

Transformation of Methanol to Hydrocarbons using Modified HZSM-5 catalyst

Syed Saif Ali and Hasan Akhtar Zaidi*

Department of Chemical Engineering,
Aligarh Muslim University, Aligarh-202002, INDIA.
email: hasan.azaidi@gmail.com (H. A. Zaidi)

(Received on: November 10, 2020)

ABSTRACT

HZSM-5 catalyst was modified with barium oxide and cadmium oxide and used for the production of hydrocarbons in a fixed bed reactor was investigated. Barium oxide and cadmium oxide content such as 1wt%BaO and 0.1wt%CdO were doped over HZSM-5 and prepared using the wet impregnation technique. It was found the BaO and CdO get dispersed uniformly over the HZSM-5 catalyst. BaO/CdO film directly influences the formation of crystals, catalyst area, pore-volume, and catalyst reaction. 1wt%BaO/0.1wt%CdO-HZSM-5 catalyst was modified by mild dealumination in 1 M oxalic acid solution, named Cd-Ba/HZOX, and exhibited significant improvement in catalyst stability and hydrocarbon yield. The catalyst properties were investigated by XRD, SEM, and BET analysis. The significant products obtained were methane, ethylene, propylene, dimethyl ether, benzene, toluene, ethylbenzene, xylene, isopropyl benzene, ethyl toluene, and trimethyl benzene and tetra methylbenzene [T=673 K, P=1atm and WHSV=9.5–19h⁻¹]. It was investigated that the Cd-Ba/HZOX catalyst showed better stability than the HZSM-5(HZ), 1wt%BaO-HZSM-5 (Ba/HZ), and 1wt%BaO-0.1wt%CdO/HZSM-5 (Cd-Ba/HZ) catalyst, and this study was made based on the effect of run time.

Keywords: HZSM-5, Methanol to hydrocarbons, yield, conversion, deactivation.

INTRODUCTION

Methanol provides ways to produce petrochemical and hydrocarbons products from coal and natural gas via syngas. Technologies are used to convert carbon sources such as

coal, biomass, heavy oil, etc., into syngas. Syngas can be easily converted into methanol, which can be transformed into various C₁ to C₁₀ range gasoline hydrocarbons with improved activity and high selectivity.¹⁻⁴

HZSM-5 is a crystalline alumina silicate zeolite with a well-defined porous structure (<2 nm), high surface area, uniform micropores, and stronger acidity improved activity and high selectivity in the MTH reaction. The ZSM-5 catalyst having a defined pore structure and stronger Brønsted acidity leads to hydrocarbons production from methanol (especially aromatics).^{2,5-9} Carbocation is adsorbed on strong acidic sites and formed polycondensed aromatics due to growth mechanisms during MTH reaction. The blockage of pore and intersection in the catalyst results in coking, which disturbs the diffusivity of the reactant into active sites. So, deactivation from coking is the major problem for commercial plants.³ Deactivation of catalyst is an important aspect that needs to be controlled. The rate of deactivation can be reduced by treating the catalyst with the oxalic acid solution at a mild concentration. Higher concentration may lead to the removal of a significant amount of acidic sites. H-beta catalyst was used with varying aluminum metal impregnation and is dealuminated using oxalic acid, which significantly enhances coke formation resistance. Better catalytic activity was obtained with enhanced catalyst stability.¹⁰ The Zn/Cu-HZSM-5 catalyst was dealuminated using oxalic acid with the mild treatment of 2 minutes to avoid the removal of a significant amount of acidic sites. After treatment, a better catalytic activity was observed due to an improved lifetime of 18 h.⁵ HZSM-5 catalyst was used for the MTG reaction, and the dealumination step was performed using oxalic acid, which increased catalytic stability. The amount of Brønsted acid sites on the catalyst framework was reduced by dealumination, hence lowering the deactivation rate.¹¹⁻¹³

In the present study, a suitable catalyst is prepared to increase the yield of hydrocarbons. Cd-Ba/HZOX, Cd-Ba/HZ, Ba/HZ and HZ were used during the methanol transformation into hydrocarbons. The catalyst's deactivation occurs because of coke deposition on its surface, which reduces the catalyst activity. Oxalic acid treatment over Cd-Ba/HZ was useful as it increased the catalyst stability and lowered the rate of coke formation.

