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Catalytic conversion of methanol to gasoline range hydrocarbons

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Abstract

The catalytic conversion of methanol to hydrocarbons of gasoline range has been studied over HZSM-5, ZnO/HZSM-5, CuO/HZSM-5 and CuO/ZnO/HZSM-5. The selectivity of methanol conversion to hydrocarbon has been found to be a function of CuO/ZnO/HZSM-5 concentration. A comparison has been done to study the conversion and yield of different metal oxides doped on the catalyst. The catalysts were prepared by means of impregnation technique followed by heat treatment at 550 °C for 5 h. The copper and zinc oxide loading over HZSM-5 (Si/Al = 45) catalyst were 7 wt.% each. These catalysts were characterized by X-ray diffraction and surface area analysis. The performances of the catalysts were evaluated by conducting experiments in a fixed bed reactor (i.d.: 19 mm) made of stainless steel. Experiments were conducted at 1 atm and 400 °C at constant flow rate of methanol. The major products were ethylene, propylene, dimethyl ether, toluene, ethyl benzene, ethyl toluene, trimethyl benzene and tetra methylbenzene. Investigations have also been done to study the catalyst deactivation. The catalysts were mainly deactivated due to deposition of coke. Addition of ZnO over CuO/HZSM-5 significantly reduces the coke without affecting product yields. Over a ZnO/HZSM-5 catalyst, the coke formation was reduced compared to a CuO/HZSM-5 catalyst. ZnO/CuO/HZSM-5 enhanced the aromatics yield to 69 wt.% as compared to yield of 66.9 wt.% over ZnO/HZSM-5. The product compositions are compared and discussed.

Keywords: HZSM-5; CuO/HZSM-5; CuO/ZnO/HZSM-5; ZnO/HZSM-5; Methanol conversion

1. Introduction

Methanol could be one of the main fuels used in future transportation when petroleum wells are depleted. Methanol is produced from synthesis gas (mixture of carbon mono oxide and hydrogen), which is formed by steam reforming of natural gas or gasification of coal or from biomass. Methanol is available in abundance, therefore it has been used as a raw material for the production of gasoline and olefins. It can be obtained from renewable sources such as biomass.

Catalytic conversion of methanol to gasoline and olefins attracted many researchers when the price of fuel started to increase. The literature concerning conversion of methanol to hydrocarbons over zeolite catalyst is extensive [1–13]. In 1970s, Mobile researchers found that methanol could be converted to gasoline over mesoporous selective zeolites. Conversion of hydrocarbons from methanol using ZSM-5 has been investigated by Chang and Silvestri [7]. Dubois et al. [6] reported the effect of transition metals Co, Mn and Ni over SAPO-34 molecular sieve to check the activity and conversion.

Al-Jarallah et al. [3] studied the effect of metal impregnation on high silica zeolites of the pentasil type MFI structure to investigate the methanol conversion to light alkenes. Tsoncheva and Dimitrova [11] converted methanol to hydrocarbons over different zeolite catalysts. Freeman et al. [5] investigated the conversion of methanol to hydrocarbons over Ga_2O_3/HZSM-5 and Ga_2O_3/WO_3 and the effect of loading Ga_2O_3 on to HZSM-5 on conversion and yield of hydrocarbons.

Doping metal oxides such as CuO into the HZSM-5 framework usually results in the generation of additional acidic sites, and thereby modifies the acidity of the parental material. It facilitates the dehydrating activity of the catalyst and also helps to form higher molecular weight hydrocarbons in the gasoline range.

The objective of this study was to compare CuO/ZnO and CuO supported HZSM-5 and HZSM-5 under the same operating conditions such as temperature, pressure and flow rate, and to investigate the conversion and yield of hydrocar-

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bons. CuO/ZnO loaded over HZSM-5 was prepared, characterized and experimented for their performance of methanol conversion.

