis shown in Figure 6 show the nature of acidity of the ZSM-5 zeolites. Figure 6A gives the comparison between the spectra of the desilicated H-ZSM-5 zeolite and the undesilicated H-ZSM-5 zeolite. It is

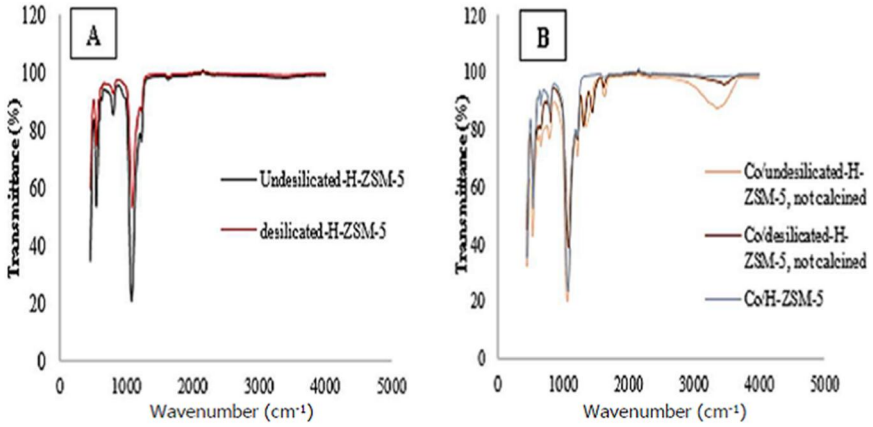


**Figure 6.** The FT-IR spectra of (A) desilicated and undesilicated-H-ZSM-5 zeolites, (B) Co/undesilicated H-ZSM-5 and Co/desilicated-H-ZSM-5 before calcination, Co/H-ZSM-5 catalyst.

known that zeolite is an alumino-silicate material. According to Figure 6A and 6B, the band 433 $cm^{-1}$ could be attributed to the T–O bending vibration of internal tetrahedral (where T = Si or Al). The band 542 $cm^{-1}$ is for the double ring; band 797 $cm^{-1}$ for the external symmetric stretch as reported by Zhao et al. (2015). The T–O bending vibration of internal tetrahedral (where T = Si or Al), especially for the internal asymmetric stretch and the external asymmetric stretch could be observed at band 1076 $cm^{-1}$ and 1220 $cm^{-1}$, respectively, agreeing with previous reports (Coates 2006; Zhao et al. 2015; Hosseinpour et al. 2016; Rostamizadeh and Taeb 2015). These identified absorption bands are considered as characteristic signals for the framework vibration of ZMS-5 zeolite. Both desilicated H-ZSM-5 and undesilicated H-ZSM-5 zeolite exhibit these characteristics. However, the intensity of the internal asymmetric stretch at 1076 $cm^{-1}$ decreased in the desilicated zeolite, attributable to the removal of silica by the desilication.

For H-ZSM-5 zeolite, presence of hydroxyl (-OH) group could be identified at band 3570–3200 $cm^{-1}$, which was well pronounced before calcination at band 3409 $cm^{-1}$ for Co/undesilicated H-ZSM-5 catalyst; and at band 3506 $cm^{-1}$ for the Co/desilicated-H-ZSM-5 (see Figure 6B). According to Coates (2006), the hydroxyl anion alters the structure of zeolite ([Al – Si – O]) by introducing that of a silanol group, a functional group in silicon chemistry with the connectivity Si–O–H. The IR band located at 3506 $cm^{-1}$ signifies a strong BrØnsted acid or acidic hydroxyl Si-OH-Al sites, which is closely similar to the IR at band 3610 $cm^{-1}$ at which Holm et al. (Holm et al. 2009) reportedly observed strong BrØnsted acid or acidic hydroxyl Si-OH-Al sites. Upon desilication in diluted 0.2 M NaOH, the intensity of band of Si-OH-Al groups in zeolite reduced and narrowed as represented in Figure 6B, attributable to partly amorphization of zeolite, agreeing with the observation of Sadowska et al. (Sadowska et al. 2013), though a complete disappearance of Si-OH-Al band was reported by the authors when the treatment was with 1 M NaOH. NaOH solution is believed to have reduced the acidity of zeolite regardless of the ion exchange with $NH_4^+$.

### *Performance evaluation of the catalysts*

The Co/H-ZSM-5 zeolite catalyst was tested during F-T synthesis to evaluate its performance. Carbon monoxide conversion and selectivity of hydrocarbons products were the performance evaluators. In addition, performance of catalysts prepared with undesilicated H-ZSM-5 zeolite was compared to those prepared using desilicated H-ZSM-5 zeolite to assess the effect of desilication on the performance of the catalysts. A further investigation on whether the temperature treatment during desilication method and promotion of catalyst on H-ZSM-5 can influence the performance of Co/desilicated-H-ZSM-5 during F-T synthesis was also carried out. The tests were carried out using the following conditions: $H_2/CO$ of 2.5, reaction temperature of 250 °C, total

pressure of 15 bar, flow rate of 1200 gas hourly space velocity (GHSV) and 0.5 g catalyst.

