Methanol to Gasoline Conversion over CuO / ZSM-5 Catalyst Synthesized and Influence of Water on Conversion

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Abstract: Conversion of Methanol to Gasoline (MTG) process is accomplished by the synthesis of ZSM-5 zeolite catalyst to produce high-quality gasoline. The generated catalyst had an area of Zeolite and CuO / ZSM-5 (2%) and CuO / ZSM-5 (4%) 300 m^2g^{-1} and 284 m^2g^{-1} and 254 m^2g^{-1}. Structure and morphology of synthesized catalysts were studied by such analyses as BET, XRF, SEM, XRD. CuO / ZSM-5 (4%) (70% water / 30% methanol feed) catalyst resulted in increased activity for the conversion of methanol to hydrocarbons of gasoline range especially aromatics. Using (70% water / 30% methanol feed) with catalyst CuO / ZSM-5 (4%) led to improving the performance of catalysts and increased aromatic and decreased conversions. The main products of the aromatic were C_7H_8, $(CH_3)_2C_6H_4$, C_8H_{10}, $CH_3C_6H_4C_2H_5$, $C_{10}H_{14}$, $C_6H_4(C_2H_5)_2$, and $C_6H_5(CH_2)_3CH_3$. Also, water on ZSM-5 and CuO / ZSM5 play an important role in the of aromatic products.

Keywords: ZSM-5 zeolite catalyst, fixed-bed reactor, specific surface, water, sonochemistry

1. Introduction

The zeolites are crystal aluminum silicates and hydrated alkaline metals and alkaline earth which contain the 3D network which is composed of $[SiO4]^{4-}$ and $[AlO4]^{4-}$ tetrahedrons. Such catalysts are used in Fluid Catalytic Cracking (FCC), hydrocracking, desulfurization of gasoline, isomerization of light paraffin, Methanol to Gasoline, or Gasoil conversion, and methanol to propylene (MTP) and methanol to dimethyl ether (DME) processes [1-4]. Among all these acidic catalysts, ZSM-5 with medium size and porosity is more applied in petrochemical industries. The high efficiency of Zeolites as a catalyst is due to high morphology and its special properties including a specific crystalline structure, high level, uniform pores, high thermal stability, and selectivity which result in the formation of the proper catalyst [5-8]. In refineries, Zeolite catalysts are the main source of gasoline and octane efficiency improvement as well as the production of lubricants and clean fuel. There is plenty of evidence that shows that limited petroleum resources are not able to supply global energy demands. General consumption of fuel is about 116.45 million tons per day which is being increased with a growth of more than 3%. Given this rate, consumption will reach 162.28 million tons per day in 2020 [9, 12]. Conventional methods for gasoline production generally are crude oil distillation and such processes as alkylation and catalytic cracking, although the process of converting coal to liquid is conducted in some countries with coal resources. Given the critical importance and urgent need for fuel as well as increasing demand for fuel, some alternative methods should be found to produce it. Methanol to Gasoline process, which is a part of the general process of gas to a liquid, is a suitable alternative process. Since gasoline is often used in transportation and production of crude oil and it is going to be terminated with current consumption trends [13-15]. Given the limited current global petroleum resources, it seems necessary to find modern practices to produce valuable fuels like gasoline. One of these practices is MTG. So far, plenty of efforts have been accomplished to produce diverse hydrocarbons through methanol [16-20]. The conducted studies include an evaluation of the process, catalyst, and operational conditions to implement the reactions. Among Zeolite catalysts, ZSM-5 and SAPO-34 are suitable for the accomplishment of this process and they have been studied more frequently. The main recognized mechanism for the MTG process is Methanol to Dimethyl ether which is an equilibrium reaction and the following rehydration, it is converted to light olefins such as ethylene and propylene [21-25]. These olefins are converted to aromatics inside pores of the catalyst and other hydrocarbons are converted to gasoline within the boiling point range [28-31]. With measured volumetric flow and molar composition of the gaseous product at ambient temperature and pressure, gas density and mass flow were calculated via literature correlations and by known mass flows and compositions (weight percent) of oil cut and aqueous solution,