2. Experimental

HZSM-5 (Si/Al = 45), the catalyst used for MTG, was supplied by Süd Chemie (Germany). Amounts of CuO/ZnO 7 wt.% each and 0.5 wt.% ZnO were doped on the HZSM-5. In our previous work, the effect of copper oxide loading on HZSM-5 was studied. It was found that on increasing the CuO content, the yield and conversion increased [13]. All these catalysts were prepared by standard impregnation technique [15,16]. NH_4OH solution was added to the slurry of the catalyst wetted with copper nitrate solution to increase the pH to 5. The solution was stirred for 12 h. The catalyst slurry was transferred to a rotary evaporator to remove excess water under vacuum. The pellets were dried at 120 °C for 12 h followed by calcination at 550 °C for 5 h. Three different catalysts were prepared by impregnation over HZSM-5 by CuO or ZnO and CuO/ZnO. The final weight percent of the metal oxide as indicated in Table 1 was determined by metal trace analyzer (Metrohm, Switzerland).

The total surface area and pore size of the catalysts were determined with a Micromeretics ASAP-2010 by nitrogen adsorption at 77 K. Prior to the analysis, the catalysts samples were pretreated for 4 h at 150 °C under vacuum.

Table 1
Properties of various metal impregnated HZSM-5 catalysts

Catalyst	Metal content (wt.%)		S_{BET} (m^2/g)	Pore volume (cm^3/g)
	CuO	ZnO		
HZSM-5	0	0	290.0	0.39
ZnO/HZSM-5	0	7	244.0	0.347
CuO/HZSM-5	7	0	254.6	0.33
CuO/ZnO/HZSM-5	7	0.5	241.6	0.36

X-ray diffraction pattern of catalysts were taken in order to characterize the phases and crystallinities of the modified HZSM-5. All the prepared samples were analyzed at room temperature by X-ray diffraction using a Bruker D8 Advance X-ray diffractrometer with monochromatic Cu Kα radiation (wavelength $\lambda = 1.5406$ Å at 2θ range from 2° to 40°).

All the catalysts were compared for their performance by conducting experiments in a fixed bed reactor under identical conditions. Liquid methanol was pumped from a graduated burette using a microtube pump (Eyela, Tokyo Rikakikai Co. Ltd.) at a flow rate of 0.5 ± 0.1 ml/min. Methanol was passed through a preheater maintained at a temperature of 150 °C. This stream was mixed with nitrogen and passed to the reactor. The schematic diagram of the experimental setup has been shown in Fig. 1. The tubular reactor was made up of stainless steel tube (i.d.: 19 mm). The reactor was heated in three zones by means of electric furnace at 400 °C. The total length of reactor was 770 mm. One thermocouple was at-

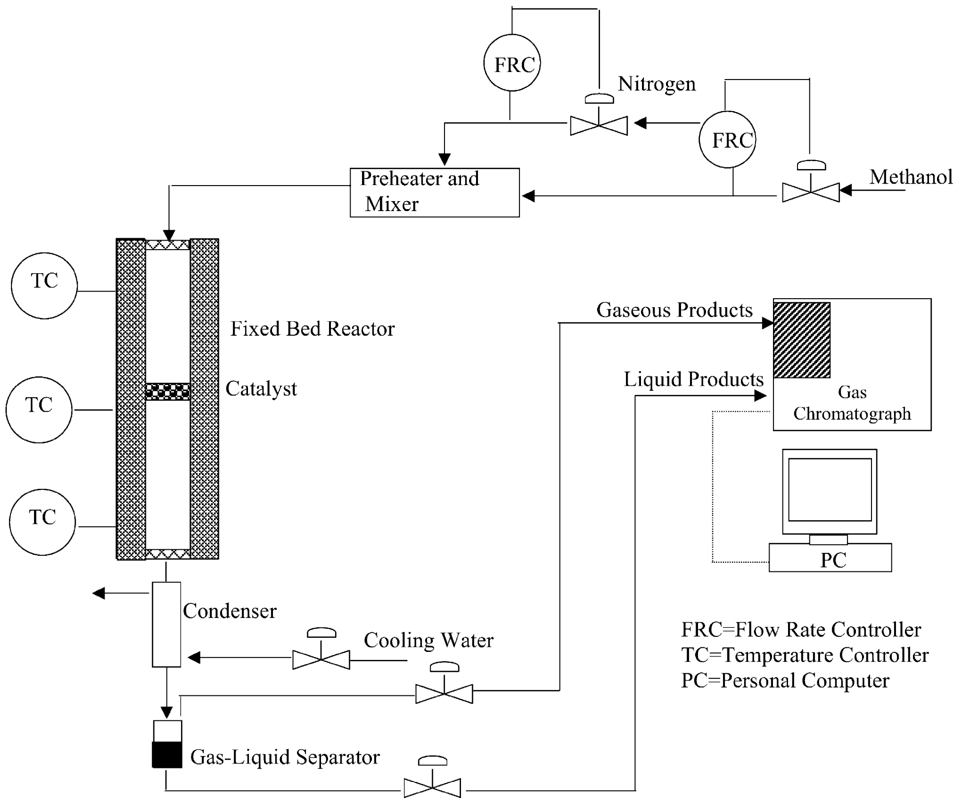

Fig. 1. Schematic diagram of experimental setup.

