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High silica REHY zeolite with low rare earth loading as high-performance catalyst for heavy oil conversion

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ABSTRACT

Study on the rare earth exchange performance was carried out with high silica, normal silica and low silica NaY zeolites with framework SiO_2/Al_2O_3 ratios of 5.8, 4.8 and 4.6, respectively. It is found that the silicon content of the starting NaY zeolite is one of the significant factors in determining the ion exchange efficiency. The higher the framework SiO_2/Al_2O_3 ratio is, the less selective to the rare earth ions the zeolite will be. However, the efficiency of the use of rare earth ions are comparable to each other when the concentration of rare earth in the ion exchange solution is less than 6 wt.%, no matter the level of the framework SiO_2/Al_2O_3 ratio of the starting zeolites. Comparison of the hydrothermal stability of the rare earth and ammonium exchanged zeolites (REHY) indicates that the REHY sample prepared from the high silica NaY and with the lowest rare earth loading (2.9 wt.%) exhibits the best hydrothermal stability. The reaction studies indicate that the catalyst containing this REHY zeolite shows much better activity and product selectivity in the catalytic conversion of heavy oil than another REHY zeolite prepared from the normal silica NaY zeolite and having a rare earth loading as high as 6.6 wt.%, which is highly probably due to the superior hydrothermal stability of the former zeolite. It is suggested that the REHY zeolite with a low level of rare earth loading prepared from the high silica NaY can be considered as an alternative catalyst for the catalytic conversion of gas oil.

1. Introduction

Ion exchange with rare earth ions is a common way to improve the framework stability [1–5] and catalytic activity of zeolites [6–9]. Among the successful implementations the preparation of the rare earth-containing HY zeolite (REHY) is a typical example. REHY zeolite, which contains both rare earth and hydrogen ions has been one of the most important hydrocarbon cracking catalysts in the petroleum refining industry for many years. Typical prior art REHY zeolites often contain, however, a relatively high concentration of rare earth ions in order to impart the desired thermal and hydrothermal stability necessary for its application in the petroleum refining industry. Nowadays, the rare earth elements are playing a growing role in the drive toward a high-tech economy, in everything from magnets for electric motors and generators to catalysts for fuel production [10,11]. In the case of the oil processing industry, for example, the fluid catalytic cracking industry, the fresh catalyst consumption per day may be up to several tons. Lowering the rare earth content of the catalyst is a good way of cutting down the consumption of rare earth elements so as to decrease the final cost of the product and to protect limited rare earth resources. However, the problem is how to guarantee the thermal and especially the hydrothermal stability of the REHY zeolite when the rare earth loading in this zeolite is reduced.

NaY zeolites with elevated SiO_2/Al_2O_3 ratios have been successfully synthesized without the use of template agents [12,13]. Recent studies have shown that these new types of high silica NaY zeolites are promising catalyst in the catalytic conversion of hydrocarbons [14–16]. Obviously, it is the higher SiO_2/Al_2O_3 ratio of these newly emerging high silica NaY zeolites that contributes finally to such interesting changes in the catalytic performances. Inspired by these discoveries, a candidate approach was suggested for the preparation of REHY zeolite using the high silica NaY zeolite as the starting material. Although the study of rare earth exchanged Y zeolite has been extensively reported previously, a detailed investigation on

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