PhD Thesis

HETEROGENEOUS REACTIONS (Valorisation of Acetone via Hydrogenation and Steam Reforming)

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Abstract

The current scenario of declining energy reserves demands extensive utilization of renewable resources and low value byproducts. Acetone is a byproduct of cumene process for phenol production. The acetone market is not able to keep pace with production. It is, therefore, essential to find ways for converting acetone into value added products through heterogeneous catalysis. In this work, acetone is used to synthesize isopropanol, methyl isobutyl ketone via hydrogenation and H_2 rich syngas by steam reforming at atmospheric pressure using inexpensive non-noble metal based mixed oxide and olivine supported catalysts. A series of Cu-Al mixed oxides, Ni-Co-Mg-Al mixed oxides and Ni-Co/olivine catalysts were synthesized from cheap precursors using co-precipitation and wet impregnation methods. The catalysts were characterized using BET, XRD, FESEM (coupled with EDS), CO_2-TPD, NH_3-TPD, H_2-TPR, TGA and CHNS. The activity of the catalyst was evaluated in a continuous packed bed reactor. The performance of the catalyst was tested by varying temperature, feed molar ratio and space- velocity. From kinetic study, rate equations based on power law model and L-H-H-W kinetic model were derived and validated.

The vapor phase hydrogenation of acetone was carried out over Cu-Al mixed oxide catalysts. The optimum conditions for isopropanol synthesis are: Cu:Al atomic ratio, 0.5; reaction temperature, 175 ^oC; H_2/CH_3COCH_3 molar ratio, 1; space-velocity, 0.126 kmol acetone/kg cat h. A 98 % selectivity for isopropanol was achieved under these conditions. The activation energy of the reaction was determined to be 44.3 kJ/mol. The optimum conditions for synthesis of methyl isobutyl ketone are: Cu:Al atomic ratio, 0.25; reaction temperature, 250 ^oC; H_2/CH_3COCH_3molar ratio, 1; space-velocity, 0.047 kmol acetone/ kgcat h. Under these conditions, the selectivity of methyl isobutyl ketone

was obtained as 74 %. The activation energy of the MIBK synthesis reaction was determined from LHHW type kinetic model as 81 kJ/mol.

The steam reforming of acetone was tested over Ni-Co-Mg-Al mixed oxides and Ni-Co/Olivine catalysts. Around 99 % conversion of acetone and 80 % hydrogen selectivity was obtained over both the catalysts. The optimum conditions for mixed oxides catalyst are: reaction temperature, 550 ^{o}C; steam:acetone (molar), 8:1; space-time, 24 kg cat h/kmol acetone. The optimum conditions in case of olivine supported catalysts are: reaction temperature, 550 ^{o}C; steam:acetone (molar), 6:1; space-time, 24 kg cat h/kmol acetone. The activation energies of the complex reforming process were determined from heterogeneous kinetic models as 44 kJ/mol with mixed oxide catalyst and 63 kJ/mol with Ni-Co/Olivine catalyst, respectively.

Keywords: Heterogeneous reactions, Hydrogenation, Hydrotalcites, Steam reforming, Mixed oxides, Olivine, Ni-Co catalyst