

Attrition Resistant Fischer-Tropsch Catalysts Based On FCC Supports

Final Report

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ABSTRACT

Commercial spent fluid catalytic cracking (FCC) catalysts provided by Engelhard and Albemarle were used as supports for Fe-based catalysts with the goal of improving the attrition resistance of typical F-T catalysts. Catalysts with the Ruhrchemie composition (100 Fe/5 Cu/4.2 K/25 spent FCC on mass basis) were prepared by wet impregnation. XRD and XANES analysis showed the presence of Fe₂O₃ in calcined catalysts. FeC_x and Fe₃O₄ were present in the activated catalysts. The metal composition of the catalysts was analyzed by ICP-MS. F-T activity of the catalysts activated *in situ* in CO at the same conditions as used prior to the attrition tests was measured using a fixed bed reactor at T = 573 K, P = 1.38 MPa and H₂:CO ratio of 0.67. Cu and K promoted Fe supported over Engelhard provided spent FCC catalyst shows relatively good attrition resistance (8.2 wt% fines lost), high CO conversion (81%) and C₅+ hydrocarbons selectivity (18.3%).

Keywords: Fischer-Tropsch synthesis, spent FCC materials, Attrition, Jet-cup

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NOMENCLATURE

(P)	Precipitated
(B)	Binder
CAER	Center of Advanced Energy Research
NETL	National Energy Technology Laboratory
SBCR	Slurry Bubble Column Reactor
WGS	Water Gas Shift
XRD	X-Ray Powder Diffraction
TPR	Temperature Programmed Reduction
SEM	Scanning Electron Microscope
EDXS	Energy Dispersive X-Ray Spectroscopy
PSD	Particle Size Distribution
FTS	Fischer-Tropsch Synthesis
TOS	Time on Stream
STSR	Stirred Tank Reactor

ATTRITION RESISTANT FISCHER-TROPSCH CATALYSTS BASED ON FCC SUPPORTS

1.0 Introduction: Problem Definition

Clean, efficient fuels can be produced using the Fischer-Tropsch Synthesis (FTS), which is the reaction of CO and H₂ (syngas), typically using iron-or cobalt-based catalysts. A number of plants are currently either under construction or in the planning stage (Table 1; Anon, 2004).

Table 1. Near-term Fischer Tropsch plants		
	Plant site	
	Nigeria, Escravos	Qatar, Ras Laffan
Scheduled startup	2007	2005
Design capacity (Mbbpd)	34	34
F-T unit technology	Sasol	Sasol
Investment estimate/daily capacity barrel (\$/bbl)	23,500	23,500

In addition to Sasol’s coal-based FT plants in South Africa, two natural gas-based plants have been operating over the past 10 years: Shell’s 15,000 b/d plant at Bintulu, Malaysia and a government-owned 20,000 b/d plant at Moss Bay in South Africa (Thackery, 2004). At least 24 proposals for FT projects have been announced in the past two years, most for large plants of 100,000 b/d or more. These activities clearly show that improvements and innovations in FTS are underway. Given recent trends in energy prices, FTS is likely to be even more important to the production of clean fuels.

Coal-based FTS. This process is also strategically important to the U.S. because of its vast coal reserves, and because FTS represents the best means to make high quality transportation fuels and liquid products from coal. In addition to other technical issues, heat removal is a major reactor design challenge. Recent progress in this area has focused on the use of a slurry bubble

column reactor (SBCR), originally developed commercially in the early 1990's by Sasol. A 5-m diameter, 2500 b/d was brought on line during this time and operated for 10 years (Davis, 2003). These reactors are conceptually simple and inexpensive, but still permit high catalyst and reactor productivity. It is generally thought that this will be the reactor of choice for commercial, coal-based FTS in the United States.

Since modern coal gasification plants produce a syngas that is relatively lean in H₂ (H₂/CO \cong 0.5-0.7), a catalyst which is active for the FTS reaction ($\text{CO} + 2 \text{H}_2 \rightarrow -\text{CH}_2- + \text{H}_2\text{O}$) and the water-gas shift (WGS) reaction ($\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$) is required. The overall reaction on these catalysts is thus $2\text{CO} + \text{H}_2 \rightarrow -\text{CH}_2- + \text{CO}_2$. This allows the efficient use of low H₂/CO syngas. Iron-based catalysts, which are active shift catalysts, are thus preferred over cobalt-based catalysts; which are not. Iron is also much less expensive than cobalt.

There are two major barriers to the widespread commercialization of FTS using SBCRs:

- (i) severe attrition of currently available iron-based catalysts. This attrition causes plugging, fouling, difficulty in separating the catalyst from the wax product, and loss of the catalyst. Each of these effects can result in very poor process economics.
- (ii) production of a non-selective product slate of C₁ to C₆₀⁺ hydrocarbons, requiring expensive downstream separation and processing, again resulting in poor economics.

This project addresses both of these two barriers by developing attrition-resistant chain-limiting iron-based F-T catalysts for SBCRs that maximize the production of C₁₀ to C₂₀ hydrocarbons, while limiting the production of light gases and C₂₀⁺ hydrocarbons.

Hampton University, in collaboration with Louisiana State University, has put together an exceptional research team. Also, a major commercial catalyst manufacturer, SUD CHEMIE, INC, will be providing guidance to the project and cost sharing.

2.0 EXECUTIVE SUMMARY

Fischer-Tropsch (F-T) technology can be briefly defined as the means used to convert coal or natural gas derived synthesis gas containing H₂ and CO into clean hydrocarbons using iron or cobalt based catalysts [1-3]. This can be expressed as (eqⁿ-1),



For coal derived syngas, which typically has a low H₂/CO ratio of 0.5-0.7, Fe-based catalysts are preferred for F-T synthesis over cobalt-based catalysts due to iron's excellent water-gas shift (WGS) activity (eqⁿ-2) and their low cost [4, 5].



However, catalyst attrition, causing plugging of downstream filters, product contamination and increased slurry viscosity, which leads to mass transfer limitations and eventually reactor shutdown is one of the major problems encountered with the industrial application of the Fe F-T catalysts in the slurry bubble column reactors (SBCRs) [6, 7]. A SBCR has been considered as the preferred industrial reactor for the F-T synthesis due to its low capital cost, low pressure drop across the reactor, excellent heat transfer efficiency and capability of on-line catalyst addition and removal [8, 9]. Fe-based catalysts are known to undergo attrition during exposure to syngas at elevated temperatures [10] and their resistance to attrition must be improved for use in SBCRs.