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conversion and each component mass percent in whole products can be calculated by mass balance. Methanol conversion was calculated through equations (1) and (2) [35-39]:

$$X_{MeOH} = \frac{F_{MeOH_{in}} - (F_{MeOH_{out}} + 2F_{DME})}{F_{MeOH_{in}}} \tag{1}$$

$$X_{MeOH} = \frac{\dot{M}_{MeOH_{in}} - (\dot{M}_{MeOH_{out}} + 1.391\dot{M}_{DME})}{\dot{M}_{MeOH_{in}}} \tag{2}$$

The main aim of the present investigation is to study the effect of CuO loading on ZSM-5 support for conversion of methanol to gasoline range hydrocarbons. A series of CuO / ZSM-5 catalysts were prepared, characterized and experimented for their performance on methanol conversion and hydrocarbon yield. The effects of run time on methanol conversion and hydrocarbon yield with various CuO / ZSM-5 catalysts have been studied. Zeolites as catalysts have many unique properties such as acidity, shape-selectivity, high surface area and structural stability.

2. Materials and methods

2.1 Materials

Sodium aluminate (technical grade) was purchased Riedel-deHaen. Silicic acid (96.6%), tetrapropylammonium bromide (98%), sodium hydroxide (97.5%), methanol (99.9%), ethanol (96%), and copper (II) nitrate (99.9 %) ammonium nitrate (99.95%) was supplied by Merck. All the chemicals used in this research were of analytical grade.

3. Zeolite catalyst synthesis and CuO / ZSM-5

Gel Preparation: The preparation zeolite catalyst, tetrapentyl ammonium bromide was diluted with H_2O and stirred for 20 min. The template was added to the blend of Tetraethyl orthosilicate and H_2O via a syringe pump. Prepared blended stirred on a hot-plate at 40°C and 300 RPM for 3 hrs. Now, $Na_2Al_2O_4$ and H_2O added together in another Beaker, and the rest of NaOH was injected into $Na_2Al_2O_4$ blend followed by roughly stirring for 3 hrs. The second blended added to the first solution drop-wise in 3 hrs, then agitated for 1 hour. As the pH of the prepared Gel has to be adjusted at 10, Sulfuric acid was employed as an acidity control agent. The aging sessioned performed for the gel at 400°C and 300 RPM for 25 hrs. The Prepared gel was transferred into a 180 ml Teflon lined autoclave and kept at 180°C for 50 hrs, using a programmable lab oven. Synthesized catalyst powder was obtained after several times washing with distilled H_2O till pH value reached 7 Drying & calcination: Prepared catalyst was dried overnight at 90°C and then calcined at 50°C for 10 hrs. The resultant product was dried at 110°C for 12 hours and calcined at 500°C for 5 hours [9, 12].

4. Reactor test

Figure 1 shows the process flow diagram (PFD) of the experimental rig. To carry out experimental runs in the MTG reaction, 1.5 g of the calcined sample with 4 g of Sic were loaded in the catalyst bed under atmospheric pressure. Before feeding the fixed bed reactor, an N_2 flow at 550°C was passed through the loaded sample for 1 hour to dehumidify and to activate the catalyst. After that, the temperature was regulated to the reaction temperature of 425°C. The output products of the reaction were analyzed by a gas online chromatography (Agilent GC 7890A) which was equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD).