EXPERIMENTAL

Catalyst preparation

1wt% BaO-HZSM-5, 0.1wt% CdO-1wt% BaO-HZSM-5 were produced by the wet impregnation technique. NH₄-ZSM-5 (Si/Al = 50) was calcined in a muffle furnace under the airflow at 823 K for 5 h to prepare the HZSM-5 catalyst. Ba and Cd precursor Ba(NO₃)₂.6H₂O and Cd(NO₃)₂.6H₂O were procured from Merck, Germany. Satisfying 1wt% BaO and 0.1wt% CdO were dissolved in deionized water, were mixed, and stirred well. The 1wt% BaO and 0.1wt% CdO denoted as Ba/HZ, and Cd-Ba/HZ were obtained after drying at 383 K overnight and calcined at 823 K for 5 h to remove the residual precursor salt materials and oxide the active metal. Dealumination of Cd-Ba/HZ was done using 1 M

oxalic acid for 2 min at 323 K. It was then washed with deionized water and denoted as Cd-Ba/HZOX.

Catalyst characterization

The X-ray diffraction (XRD) was used to check the crystallinity behavior of the catalyst samples using Rigaku D/Max 2500. The X-ray diffraction pattern was checked in the range of 2θ from 5 to 50° with Cu-K α radiation ($\lambda = 1.54439 \text{ \AA}$) under 40 kV and 100 mA. The catalyst's morphology and structure were studied using the Hitachi S-3700N scanning electron microscope (SEM). The catalyst's textural properties were analyzed using N₂ adsorption-desorption isotherm at 77 K using Belsorb Max, Japan.

Catalyst evaluation: MTH reaction

MTH reaction was conducted at 673 K and atmospheric pressure in a fixed bed reactor using a 0.5 g catalyst.^{5,12-13} All the samples were checked based on the performance in the transformation of hydrocarbons from methanol. Before reaction, the sample of 0.5 g was preheated in nitrogen at 673 K for 2 h to remove absorbed moisture. For maintaining the isothermal conditions, the catalyst was placed in the central part of the reactor. The liquid methanol was evaporated by pre-heater at 473 K to vaporize the methanol. Then it was supplied to the pre-heater via a syringe pump. After pre-treatment, the weight hourly space velocity was varied from 9.5–19 h⁻¹, and the temperature inside the reactor was set constant. The reactor's product outlet was subjected to the condenser.

The analysis of liquids and gaseous hydrocarbons was performed in a gas chromatograph (GC-2014 Shimadzu) embedded with a flame ionization detector (FID). Gases such as carbon dioxide, carbon monoxide, etc., were detected using a thermal conductivity detector (TCD). Methanol transformation and hydrocarbons yield were calculated by:

RESULTS AND DISCUSSIONS

Catalysts characterization

Figure 1 shows that the Pattern shifts weren't detected, which shows that the amount of BaO and CdO on HZSM-5 and oxalic acid treatment over the Cd-Ba/HZ catalyst don't change the crystallinity parent ZSM-5. At the same time, the XRD peaks were reduced with an increasing amount of BaO and CdO.

The average sizes of ZSM-5 catalyst crystals were calculated by using the Scherrer equation between $2\theta = 7-10^\circ$:

$$L = K\lambda/\beta\cos\theta \quad (1)$$

L, K, β denotes average crystal size, crystal shape factor, and full width at half maximum (FWHM) of a selected peak at 2θ diffraction angle, respectively. The average crystal size of catalysts is mentioned in Table 1.

The catalyst particle's size distributions were investigated with SEM, and representative micrographs of the different samples are given in Figure 2 (a) and 2(b). To

study the structure of catalysts, SEM was used. This SEM showed that crystal grows in spherical polycrystalline aggregates, and particles of irregular shape were also present,^{5,7}, as shown in Figure 2 (a) and 2 (b).