### *Effect of desilication*

Under the process conditions mentioned in Performance evaluation of the catalysts section, the CO conversion obtained over Co/H-ZSM-5 (un-desilicated) was 49.7% (see Table 2). Daramola et al. (Daramola et al. 2017) reported CO conversion of 53.77% under similar conditions while Sartipi et al. (Sartipi et al. 2014) reported CO conversion of 62% (un-desilicated) under different process conditions (reaction temperature of 240 °C, 2.4 $m^3_{STP}.kg_{cat}^{-1}.h^{-1}$, and $H_2$/CO = 2; see Table 3). The slight difference in CO conversion of Daramola et al. (Daramola et al. 2017) and the conversion in this study could be attributed to the difference in the reaction time. In this study, CO conversion was calculated every 2 h for 73 h after attaining a steady state within 25 h (as presented in Figure 7), which gives an average conversion of 49.7%, while Daramola et al. (Daramola et al. 2017) recorded CO conversion every 2 h for about 96 h with an average of CO conversion of 53.77%. The disparity in CO conversion of Sartipi et al. (Sartipi et al. 2014) and this study could be attributed to the difference in process conditions. Figure 7 shows that the CO conversion obtained from Co/un-desilicated H-ZSM-5 catalyst was very unstable in comparison to the CO conversion obtained from the Co/desilicated H-ZSM-5 catalyst. Furthermore, Calleja et al. (Calleja et al. 1995) reported that a high $H_2$/CO ratio enhances high CO conversion. Comparing the CO conversion of 75% reported by Sartipi et al. (Sartipi et al. 2014) for Co/desilicated H-ZSM-5 catalyst with the CO conversion of 84.2% obtained in this study for Co/desilicated H-ZSM-5 catalyst (desilicated at 55 °C), clearly confirms the submission of Calleja et al. for enhanced CO conversion at higher $H_2$/CO ratio because this study used $H_2$/CO ratio of 2.5 while Sartipi et al. used $H_2$/CO of 2.

Results of testing of the Co/desilicated H-ZSM-5 catalyst reveal that the CO conversion dramatically increased to >75%. The increase in CO conversion can be attributed to an increase in cobalt dispersion or Co loading due to an increase in surface area of the H-ZSM-5 by desilication. This result agree with the report of Mochizuki et al. (2012) and Yusuf et al. (2023) where the conversion of soya bean during transesterification reaction to produce biodiesel was increased to 94.% as a result of desilication of ZSM-5 zeolite that was used as the support for the catalyst. The CO conversion of the Co supported on un-desilicated H-ZSM-5 zeolite increased from 49.7% to 76.9% for H-ZSM-5 support desilicated at 40 °C; to 84.2% for for H-ZSM-5 support desilicated at 55 °C and to 79.9% for H-ZSM-5 support desilicated at 70 °C. Sartipi et al. (Sartipi et al. 2014) reported CO conversion of 75% for their Co/meso-H-ZSM-5 catalyst whose desilication was done at 70 °C (note that the testing was carried out at reaction temperature 240 °C and $H_2$/CO = 2; see Table 3). According to Calleja et al. (Calleja et al. 1995), increasing $H_2$/CO ratio increases CO conversion. The CO conversion over Co/H-ZSM-5 (un-desilicated) is low since it is prevented by diffusion limitations of reactants caused by micropore sizes of H-ZSM-5 and poor metal dispersion over

**Table 2.** CO conversion during FT synthesis using Co-based catalyst supported on desilicated H-ZSM-5 supports.

| Catalyst | Average conversion (%) |
|---|---|
| Co/H-ZSM-5 | 49.7 |
| Co/H-ZSM-5 (support desilicated at 40 °C) | 76.9 |
| Co/H-ZSM-5 (support desilicated at 55 °C) | 84.2 |
| Co/H-ZSM-5 (support desilicated at 70 °C) | 79.8 |

**Table 3.** Results compared with literature.

| Process conditions | Catalyst | $\%X_{CO}$ | Selectivity to $C_1$ | Selectivity to $C_2 - C_4$ | Selectivity to $C_{5+}$ |
|---|---|---|---|---|---|
| 1200 $mL^{-1}.gcat^{-1}.h^{-1}$,15 bar, 250 °C, $H_2$/CO = 2.5 (This study) | Co/H-ZSM-5 | 49.7 | 47.8 | 43.4 | 8.8 |
| | Co/H-ZSM-5(40) | 76.9 | 49.8 | 39.7 | 12.3 |
| | Co/H-ZSM-5(55) | 84.2 | 21.7 | 30.4 | 47.9 |
| | Co/H-ZSM-5(70) | 79.8 | 21.5 | 49.5 | 29.0 |
| 2400 $mL^{-1}.gcat^{-1}.h^{-1}$,15 bar, 240 °C, $H_2$/CO = 2 (Sartipi et al.,2014) | Co/H-ZSM-5 | 62 | 21 | 16 | 50 |
| | Co/meso-H-ZSM-5(70) | 75 | 16 | 14 | 55 |
| 1200 $mL^{-1}gcat^{-1}.h^{-1}$,15 bar, 250 °C, $H_2$/CO =2.5 (Daramola et al. ,2017) | Co/H-ZSM-5 | 53.7 | 34.6 | 50.4% | 15% |

Xco = CO conversion.

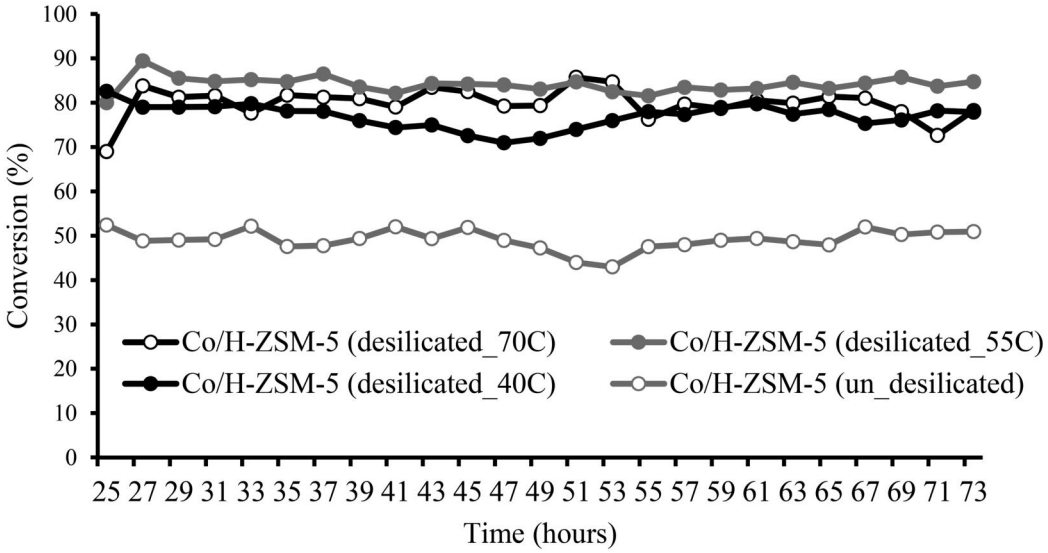


**Figure 7.** Time on the stream of CO conversion recorded every 2 h for 73 h during FTS after attaining a steady state at 25 h. Experimental conditions: Reaction temp.: 250 °C, total pressure: 15 bar, $H_2$/CO: 2.5, GHSV = 1200, amount of catalyst: 0.5 g.