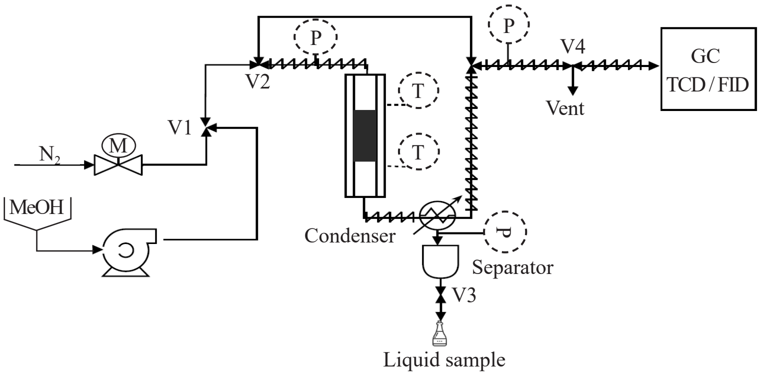

Figure 1. Experimental system for evaluation of ZSM-5 catalyst synthesis performance for Methanol to Gasoline conversion

5. Results and discussion

5.1 Characterization analysis

5.1.1 X-ray diffraction (XRD) analysis

Figure 2 X-ray diffraction (XRD) images to determine the crystalline phase, Phase purity and crystallinity are the catalysts synthesized. By comparing the obtained patterns and the reference patterns, we conclude all samples had ZSM-5 angles of 8-10°C [13] sharp peaks at 8, 9, 10, 11, 14, 14.7, 23.1, 24 and 32 crystal faces, respectively [9, 12]. The crystallite sizes were determined peak via Scherrer's equation that is indicated in Table 1.

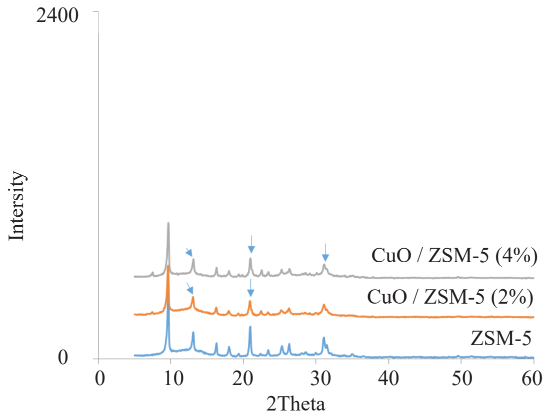

Figure 2. XRD patterns of the parent

Table 1. Results of Brunauer-Emmett-Teller (BET) analysis

Catalyst	Si / AL	SiO_2 / Al_2O_3	BET surface area (m^2/g)	Crystal size (nm)	Pore volume (cm^3/g)
ZSM-5	15	30	300	17	0.38
CuO / ZSM-5 (2%)	11	22	278	29	0.35
CuO / ZSM-5 (4%)	10	20	250	30	0.32

Catalyst	V_{Total} / cm^3g^{-1}	V_{Micro} / cm^3g^{-1}	V_{Meso} / cm^3g^{-1}
ZSM-5	0.417	0.102	0.315
CuO / ZSM-5 (2%)	0.315	0.101	0.214
CuO / ZSM-5 (4%)	0.214	0.100	0.115

5.1.2 Scanning electron microscope (SEM) and EDX analysis

SEM and EDX were used to study the morphology shape and size of the synthesized crystals. Figure 3 and Table 3 show the images of the SEM for 3 synthesized samples. The SEM images of the samples show that the morphology of all the samples as expected for ZSM-5 is regular and the dominant phase in all samples is ZSM-5, CuO / ZSM-5 (2%), and

CuO / ZSM-5 (4%). Considering pH and surface specifications such as isoelectric charge, there is an obvious possibility for metal deposition out of the frame and / or catalyst pores. This distribution leads to catalyst malfunction which shall be fast deactivation, lower conversion, and product selectivity reduction.