In recent years, several research groups have studied attrition properties of iron based F-T catalysts [4, 11-13]. The major relevant finding from previous studies has been that precipitated unsupported Fe F-T catalysts disintegrate easily into smaller particles [6, 14, 15]. In several studies it was found that even some spray-dried Fe F-T catalysts are not attrition resistant [12, 16-18]. However, Goodwin and coworkers [4, 13, 19], and Pham and coworkers [11, 15] were

able to prepare Fe based F-T catalysts of sufficient attrition resistance using a spray drying method.

Gangwal *et al.*, claimed that Fe or Co impregnated over spent fluid catalytic cracking (FCC) catalysts poisoned with heavy metals such as Ni and V were active in F-T synthesis and are attrition resistant [20]. They used commercial spent FCC catalysts as the supports without any further regeneration or passivation. Also they reported that spent FCC catalysts are more attrition resistant than fresh FCC catalysts. FCC is a particularly well known and widely used process in the oil refineries to crack the heavy oil into smaller hydrocarbon chains used to produce gasoline and heating oil. FCC catalysts are typically composed of 5-40% zeolite Y dispersed in a matrix of synthetic silica-alumina, semi-synthetic clay derived gel or kaolin clay [21, 22]. Worldwide, the production of this important class of catalysts is about 300,000 tons/year for 350 FCC units worldwide [22], 500 tons/day of which spent FCC catalyst is disposed after use. Only 5% of this finds reuse in applications such as cement, asphalt and brick and the remainder is disposed as landfills [20, 22]. With growing environmental concern, land filling is becoming more costly and increasingly less desirable. The use of spent FCC catalyst is advantageous in both economical and environment aspects, due to its low cost and reuse of waste catalyst. Further, the presence of zeolite might improve the selectivity of F-T products towards C₅-C₁₂ hydrocarbons [23].

The objective of the present research is to study the role of spent FCC catalysts as supports for Fe F-T catalysts to improve their resistance to attrition and to study their F-T activity. However, improvement in attrition resistance at the expense of activity and selectivity is not desirable.

3.0 Experimental

F-T synthesis was studied in a fixed bed reactor at a temperature of 573 K and pressure equals to 1.38 MPa. Nominal Ruhrchemie catalyst composition 100 Fe/5 Cu/4.2 K/25 SiO₂ (on a mass basis) was taken as a baseline to synthesize the catalysts. These catalysts were prepared by incipient wetness replacing SiO₂ with spent FCC material as a support. The Ruhrchemie catalyst is a robust precipitated iron catalyst for the F-T synthesis and was used initially in commercial fixed bed reactors at Sasol in South Africa [24, 25]. Two different commercial spent FCC catalysts were procured from Engelhard and Albemarle Corporation for this purpose and were used in this study without any further modification.

3.1 Catalysts Preparation

The catalysts were prepared by wet impregnation method to get Ruhrchemie composition (100 Fe/5 Cu/4.2 K/25 SiO₂). The active metals were impregnated on to the spent FCC support step wise in the sequence of K, Fe and Cu. In a typical experiment, the requisite amount of KHCO₃ dissolved in H₂O was added to the spent FCC support. The excess water was removed using rotary evaporator under vacuum and at 363 K and continued for 2 h. After cooling to room temperature, an aqueous solution of Fe(NO₃)₃ · 9H₂O was added slowly and excess water was removed using the rotary evaporator. Then an aqueous solution of Cu(NO₃)₂ · 2.5H₂O was added slowly to the catalyst and the drying procedure was repeated. Then the catalyst was dried in oven at 393 K for 5 h and calcined in air at 723 K for 2 h. The catalysts were designated as Fe-Cu-K/Engelhard and Fe-Cu-K/Albemarle.

3.2. Catalyst Activation

Prior to the attrition studies, the calcined Fe-Cu-K/spent FCC catalysts were activated in presence of CO at ambient pressure and at a temperature of 553 K. The catalysts were first heated in a quartz reactor to a temperature of 553 K at 2 K min⁻¹ in presence of helium. After attaining the temperature 553 K, the gas flow was changed to 50% CO, balance helium at a total flow rate of 600 cc min⁻¹ gcat⁻¹ for 24 h. After activation, the reactor was cooled down to room temperature under helium flow and then the catalysts were passivated by passing 1% O₂, balance helium for 4 h. After passivation, the catalyst was unloaded from the reactor carefully and stored in a sealed container. These catalysts were used for attrition tests.

3.3 Catalyst Characterization

BET S.A., pore volume and pore size of the calcined, activated catalysts and spent FCC supports were measured using autosorb (AS-1, M/S Quantachrome) by adsorbing N₂ at its liquefaction temperature 77 K. These samples were degassed at 423 K for 2 h prior to N₂ adsorption-desorption process. ICP-MS analysis was used to measure the metal composition of the catalysts. Powder X-ray diffraction analysis of the calcined catalysts was done by using Cu-K_α radiation and Co-K_α radiation was used for CO activated catalysts. These samples were scanned in the 2θ range of 10-80° at 1° min⁻¹ of scan speed. These patterns were recorded on Siemens D5000 automated powder X-ray diffractometer. Phase identification was done by using ICDD database. H₂-TPR experiments were carried out in a fixed bed micro reactor system. 50 mg of the sample was placed in a 6 mm i. d. reactor tube and reduced in a 10% H₂/Ar mixture while the temperature was linearly ramped from 323 K to 1073 K at 5 K min⁻¹. A thermal conductivity detector (TCD) was used to monitor H₂ consumption as a function of temperature.

The Fe K-edge XANES scans were taken at the J. Bennett Johnston Sr., Center for Advanced Materials and Devices (CAMD), Louisiana State University, which operates its storage ring with an electron energy of 1.3 GeV and a current typically between 90 and 190 mA. The monochromator crystals used were Ge (220) and the resolution at the energies studied is ~2

eV. The Fe standards used were Fe₂O₃ (99.85+% metals basis Alfa Aesar[®]), Fe₃O₄ (99.95% metals basis Alfa Aesar[®]), FeO (99.5% metals basis Alfa Aesar[®]), and a 7.5 μm thick α-Fe foil positioned after the transmission chamber for calibration purposes. A θ-Fe₃C standard was synthesized using a CO TPR of Fe₂O₃, using a similar procedure to the literature [26]. Athena as well as IFEFFIT software were used in the data analysis [27].

3.4 Attrition tests

Catalyst attrition testing was performed by Sud-Chemie in a jet cup system based on ASTM design as described previously [28]. In a typical attrition test, 5 g of the activated catalyst sample was charged in to the sample cup and then attached to the settling chamber. After all joints were sealed, wet air was introduced into the sample at a controlled flow rate of 21 l min⁻¹ and at a pressure of 3.5 bar. After 1 h time-on-stream (TOS), the air flow was stopped and the weight of fines collected by the downstream filter was determined and "weight percentage of fines lost" calculated.