tached to the top whereas another one had been inserted from the bottom of the reactor to measure the axial temperature profile. A circular plate containing holes was welded to the upper thermo-well and serves as the catalyst retaining support. The weighted catalyst was placed in the central portion of the reactor where isothermal conditions were maintained.

The products from the reactor passed through the condenser maintained at −5 °C to remove all the condensables. The non-condensables were passed through a gas sampler, a gas flow meter, and then vented.

The gaseous and liquid products were analyzed by two gas chromatographs using thermal conductivity detector (TCD) and flame ionization detector (FID). The TCD column was used for the determination of N_2, CH_4 and any CO and CO_2 formed during reaction. N_2 gas was used as an internal standard for subsequent gas analysis. The FID column was used for the determination of hydrocarbon gases and liquid products. All hydrocarbon gases were analyzed by using a Porapak-Q column (i.d.: 2 mm, length: 6 ft). The liquid hydrocarbons were determined by using a capillary column (Petrocol DH, $L = 60$ m, i.d. = 0.25 mm fused silica), on a FID mode. The oven, injector and detector temperature were maintained at 80, 130 and 140 °C, respectively.

3. Results and discussion

Fig. 2 shows the XRD pattern of CuO/ZnO, and CuO catalyst and a comparison with the starting HZSM-5 catalyst. XRD pattern of these catalyst were mostly amorphous (no sharp peaks of CuO and ZnO) indicating the structure of zeolites remains intact after the different treatment procedures. However, the obtained intensities differ depending upon preparation methods and on CuO/ZnO content. The higher intensity was observed for the starting zeolite (HZSM-5). The decrease in the intensities may be due to higher absorption coefficient of CuO/ZnO [16].

The surface area and pore volume of the catalyst were determined by the BET method. These results are shown in Table 1. The total surface area of the catalysts decreased with increasing copper/zinc oxide loading. The volume of N_2 adsorbed decreases with increasing copper/zinc oxide content due to partial coverage of the surface with copper/zinc oxide [15,16].

The 0.5 wt.% ZnO loaded on a CuO/HZSM-5 catalyst shows increased resistance towards deactivation as compared to the CuO/HZSM-5 catalyst. Fig. 3 shows a comparison of products distribution obtained with various metal oxide (Cu/Zn) doped HZSM-5 catalysts at 400 °C and atmospheric pressure. Preliminary experiments carried out with the HZSM-5 catalyst at the same temperature, pressure and flow rate also showed that aromatic compounds are dominant in the products [5,14]. Figs. 4 and 5 show the product distribution of gaseous and liquid products, respectively over CuO/ZnO/HZSM-5 catalyst. The detailed conversion and product distribution with all the catalysts studied are shown in Table 2. There was a significant increase in conversion of methanol on incorporation of CuO loading. The