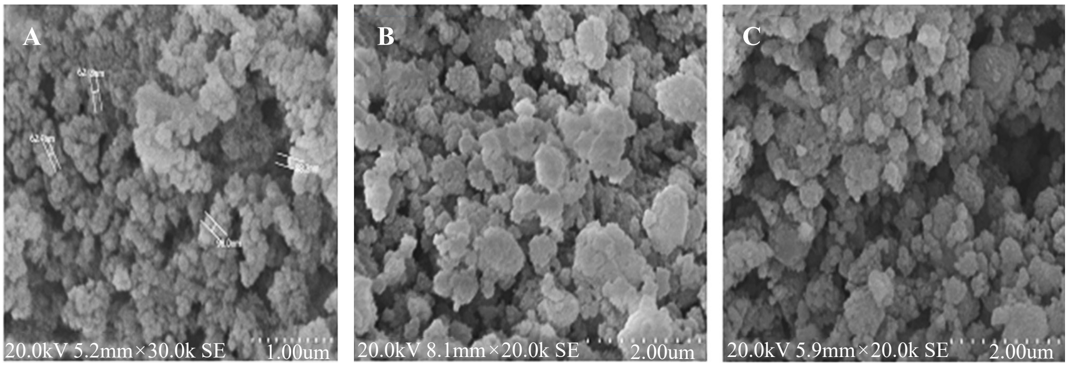

Figure 3. SEM patterns of the parent (A) ZSM-5(B) CuO / ZSM-5 (2%) (C) CuO / ZSM-5 (4%)

Table 2. EDX pattern for promoted / pure catalyst batches

Element		Pure	CuO 2%	CuO 4%
	O	65.4	66.8	68.0
Elemental Analysis	Al	0.82	0.78	0.73
	Si	33.78	32.3	31.2
	CuO	0	0.12	0.07

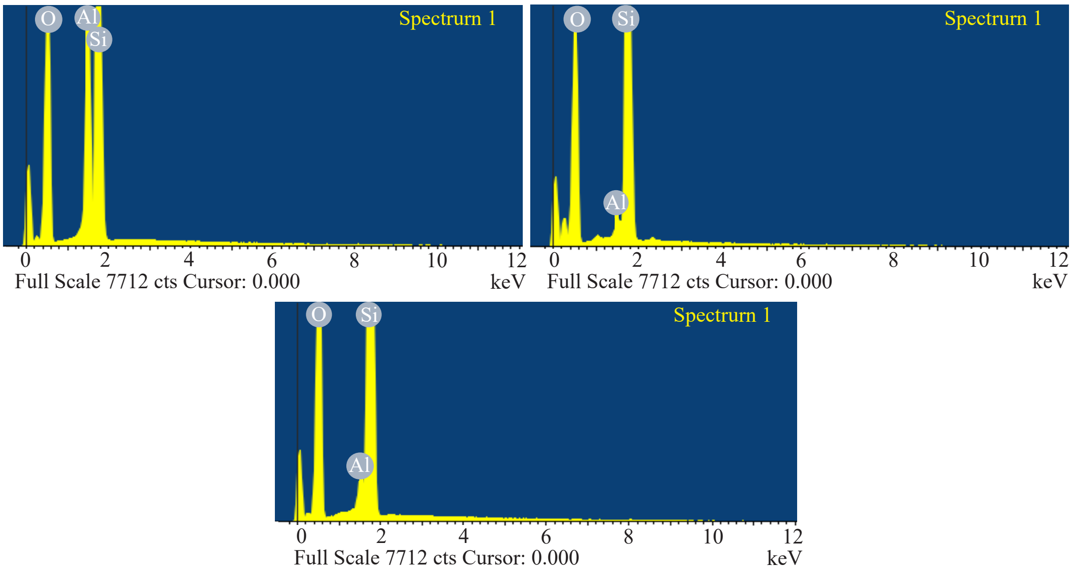

Figure 4. EDX pattern for promoted / pure catalyst batches

5.1.3 (TPD) analysis

The synthesized catalyst was studied using Micrometrics Autochem 2920 unit (equipped with TCD) to determine acidity and acid site distribution operates with He as carrier and ammonia during adsorption. The sample preparation was performed at 500ºC for 2 hours followed by cooling at 100ºC. Figure 3 illustrates the TPD results of parent ZSM-5 zeolite over temperature range of 100 to 900ºC. Two main peaks are observed with maximum at 200ºC and 415ºC, which is attributed to weak / medium and strong acid sites, respectively. The results of TPD analysis are suitably in line with the aluminum presence in Zeolite composition [9].