3.5 Activity studies

The F-T reaction was carried out in a continuous flow fixed bed high pressure reactor. In a typical experiment, 1 g of the catalyst was loaded in to the reactor and was activated in presence of 50% CO balance N₂ at 553 K, as previously described. After activation, the reactor was flushed with N₂ flow at 100 SCCM for 1 h. After flushing with N₂, the reaction was carried out at 573 K, H₂:CO of 0.67 and at a pressure equals to 1.38 MPa. The reaction mixture was

diluted with N₂ at a ratio of 1:5 (N₂:syngas) and total GHSV equals to 3600 h⁻¹. The catalyst was diluted with 5 g quartz sand prior to loading in to the reactor to minimize the hotspots due to the exothermic nature of the reaction. The hot trap and reactor vent lines were maintained at 423 K and cold trap was maintained at 275 K. The gaseous products were analyzed *in-situ* using GC equipped with FID and TCD. Liquid and wax products were collected periodically and their

^c measured at P/P₀ = 0.99, ^d measured using t-plot method

weights were measured by a mass balance and were analyzed by using GC. The CO conversion k//and product selectivities are calculated as follows:

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

$$\% \text{ 'C' selectivity of product} = \frac{[\text{no. of moles of product formed} \times \text{no. of C atoms present}]}{[\text{no. of moles of CO consumed}]} \times 100$$

Table 1. Textural property of the catalysts

Catalyst	BET S.A. (m ² g ⁻¹)	Total pore ^c volume(cc g ⁻¹)	Pore size (nm)	micropore area ^d (m ² g ⁻¹)
Albemarle	148	0.15	4.07	101.4
Engelhard	101	0.1	4.3	56.9
^a Fe-Cu--K/Albemarle	31	0.07	9.4	3.2
^a Fe-Cu-K/Engelhard	27	0.06	9.9	2.0
^b Fe-Cu-K/Albemarle	38	0.08	8.7	4.2
^b Fe-Cu-K/Engelhard	37	0.09	9.4	3.7

^a calcined catalysts, ^b catalysts activated in presence of CO

^c measured at P/P₀ = 0.99, ^d measured using t-plot method

4.0 Results and discussions

4.1 Textural properties and metal analysis

Table-1 shows the textural properties of spent FCC supports, calcined and CO activated Fe-Cu-K/spent FCC catalysts. Pore size distributions of spent FCC supports as well as calcined and carbided catalysts were presented in figure-1A and B. The BET surface areas of the supports were found

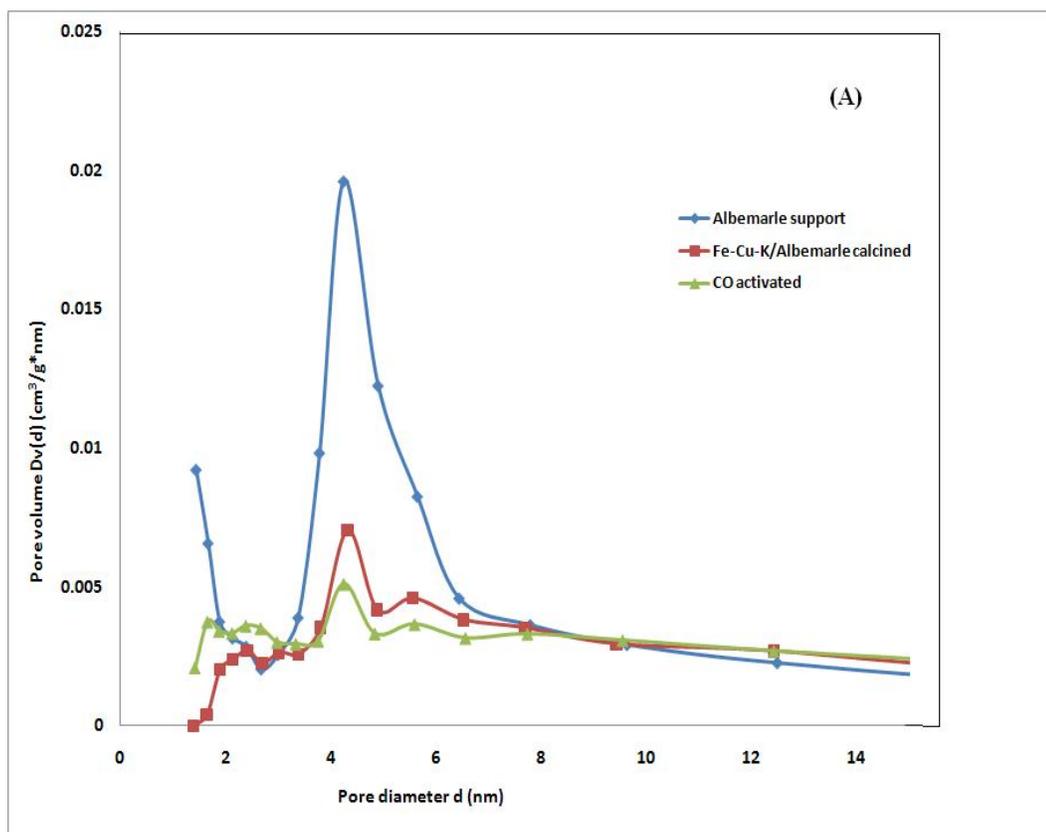
Table 2 Metal composition from ICP-MS analysis

Catalyst		Metal composition (parts by wt)*							
		Fe	Cu	K	Si	Al	Ti	V	Zr
Ni	Ca								
Engelhard ^a		0.58	-	-	23.9	20.7	0.7	0.08	0.02
0.05	0.02								
Albemarle ^a		0.54	-	-	21.9	22.1	0.7	0.08	0.01
0.02	0.04								
Fe-Cu-K/Engelhard ^b		45.1	1.95	1.3	5.5	5.8	0.22	<0.05	0.001
0.01	0.02								
Fe-Cu-K/Albemarle ^b		44.3	1.92	1.3	6.3	5.5	0.23	<0.05	0.002
0.015	0.02								

* measured from ICP-MS analysis, ^a spent FCC supports, ^b calcined catalysts

to be 101 m² g⁻¹ and 158 m² g⁻¹ for Engelhard and Albemarle materials respectively. The calcined and activated catalysts have far less surface areas compared to the spent FCC supports. This can be attributed to the addition of Fe, Cu and K over spent FCC supports which, in turn leads to blocking the pores of spent FCC support. The reduction in the pore size distribution from spent FCC support to calcined and activated catalysts is seen in both cases (Figure-1&Table-1). The CO activation of the calcined catalysts leads to a small increase in surface area. The change in pore volume was negligible. These findings are in good agreement with Zhao *et al.* [29]. The metal composition of the catalysts was shown in Table-2. An ICP-MS analysis

(Table-2) show Si to Al ratios of the supports are 0.99 and 1.16 for Engelhard and Albemarle supports respectively and remains constant after loading of Fe, Cu and K metals. Also metal analysis shows that both the spent FCC supports were poisoned with heavy metals such as Ti, V, Ni, Zr and Ca in trace amounts. It is known that during the process FCC catalysts are contaminated with heavy metals [20, 22]. The compositions of both the calcined F-T catalysts (100 Fe/4.3 Cu/2.8 K/25 Engelhard & 100 Fe/ 4.3 Cu/2.9 K/26.6 Albemarle) are found to be close to the target Ruhrchemie catalyst composition. The carbon analysis shows both the spent FCC supports contain 0.12wt%C, while calcined catalysts show 0.18wt%C (Albemarle supported) and 0.2 wt% C (Engelhard supported). The increase in C content may be due to KHCO_3 that does not decompose during calcinations.