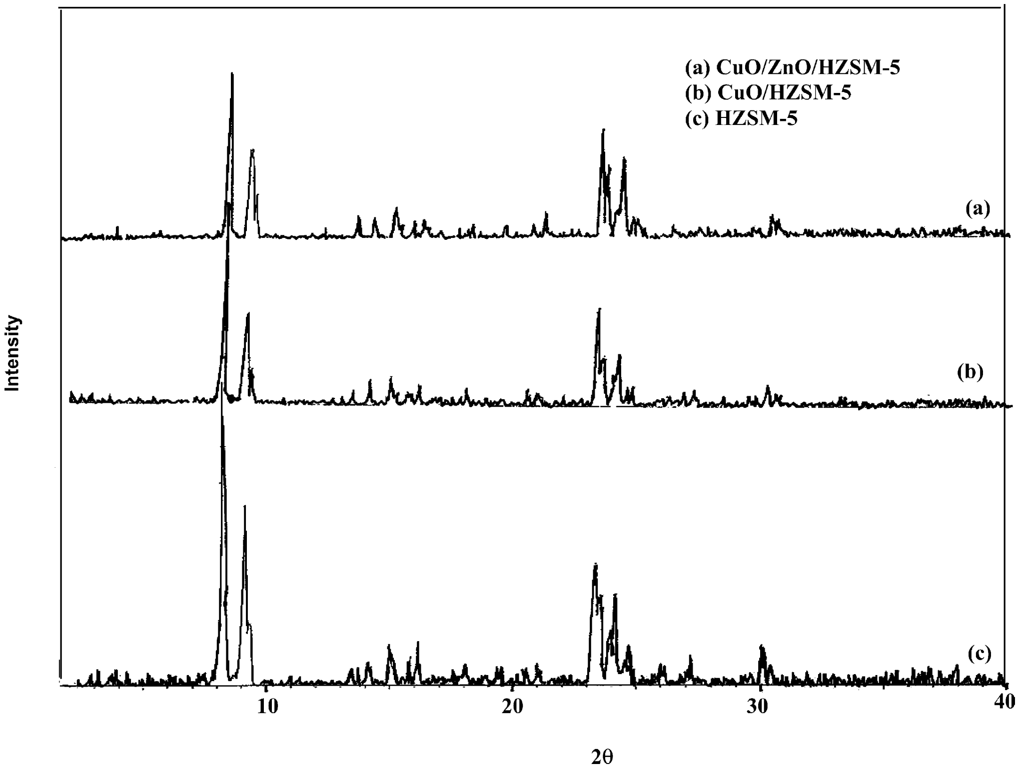

Fig. 2. XRD patterns for copper oxide impregnated catalysts.

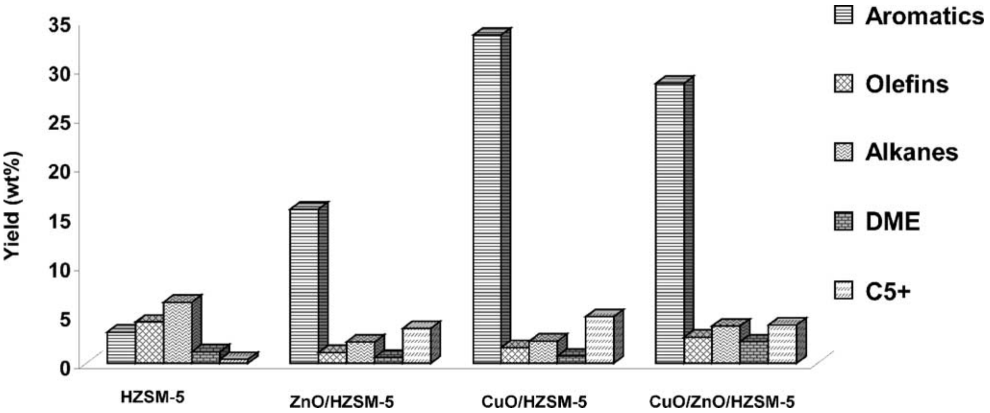

Fig. 3. Product distribution of hydrocarbons over various metal impregnated catalysts [$T = 400\,^{\circ}\text{C}$, $P = 1$ atm and $\text{W/F}_{\text{A0}} = 4.14$ ($\text{g}_{\text{cat.}}$ h/mol methanol fed)].

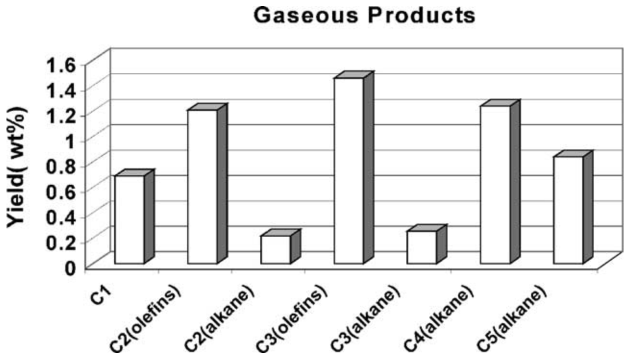

Fig. 4. Product distribution for methanol conversion to hydrocarbons over CuO/ZnO/HZSM-5 [$T = 400\,^{\circ}\text{C}$, $\text{W/F}_{\text{A0}} = 4.14$ ($\text{g}_{\text{cat.}}$ h/mol methanol fed)].