H-ZSM-5 support. The highest CO conversion obtained for this research over Cobalt supported by H-ZSM-5 (desilicated at 55 °C) is 84.2%. The alkaline treatment temperature of 55 °C in 0.2 M NaOH can be regarded as optimal amongst other investigated alkaline treatment temperatures (i.e. 40 °C and 70 °C). This agrees with the observation of Groen et al. (2004). In the study reported by Groen et al.(Groen et al. 2004), where the effect of alkaline treatment of ZSM-5 zeolite in 0.2 M NaOH for 30 min at different temperatures (from 308 K to 358 K) was investigated, the authors observed broadening in the pore-size distribution that led to a higher mesopore volume until 338 K. After 338 K, this property decreased. Consequently, the authors reported an optimal temperature of 338 K (65 °C) for the alkaline treatment of ZSM-5 in a 0.2 M NaOH aqueous solution for 30 min.

The development of bi-functional Co/H-ZSM-5 catalyst in this study is expected to break or challenge the Anderson-Schulz-Flory (ASF) product distribution, which states that in most conventional FT catalysts, the products follow the ASF distribution, yielding a maximum selectivity of gasoline ($C_5$ – $C_{11}$) and diesel ($C_{12}$ – $C_{20}$) hydrocarbons, 45% and 30% for $C_5$ – $C_{11}$ and $C_{12}$ – $C_{20}$, respectively. Literature reveals that zeolite, which is acidic, acts as a determining factor for product distribution since its function is hydrocracking and isomerization once hydrocarbons are formed by F-T catalyst. Methane is referred as $C_1$ and $C_2$ – $C_4$ are considered a lower or middle distillate. Methane selectivity in Table 3 is the average methane relative to both Olefins and paraffins while methane selectivity in Figure 8 and Figure 9 is the methane percentage relative to paraffins only.

Under the same conditions given in Performance evaluation of the catalysts section, the product distribution in terms of both olefins and paraffins selectivity, comparing the performance of cobalt metal loaded on H-ZSM-5 (un-desilicated) and H-ZSM-5 (desilicated) zeolite was studied. The bi-functional catalyst (Co/H-ZSM-5) is more selective to olefins over paraffins. The highest selectivity to methane ($C_1$) was 58.9%, with only 8.8% $C_{5+}$ selectivity over Co/H-ZSM-5 (un-desilicated) where methane selectivity is closely analogous to 53% reported by Daramola et al. (Daramola et al. 2017) under the same conditions (see performance evaluation of the catalysts section). Sartipi et al. (Sartipi et al. 2014) reported the selectivity of methane ($C_1$) and $C_{5+}$ as 21% and 50%, respectively (see Table 3). Methane selectivity of this study is almost three times higher than that of Sartipi et al. (Sartipi et al. 2014). This could probably be due to a higher $H_2$ diffusion rate in the zeolite surface than CO diffusion. This was evidenced by Vervloet et al. (2012) that higher $H_2$/CO ratio yields higher methane production. Co/H-ZSM-5