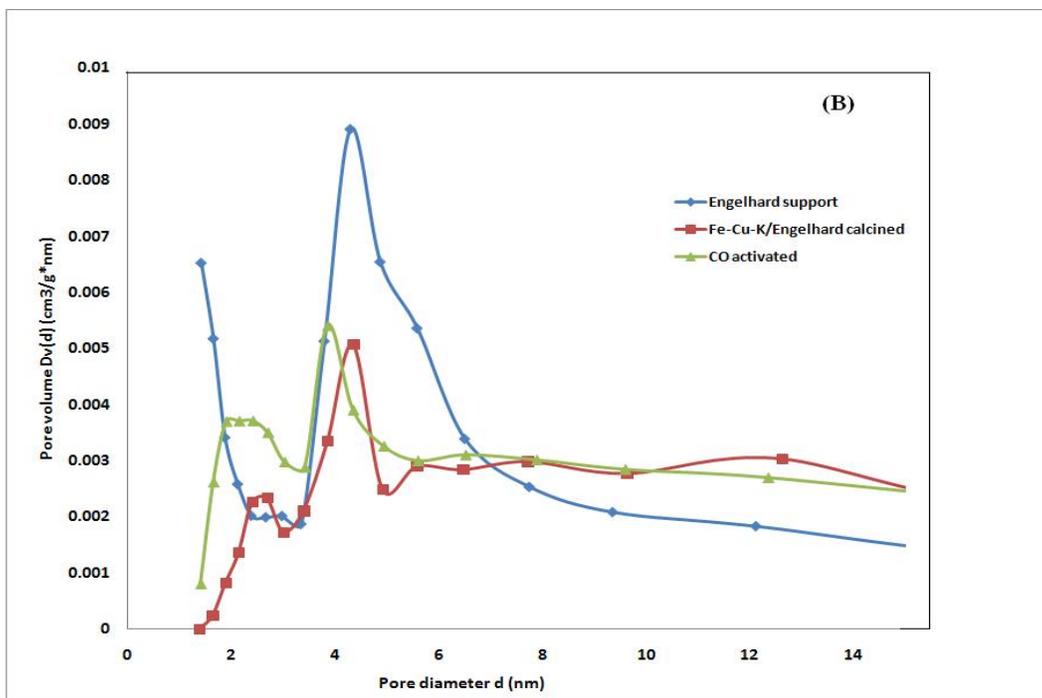


Figure 1. Pore size distribution curves of spent FCC Support, calcined and activated Fe-Cu- K/ spent FCC catalysts.

4.2 TPR results

The H₂-TPR profiles of the Cu, K promoted Fe loaded over spent FCC supports and spent FCC supports alone are presented in Figure-2. Spent FCC supports alone without any active metal show no reduction peak. The reduction profiles of calcined Fe- Cu-K/spent FCC catalysts shows two main stages of reduction at about 573-593 K and 853-893 K. The low temperature peak corresponds to the reduction of Fe₂O₃ to Fe₃O₄ and CuO to Cu [30]. The presence of Cu in the catalysts shifts the reduction of Fe₂O₃ to Fe₃O₄ towards lower temperatures. Cu crystallites nucleate during reduction of CuO and provide H₂ dissociation sites that lead to reactive hydrogen species capable to reduce Fe oxides at a relatively low temperature [30]. In the first stage, Albemarle-spent FCC supported catalyst shows two distinct reduction peaks centered at 493 K and 593 K. In case of Engelhard-spent FCC supported catalyst shows a shoulder at 473 K and

another peak at 573 K. In both the cases, the first peak corresponds to the reduction of CuO to Cu and the second corresponds to the reduction of Fe₂O₃ to Fe₃O₄ [31]. The second stage of the reduction shown at 853-893 K corresponds to the reduction of Fe₃O₄ to metallic iron. Engelhard (spent FCC) supported catalyst shows relatively lower reduction temperatures at all stages by approximately 20 K, which can be attributed to interactions between Cu and Fe.

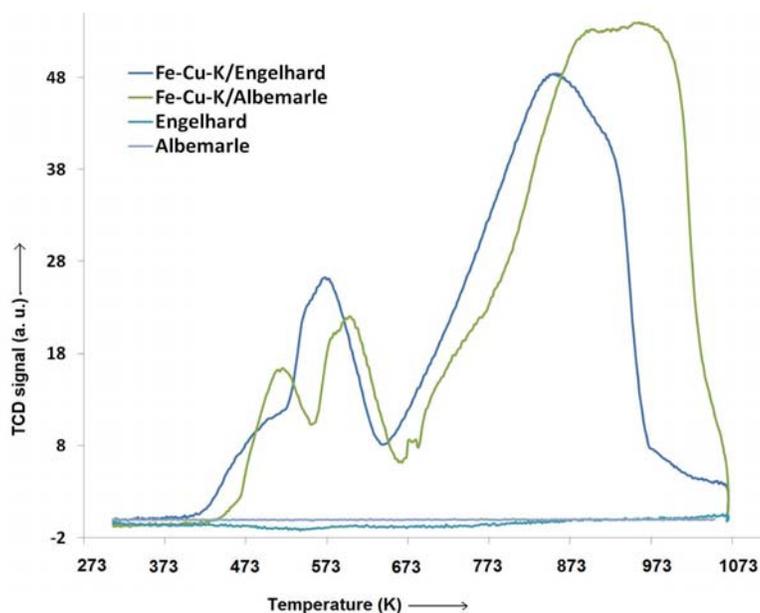


Figure 2. H₂-TPR profiles of Cu, K promoted Fe supported over spent FCC catalysts and pure spent FCC supports.