Meanwhile, the SEM micrographs of the HZ and Cd-Ba/HZOX zeolite show structure and morphology indicate that the addition of cadmium oxide, barium oxide had little influence on the morphology of the HZSM-5 catalyst. Treatment with 1 mol/L oxalic acid led to no change in the ZSM-5 zeolite morphology. The image is shown in Figure 2 (a), and 2 (b) indicate that the HZSM-5 catalyst was quite spherical.

It can be seen from Table 1 that catalyst decreased from 401 m²/g on HZ to 367 m²/g simultaneously; pore volume also decreases from 0.29 to 0.21 cm³/g with metal doping. The decrease in the catalyst's pore volume and surface area could be due to the metal solution's diffusion in zeolite catalysts' pores.

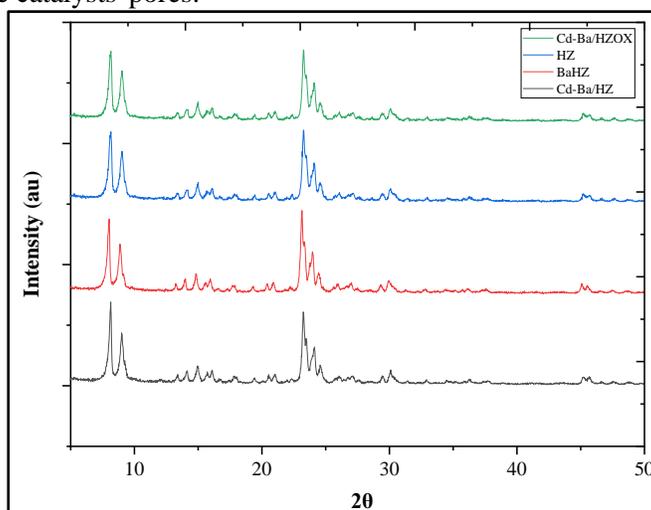


Figure 1. XRD patterns for modified and un-modified HZSM-5

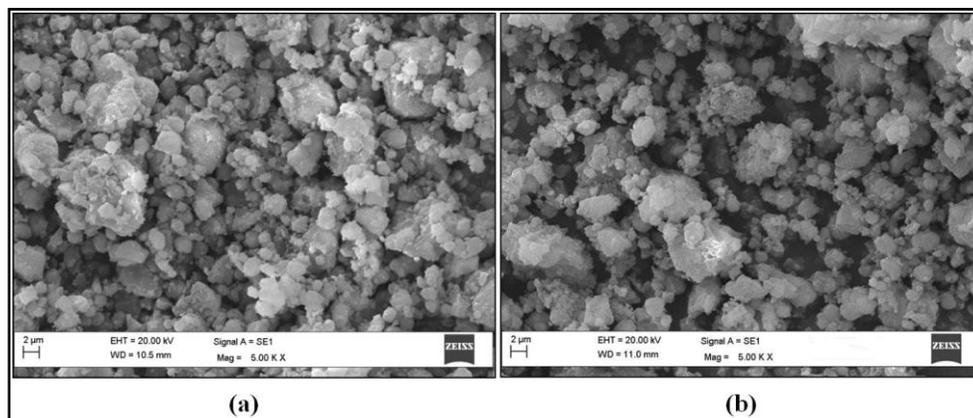


Figure 2. SEM micrographs of the sample (a) HZ and (b) Cd-Ba/HZOX catalysts

In Figures 3 and 4, the transformation of methanol and hydrocarbons yield was affected due to doping of barium oxide and cadmium oxide over HZSM-5 catalyst with time on stream. The transformation of methanol and the yield of hydrocarbons using Ba/HZ catalysts were enhanced compared with the HZ catalyst. Hydrocarbons such as methane, ethylene, propylene, dimethyl ether, toluene, ethylbenzene, xylene, trimethylbenzene, tetramethyl benzene, and C₅⁺ hydrocarbons were the major products formed. The acidic properties and activity of the catalyst were studied by many researchers based on the dehydration of methanol.^{2,4,12}