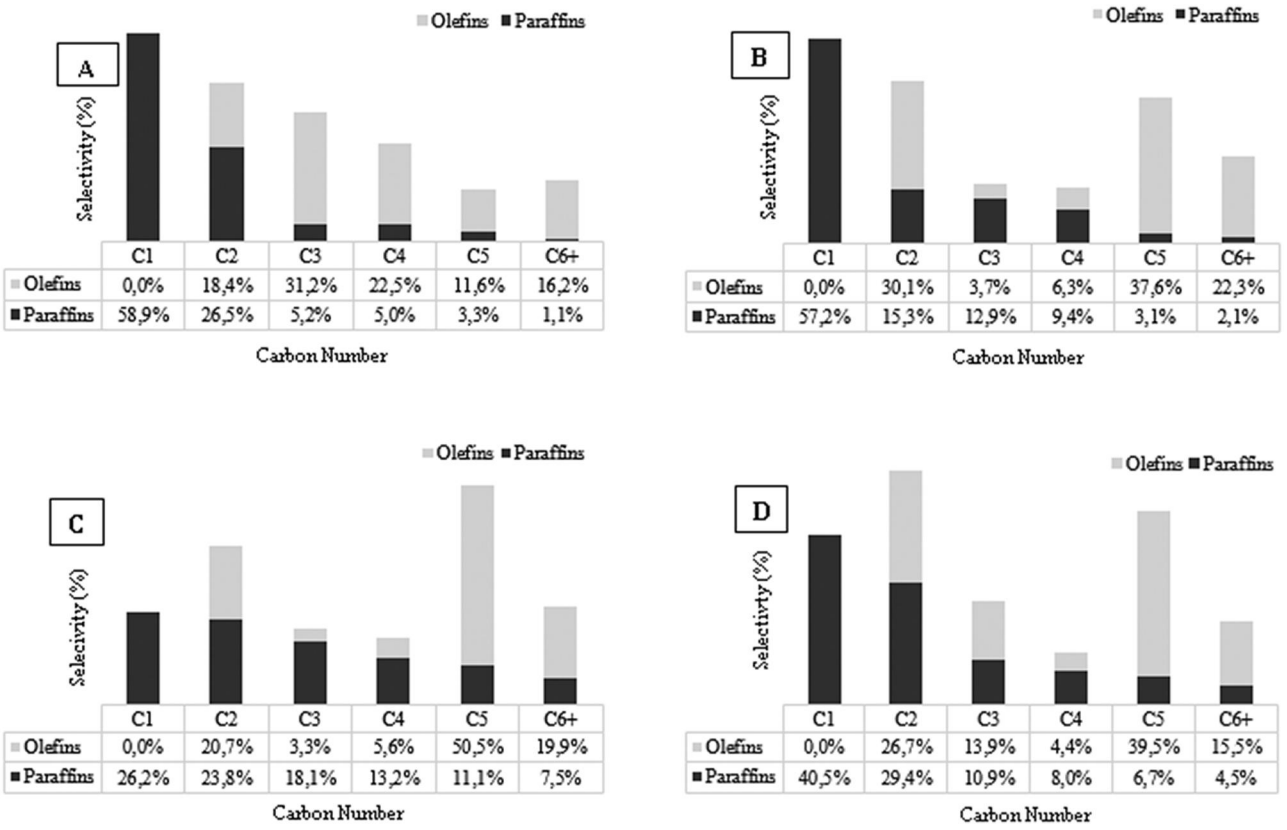


**Figure 8.** Product distribution of paraffins and olefins during F-T synthesis. A = Co/H-ZSM-5(un-desilicated), B = Co/H-ZSM-5 (desilicated 40 °C), C = Co/H-ZSM-5 (desilicated 55 °C) and D = Co/H-ZSM-5 (desilicated 70 °C). Experimental conditions: Reaction temp.: 250 °C, total pressure: 15 bar, $H_2$/CO: 2.5, GHSV = 1200, amount of catalyst: 0.5 g.

catalyst (see Figure 8A) proved to be favorable toward lower hydrocarbons ($C_2$ – $C_4$). Selectivity to paraffin $C_2$ was 26.5%, and to olefin $C_3$ was 31.2%. Thereafter, selectivity decreased from $C_3$ to $C_4$ due to over cracking of HCs in the zeolite, which further resulted in a poor selectivity to desired products ($C_5$ – $C_{6+}$) with $C_5$ and $C_{6+}$ paraffin of 3.3% and 1.1%, respectively, together with $C_5$ and $C_{6+}$ olefins of 11.6% and 16.2%. Daramola et al.(Daramola et al. 2017) reported $C_5$ paraffin and $C_5$ olefins of 4% and 8%, respectively. However, the overall (both paraffins & olefins) $C_5$ – $C_{6+}$ selectivity in this study was calculated to be 16.1%, which is closely equal to 15% reported by Daramola et al.(Daramola et al. 2017). In summary, the presence of micropores of acidic zeolite sites causes over-cracking of primary hydrocarbons because of the slow transportation of products inside zeolite reported (Bao et al. 2009). Apart from the ~50% CO conversion of syngas to liquid fuels, the gasoline-range or higher HCs were poorly produced. However, the introduction of meso-porosity into H-ZSM-5 zeolite *via* desilication enhanced the selectivity of these gasoline-range hydrocarbons (GRHs), see Figure 8B–D.

The product selectivity depends on the desilication temperature for mesoporous ZSM-5. For the meso-H-ZMS-5 prepared using 40 °C treatment temperature, which is denoted as Co/H-ZSM-5(40), the methane ($C_1$) and $C_2$ – $C_4$ selectivity decreased to 57.2% and 37.9%, respectively, while $C_5$ – $C_{6+}$ selectivity increased from 8.8% to 12.3%. In more detail (see Figure 8A and 8B), the selectivity to $C_2$ paraffin decreased from 26.5% to 15.3%, and the selectivity to $C_3$ and $C_4$ olefin decreased from 31.2% to 3.7% and 22.5% to 6.3%, respectively. The performance of Co/H-ZSM-5(40) catalyst significantly increased the selectivity to $C_5$ and $C_{6+}$ olefin hydrocarbons from 11.6% to 37.6% and 16.2% to 22.3%, respectively. Through results observation, the desilicated-H-ZSM-5 prepared using 0.2 M NaOH aqueous solution at 40 °C had no major influence on paraffin higher hydrocarbons.

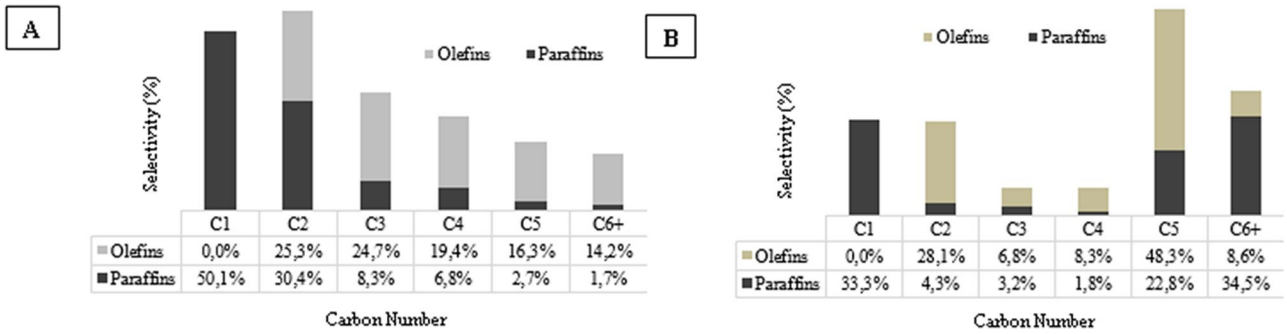


**Figure 9.** Product distribution of paraffins and olefins during F-T synthesis. A = Co/H-ZSM-5(un-desilicated), B = Co/H-ZSM-5 (desilicated 40 °C), C = Co/H-ZSM-5 (desilicated 55 °C) and D = Co/H-ZSM-5 (desilicated 70 °C). Experimental conditions: Reaction temp.: 250 °C, total pressure: 15 bar, $H_2$/CO: 2.5, GHSV = 1200.

