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Short communication

Characterization and application of a Pt/ZSM-5/SSMF catalyst for hydrocracking of paraffin wax

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ABSTRACT

The microstructured Pt/ZSM-5/SSMF catalysts, for hydrocracking of paraffin wax, have been developed by impregnation method to place Pt onto thin-sheet ZSM-5/SSMF composites obtained by direct growth of ZSM-5 on the sinter-locked stainless steel microfibers (SSMF). The best catalyst is the one with ZSM-5 having a SiO_2/Al_2O_3 weight ratio of 200, delivering ~95% conversion with 77.5% selectivity to liquid products or 64.4% selectivity to naphtha at 280 °C. This new approach is capable of increasing the naphtha selectivity with high activity maintenance in comparison with the literature catalysts.

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1. Introduction

The hydrocracking of paraffines over bifunctional catalysts has received increasing attention during the last decades [1–3]. The hydrocracking properties are affected by activity of the metal and the type of carriers. Catalysts based on group VIII metals (Ni, Mo, W) and Nobel metals have been reported in many publications [4–6]. Previous studies showed that the carrier type was important to improving the yield and selectivity of hydrocracking in regard to the acidity and pore structure of catalyst [7–9]. Amophous silica–alumina, ZSM-22, ZSM-5 and additional zeolites in amorphous silica–alumina have been extensively studied to exclude the relationship between carrier propertie (e.g., acidity and pore structure) and catalytic performance [10,11]. The traditional catalysts with additional ZSM-5 in carriers have proven to be most promising while their poor heat and mass transfer properties lead to deep hydrocracking [12]. As a result, very high conversion is achievable but the selectivity to middle distillates is lowered with lots of gas formation.

Furthermore, Jiang et al. [13] reported that the microfibrous entrapped Pt/SAB catalyst (MFEC) had good heat transfer properties while the conversion yield and selectivity of middle distillates were lower than traditional catalysts. The degeneration of supports happened during the calcinations with high temperature when MFEC were prepared. Chen et al. [14,15] illustrated the preparation of a novel zeolite membrane/PSSF composites for toluene adsorption. Microfiber based zeolite membrane is very suitable for the design of catalytic and adsorption fixed beds with a porosity gradient and various shapes. Zeolites layers which grow on the metal with controlled thickness, shapes and different Si/Al ratio can benefit the catalytic properties and can avoid the degeneration of supports with high temperature calcination [16].

In this study, microstructured Pt/ZSM-5 were developed and examined in hydrocracking paraffin wax on a fixed bed reactor. Such Pt catalysts were prepared by impregnation method using composite supports of ZSM-5/SSMF which were obtained by directly growing ZSM-5 (SiO_2/Al_2O_3 weight ratio ranged from 100 to 250) onto a sinter-locked substrate of stainless steel microfibers. The catalytically relevant physiochemical properties of the resulting catalysts in terms of morphology, acid strength and amount, and crystalline phases were studied by SEM, NH3-TPD and XRD.

2. Experimental

2.1. Catalyst preparation

A sinter-locked microfibrous structure with entirely open 3D porous network, consisting of 15 vol.% 316-L stainless steel fibers (20 μm in dia.) and 85 vol.% voidage, is utilized as substrate (denoted as SSMF), which is taken from Western Metal Material Co. Ltd. (China). To remove any contamination, the microfibrous substrate is soaked in HCl (1 wt.%) aqueous solution for 0.5 h, sonicated in acetone for 5 min, thoroughly washed using water, and then dried at 80 °C in air.

The SSMF substrates were seeded with the ZSM-5 nanocrystals using dip-coating method as previously described elsewhere [16]. The dip-coating suspension was prepared by adding 1 wt.% ZSM-5 seeds