Table 1. Structural properties and BET analysis of parent and modified HZSM-5 catalysts

S. No	Catalyst	BET surface area (m ² /g)	Pore volume (cm ³ /g)	Average crystal size (nm) ^a
1	HZ	401	0.29	44.32
2	Ba/HZ	386	0.24	39.81
3	Cd-Ba/HZOX	380	0.26	46.57
4	Cd-Ba/HZ	367	0.21	42.96

^aEstimated by Scherrer equation from XRD spectra

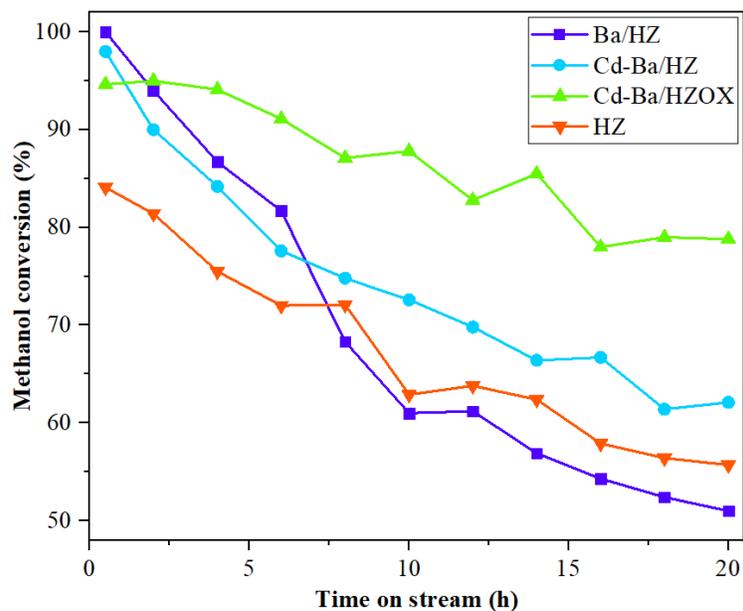


Figure 3. Methanol conversion versus time in a fixed bed reactor [T = 673K, P = 1 atm, WHSV (g of methanol fed/g of catalyst*h) = 9.504]

The rate of deactivation of the Ba/HZ catalyst was faster as compared to the HZ(OX) catalyst. Different catalysts such as HZ, Ba/HZ, Cd-Ba/HZ, and Cd-Ba/HZOX were compared with time on stream, as shown in Figure 3. The transformation of methanol was decreasing with increasing run time. The methanol transformation using Ba/HZ, Cd-Ba/HZ, Cd-Ba/HZOX, and HZ were 100%, 98%, 94.63%, and 84.09%, respectively, and after 20 h of a run, it decreases to 79.5%, 72%, 66.4%, and 54.6%, respectively as represented in Figure 3.

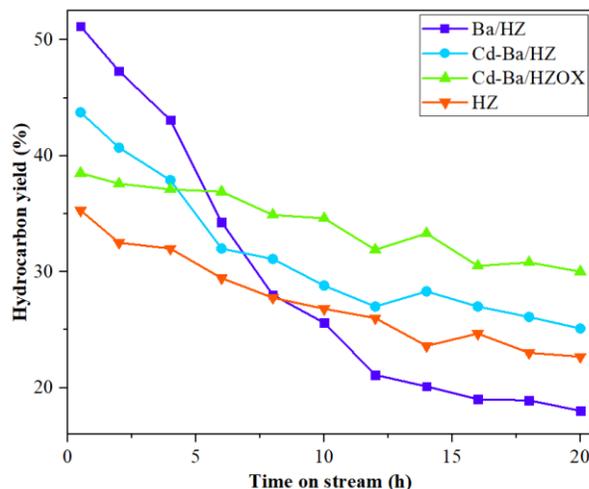


Figure 4. Hydrocarbon yield versus time in a fixed bed reactor [T = 673K, P = 1 atm, WHSV (g of methanol fed/g of catalyst*h) = 9.504]