Further increases in NaOH temperature treatment to 55 °C for mesoporous H-ZSM-5 increased the $C_5$ – $C_{6+}$ selectivity to 47. 9% and dramatically decreased $C_1$ selectivity to 26.2%. Figure 8C depicts the product distribution results of Co/desilicated H-ZSM-5 catalyst desilicated at 55 °C using 0.2 M NaOH, which is denoted as Co/H-ZSM-5(55). Comparing Figure 8B and Figure 8C, the selectivity to $C_3$ & $C_4$ paraffin and olefins remains unchanged. Interestingly, about 50% significant drop toward $C_1$ and $C_2$ selectivity was observed. For instance, selectivity to $C_2$ hydrocarbons decreased from paraffin (15.3%) and olefin (30.1%) to 11.2% and 6.7% for paraffin and olefin, respectively. It is important to mention an increase in $C_5$ hydrocarbons (from 37.6% to 56.5% $C_5$ olefin) was observed. It can be concluded that the performance of desilicated-Co/H-ZSM-5(55) catalyst, could also be attributed to the mesoporosity of the support after desilication (see Figure 8C) allowing an easier and faster access to higher hydrocarbons compared to the performance of Co/H-ZSM-5(40) catalyst (see Figure 8B). Groen et al. (Groen et al. 2004) reported an increase of BET surface area to 550 $m^2$/g for ZSM-5 desilicated at about 65 °C using 0.2 M NaOH aqueous solution.

Unexpectedly, the performance of desilicated-Co/H-ZSM-5(70) catalyst during FTS brought about no better results (Figure 8D) when compared to the results in Figure 8C. This can be attributed to production of more undesirable methane (40.5%) and $C_2$ – $C_4$ selectivity (49.5%) with a drop in $C_5$ – $C_{6+}$ selectivity (29.0%). However, the use of Co/H-ZSM-5(70) catalyst maintained high selectivity to some hydrocarbons (HCs). For instance, selectivity to $C_5$ olefins slightly increased to 39.5%. The higher selectivity to ($C_5$ – $C_{6+}$) can be the result of the weak acidity of catalysts. Though no experimental investigation, such as $NH_3$-TPD of the catalyst, was carried out in this study to confirm this because this instrument was faulty at the time this study was carried out, our discussion was based on previous studies. For instance, the study from Su et al. (2019) on the conversion of syngas to light olefins resulting in high olefin/paraffin ratio using ZnCrOx/AlPO-18 bi-functional catalysts confirm this speculation. In addition, the work of Wang et al. (2020) on effective iron catalysts supported on mixed $MgO-Al_2O_3$ for Fischer – Tropsch synthesis to olefins provide a similar explanation to the reported observation of this study. In other words, desilication increased the catalytic activity; caused a loss in the acidity of zeolite, thus improved the selectivity of HCs (Yusuf et al. 2023). A clear observation between Figure 8B and Figure 8D is that although desilicated Co/H-ZSM-5(70) catalyst outperformed desilicated Co/H-ZSM-5(40), in terms of gasoline-range ($C_5$-$C_{6+}$) hydrocarbons, it cannot be recommended due to its hydrocracking characteristics. In terms of overall performance, the best results were achieved over desilicated-Co/H-ZSM-5(55) (i.e. CO coversion 84.25; $C_{5+}$ selectivity of 47.9%).

According to a few studies reported in literature, presence of the $Na^+$ in the support from the alkaline desilication of the support could enhance catalyst selectivity (Xiong et al., 2015; Zhao et al. 2018). For instance, the studies by Zhao et al. (2018) for $\gamma$-$Al_2O_3$ support and by

Auepattana-Aumrung et al. (2020) for the ZSM-5 support reported that presence of $Na^+$ in their catalysts enhanced the conversion and selectivity of their catalysts. These authors also reported that presence of $Na^+$ can reduce the acidity of catalyst support, thereby preventing or reducing the rate of coke formation. The enhanced CO conversion and selectivity displayed by the Co-based catalysts supported on H-ZSM-5 desilicated using 0.2 M NaOH might be partly attributed to the presence of residual $Na^+$ observed in the catalyst support (see the EDX results presented in Figure 5). This explanation is speculative based on reported studies; such as studies have shown that presence of $Na^+$ can reduce the acidity of catalyst support as demonstrated by Zhao et al. (2018) for the $\gamma$-$Al_2O_3$ and Auepattana-Aumrung et al. (2020) for the ZSM-5 support.

### *Effect of Ca promotion*

Since a higher conversion was obtained from Co/H-ZSM-5(55) catalyst as reported in Table 2; thus, investigation of effect of promotion with Ca was carried out using this catalyst. Both un-desilicated and desilicated catalysts were promoted with Ca and tested under the same conditions. Calcium promoted catalysts of both Co/H-ZSM-5 and Co/H-ZSM-5(55) are denoted as Ca-Co/H-ZSM-5 (un-desilicated) and Ca-Co/H-ZSM-5(55) (desilicated at 55 °C). The addition of Ca to Co/H-ZSM-5 improved the activity of the catalysts. By promoting with calcium, CO conversions increased to 50.2% and 90.9% for Ca-Co/H-ZSM-5 and Ca-Co/H-ZSM-5(55), respectively (see Table 4). These results agree well with the outcome of the investigation of Tao et al. (Tao et al. 2006) where the authors have reported that presence of calcium as a promoter in their catalyst favors the dissociative adsorption of CO but suppresses $H_2$ adsorption during F-T synthesis reaction.

The selectivity for the catalysts to $C_5$ – $C_{6+}$ paraffin over olefin, calculated using Equation (4) was also influenced by the calcium promotion.