4.3 XRD results

Powder X-ray diffraction patterns of both calcined and CO pretreated catalysts are presented in Figure-3. The patterns of the calcined Fe-Cu-K/Spent FCC catalysts show strong peaks at 2θ values of 24.2°, 33.2°, 35.7°, 40.8°, 49.6°, 54.2° and 64.1°, which represent catalysts comprised entirely of α -Fe₂O₃ (rhombohedral hematite) phase [32]. The catalysts pretreated in

presence of CO at 553 K exhibits the peaks for Fe₃O₄ (magnetite) and χ -Fe₅C₂ (Hägg carbide). Both magnetite and Fe-carbide have a peak at 2 θ value of 43.6°. Several researchers reported the phase of the activated catalysts will depend strongly on the pretreatment conditions employed [12, 29]. Kalakkad *et al.* reported that the 100% intensity peak for magnetite occurs at 35.6° and the ratio of the 35.5° to and the 43° peak areas should be around 3.33 if only magnetite was present in the sample [12]. The ratio would decrease if there was an Fe-carbide phase present along with magnetite. Using this approach, they report that the catalyst sample exposed to CO at 543 K contained both magnetite and Fe-carbide phases. Zhao *et al.* reported that catalysts carburized under higher flow rates (375 cm³ min⁻¹) of CO mainly consists of magnetite and χ -carbide (Fe₅C₂) and a syngas activated catalyst consisted of magnetite and ϵ -carbide [29].

4.4 XANES results

The Fe K-edge XANES spectra for the standards, as well as the fresh calcined and activated Albemarle and Engelhard catalysts are presented in Figure-4. As expected, the XANES spectra of the fresh calcined catalysts were in good agreement with the Fe₂O₃ standard. After CO activation (conditions previously discussed) the Fe in the catalyst was found to be a mixture of the Fe₃O₄ and Fe_xC phases. A Principal Component Analysis [33] of the Albemarle and Engelhard XANES spectra confirmed the presence of θ -Fe₃C, Fe₂O₃, Fe₃O₄ and excluded α -Fe, FeO, which is consistent with the literature for a CO pretreated Fe-based FT catalyst [26, 34-36]. An assumption made in the least squares fitting was that the XANES contribution from the iron carbide (Fe_xC) would be close agreement to the θ -Fe₃C standard, which was also assumed in previous studies [26, 34, 36]. The least squares fitting results are in Table-3. The results of the fit were in good agreement with the XRD data, suggesting that the Fe in the fresh calcined catalyst

is present as Fe_2O_3 . In addition, the activated catalyst is a combination of Fe_xC and Fe_3O_4 , which is also consistent with the XRD analysis; it was observed that after CO activation that the Engelhard-spent FCC supported catalyst was slightly more carburized than the Albemarle-spent FCC supported catalyst.

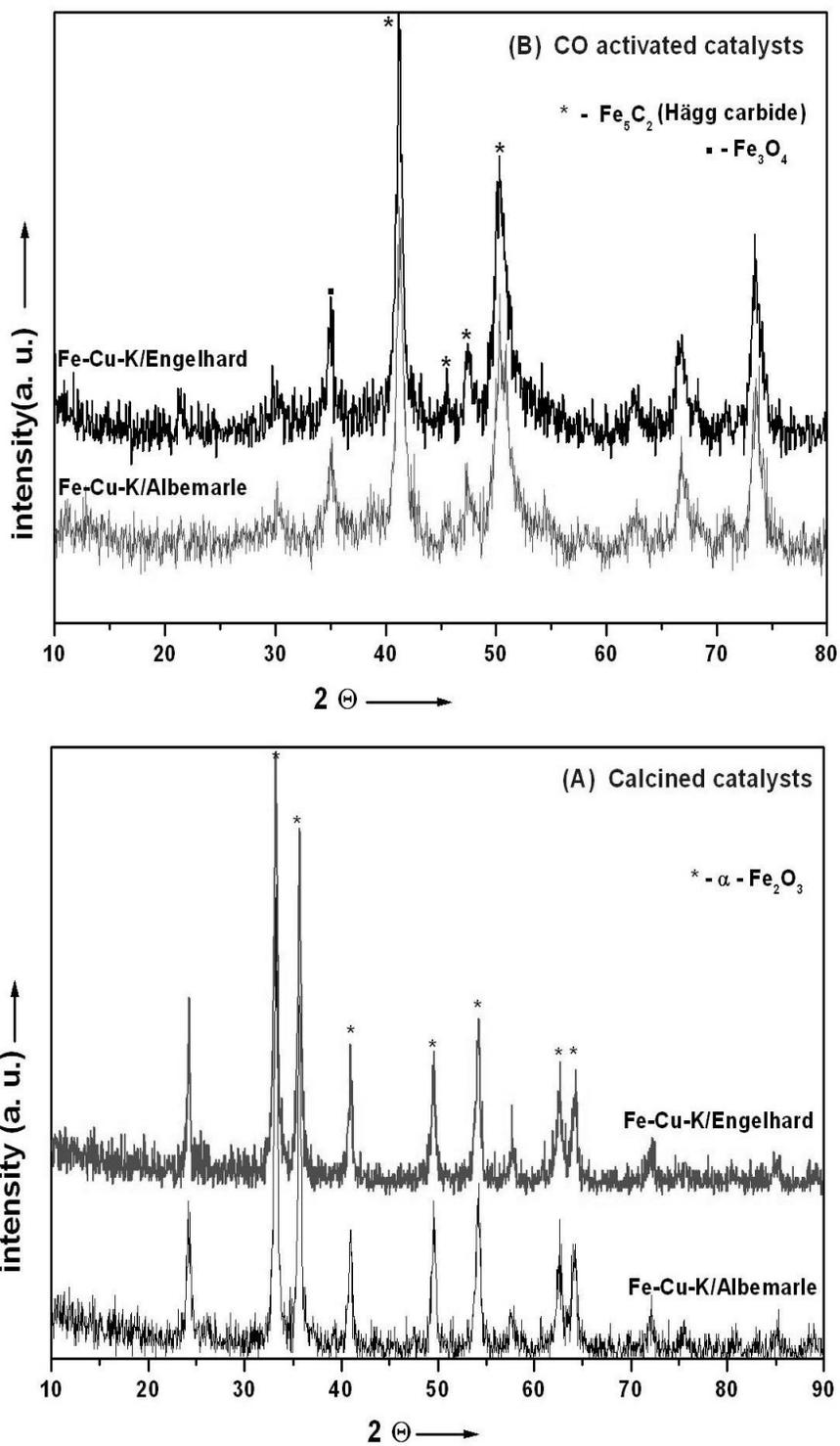


Figure 3. Powder X-ray diffraction patterns of (A) calcined catalysts and (B) CO activated catalysts.