The product's hydrocarbon yield versus time on stream is shown in Figure 4. As the reaction proceeds, the amount of hydrocarbons gets reduced. Figure 4 shows HZ, Ba/HZ, Cd-Ba/HZ, and Cd-Ba/HZOX catalysts, such as how hydrocarbons yield decreases with an increase in reaction time. The starting hydrocarbon yield of Ba/HZ, Cd-Ba/HZ, Cd-Ba/HZOX, and HZ were 51.17%, 43.75%, 38.51%, and 35.29%, respectively, and 20 h run hydrocarbons yield decreases to 40.1%, 33.1%, 27.67%, and 25.55%, respectively. The highest transformation and yield of hydrocarbons was displayed by the 1wt%BaO modified HZSM-5 catalyst. Figures 3 and 4 show the comparison between a non-treated oxalic acid catalyst and an oxalic acid-treated HZSM-5 catalyst. It was observed that non-treated oxalic acid catalyst shows a shorter lifetime due to which it has less conversion capacity.

Table 2 shows methanol conversion and hydrocarbon yield using catalysts like HZ, Ba/HZ, Cd-Ba/HZ, and Cd-Ba/HZOX. The aromatic weight percentage of different catalysts were found to be: HZ = 35.79, Cd-Ba/HZOX = 38.51, Ba/HZ = 51.17, and Cd-Ba/HZ = 43.75. The highest aromatic content was found to be in Ba/HZ catalyst. This high aromatic content causes higher coke formation over the catalyst (Ba/HZ) surface during the MTH process. In contrast, Cd-Ba/HZOX catalyst gave lower aromatics, and as a result, there is less coke content over the catalyst surface. This is also because there are fewer acidic sites

due to cadmium doping and a further reduction in coking due to catalyst oxalic acid treatment.

Table 2. Product distributions for the conversion of methanol over different catalysts [T = 673 K, WHSV (g of methanol fed/g of catalyst*h) = 9.504, P = 1 atm]

Compound	HZ	Cd-Ba/HZOX	Ba/HZ	Cd-Ba/HZ
Conversion (%)	84.09	94.63	100	98
	Yield (wt %)			
CH₄	1	0.89	0.33	0.7
C₂	2.35	2.16	1.96	2.4
C₃	4.47	2.42	1.85	2.2
C₄	1.1	1.45	0.91	1.2
C₅	2.12	0.84	0.55	1.6
C₅⁺	6.8	7.36	10.08	8.1
C₆H₆	0.27	0.13	1.2	0.85
C₇H₈	0.72	2.95	4.85	2.2
C₈H₁₀	6	7.58	11.2	9.4
C₉H₁₂	7.8	8.38	12.98	10.1
C₁₀H₁₄	Tr. •	1.55	3.53	2.8
CH₃OCH₃	2.16	2.8	1.73	2.2
Hydrocarbons yield (wt % feed)	34.79	38.51	51.17	43.75
Water (wt % feed)	30.3	35.8	38.19	37.8
Others (wt %)*	18.5	20.32	10.64	16.45

*Include CO and CO₂

•Traces

The present studies show that using Cd-Ba/HZOX catalyst converted a higher amount of methanol to hydrocarbons than other catalysts. It was deduced that new active sites are formed which were more suitable for the production of hydrocarbons.

CONCLUSIONS

Cd-Ba/HZOX showed very high reactivity and selectivity as compared with Cd-Ba/HZ, Ba/HZ, and HZ catalyst in methanol conversion to hydrocarbons. The major products obtained methanol conversions were methane, ethylene, propylene, dimethyl ether, benzene, toluene, ethylbenzene, xylene, isopropyl benzene, ethyl toluene, and trimethyl benzene, and tetra methylbenzene. The oxalic acid treated HZSM-5 catalyst (Cd-Ba/HZOX) showed more resistance to deactivation and further decreased the aromatic hydrocarbon yield. Before the catalyst gets completely deactivated, a considerable amount of methanol is converted to hydrocarbons.