total methanol conversion reached 97% at a CuO loading of 7 wt.%. The product distribution was also significantly improved. The major products of the reaction were methane, ethylene, propylene, dimethyl ether, toluene, ethyl benzene, xylene, isopropyl benzene, ethyl toluene, and trimethyl benzene and tetra methylbenzene. As can be seen from the product distribution, C_5–C_{10} hydrocarbons were the major products. All these products were identified from their retention times by comparison with authentic samples.

The aromatics distribution with the different zeolite catalysts strongly depends upon their pore size and acidic sites. Slow hydride transfer from alkenes, disproportionate into alkanes and aromatics compounds. The hydrocarbon product distribution depends mainly on the conversion reaction due to the structure of the zeolite and also due to steric restriction and secondary process such as hydrogen transfer activity and coking.

The aromatic content over the HZSM-5 catalyst was 21 wt.% on a water-free basis, and catalyst containing 7 wt.% CuO and 0.5 wt.% ZnO resulted an increase in aromatic content up to 69 wt.%.

The transformation of methanol to various products may be explained by the following mechanisms. In a pri-

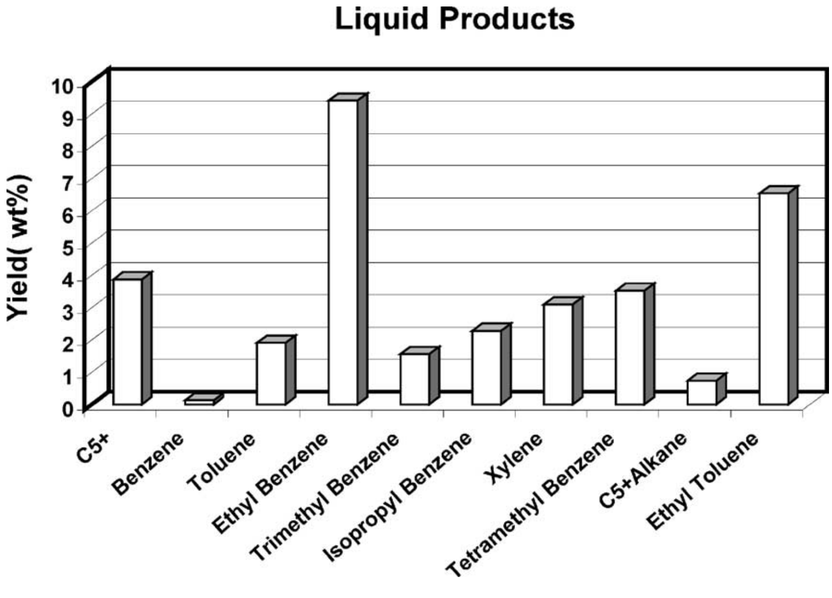

Fig. 5. Product distribution for methanol conversion to hydrocarbons over CuO/ZnO/HZSM-5 [$T = 400\,^{\circ}\text{C}$, $\text{W/F}_{\text{A0}} = 4.14$ ($\text{g}_{\text{cat.}}$ h/mol methanol fed)].

Table 2
Conversion and hydrocarbons product distribution for the catalytic conversion of methanol

Compound	CuO/HZSM-5	CuO/ZnO/HZSM-5	ZnO/HZSM-5	HZSM-5
Conversion (wt.%)	97	95	60	38
Yield (wt.%)				
CH_4	0.33	0.69	0.39	0.99
C_2	0.957	1.23	0.56	1.35
C_3	0.85	1.72	0.72	3.47
C_4	0.61	1.24	0.51	1.89
C_5	0.55	0.84	0.34	2.12
C_{5+}	6.1	4.36	4.3	1.0
C_6H_6	0.1	0.127	0.19	0.27
C_7H_8	3.34	1.91	0.732	0.72
C_8H_{10}	12.2	12.58	7.0	1.1
C_9H_{12}	12.98	10.38	5.28	1.1
$C_{10}H_{14}$	3.43	3.523	1.86	0
CH_3OCH_3	0.73	2.2	0.6	1.16
Aromatics[a]	76.5	69.4	66.9	20.9
Total hydrocarbon (wt.%)	42.16	41.1	22.5	15.2
Water (wt.%)	41.8	36.68	35.7	19.38
Others[b] (wt.%)	13.04	17.2	1.8	3.42

Reaction conditions: W/F_{A0} ($g_{cat.}$ h/mol methanol fed) $= 4.138$, 400 °C and 1 atm; CuO/ZnO/HZSM-5 represents 7 wt.% CuO and 0.5 wt.% ZnO; CuO/HZSM-5 represents 7 wt.% of CuO; ZnO/HZSM-5 represents 7 wt.% of ZnO.

