Structure and activity of Ni_2P/desilicated β catalysts for hydrocracking of polycyclic aromatics

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Abstract: Ni_2P catalysts supported on β (β) and desilicated β (DS-β) zeolites were prepared by temperature-programmed reduction, and the structural and chemical properties were analyzed by N_2 physisorption, TEM, XRD, EXAFS, pyridine-TPD, and CO uptake. The catalytic activity was tested at 653 K and 6.0 MPa in a fixed bed reactor for the hydrocracking of 1-methylnaphthalene and phenanthrene into benzene, toluene, and xylene. In the hydrocracking, the Ni_2P/DS-β showed better activity and stability for hydrocracking of polyaromatic hydrocarbons than the Ni_2P/β catalyst. In addition, the Ni_2P/DS-β maintained the stability in terms of catalytic activity and local structure, while the Ni_2P/β suffered from coke formation.

Keywords: Ni_2P, hydrocracking, desilication.

1. Introduction

Adsorption of aromatic species on the strong acidic site allows their extended stay leading to condensed aromatic carbon on the acidic site. Hydrogen spillover from the Ni_2P in the neighbor of acidic site may partially hydrogenate the strongly adsorbed species into products that are easier to crack. This catalytic cracking step is sensitive to the zeolite's crystallite structure and acidity [1-2]. Post-synthetic desilication using alkaline solutions represents a simple and scalable method to introduce mesopores in zeolites [3]. The objective of this work is to study the effect of desilication β zeolite(DS-β) on the catalytic hydrocracking of polycyclic hydrocarbons.

2. Experimental

The desilicated β zeolite(DS-β) was prepared by combining β zeolite with 0.2M aqueous solutions of NaOH/TPAOH(tetrapropylammonium hydroxide) mixture at 353K for 30 min at a mass ratio of solution to zeolite of 30. The amount of Ni loading was fixed at 1.5 mmol g^{-1} of support with the initial P/Ni ratio in the precursors of 2.0. The supported nickel phosphate precursor was prepared by incipient wetness impregnation of a solution of nickel nitrate and ammonium phosphate, followed by drying at 373 K for 7 h and calcination at 673 K for 4 h. The resulting precursor phosphates were reduced to the corresponding phosphides by TPR from 298 to 873 K (at 5 $Kmin^{-1}$) in quartz U-tube reactors using 100 cm^3min^{-1} H_2 flow. After reduction, the phosphides were cooled to room temperature under 100 cm^3min^{-1} He flow followed by passivation under 0.1 % O_2/He flow (100 cm^3min^{-1}) for 4 h.

Hydrocracking was carried out at 653K and 6.0MPa in a continuous-flow reactor using a model feed mixture containing 2- to 3- ring aromatic compounds. The feed liquid was prepared by combining 15 wt% phenanthrene in 1-MN. Quantities of catalysts loaded in the reactor were 1.0 cm^3 for the Ni_2P catalysts with corresponding liquid hourly space velocity of 0.5 h^{-1}. Before the hydrocracking reaction, the passivated catalysts were pretreated for 2 h at 723 K under H_2 flow of 100 cm^3min^{-1}. The fresh and spent catalysts were characterized by BET, CO uptake, Pyridine-TPD, FT-IR, TEM, X-ray diffraction (XRD), and extended X-ray absorption fine structure (EXAFS).

3. Results and discussion

Fig. 1 shows N_2 adsorption/desorption isotherms of the supports. For the both zeolites, their isotherms corresponded with type IV, exhibiting a remarkable H3-shaped hysteresis loops at P/P_0=0.7–1.0 typical for capillary condensation of mesoporous materials. The hysteresis loop of β can be explained by the existence of non-rigid aggregates of plate-like particles or assemblages of slit-shaped pores [4]. It is noted that the hysteresis loop of the desilicated β(DS-β) is further developed with the formation of wider ranges of mesoropores. Again, this is due to the desilication treatement.

Fig. 2 shows the hydrocracking activity test results. The Ni_2P/DS-β exhibited a high BTX yield of 45.9 wt%, while the Ni_2P/β gave a little lower BTX yield of 43.2 wt%. Considering the high activity of Ni_2P for 2, 3-ring aromatic compounds conversion reaching over 99% in both cases, the difference in the BTX yield can be related with the pore accessibility. Moreover, a decrease in BTX yield was found over the Ni_2P/β catalyst over a longer reaction time, particularly exceeding, which suggests that the Ni_2P/β catalyst undergoes a loss in cracking activity probably due to a coke deposit on acid sites.

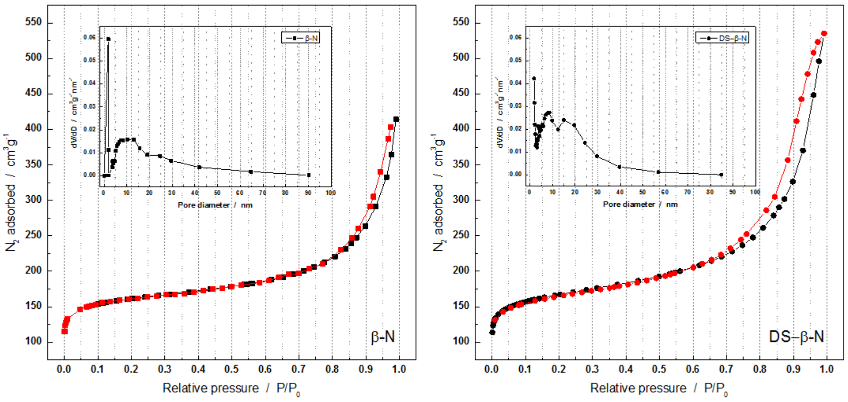

Figure 1. N_2 adsorption/desorption isotherms and pore size distributions for β and DS-β.

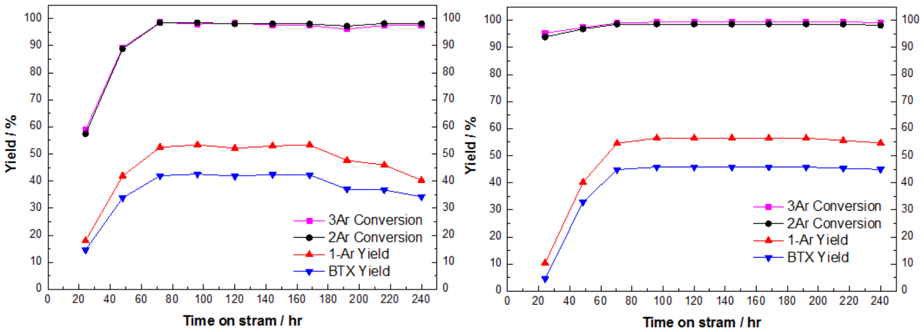

Figure 2. Activity tests for polycyclic hydrocarbons hydrocracking at 6.0MPa, 653K, and LHSV of 1.0 h^{-1}.

4. Conclusions

The effect of desilication on the catalytic activity was investigated using Ni_2P catalysts supported on zeolite β. The Ni_2P/DS-β showed a high activity and stability for hydrocracking of PAHs compared to the Ni_2P/β, with exhibiting a high BTX yield (45.9% vs. 43.2%). The characterizations demonstrated that the DS-β features abundant inter-crystalline mesopores to provide better dispersion for Ni_2P catalysts and accessibility toward acid sites, offering remarkable activity in the PAHs hydrocracking with less coke formation.

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