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研究论文

载体酸性对 $Mo/HZSM\text{-}5\text{-}Al_2O_3$ 催化剂上烯烃歧化反应性能的影响

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摘要 在固定床反应器上考察了 $Mo/HZSM\text{-}5\text{-}Al_2O_3$ 催化剂上乙烯与 2-丁烯歧化制丙烯反应的性能. 结合 X 射线衍射、NH_3 程序升温脱附、吡啶吸附红外、H_2 程序升温还原和程序升温氧化等表征结果发现, 载体酸性的差异导致催化剂酸性和 Mo 物种落位方式不同. 载体酸性较强时, 催化剂积炭严重, 反应稳定性差; 载体酸性较弱时, Mo 物种在分子筛孔道内以 $(Mo_2O_5)^{2+}$团簇形式存在, 而在 Al_2O_3 表面形成较多易还原的六配位 Mo 物种, 催化活性低, 并呈现出一定的诱导期; 适中酸性的载体有利于 Mo 物种的分散和活化, 表现出了最佳的歧化反应活性.

关键词: 乙烯 ??丁烯 ??歧化反应 ??丙烯 ??载体酸性 ??HZSM-5?分子筛 ??氧化铝

Abstract: $Mo/HZSM\text{-}5\text{-}Al_2O_3$ catalyst samples, where the HZSM-5 had different Si/Al ratios (12, 42, and 213), were prepared and evaluated in a fixed-bed reactor. Effects of support acidity changes on the catalytic performance of $Mo/HZSM\text{-}5\text{-}Al_2O_3$ in the metathesis of ethene and 2-butene to propene were investigated. NH_3 temperature-programmed desorption and pyridine infrared spectra revealed that the differences in support acidity led to the different anchoring modes of Mo species on the composite supports. Quick deactivation phenomena were observed on $Mo/HZSM\text{-}5\text{-}Al_2O_3$ (Si/Al = 12) due to the high acidity density of the catalyst. For $Mo/HZSM\text{-}5\text{-}Al_2O_3$ (Si/Al = 213), more Mo species dispersed on the alumina in octahedral form and those locating in the zeolite channels existed in the state of $(Mo_2O_5)^{2+}$ clusters evidenced by ultraviolet-visible diffuse reflectance spectroscopy and H_2 temperature-programmed reduction results. Such distribution was linked with the low metathesis activity and the appearance of the induction period on $Mo/HZSM\text{-}5\text{-}Al_2O_3$ (Si/Al = 213). $Mo/HZSM\text{-}5\text{-}Al_2O_3$ (Si/Al = 42) sample demonstrated the best catalytic activity and reaction stability among the three samples. This was attributed to its suitable acidity amount and optimal distribution of Mo species on the support.

Keywords: ethene, butene, metathesis reaction, propene, support acidity, HZSM-5 zeolite, alumina

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