**Table 4.** Effect of low pressure on CO conversion over calcium promoted Co/H-ZSM-5 catalyst during FT synthesis.

| Catalyst | Pressure (bar) | CO conversion (%) |
|---|---|---|
| Ca-Co/H-ZSM-5 (55) | 8 | 47.7 |
| Ca-Co/H-ZSM-5 (55) | 2 | 17.4 |

According to Equation (4), a decrease in the olefin ratio indicates an increase in paraffin. The results show that $C_6$ olefin ratio decreased from 93.5% for Co/H-ZSM-5 catalyst (undesilicated) to 89.5% for Ca-Co/H-ZSM-5 (undesilicated). $C_5$ olefin ratio decreased from 77.0% for Co/H-ZSM-5(55) (desilicated) to 68.0% for Ca-Co/H-ZSM-5(55) (desilicated), while $C_{6+}$ olefin ratio dropped from 47.5% for Co/H-ZSM-5 (desilicated) to 19.9% for Ca-Co/H-ZSM-5(55) (desilicated).

$$Olefin\ \ Ratio = \frac{Olefin}{Olefin + Paraffin} \tag{5}$$

Ngantsoue-Hoc et al. (2002) reported that the fraction of alkene (olefin ratio) decreased as the CO conversion increased for both unpromoted and calcium promoted catalysts. In general, the $C_5$ – $C_{6+}$ selectivity continued to increase after the promotion of the catalysts. $C_5$ – $C_{6+}$ selectivity increased to 9.7% from 8.8% (unpromoted Co/H-ZSM-5) and to 57.2% from 47.9% (unpromoted Co/H-ZSM-5(55)). Figure 9B shows that both $C_5$ and $C_{6+}$ paraffin drastically increased from 11.1% to 22.8% (for promoted Co/H-ZSM-5) and from 7.5% to 34.5% ((promoted Co/H-ZSM-5(55)). From these data and according to those reported by De La Osa et al. (2011) and Bao et al. (Bao et al. 2009), $C_{5+}$ selectivity increased due to the promotion of the catalyst (in this case, calcium promotion).

Promoting the catalysts with calcium enhanced the selectivity of the catalyst to $C_5$ – $C_{6+}$ selectivity. Re-adsorption of smaller reactive products (such as ethene and propene) toward increasing longer hydrocarbons ($C_{5+}$) has been attributed to the presence of Ca as a promoter in Co/zeolite-based catalysts (Schulz and Claeys 1999; Van Der Laan and Beenackers 1999; De La Osa et al. 2011). Similar observation is seen in this study. Thus, presence of Ca in the catalyst has enhanced the selectivity of the catalyst toward a longer chain hydrocarbon ($C_5$ – $C_{6+}$). The retained high selectivity to higher hydrocarbons ($C_5$ – $C_{6+}$) manifests the advantage of the presence of calcium in cobalt-based catalyst which is known for its re-adsorption of smaller reactive products (such as ethene and propene) into increasing, adding to ($C_{5+}$) longer hydrocarbons (Schulz and

Claeys 1999; Van Der Laan and Beenackers 1999; De La Osa et al. 2011).

## Conclusion

From microporous H-ZSM-5 zeolite (Si/Al = 47), a mesoporous H-ZSM-5 zeolite was successfully obtained *via* alkaline desilication using 0.2 M NaOH aqueous solution for 30 min at treatment temperatures 40 °C, 55 °C, and 70 °C. Co-based catalysts were synthesized using the H-ZSM-5 zeolite (un-desilicated and desilicated) as the catalyst support. The prepared catalysts were promoted using calcium to enhance their catalytic reactivity (i.e., conversion and selectivity). The promoted and unpromoted catalysts were tested in F-T synthesis for production of gasoline-range ($C_5$ – $C_{6+}$) hydrocarbons from syngas.

CO conversion increased from about 50% for the Co catalyst, supported on undesilicated H-ZSM-5, to >75% for Co catalyst, supported on desilicated H-ZSM-5. The high selectivity to $C_5$ – $C_{6+}$ was recorded for Co/HZSM-5 catalyst prepared using H-ZSM-5 zeolite desilicated at 55 °C. A 60% selectivity of higher-HCs ($C_5$ – $C_{6+}$), including both paraffins and olefins was obtained over Co/HZSM-5 (55) catalyst. The Co catalyst supported on the desilicated H-ZSM-5 displayed a reduced selectivity to both methane ($C_1$) and lower-HCs ($C_2$ – $C_4$).

In conclusion, this study highlights a new approach for further improvement of $C_5$ – $C_{6+}$ selectivity in FT synthesis. However, understanding the effect of varying the concentration of NaOH solution during desilication on the formation of mesoporosity and performance of catalyst obtained thereof might be important. In addition, MgO-based catalyst, a study from Wang et al. where MgO has been introduced to the catalyst can be studied further for further improvement of $C_5$–$C_{6+}$ selectivity in FT synthesis because according to the authors the catalyst displayed improved CO conversion and promoted olefin-to-paraffin ratio with $C_4$ and $C_5$ obtained for 50% MgO-loaded catalyst (Wang et al., 2020).

## Acknowledgments

The authors acknowledge University of the Witwatersrand and University of Pretoria in South Africa for providing an enabling environment to perform the experiment.

## Disclosure statement

No potential conflict of interest is reported by the authors.

## References

Abelló S, Bonilla A, Pérez-Ramírez J. 2009. Mesoporous ZSM-5 zeolite catalysts prepared by desilication with organic hydroxides and comparison with NaOH leaching. Appl Catal, A. 364(1-2):191–198. doi: 10.1016/j.apcata.2009.05.055.

Auepattana-Aumrung C, Suriye K, Jongsomjit B, Panpranot J, Praserthdam P. 2020. Inhibition effect of Na + form in ZSM-5 zeolite on hydrogen transfer reaction via 1-butene cracking. Catal Today. 358:237–245. doi: 10.1016/j.cattod.2019.08.012.

Bao A, Liew K, Li J. 2009. Fischer–Tropsch synthesis on CaO-promoted Co/Al2O3 catalysts. J Mol Catal A: Chem. 304(1-2):47–51. doi: 10.1016/j.molcata.2009.01.022.

Calleja G, de Lucas A, van Grieken R. 1995. Co/HZSM-5 catalyst for syngas conversion: influence of process variables. Fuel. 74(3):445–451. doi: 10.1016/0016-2361(95)93480-2.

Che M, Védrine JC. 2012. Characterization of solid materials and heterogeneous catalysts: from structure to surface reactivity. Germany: John Wiley & Sons.