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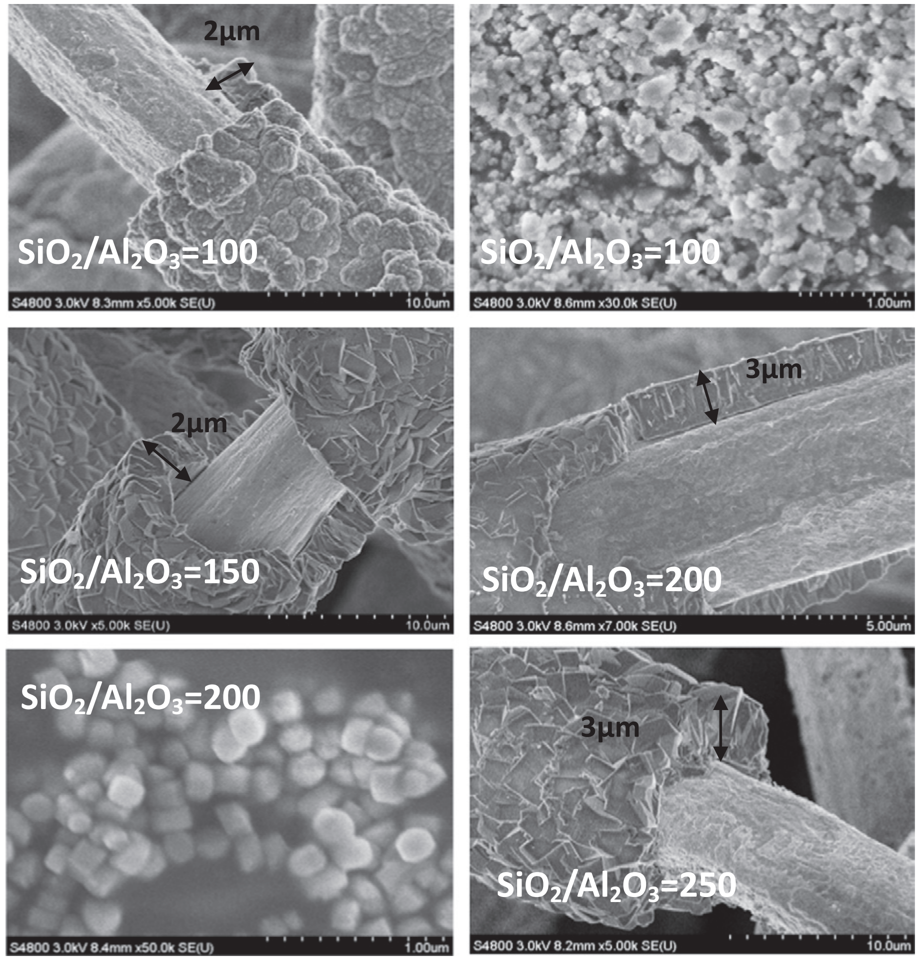

Fig. 1. SEM micrographs of Pt/ZSM-5/SSMF catalyst.

(SiO_2/Al_2O_3 ratio = 180; crystal size: 100–200 nm) into a silica sol-gel (1 wt.% SiO_2) and its pH was adjusted to 2.3 using 1 wt.% HCl aqueous solution prior to the dip coating. Seeding of the ZSM-5 was performed by slowly dipping the SMF substrates into the above suspension for 10 s, followed by drying at 25 °C for 14 h and calcining at 450 °C for 2 h in air. Such seeded SSMF was placed vertically in autoclave filled with synthesis gel. The gel composition in molar ratio was as follows: tetraethyl orthosilicate (TEOS)/tetrapropylammonium hydroxide (TPAOH)/NaOH/$NaAlO_2$/H_2O = 1/0.25/0.4/n/250 (n = 0.01, 0.0067, 0.005 or 0.004; corresponding to the gel SiO_2/Al_2O_3 weight ratio of 100, 200, 300, or 900). When Si/Al ratio is less than 100, the zeolite layer is prone to agglomeration and the crystal size is too small. While Si/Al ratio is too big, the seed crystal is difficult to coat on the substrate because the binding force of the large size of the seed crystal and the substrate is weak [17]. The best crystal size is from 100 to 200 nm, so we choose the Si/Al ratio is from 100 to 250. After hydrothermal

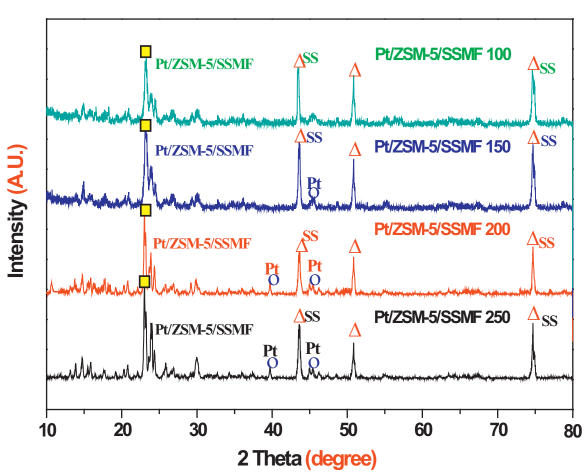

Fig. 2. XRD of different Pt/ZSM-5/SSMF catalyst.

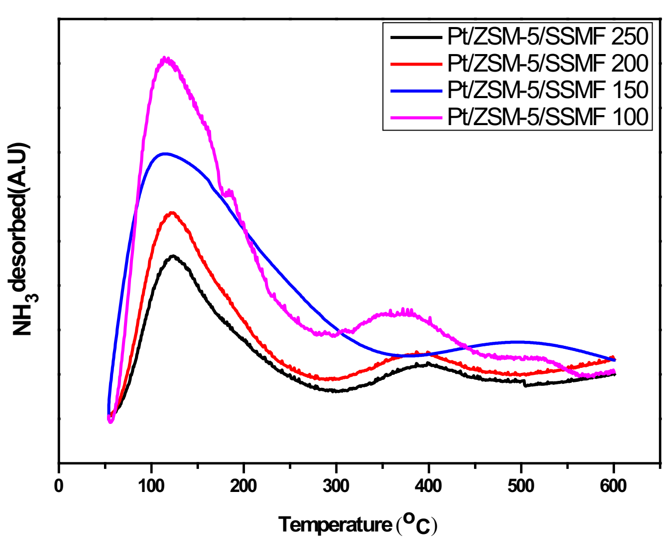

Fig. 3. NH_3-TPD curves of Pt/ZSM-5/SSMF catalyst.

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