CATALYTIC CONVERSION OF METHANOL TO GASOLINE RANGE HYDROCARBONS OVER ZnO/CuO/HZSM-5 CATALYST

by

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DEPARTMENT OF CHEMICAL ENGINEERING

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DOCTOR OF PHILOSOPHY

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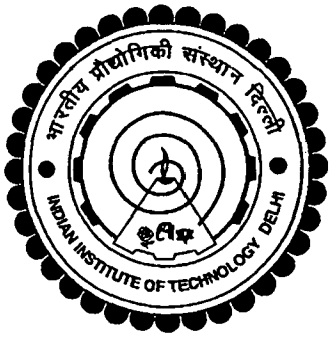

INDIAN INSTITUTE OF TECHNOLOGY DELHI

August, 2005

Methanol
Hydrocarbons
Catalytic Conversion

DEDICATED

TO

MY PARENTS

CERTIFICATE

This is to certify that the thesis entitled, **"CATALYTIC CONVERSION OF METHANOL TO GASOLINE RANGE HYDROCARBONS OVER ZnO/CuO/HZSM-5 CATALYST"** being submitted by **Mr. Hasan Akhtar Zaidi** to the Indian Institute of Technology, Delhi for the award of Doctor of Philosophy is a record of bonafide research work carried out by him under my guidance and supervision in conformity with the rules and regulations of Indian Institute of Technology Delhi.

The research report and results presented in this thesis have not been submitted, in part or full, any other university or institute for the award of any degree or diploma.

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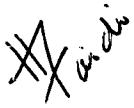

Hasan Akhtar Zaidi

ABSTRACT

Methanol could be one of the main sources of hydrocarbon fuels used in future transportation. Catalytic conversion of methanol to hydrocarbons has attracted many researchers due to the hike in prices of petroleum products and limited petroleum reserves. The development of a suitable catalyst for the methanol transformation to gasoline process can result in several benefits; such as improved conversion; product yields and lower coke deposition.

The present work aims at development of a suitable catalyst and investigations on kinetics and deactivation studies on catalytic conversion of methanol to gasoline range of hydrocarbons. A series of CuO/HZSM-5 catalysts were prepared by wet impregnation technique. In order to improve the dispersion of CuO, the impregnated catalysts were treated with ZnO. The loading of ZnO onto CuO/HZSM-5 was kept between 0 and 0.5 wt%. Another batch of the catalyst was prepared by treating ZnO/CuO/HZSM-5 pellets with 1 molar oxalic acid in deionized water at 353 K. The treated pellets were washed thoroughly with deionized water and finally dried overnight followed by calcinations for 5 hours at 823 K.

The surface area and pore volume of these catalysts were determined by using BET surface area analyzer Micromeretics, USA (ASAP-2010) by adsorption with liquid nitrogen at 77 K. Metal trace analyzer determined the final metal oxide content. TGA profiles were recorded to analyze the weight loss during heat treatment and to estimate the coke content

on the surface of the catalysts. The X-ray diffraction patterns and scanning electron micrographs of the catalyst were also taken in order to investigate the surface morphology of the catalysts. There was no new phase formation during heat treatment and CuO doping.

The prepared catalysts were compared by conducting runs in a fixed bed tubular reactor at 673 K. Addition of CuO on the HZSM-5 catalyst significantly increased the conversion as well as the yield of desired products (C_5^+ non aromatic and aromatic hydrocarbons). The major reaction products were methane, ethylene, propylene, dimethyl ether, pentane, toluene, ethyl benzene, xylene, isopropyl benzene, ethyl toluene, trimethyl benzene and tetramethyl benzene.

There was a significant loss in catalytic activity with time on CuO doped HZSM-5 catalysts. Incorporation of 0.5 wt% ZnO on the 7 wt% CuO with HZSM-5 catalyst significantly reduced the deactivation without significantly affecting the methanol conversion and products yield. Treating this catalyst with oxalic acid further reduced deactivation. Based on comparative studies for high methanol conversion, better product yields and improved catalytic activity, 0.5wt%ZnO/7wt%CuO/HZSM-5 catalyst was selected for further studies. Effect of process variables such as temperature, space-time and partial pressure on conversion and hydrocarbon products yield was investigated using this catalyst.

Yield of aromatic hydrocarbons increased by increasing the contact time while the yield of lighter olefins decreased. Olefins and DME were the intermediate in the methanol

conversion to hydrocarbons. At low contact time high yield of olefins and DME were reported. Similarly yield of olefins and DME decreased with increase in partial pressure of methanol above 90 kPa. Reaction was favorable at lower partial pressure of methanol and higher yields of liquids (C_{5+}) hydrocarbons were observed. The kinetic equations for various models have been formulated considering elemental steps for the mechanism. These models were proposed taking into account the autocatalytic nature of the reaction and the disappearance of oxygenates (methanol+dimethy ether), which was accelerated by the reaction of oxygenates with olefins. The weight fraction of oxygenates, light olefins and rest of the hydrocarbons obtained at different contact time, were used to validate the kinetic model. Optimization of the given objective function was carried out for the estimation of the kinetic parameters for each of the kinetic models.

The deactivation of the catalyst for transformation of methanol to hydrocarbon is mainly due to coke deposition. There was a reduction in conversion and products yield due to coke deposition. The total amount of coke deposited on different catalyst was determined using thermogravimetric analyzer. The monolayer-multilayer coke growth model is described to study the coke formation kinetics. Coke formation on catalyst as a function of time was described by taking into account a simultaneous formation of coke over the surface of the catalyst and multilayer coke deposition. Hence the total rate of coke formation was described as the addition of growth velocities of multilayer and monolayer. The final deactivation model contained seven parameters given as maximum coke of monolayer on catalyst (C_{max}), rate constants k_1, k_2, activation energies E_1, E_2 and deactivation parameters α_1 and α_2. These parameters were determined by fitting experimental data for 18 hours run

against the model predicted data by using a non-linear regression technique. The results indicated that monolayer coke had more deactivating effect on the activity of catalysts. The activation energy for the monolayer formation was smaller than that for multilayer formation, which agrees with the fact that monolayer growth over solid surface is catalyzed. The results indicated that both monolayer as well as multilayer coke deactivates the catalyst activity. The model predictions were in good agreement with the experimental data.

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