

盐酸溶液和水热脱铝 HEU-1 分子筛的表征及其催化裂解性能

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摘要 采用 HCl 溶液和/或水热处理 HEU-1 分子筛, 利用 X 射线衍射、N₂ 吸附-脱附、X 射线荧光光谱、NH₃ 程序升温脱附、吡啶吸附傅里叶变换红外光谱和铝固体核磁共振等对脱铝处理的 HEU-1 分子筛进行了表征, 并考察了脱铝 HEU-1 分子筛上正己烷的催化裂解性能. 结果表明, 采用 HCl 溶液处理 HEU-1 分子筛, 能有效脱除非骨架铝, 可调变样品的弱酸中心; 而水热处理 HEU-1 分子筛, 能有效脱除骨架铝, 可调变样品的强酸中心. 水热处理和 HCl 溶液处理有效结合可以达到同时调变 HEU-1 分子筛的酸类型和酸密度的目的. 脱铝 HEU-1 分子筛上正己烷催化裂解反应结果表明, 氢转移反应被明显抑制, 丙烯选择性提高. 600 ° C 水热处理后再用 HCl 溶液处理的 HEU-1 分子筛于 625 ° C 反应时丙烯选择性由未改性的 21.9% 提高到 35.2%, 活性稳定性也由不足 10 h 提高到 40 h.

关键词: HEU-1 分子筛 脱铝 水热处理 盐酸溶液处理 催化裂解 丙烯

Abstract: A series of modified HEU-1 zeolites were prepared using hydrochloric acid treatment, hydrothermal treatment, and a combination of these. The parent and modified HEU-1 zeolites were characterized by X-ray diffraction, N₂ adsorption-desorption isotherms, X-ray fluorescence, temperature-programmed desorption of ammonia, Fourier-transform infrared spectroscopy of adsorbed pyridine, and ²⁷Al solid-state magic-angle spinning nuclear magnetic resonance techniques. The catalytic cracking performances of the modified HEU-1 zeolites were evaluated on a fixed-bed microreactor at 625 ° C, atmospheric pressure, and an n-hexane weight hourly space velocity of 2.0 h⁻¹. The results showed that extra-framework alumina could be removed by directly treating with hydrochloric acid, and framework alumina could be removed by hydrothermal treatment. Acidity characterization showed that the weak acid sites of HEU-1 zeolites could be adjusted using acid treatment, and the number of strong acid sites could be reduced using hydrothermal treatment. The framework n_{Si}:n_{Al} ratio was improved by using a combination of hydrothermal treatment and acid leaching. The acidities of the HEU-1 zeolites were adjusted and both the mesopore volume and external surface area were enhanced. In n-hexane cracking reactions, the dealuminated HEU-1 zeolite obtained by hydrothermal treatment for 4 h at 600 ° C and then washing with hydrochloric acid exhibited the highest propylene production as a result of suppression of the hydrogen transfer reaction. At 625 ° C, the selectivity for propylene on HEU-1(HT4-HCl) increased to 35.2% from 21.9%, and the lifetime of HEU-1(HT4-HCl) was also prolonged from not more than 10 to 40 h.

Keywords: HEU-1 zeolite, dealumination, hydrothermal treatment, hydrochloric acid treatment, catalytic cracking, propylene

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