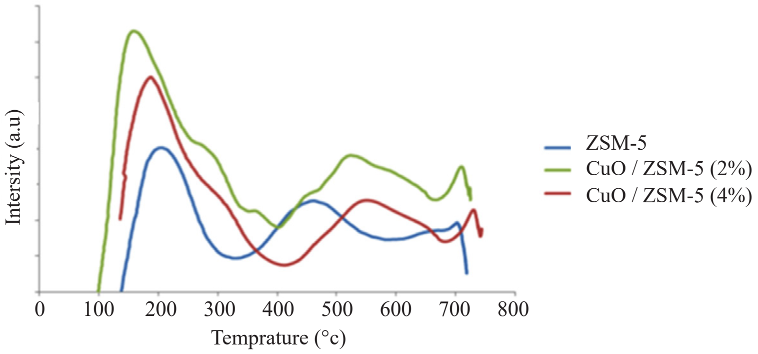

Figure 5. NH_3**-TPD analysis for prepared catalyst**

5.1.4 N_2 adsorption-desorption isotherms analysis

Figure 6 shows N_2 adsorption-desorption which is used to determine the porosity, specific surface area, and physisorption isotherms. All samples exhibit a typical reversible type IV adsorption isotherm as defined by International Union of Pure and Applied Chemistry (IUPAC). The hysteresis loop is very similar to the H_3 type N_2 adsorption-desorption isotherms with hysteresis characterization. Three different stages are observed in the isotherms. At low relative pressure ($P/P0 < 0.4$), adsorption occurs only as of the monolayer on the pore walls. As the relative pressure increases ($P/P0 > 0.4$), a hysteresis loop is observed which is a characteristic of capillary condensation of nitrogen in mesoporous. At higher pressure ($P/P0 > 0.95$), again another linear region is observed. This part is attributed to the multilayer N_2 adsorption on the external surface of the materials. There is no limiting uptake observed over the high range of P/P0, which is characteristic of aggregates with plate-like particles [9, 32].

