DIRECT CONVERSION OF METHANE TO HIGHER HYDROCARBONS OVER Ga/Zn PROMOTED Mo/HZSM-5 CATALYSTS

by

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DEPARTMENT OF CHEMICAL ENGINEERING

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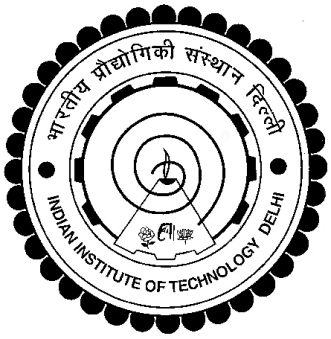
to the



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Dedicated to the memory of

My grandmother

Late smt. Jashoda devi

CERTIFICATE

This is to certify that the thesis entitled, **"DIRECT CONVERSION OF METHANE TO HIGHER HYDROCARBONS OVER Ga/Zn PROMOTED Mo/HZSM-5 CATALYSTS"** being submitted by **Mr. Sachchit Kumar Majhi** 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, to any other university or institute for the award of any degree or diploma.

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(Sachchit Kumar Majhi)

ABSTRACT

Due to the high abundance of natural gas, the direct conversion of methane to higher hydrocarbon in the absence of oxygen has been recognized as a potential catalytic process. The direct conversion method can eliminate the intermediate costlier step of production of synthesis gas towards hydrocarbon production. In the present investigation an attempt has been made to convert methane into higher hydrocarbon by direct conversion (non-oxidative) methods.

Ga and Zn promoted Mo/HZSM-5 catalysts prepared by wet impregnation method were characterized by surface area, pore volume, pore size distribution, X-ray diffraction (XRD), scanning electron microscopy (SEM), temperature programmed reduction (TPR); H_2 pulse chemisorption, temperature programmed desorption (NH_3-TPD) and Thermogravimatric analysis (TGA) techniques. The surface area and the pore volumes of the catalysts decreased from 262 to 236 m2/g with an increase in the molybdenum content of 0-8% whereas the pore volume decreased from 0.34 to 0.28 cm^3/g. From the XRD and FTIR analysis, it was revealed that there was no significant change in the framework of HZSM-5 after the metal impregnation. The H_2-TPR study confirmed that the reduction process of molybdenum oxide takes place in three steps. The first step is attributed to the reduction of MoO_3 to MoO_2 (~450 ^OC) whereas the second step observed is due to the reduction of MoO3 to MoO (~700 ^OC). The third step for the crystalline MoO to metallic Mo which generally occurred at high temperature (>900 ^OC). Incorporation of Mo, Ga and Zn species into HZSM-5 reduced the concentration of Bronsted acid site, while increasing the Lewis acid site as confirmed by the NH_3-TPD analysis. This is due to the fact that Bronsted acid centers of HZSM-5 are covered partly by Mo, Ga and Zn oxides, which reduced the Bronsted

acidity. Second, part of the metal species exchanged with Bronsted acid centers and was responsible for the increase in Lewis acid centers.

The performance of catalysts was evaluated in a differential packed bed reactor over a wide range of operating conditions. The experimental conditions were as follows: T=550-850 ^{O}C; CH4 GHSV=1200-4000 mL/h/gcat, P=1atm. Results suggested that the 5%Mo/HZSM-5 catalyst with silica to alumina ratio 55 is most suitable for methane activation. Investigations revealed that Mo/HZSM-5 catalysts promoted by Ga and Zn are effective for the conversion of methane to higher hydrocarbons. Effect of run time on production distribution were also studied to understand the deactivation of the catalyst.

The effect of methanol as co-feed on methane conversion was studied in order to improve product selectivity and methane activation rate. It was found that by adding of small quantities of methanol in the feed stream, methane conversion is possible at 550 ^{O}C. Total methane conversion was 19.2% with 90% aromatic selectivity over 2%Zn-5%Mo/HZSM-5 at 650 ^{O}C when CH_4/CH_3OH (mol/mol) was 5.5. The probable reason of higher conversion is that the methanol react over the acidic side of zeolite whereas methane react over metal side and form CHx type of intermediate which comes from either the methane and/or methanol side, undergo oligomerization and aromatization reaction to form olefins and aromatics. The main reaction products were ethylene, ethane, propylene, propane, butylene, butane, benzene, ethyl benzene, toluene xylene and some other higher aromatics. The selectivity was about more than 75% in each case.

Effect of propane was also investigated as a co-reactant with methane to improve the catalyst selectivity. Methane conversion reached 17.2 % and the selectivity of aromatic products reached above 80.0% at a CH_4 space velocity 3540 mL/h.gCat and 650 ^{O}C.

Propane conversion was found higher when methane to propane molar ratio was low. Lower methane to propane ratio leads to form a reaction intermediate from the propane side which couple with methane to form higher hydrocarbon. At higher methane to propane ratio (1:1), a part of the propane converts to methane during the reaction.

A reaction mechanism was proposed based on available literature and products distribution obtained. Kinetic study was carried out for the methane conversion over 2%Zn-5%Mo/HZSM-5 catalyst. Due to interdependency of preexponential factor and activation energy a reparameterization of rate equation was done and kinetic parameters were obtained by regression technique. The activation energy as calculated was found to be 81.3 kJ/ mol, and the frequency factor was 1.368×103 kmol/kgcath. The activation energy for methane conversion in the presence of methanol and propane as co-feed were 61.6 and 72.3 kJ/ mol respectively.

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