Coates J. 2006. Interpretation of infrared spectra, a practical approach. In Meyers RA, editor. Encyclopedia of analytical chemistry: applications, theory and instrumentation. Chichester: John Wiley and Sons Ltd. p. 10815–10837.

Dagle RA, Lizarazo-Adarme JA, Dagle VL, Gray MJ, White JF, King DL, Palo DR. 2014. Syngas conversion to gasoline-range hydrocarbons over $Pd/ZnO/Al_2O_3$ and ZSM-5 composite catalyst system. Fuel Process Technol. 123:65–74. doi: 10.1016/j.fuproc.2014.01.041.

Dancuart L, Steynberg A. 2007. Fischer-Tropsch based GTL technology: a new process? Studies in Surface Science and Catalysis. 163:379–399. doi: 10.1016/S0167-2991(07)80490-3.

Daramola MO, Matamela K, Sadare OO. 2017. Effect of $CO_2$ co-feeding on the conversion of syngas derived from waste to liquid fuel over a bi-functional Co/H-ZSM-5 catalyst. J. Environ Chem. Eng. 5(1):54–62. doi: 10.1016/j.jece.2016.11.019.

De la Osa A, De Lucas A, Romero A, Valverde J, Sánchez P. 2011. Fischer–Tropsch diesel production over calcium-promoted Co/alumina catalyst: effect of reaction conditions. Fuel. 90(5):1935–1945. doi: 10.1016/j.fuel.2010.12.024.

Downs RT, Hall-Wallace M. 2003. The American Mineralogist crystal structure database. Am Mineral. 88(1):247–250.

Dry ME. 2002. High quality diesel via the Fischer–Tropsch process–a review. J of Chemical Tech & Biotech. 77(1):43–50. doi: 10.1002/jctb.527.

Groen JC, Peffer LAA, Moulijn JA, Pérez-Ramírez J. 2004. Mesoporosity development in ZSM-5 zeolite upon optimized desilication conditions in alkaline medium.

Colloids Surf, A. 241(1-3):53–58. doi: 10.1016/j.colsurfa.2004.04.012.

Matamela K. 2016. Synthesis and performance evaluation of Co/H-ZSM-5 bi-functional catalyst for Fischer-Tropsch synthesis [MSc dissertation]. South Africa: University of the Witwatersrand.

Mochizuki H, Yokoi T, Imai H, Namba S, Kondo JN, Tatsumi T. 2012. Effect of desilication of H-ZSM-5 by alkali treatment on catalytic performance in hexane cracking. Appl Catal, A. 449:188–197. doi: 10.1016/j.apcata.2012.10.003.

Holm MS, Hansen MK, Christensen CH. 2009. One-Pot" Ion-Exchange and Mesopore Formation During Desilication. Eur J Inorg Chem. 2009(9):1194–1198. doi: 10.1002/ejic.200801194.

Hong Y, Fripiat J. 1995. Microporous characteristics of H Y, H-ZSM-5 and H-mordenite dealuminated by calcination. Microporous Materials. 4(5):323–334. doi: 10.1016/0927-6513(95)00038-B.

Hosseinpour M, Amiri H, Ahmadi SJ, Mousavian MA. 2016. The role of supercritical water on the rapid formation of ZSM-5 nanocatalyst. J. Supercrit. Fluids. 107(2016):479–485. doi: 10.1016/j.supflu.2015.06.013.

Jahangiri H, Bennett J, Mahjoubi P, Wilson K, Gu S. 2014. A review of advanced catalyst development for Fischer-Tropsch synthesis of hydrocarbons from biomass derived syngas. Catal. Sci. Tech. 4(8):2210–2229. doi: 10.1039/C4CY00327F.

Janssen A, Schmidt I, Jacobsen C, Koster A, De Jong K. 2003. Exploratory study of mesopore templating with carbon during zeolite synthesis. Microporous Mesoporous Mater. 65(1):59–75. doi: 10.1016/j.micromeso.2003.07.003.

Lu X, Hildebrandt D, Liu X, Glasser D. 2010. Making sense of the Fischer – Tropsch synthesis reaction: start-up. Ind Eng Chem Res. 49(20):9753–9758. doi: 10.1021/ie1011933.

Müller M, Harvey G, Prins R. 2000. Comparison of the dealumination of zeolites beta, mordenite, ZSM-5 and ferrierite by thermal treatment, leaching with oxalic acid and treatment with SiCl4 by 1H, 29Si and 27Al MAS NMR. Microporous Mesoporous Mater. 34(2):135–147. doi: 10.1016/S1387-1811(99)00167-5.

Hoc N, Zhang YQ, O'Brien RJ, Luo MS, Davis BH. 2002. Fischer – Tropsch synthesis: activity and selectivity for Group I alkali promoted iron-based catalysts. Appl. Catal. A: Gen. 236:77–89.

Ogura M, Shinomiya S-y, Tateno J, Nara Y, Nomura M, Kikuchi E, Matsukata M. 2001. Alkali-treatment technique—new method for modification of structural and acid-catalytic properties of ZSM-5 zeolites. Appl Catal, A. 219(1-2):33–43. doi: 10.1016/S0926-860X(01)00645-7.

Rostamizadeh M, Taeb A. 2015. Highly selective Me-ZSM-5 catalyst for methanol to propylene (MTP). J. Ind. Eng. Chem. 27:297–306. doi: 10.1016/j.jiec.2015.01.004.

Sadowska K, Wach A, Olejniczak Z, Kuśtrowski P, Datka J. 2013. Hierarchic zeolites: zeolite ZSM-5 desilicated with NaOH and NaOH/tetrabutylamine hydroxide. Microporous Mesoporous Mater. 167:82–88. doi: 10.1016/j.micromeso.2012.03.045.

Santos VP, Borges L, Sartipi S, van der Linden B, Dugulan AI, Chojecki A, Davidian T, Ruitenbeek M, Meimac GR, Kapteijn F. et al. 2017. High-temperature Fischer-Tropsch synthesis over FeTi mixed oxide model catalysts: tailoring activity and stability by varying the Ti/Fe ratio. Appl Catal, A. 533:38–48. doi: 10.1016/j.apcata.2017.01.002.