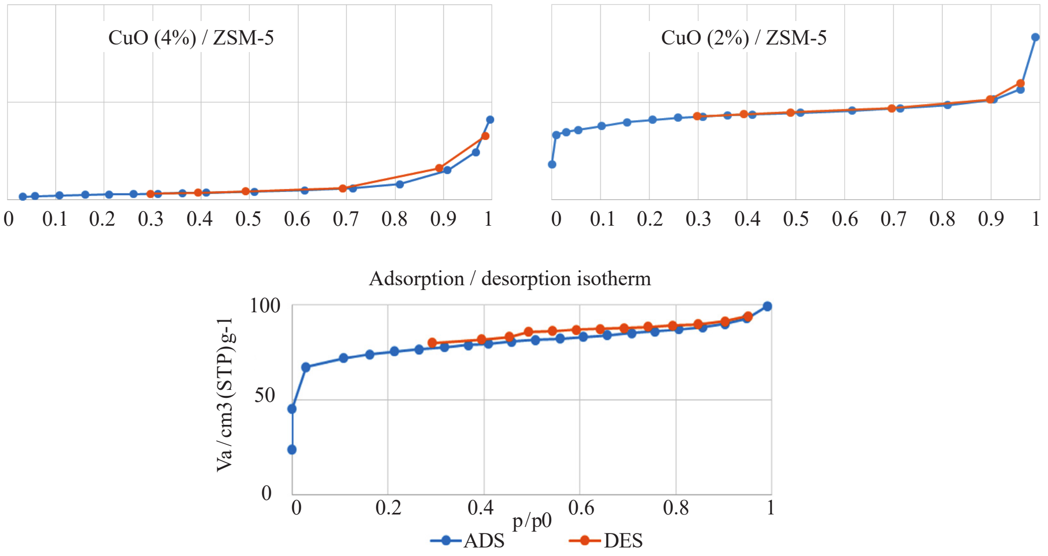

Figure 6. N_2 **adsorption-desorption isotherms**

5.1.5 Catalyst performance

Table 3 compare selectivity of production of gasoline hydrocarbon groups by using the catalyst of CuO(4%) / ZSM-5 and input methanol ratios of 30% and 100%. A major portion of produced gasoline compositions is dedicated to aromatics by using methanol feed of 30% while lower light olefin compositions and lower conversions are seen. Table 4 compare selectivity of production of gasoline hydrocarbons. As it can be seen from the Table 4, using methanol feed of 30%, the rate of the hydrocarbons heavier than octane was significantly increased. Table 4 shows the selectivity of the produced gasoline hydrocarbons, demonstrating a lower amount of olefin and light alkanes and heavier aromatics, especially xylene and ethyl toluene. Therefore, using a methanol feed of 30%, the process is argued to be improved and the final reaction of heavier hydrocarbons and aromatics production was substantially increased, which may be due to higher methanol rate over the catalyst or burning coke with water steam and catalyst recovery during the process. Table 4 major portion of produced gasoline compositions is dedicated to aromatics by using catalysts CuO / ZSM-5(4%) with methanol feed of 30% while lower light olefin compositions and increased Xylene are seen.

Table 3. The selectivity of produced gasoline hydrocarbons

Compound	ZSM-5	CuO / ZSM-5 (2%)	CuO / ZSM-5 (4%)
Methanol input (%)	100	30	30
Conversion (mol%)	99.5	94.6	93.3
Aromatics	40	65	75
Iso-paraffins	7.5	2.5	2.5
Naphthenes	2.0	3.6	2.3
Olefins	34.0	5.4	2.8
Paraffins	2	2.0	0.8
Unknown	1	4.5	4.9

Table 4. The selectivity of produced gasoline hydrocarbons

Compound	ZSM-5	CuO / ZSM-5 (%2)	CuO / ZSM-5 (%4)
Methanol input (%)	100	30	30
	Yield (%)		
Benzene	1.3	0.4	0.1
Toluene	6.4	6.5	3.8
Xylene	28.0	45.1	56.7
Ethylbenzen	1.2	1.3	1.6
Ethyltoluene	3.3	3.5	5.8
Propylbenzene	0.1	0.2	0.3
Ethyldimethylbenzene	0.1	0.2	0.4
Trimethylbenzene	0.4	2.7	1.9
Diethylbenzene	0.4	0.5	0.7
Butylbenzene	2.8	2.5	7.9
Olefins	37.0	35.0	15.5
Water	19	2.1	5.3

6. Conclusion

This work shows that zeolite has a good effect on the transformation of methanol to gasoline. Noticeable growth in selectivity to aromatics and higher hydrocarbons was observed over the ZSM-5 catalyst which was prepared using sonification. CuO / ZSM-5 (4%) (70% water / 30% methanol feed) catalyst resulted in increased activity for the conversion of methanol to hydrocarbons of gasoline range especially aromatics. Using methanol feed 30% with catalyst CuO / ZSM-5 (4%) led to improving the performance of catalysts and increased aromatic and decreased conversions. The main products of the aromatic were C_7H_8, $(CH_3)_2C_6H_4$, C_8H_{10}, $CH_3C_6H_4C_2H_5$, $C_{10}H_{14}$, $C_6H_4(C_2H_5)_2$, and $C_6H_5(CH_2)_3CH_3$. Also, water on ZSM-5 and CuO / ZSM-5 play an important role in the of aromatic products.

Conflict of interest

The authors declare that they have no conflict of interest.

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