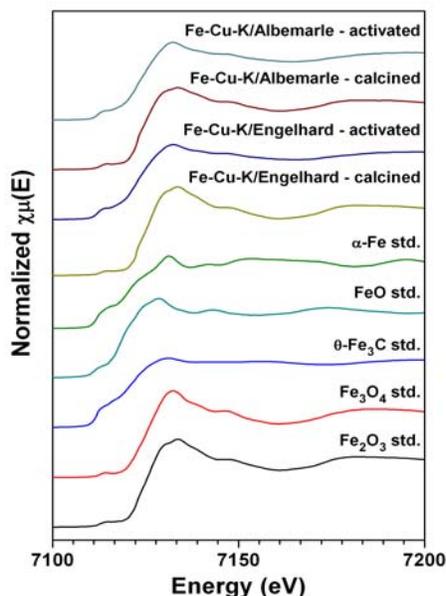


Figure 4. Normalized Fe K-edge XANES of Fe standards, calcined and activated Fe-Cu k/spent FCC catalysts.

Table 3

Least squares fitting results for calcined and activated Fe-Cu-K/spent FCC catalysts.

Catalyst	Condition	Fe ₂ O ₃ (%)	Fe ₃ O ₄ (%)	FeC _x (%)
Fe-Cu-K/Engelhard	calcined	100	0	0
	activated	0	52.3±1.6	47.7±1.6
Fe-Cu-K/Albemarle	calcined	100	0	0
	activated	0	63.7±1.1	36.3±1.1

4.5 Attrition results

Attrition of catalysts as determined by jet cup measurement is given in Table-4. Both the spent FCC supports shows negligible attrition. The addition of Fe, Cu and K to the spent FCC supports leads to increase in the lost of fines (wt%), likely due to breakup of Fe-carbide into smaller particles. These iron catalysts show appreciable attrition resistance in comparison of literature studies, in which the attrition tests were conducted under similar conditions [29, 37]. Zhao *et al.* synthesized the spray-dried, Cu- and K- promoted Fe catalyst containing 9.1 wt% of silica binder

[29]. This catalyst was tested for attrition by jet cup method after pretreatment with CO at 553 K and wt% of fines lost was found to be 7.5-7.7, slightly lower than the present results (8.2-9.3 wt%). Similar results were also observed in a related study by Zhao et al. [37]. The attrition test conditions employed in the present study are more severe than employed by Zhao *et al.* [29, 37].

4.6 F-T Activity results

F-T synthesis performances of the catalysts were measured in a fixed bed reactor at $T = 573$ K, $P = 1.38$ MPa, $H_2/CO = 0.67$ and GHSV of 3600 h⁻¹. The activities, stabilities and selectivities were tested over a period of 24 h. The effect of reaction time on CO and H₂ conversion over both the Fe-Cu-K/spent FCC catalysts over time on stream are presented in Figure-5.

Table 4 Jet cup attrition test results

Catalyst	Fines lost (wt%)^{a, b}
Engelhard	1.2
Albemarle	0.8
Fe-Cu-K/Engelhard ^c	8.2
Fe-Cu-K/Albemarle ^c	9.3

^a Weight percentage of fines =
(weight of fines collected/weight of total catalyst recovered) X 100

^b Error: ±10% of the value measured

^c Catalysts activated in presence of CO at 553 K

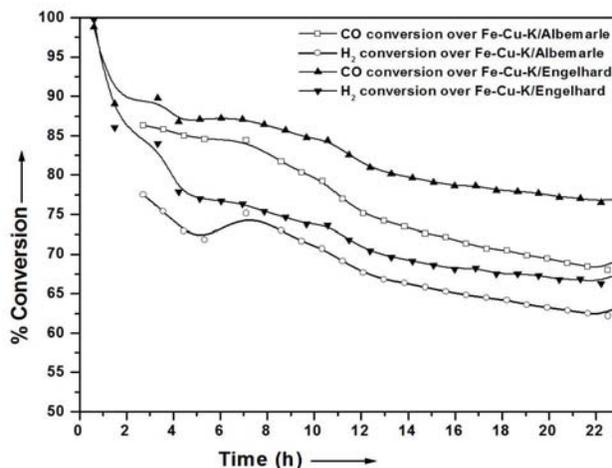


Figure 5. CO and H₂ conversion as a function of time on stream.

The initial conversion of CO is similar on both catalysts (86.3% over Albemarle spent FCC and 89% over Engelhard spent FCC). As the reaction proceeds, the conversion drops down continuously over Albemarle-spent FCC supported catalyst and reaches down to 68% at 24 h. For the catalyst supported over Engelhard-spent FCC, CO conversion decreases to 81% after 12 h, and then less rapidly thereafter. The loss of activity with time on stream can be the result of one or more of following reasons: (i) deposition of inactive carbonaceous layer, (ii) sintering of metal particles, (iii) phase transformations in the FT component and (iv) coking of zeolitic component [23,38]. Deposition of inactive carbonaceous compounds through Boudouard reaction is the most common way of Fe catalysts deactivation as shown in Eqs.(3) and (4) [38].



Pour et al. studied the HZSM-5 zeolite supported Fe catalysts and found that the CO conversion decreased from 97% to 85% at 200 h and to 70% at 1400 h on stream. They attributed the loss of activity to coking of the zeolite component, migration of the iron catalyst alkali promoters under synthesis conditions and dealumination of zeolites crystals caused by the presence of water[23].

The catalyst reported in the present study use spent FCC material as supports, which contain zeolites that might cause the catalyst deactivation. The Engelhard-spent FCC supported catalyst is significantly more active than the Albemarle catalyst. The same trend is observed in case of H₂ conversion. These spent FCC supported Fe catalysts show high activity in comparison with the Fe catalysts supported over conventional supports like SiO₂ and Al₂O₃ prepared in an analogous way[39,40}. Bukur et al. studied SiO₂ and Al₂O₃ supported Fe catalysts with a composition of 100Fe/5Cu/6K/139SiO₂ and 100Fe/5 Cu/9K/139Al₂O₃ for F-t synthesis in stirred tank slurry reactor at 533K/ 1.5 MPa and H₂/ CO= 0.67[39]. They found that Al₂O₃ supported catalyst showed maximum syngas conversion of 45% at 20 h on stream and then started to deactivate (35% conversion at 100h) and the activity on SiO₂ supported catalyst shows 67% conversion at 20 h on stream to 60% at 100h on stream. O'Brien et al. evaluated four different supported catalysts 100Fe/6Cu/8.1K/250-260 support material (SiO₂, MgO.SiO₂, Al₂O₃ and MgAl₂O₄ in a slurry reactor at 523 K, 1.31 MPa and H₂/CO=0.7[40]. The maximum CO conversion reported at 50h on stream was 50% over MgAl₂O₄ supported catalysts. The Fe catalyst supported over Engelhard-spent FCC reported in the present study shows CO conversion of 81% (Table 5), which is higher than in comparison with the Fe F-T catalysts prepared by conventional coprecipitation and having similar catalyst composition[39,41]. O'Brien et al. reported CO conversions of 70% with the catalyst composition of 100Fe/5Cu/4.2K/24SiO₂ and Hou et al. reported 48.5% of CO conversions over catalysts with the composition 100Fe/5Cu/4.2K/15SiO₂. Although there is slight difference in reaction conditions, the high activity of the catalysts reported here can be attributed to the difference in the support materials used and catalyst preparation method. This shows an apparent advantage of using spent FCC material as a support for Fe F-T catalysts. Table 5 shows the pseudo-steady state F-T activity of

