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Dehydration of Glycerol to Acrolein with Solid Acid Catalysts

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Abstract : Dehydration of glycerol to acrolein was conducted with solid acid catalysts in liquid phase in a batch reactor and in gas phase in a fix-bed reactor, respectively. In the liquid-phase reaction, ZSM-5, H3PO4-modified ZSM-5 and heteropolyacids including H3PW12O40•xH2O (HPW) and Cs2.5H0.5PW12O40 (CsPW) were studied as catalysts. High temperatures and high boiling point solvents such as sulfolane improved the selectivity to acrolein through suppressing the formation of polyglycerols and coke. Catalytic results and temperature-programmed desorption of ammonia showed that the yield of acrolein increased with increasing catalyst acidity within the range of weak acid strength. Weak acid sites favored the selectivity to acrolein whereas strong acid sites promoted the formation of coke. ZSM-5 possessing only acid sites led to a high acrolein yield, while heteropolyacid catalysts with strong acid sites produced a low acrolein yield. In the gas-phase reaction, HPW and CsPW supported on metal oxides such as SiO2, γ-Al2O3, SiO2-Al2O3, ZrO2 and silicate TUD-1 were studied as catalysts. HPW/TUD-1 was most active for the production of acrolein, followed by HPW/SiO2. An acrolein yield of 61 % was obtained over HPW/TUD-1. X-ray diffraction study suggested that HPW and CsPW were stable and more dispersed on SiO2, silicate TUD-1 and SiO2-Al2O3. It was found that the structures of HPW and CsPW were destroyed by interaction with γ-Al2O3 and ZrO2. Compared to CsPW/TUD-1, the higher acrolein yield with HPW/TUD-1 may be attributed to more Brønsted acid sites on HPW/TUD-1, based on preliminary pyridine adsorption IR study.

Keywords : dehydration, glycerol, acrolein, solid acid catalysts, gas-phase, liquid-phase
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