Alkylation of oluene with methanol and disportionation of toluene for production of xylenes

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Toluene, which has the lowest market demand, is always in surplus from the production of reformate and pyrolysis gasoline, whereas benzene and xylenes are in strong demand with the average annual growth rates of around 10%. Therefore, the conversion of dispensable toluene into the more valuable aromatics has an economic incentive.In this study, toluene has been used as a starting material to produce xylenes via either alkylation of low cost toluene with low cost methanol or toluene disproportionation reaction. Among these xylenes isomers, para-xylene is a valuable product because of the high demand for its production of polyethylene terephthalate resin, polyester fibers, and in the synthesis of vitamins and pharmaceuticals.In the present thesis, toluene alkylation with methanol and toluene -disproportionation runs were carried out in the vapor-phase using a fixed-bed down flow system, at atmospheric pressure and reaction temperatures between 300oC and 500oC, and using a continuous hydrogen flow of 20cm3 min-1. For the alkylation reaction, the effect of reaction temperature was investigated using methanol/toluene molar ratio of 2.5 and using a weight hourly space velocity (WHSV) of 2.6 h-1. However, the disproportionation reaction was carried out using WHSV of 2h-1. The effect of methanol/toluene molar ratio was also investigated by increasing the molar ratio from 1.0 to 2.5 at 400oC. The liquid hydrocarbon products of the two reactions were analyzed by gas chromatography. The alkylation products included a mixture of benzene in a small amount, C8 aromatics (xylenes as a major product plus ethylbenzene) and C9 aromatics (trimethylbenzenes and ethyltoluene). However, the disproportionation products contained a mixture of benzene, xylenes in a major product and small amount of trimethylbenzenes.The following catalysts were prepared to study the alkylation or disproportionation reaction:1- Two series of Pt/H-ZSM-5 and Pd/H-ZSM-5 catalysts were prepared having Pt and Pd contents of 0.1, 0.2, and 0.3wt%.2- H-ZSM-5 catalyst was treated -with HF to obtain catalysts containing 1, 2, 3, and 4%HF.3- All hydrofluorinated H ZSM-5 catalysts treated with 1, 2, 3 and 4%HF, were loaded with 0.1 or 0.3%Pt to prepare two series of catalysts.4- Bimetallic catalysts containing Pt and Pd, supported on untreated H-ZSM-5 zeolite, and on H-ZSM-5(3%HF), were prepared.5-Hydrochlorinated H-ZSM-5 catalyst containing 3%HCl was prepared.6-Hydrofluorinated H-mordenite catalysts containing 2 and 4%HF were prepared.For the evaluation of these catalysts, the following experimental analysis were used:a) The equivalent number and strength of acid sites were determined via temperature programmed desorption of presorbed ammonia (TPD).b) BET surface area and total pore volume of the catalysts were measured.c) Thermal gravitational analysis (TGA) was used to determine the deposited coke on the surface of the used -catalyst.In general, for the alkylation of toluene with methanol, the loading of H ZSM-5 with Pt or Pd increased toluene conversion during the alkylation reaction. 0.3%Pt/ H-ZSM-5 was the most selective catalyst for production of para-xylene, but the lowest catalyst for production of trimethylbenzenes.The alkylation reaction on the hydrofluorinated H-ZSM-5 catalysts containing 1, 2, 3 and 4%HF, showed higher activity for toluene conversion and xylenes production than the untreated H-ZSM-5 catalyst. All hydrofluorinated H-ZSM-5 catalysts produced para-xylene selectivities higher than the thermodynamic equilibrium values. The maximum para-xylene selectivity was obtained using the H-ZSM-5(3%HF) catalyst (40.8%).For alkylation reaction, among the hydrofluorinated 0.1%Pt/H-ZSM-5 catalysts containing 1, 2, 3 and 4%HF, the 0.1%Pt/H-ZSM-5(4%HF) catalyst was the most selective catalyst for para-xylene at 300oC. In addition, among the hydrofluorinated 0.3%Pt/H-ZSM-5 catalysts doped with 1, 2, 3 and 4%HF, the one containing 3%HF was the catalyst of choice for para-xylene selectivity at 300oC. Using bimetallic catalysts, the activity of the 0.2%Pt+0.1%Pd/H-ZSM-5 catalyst was higher than that of the 0.1%Pt+0.2%Pd/H-ZSM-5 catalyst for para-xylene selectivity, at all reaction temperatures.For disproportionation reaction, it was found that the H-ZSM-5(4%HF) catalyst was the most selective for production of para-xylene. The selectivities of the hydrofluorinated H-ZSM-5 catalysts, containing 2 and 4%HF, for para-xylene formation, were much higher than those for the hydrofluorinated H-mordenite catalysts containing the same percentage of HF.