the catalysts. The chain growth probability (α) values for the two catalysts are equal within experimental error, 0.55-0.54 (fig. 6). In this study the linear region (C₃-C₈) of the ASF plot was used [$\ln(w_n/n)$ vs. n] to calculate the α value. Time on stream studies show that methane and CO₂ selectivities increase initially up to 5 h of reaction time and no significant changes were observed at longer times (fig.7). At steady state, the CH₄ and CO₂ selectivities are found to be 5.2 % and 54.5% respectively over Albermarle-spent FCC supported catalyst and 3.9% and 49.3% respectively over Engelhard – spent FCC supported catalyst. The high CO₂ selectivities can be attributed to water-gas shift reaction. Luo et al. also found a similar CO₂ selectivity (45%) when Fe catalysts activated under CO at 543 K [42].

Table 5 F-T activity results

F-T results^a	Fe-Cu-K/Engelhard	Fe-Cu-K/Albermarle
%CO conversion^b	81.0	69.5
% selectivity (%C)		
CO ₂	49.3	54.5
CH ₄	3.9	5.2
C ₂ -C ₄ HC's	9.4	8.5
C ₅ + HC's	18.3	12.0
oxygenates	1.6	2.1
C ₂ ⁼ -C ₄ ⁼ /C ₂ -C ₄ (olefins/paraffins)	4.0	3.2
ASF (α)	0.55	0.54

^a Reaction conditions: T = 573 K, P= 1.38 MPa, H₂:CO = 0.67, GHSV=3, 600 h⁻¹

^b at 12th h of time on stream

^c calculated using C₃-C₈ region of the ASF plot.

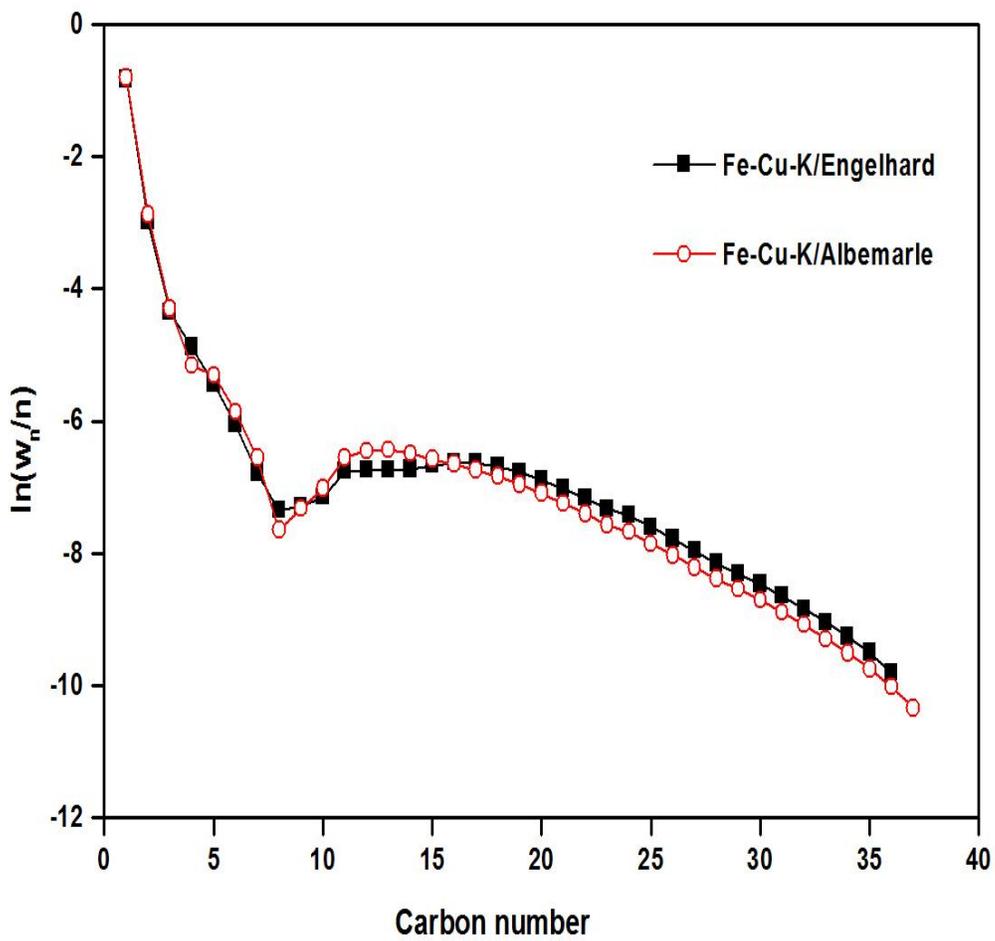


Fig. 6 Anderson- Schulz- Flory plot of chain growth.