Sartipi S, Alberts M, Santos VP, Nasalevich M, Gascon J, Kapteijn F. 2014. Insights into the catalytic performance of mesoporous H-ZSM-5-supported cobalt in Fischer–Tropsch synthesis. ChemCatChem. 6(1):142–151. doi: 10.1002/cctc.201300635.

Sartipi S, Parashar K, Makkee M, Gascon J, Kapteijn F. 2013. Breaking the Fischer–Tropsch synthesis selectivity: direct conversion of syngas to gasoline over hierarchical Co/H-ZSM-5 catalysts. Catal Sci Technol. 3(3):572–575. doi: 10.1039/C2CY20744C.

Sartipi S, Parashar K, Valero-Romero MJ, Santos VP, Van Der Linden B, Makkee M, Kapteijn F, Gascon J. 2013. Hierarchical H-ZSM-5-supported cobalt for the direct synthesis of gasoline-range hydrocarbons from syngas: advantages, limitations, and mechanistic insight. J. Catalysis. 305:179–190. doi: 10.1016/j.jcat.2013.05.012.

Sartipi S, Van Dijk JE, Gascon J, Kapteijn F. 2013. Toward bifunctional catalysts for the direct conversion of syngas to gasoline range hydrocarbons: h -ZSM-5 coated Co versus H-ZSM-5 supported Co. Appl Catal, A. 456:11–22. doi: 10.1016/j.apcata.2013.02.012.

Schulz H, Claeys M. 1999. Reactions of alpha-olefins of different chain length added during Fischer-Tropsch synthesis on a cobalt catalyst in a slurry reactor. Appl. Catal. 186(1-2):71–90. doi: 10.1016/S0926-860X(99)00165-9.

Su J, Zhou H, Liu S, Wang C, Jiao W, Wang Y, Liu C, Ye Y, Zhang L, Zhao Y. et al. 2019. Syngas to light olefins conversion with high olefin/paraffin ratio using ZnCrOx/AlPO-18 bifunctional catalysts. Nat Commun. 10(1):1297. doi: 10.1038/s41467-019-09336-1.

Tao Z, Yang Y, Zhang C, Li T, Wang J, Wan H, Xiang H, Li Y. 2006. Effect of calcium promoter on a precipitated iron–manganese catalyst for Fischer–Tropsch synthesis. Catal Commun. 7(12):1061–1066. doi: 10.1016/j.catcom.2006.05.009.

Van der Laan GP, Beenackers AACM. 1999. Kinetics and Selectivity of the Fischer–Tropsch Synthesis: a literature review. Catal. Rev. Sci. Eng. 41(3&4):255–318.

Vervloet D, Kapteijn F, Nijenhuis J, Van Ommen JR. 2012. Fischer–Tropsch reaction–diffusion in a cobalt catalyst particle: aspects of activity and selectivity for a variable chain growth probability. Catal Sci Technol. 2(6):1221–1233. doi: 10.1039/c2cy20060k.

Wang S, Yin Q, Guo J, Ru B, Zhu L. 2013. Improved Fischer–Tropsch synthesis for gasoline over Ru, Ni promoted Co/HZSM-5 catalysts. Fuel. 108:597–603. doi: 10.1016/j.fuel.2013.02.021.

Xing C, Yang G, Lu P, Shen W, Gai X, Tan L, Mao J, Wang T, Yang R, Tsubaki N. 2016. A hierarchically spherical co-based zeolite catalyst with aggregated nanorods structure for improved Fischer–Tropsch synthesis reaction activity and isoparaffin selectivity. Microporous Mesoporous Mater. 233:62–69. doi: 10.1016/j.micromeso.2015.10.021.

Xiong H, Motchelaho MA, Moyo M, Jewell LL, Coville NJ. 2015. Effect of Group I alkali metal promoters on Fe/CNT catalysts in Fischer–Tropsch synthesis. Fuel. 150:687–696. doi: 10.1016/j.fuel.2015.02.099.

Yao, J. (2011). Fisher-Tropsch synthesis using $CO_2$-cotaining syngas mixtures over cobalt and iron-based catalysts, PhD Thesis. South Africa: University of the Witwatersrand.

Yoo WC, Zhang X, Tsapatsis M, Stein A. 2012. Synthesis of mesoporous ZSM-5 zeolites through desilication and reassembly processes. Microporous Mesoporous Mater. 149(1):147–157. doi: 10.1016/j.micromeso.2011.08.014.

Yusuf BO, Oladepo SA, Ganiyu SA. 2023. Zr-modified desilicated ZSM-5 catalysts as highly active and recyclable catalysts for production of biodiesel from soybean oil: insight into improved catalyst properties, acidity and dispersion through desilication. Fuel. 351:128729. doi: 10.1016/j.fuel.2023.128729.

Wang Y, Li H-X, Li X-G, Chen D, Xiao W-D. 2020. Effective iron catalysts supported on mixed MgO – Al2O3 for Fischer – Tropsch Synthesis to Olefins. Ind Eng Chem Res. 59(25):11462–11474. doi: 10.1021/acs.iecr.0c01603.

X, Zhao X, Wei L, Cheng S, Huang Y, Yu Y, Julson J. 2015. Catalytic cracking of camelina oil for hydrocarbon biofuel over ZSM-5-Zn catalyst. Fuel Process. Technol. 139:117–126. doi: 10.1016/j.fuproc.2015.07.033.

Zhao S, Xu B, Yu L, Fan Y. 2018. Catalytic dehydrogenation of propane to propylene over highly active PtSnNa/$\gamma$-$Al_2O_3$ catalyst. Chin Chem Lett. 29(3):475–478. doi: 10.1016/j.cclet.2017.09.020.

Zhou J, Hua Z, Liu Z, Wu W, Zhu Y, Shi J. 2011. Direct synthetic strategy of mesoporous ZSM-5 zeolites by using conventional block copolymer templates and the improved catalytic properties. ACS Catal. 1(4):287–291. doi: 10.1021/cs1000976.