[a] Calculated on water-free basis.

[b] Include CO and CO_2.

mary reaction, methanol is first dehydrated to dimethyl ether (DME). In a secondary reaction, the equilibrium mixture formed of methanol, dimethyl ether and water, is then converted to light olefins. The final reaction step leads to the formation of paraffins, aromatics and higher olefins. Light olefins can oligomerize to form products in the gasoline boiling range. These products can react with oxygenates or with light olefins to produce additional gasoline products. Fig. 6 shows how the conversion of methanol decreases with increase in time on stream. The decrease is more pronounced over the CuO/HZSM-5 catalyst than over CuO/ZnO/HZSM-5. The initial conversions over CuO/HZSM-5 and CuO/ZnO/HZSM-5 were 97 and 95%, respectively, however methanol conversion decreased with time. The decrease in methanol conversion was slow for CuO/ZnO/HZSM-5 compared to CuO/HZSM-5. Fig. 7 shows the yield of hydrocarbons with respect to time. The increase in time of reaction results in a decrease in the yield of hydrocarbons. CuO/ZnO/HZSM-5 shows the slow decrease in the yield of hydrocarbon with increase in time compared to CuO/HZSM-5 catalyst. After a period of 12 h methanol conversion was reduced from 97 to 75.7% with copper oxide catalyst. Incorporation of 0.5 wt.% of ZnO on the 7 wt.% CuO catalyst significantly reduced the deactivation rate. Compared to these catalysts there was negligible loss of catalytic activity with HZSM-5 catalyst due to lower active sites available for reaction and coke formation. Addition of CuO enhances the acidic sites on HZSM-5, which are highly selective to the gasoline range of hydrocarbons, whereas ZnO reduces the deactivation during the reaction. Addition of ZnO also increases the dispersion of CuO by reducing the crystallite size, which results in more sites of CuO available for methanol adsorption thereby increases the activity of the catalyst.

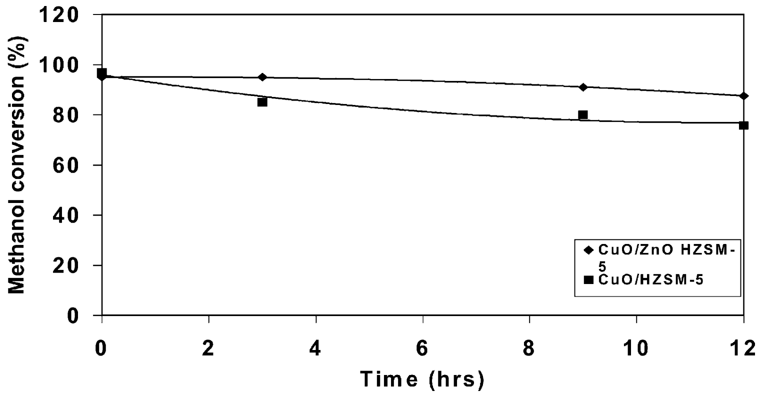

Fig. 6. Conversion of methanol vs. time with different catalysts [$T = 400$ °C, $P = 1$ atm, $W/F_{A0} = 4.14$ ($g_{cat.}$ h/mol methanol fed)].