ACKNOWLEDGEMENTS

We are thankful to the Department of Chemical Engineering, Aligarh Muslim University Aligarh-India, to support research work.

REFERENCES

1. Ahmed, S., "Methanol to olefins conversion over metal containing MFI-type zeolites", *Journal of Porous Materials*, 19, pp. 111–117 (2012).
2. Beheshti, M.S., Behzad, M., Ahmadpour, J. and Arabi, H., "Modification of H-[B]-ZSM-5 zeolite for methanol to propylene (MTP) conversion: Investigation of extrusion and steaming treatments on physicochemical characteristics and catalytic performance", *Microporous and Mesoporous Materials*, 291, pp. 109699 (2020).
3. Bjørgen, M. and Kolboe, S., "The conversion of methanol to hydrocarbons over dealuminated zeolite H-beta", *Applied Catalysis A: General*, 225, pp. 285–290 (2002).
4. Chen, J., Wright, P.A., Thomas, J.M., Natarajan, S., Marchese, L., Bradley, S.M., Sankar, G., Catlow, C.R.A., Gai-Boyes, P.L., Townsend, R.P. and Lok, C.M., "SAPO-18 catalysts and their Brønsted acid sites", *The Journal of Physical Chemistry*, 98, pp. 10216–10224 (1994).
5. Goetze, J. and Weckhuysen, B.M., "Spatiotemporal coke formation over zeolite ZSM-5 during the methanol-to-olefins process as studied with operando UV – vis spectroscopy: a comparison between H-ZSM-5 and Mg-ZSM-5", *Catalysis Science and Technology*, 8, pp. 1632–1644 (2018).
6. Hadi, N., Niaei, A., Nabavi, S.R., Shirazi, M.N. and Alizadeh, R., "Effect of second metal on the selectivity of Mn/H-ZSM-5 catalyst in methanol to propylene process", *Journal of Industrial and Engineering Chemistry*, 29, pp. 52–62 (2015).
7. Huang, J., Jiang, Y., Marthala, V.R.R., Bressel, A., Frey, J. and Hunger, M., "Effect of pore size and acidity on the coke formation during ethylbenzene conversion on zeolite catalysts", *Journal of Catalysis*, 263, pp. 277–283 (2009).
8. Inoue, Y., Nakashiro, K. and Ono, Y., "Selective conversion of methanol into aromatic hydrocarbons over silver-exchanged ZSM-5 zeolites", *Microporous Materials*, 4, pp. 379–383 (1995).
9. Kang, M. and Inui, T., "Effects of decrease in number of acid sites located on the external surface of Ni-SAPO-34 crystalline catalyst by the mechanochemical method", *Catalysis Letters*, 53, pp. 171–176 (1998).
10. Kianfar, E., Salimi, M., Pirouzfard, V. and Koohestani, B., "Synthesis of modified catalyst and stabilization of CuO/NH₄-ZSM-5 for conversion of methanol to gasoline", *International Journal of Applied Ceramic Technology*, 15, pp. 734–741 (2018).
11. Kim, S., Park, G., Kim, S.K., Kim, Y.T., Jun, K.W. and Kwak, G., "Gd/HZSM-5 catalyst for conversion of methanol to hydrocarbons: Effects of amounts of the Gd loading and catalyst preparation method", *Applied Catalysis B: Environmental*, 220, pp. 191–201 (2018).
12. Zaidi, H.A. and Pant, K.K., "Catalytic conversion of methanol to gasoline range hydrocarbons", *Catalysis Today*, 96, pp. 155–160 (2004).
13. Zaidi, H.A. and Pant, K.K., "An oxalic-acid treated ZnO/CuO/HZSM-5 catalyst with high resistance to coke formation for the conversion of methanol to hydrocarbons", *International Journal of Green Energy*, 11, pp. 376–388 (2014).