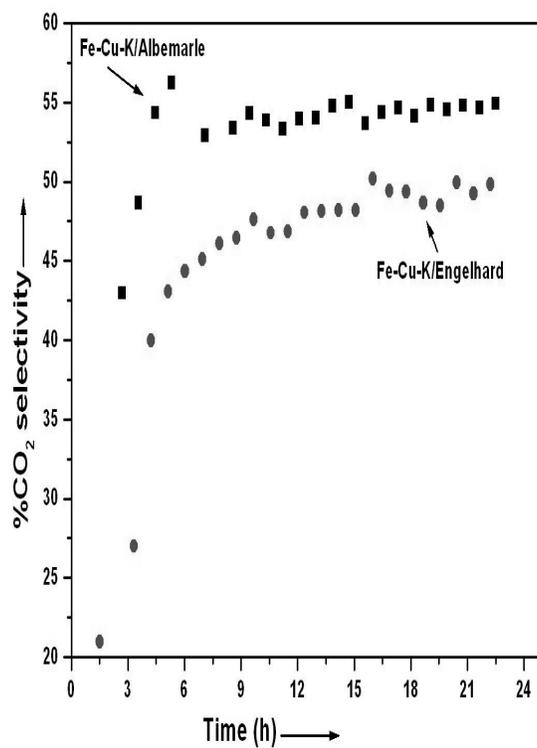
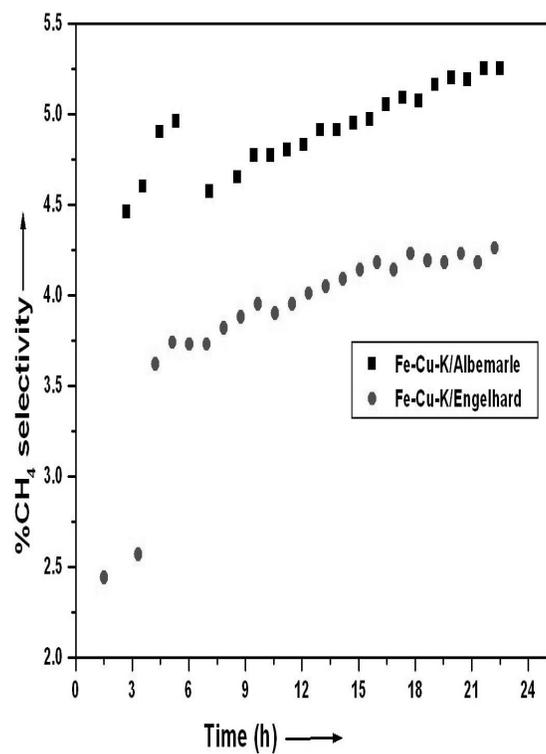


Fig. 7 Selectivity of CO₂ and CH₄ with time on stream.

C₂-C₄ hydrocarbons yield was 8.5% and 9.4% over Albemarle and Engelhard-spent FCC supported catalysts respectively at steady state (fig. 8). Albemarle-spent FCC supported catalyst shows lower C₂-C₄ olefins-to-paraffins ratio than compared to Engelhard-spent FCC supported catalyst. The C₅+ hydrocarbon selectivity was 12% and 18.5% with the oxygenates selectivity of 1.6% and 2.1% over Albemarle and Engelhard-spent FCC supported catalysts respectively. Table-6 shows the oxygenate product distribution in the aqueous product. Engelhard-spent FCC supported catalyst shows predominant formation of ethanol (41.9 ‘C’ mol %) among all the oxygenates, which is much higher than ethanol produced on Albemarle-spent FCC supported catalyst (4.8 ‘C’ mol%).

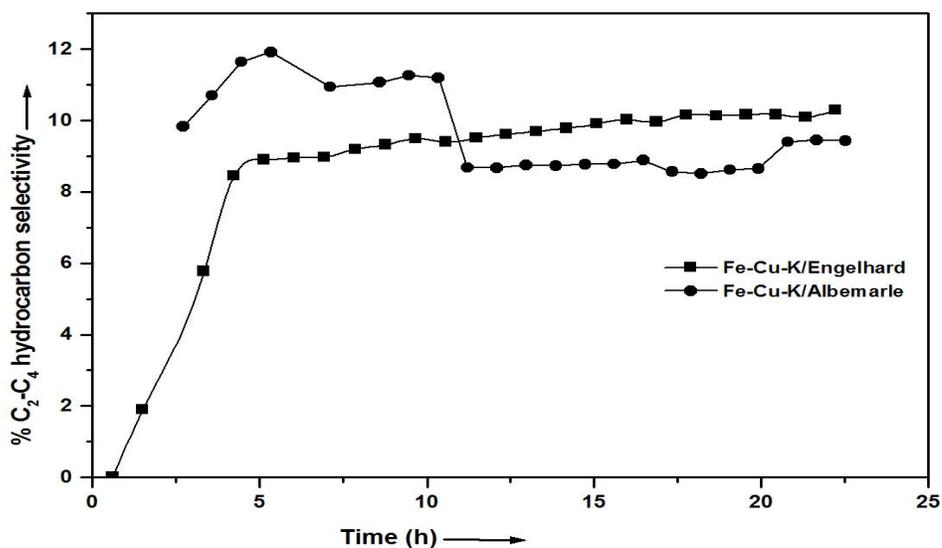


Fig 8. Selectivity of C₂-C₄ with time on stream.

Table 6 Oxygenate product distribution in aqueous samples.

Oxygenates	e-Cu-K/Engelhard mol%	Fe-Cu-K/Albemarle C mol%
acetaldehyde	4.2	6.3
methyl formate	1.4	2.9
propanal	2.8	3.7
acetone	0.7	1.1
methyl acetate	22.8	37.4
butanal	0.2	0.4
ethyl acetate	2.1	8.3
C1-OH	1.7	1.4
<i>i</i> -propanol	0.2	0.6
C2-OH	41.9	4.8
pentanal	0.9	1.2
2-butanol	0.3	0.3
C3-OH	12.2	16.2
2-methyl-1- propanol	0.8	4.3
2-pentanol	0.1	0.1
C4-OH	2.6	3.2
2-methyl-1-butanol	0.4	0.6
2-hexanol	0.1	0.2
C5-OH	1.5	2.3
2-Me-1-pentanol	0.1	0.5
4-Me-1-pentanol	0.2	0.3
3-Me-1-pentanol	0.1	0.1
C6-OH	1.6	2.4
C7-OH	1.1	1.4

The CO conversion was higher on Engelhard-spent FCC catalyst with low selectivities towards CO₂ and CH₄ and high selectivity for the formation of C₅+ hydrocarbons in comparison to Albemarle-spent FCC catalyst. This can be attributed to the greater extent of carbide formation on the Engelhard-spent FCC catalyst[38], which can be observed from least square fitting of XANES results (Table-4). The presence of different concentrations of trace metals in the spent FCC support (Table 2) might also contribute to the different product distribution.

Our preliminary studies on the Fe catalysts supported over spent FCC materials with Ruhrchemie composition using incipient wetness shows F-T synthesis activity with appreciable attrition resistance. Results obtained in this study using spent FCC catalyst as supports are encouraging; however, the stability of the catalyst should improve prior to commercial use since the deactivation rate is severe. Further optimization of the Fe-spent FCC catalyst, specifically, to improve α and catalyst deactivation, via chemical promotion should be investigated in future studies. Further studies in our laboratory are directed towards the optimization of Fe loading and to compare the F-T activity and attrition resistance of Fe-spent FCC catalysts with commercial Fe F-T catalysts.

5.0 CONCLUSIONS

Both spent FCC (Engelhard & Albemarle) supported Fe catalysts showed appreciable attrition resistance. It is concluded from the F-T activity results, that Fe can be loaded onto spent FCC materials and are active in F-T synthesis. Engelhard (spent FCC) supported Fe-Cu-K catalyst showed good attrition resistance and high C₅+ hydrocarbons selectivity in comparison to spent FCC (Albemarle) supported catalyst.

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