SELECTIVE CONVERSION OF LIGHT OLEFINS TO HIGH OCTANE-NUMBER GASOLINE ON NOVEL Fe-SILICATE CATALYSTS

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Conversion of light olefins to gasoline was investigated for various metallosilicates having the pentasil pore-opening structure. The metallosilicate was prepared by replacing the Al ingredient of the H-ZSM-5 with various metal salt at the stage of gel formation. Among various metallosilicates H-Fe-silicate was most effective and stable for the selective formation of high octane-number gasoline. The causes of this high catalytic performance was attributed to its proper acid strength and low diffusion resistance.

INTRODUCTION

Conventional processes for thermal cracking of residual oil produce a considerable amount of light olefins. The yield of valuable gasoline (C5-C11 hydrocarbons) is not so high that successive conversion of the light olefins to gasoline is demanded. As conventional catalysts for gasoline synthesis from light olefins, solid phosphoric acid, supported nickel oxide, and sulfuric acid are known[1,2]. From an industrial point of view, however, the performance of these catalysts are insufficient. Recently, it was reported that H-ZSM-5 is effective for the conversion of light olefins to gasoline fraction[3-6], however, the selectivity is not high enough, because H-ZSM-5 produces a considerable amount of gaseous light paraffins (C1-C4 paraffins) accompanied with the formation of aromatics[3,6]. The aromatization activity of H-ZSM-5 is due to the strong acid sites caused by the existence of Al cation in ZSM-5[7-9].

In order to modify delicately the acidic property and the pore diameter, we reported that Al in ZSM-5 by other elements with maintaining the pentasil pore-opening structure and the three dimensional pore
connection[10]. This was done because such pore structure of ZSM-5 is considered to be the reasons of not only the shape selectivity but also the long catalyst life[11]. Though such metallosilicate synthesis has been studied also by other authors[12,13], application to the catalytic reaction of metallosilicates has not yet been investigated extensively. The evident effect of the metal replacement on the selectivity to hydrocarbons from methanol has been reported in our previous papers[10,14]. In this paper, effects of the metal replacement on the light olefin conversion are described, and then the focus is put on the performance of H-Fe-silicate which exerted the most excellent results for gasoline synthesis among various metallosilicates tested.

**EXPERIMENTAL**

H-ZSM-5 as the authentic sample was prepared by the rapid crystallization method[10], and various kinds of metallosilicates were prepared by replacing the Al ingredient with other metal salts at the gel formation stage of the ZSM-5 preparation. All the catalysts were used as the protonated form in a grain-size of 7-15 mesh.

Fe-silicates with various Fe contents were prepared by adopting the rapid crystallization method[14]. Iron ingredient could be incorporated quantitatively up to the Si/Fe ratio 12 (10 wt% as Fe₂O₃). The XRD patterns of Fe-silicates indicated that they have the pentasil structure. The color of Fe-silicates were milky white even for the high Fe content crystals and exhibited no activity for CO hydrogenation indicating that no free Fe oxide existed in the intrastructure of the crystals. TPD profile of NH₃ from the Fe-silicates indicated that the Fe ion incorporated in the crystal is responsible for the formation of acid site and the acid strength of H-Fe-silicate is weaker than that of H-ZSM-5. From the measurements by means of SEM and EPMA it was elucidated that a small amount of Fe ingredient plays a role as nuclei in the growth of high-silica crystal and the Fe concentration inside the crystal is higher than that at its outer surface of the crystal[14]. An ordinary continuous flow reaction apparatus was used under atmospheric pressure. A 1.0 g (or ca. 1.5 ml) portion of the catalyst was packed in a tubular reactor of 6 mm inner diameter, and pretreated with an N₂ flow at 500°C for 30 min to standardize the catalyst surface condition by removal of adsorbed H₂O. The produced gas