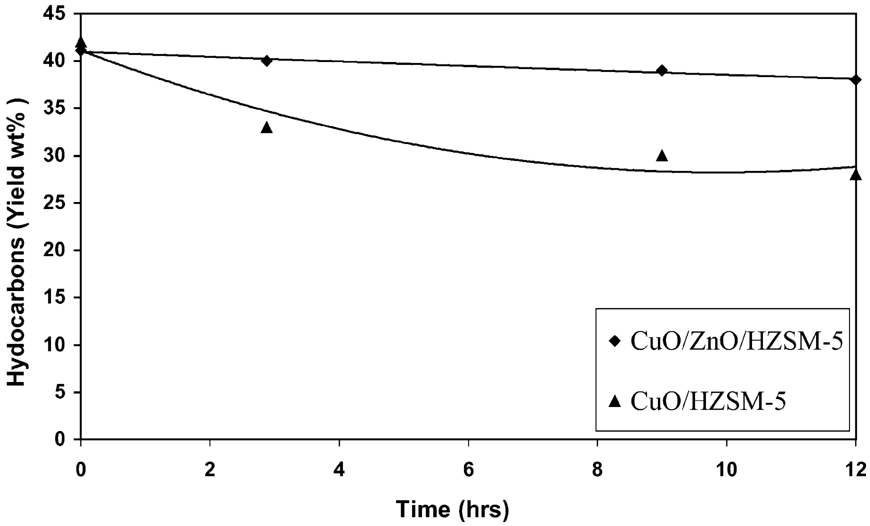

Fig. 7. Yield of hydrocarbon vs. time in a fixed bed reactor [$T = 400\,^\circ C$, $P = 1$ atm, $W/F_{A0} = 4.14$ ($g_{cat.}$ h/mol methanol fed)].

4. Conclusions

Compared to HZSM-5 catalyst, there was a significant increase in conversion and yield of aromatics over CuO/ZnO impregnated catalysts. The major reaction products were methane, ethylene, propylene, dimethyl ether, toluene, ethyl benzene, xylene, isopropyl benzene, ethyl toluene, and trimethyl benzene and tetra methylbenzene. The total wt.% of aromatics in the products was 69% with ZnO/CuO/HZSM-5 catalyst.

The present investigation suggests that incorporating CuO/ZnO into HZSM-5 significantly enhances the hydrocarbon yield. It was concluded that new active sites were created on the surface of the catalyst, which were highly selective to hydrocarbons of the gasoline range.

Addition of ZnO over CuO/HZSM leads to a catalyst, which was more resistant to deactivation. A higher amount of methanol was converted to hydrocarbons of the gasoline range before the catalyst completely deactivated.

References

[1] A.J. Marchi, G.F. Forment, Appl. Catal. 71 (1993) 91.
[2] O. Mikkelson, S. Kolboe, Micropor. Mesopor. Mater. 29 (1999) 173.
[3] A.M. Al-Jarallah, U.A. El-Nafaty, M.M. Abdillahi, Appl. Catal. 154 (1997) 117.
[4] M. Stöcker, Micropor. Mesopor. Mater. 29 (1999) 3.
[5] D. Freeman, R.P.K. Wells, G.J. Hutchings, J. Catal. 205 (2002) 358.
[6] D.R. Dubois, D.L. Obrzut, J. Liu, J. Thundimadathil, P.M. Adekkanattu, J.A. Guin, A. Punnose, M.S. Seehra, Fuel Process. Tech. 1682 (2003) 1.
[7] C.D. Chang, A.J. Silvestri, J. Catal. 47 (1977) 249.
[8] Ø. Mikkelsen, S. Kolboe, Micropor. Mesopor. Mater. 29 (1999) 173.
[9] M. Bjorgen, S. Kolboe, Appl. Catal. 225 (2002) 285.
[10] Y. Inoue, K. Nakashiro, Y. Ono, Micropor. Mesopor. Mater. 4 (1995) 379.
[11] T. Tsoncheva, R. Dimitrova, Appl. Catal. 225 (2002) 101.
[12] P. Yaragadda, C.R.F. Lund, E. Ruckenstein, Appl. Catal. 54 (1989) 139.
[13] H.A. Zaidi, K.K. Pant, in: Proceedings of the 53rd Canadian Chemical Engineering Conference, Hamilton, Ont., Paper no. 327, September 26–29, 2003.
[14] M.O. Adebajo, M.A. Long, Catal. Commun. 4 (2003) 71.
[15] P. Cañizares, A. de Lucas, F. Dorado, A. Duran, I. Asencio, Appl. Catal. 169 (1998) 137.
[16] S. Velu, L. Wang, M. Okazaki, K. Suzuki, S. Tomura, Micropor. Mesopor. Mater. 54 (2002) 113.