Enhanced Catalyst Lifetime and Selectivity in the Conversion of Methanol to Gasoline over H-ZSM-5 by Desilication with NaOH

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Introduction

The conversion of methanol to gasoline over acidic, microporous zeolite catalysts is a possible key step for the production of transportation fuels from natural gas, coal, or even biomass. Zeolites possess Brønsted acidic sites located within ordered micropores of molecular dimensions, which give rise to the successful use of zeolites as shape selective catalysts. However, diffusion limitations often hamper the efficient use of the entire zeolite crystal [1,2]. Recently, Groen and co-workers [3,4] have reported on the formation of mesopores in zeolites by treatment with dilute NaOH, so-called desilication. In this report, we adopt this desilication procedure aiming to enhance the production of an aromatics rich C_{5+} hydrocarbon mixture suitable for blending into the gasoline pool from methanol over acidic zeolite catalysts [5].

Materials and Methods

Calcined samples of ZSM-5 were treated with solutions of varying NaOH concentration (0.05 M and 0.20 M) for 2 × 4 h at 75 °C, followed by ion exchange with a 1 M NH_4NO_3 solution for 3 × 2 h at 75 °C and calcination in air at 550 °C. Catalyst characterization was carried out using standard methods. Catalytic tests were performed in a fixed bed reactor employing a partial pressure of methanol of 110 mbar in He carrier gas. The total pressure equaled atmospheric pressure. The reaction temperature was 370 °C and the weight hourly space velocity (WHSV) was 8 $gg^{-1}h^{-1}$.

Results and Discussion

Table 1 lists some of the results from the catalyst characterization. Elemental analysis showed that Si was removed from the samples, whereas the total acidity as measured by ammonia temperature programmed desorption did not change significantly as a consequence of the treatment. This indicates that extra-framework Al is present in the desilicated samples, and this was confirmed by infra-red spectroscopy (not shown). Nitrogen adsorption indicated significant mesopore formation in the two treated samples.

Figure 1 (left panel) shows the results of the catalytic tests for the conversion of methanol to hydrocarbons. Clearly, the lifetime of the catalyst is markedly improved as a consequence of the desilication procedure. Integration of the deactivation curves shows that the catalyst conversion capacity increases by a factor of 3.3 as a result of the most severe desilication procedure. Also, as seen in Figure 1 (right panel) the selectivity towards gasoline-blendable compounds is on average a factor of 1.7 higher for the most extensively desilicated sample over the entire conversion range.

Table 1. Elemental composition and N_2 adsorption characteristics of untreated and the alkaline treated samples. Pore volumes were determined using the *t*-method, and the mesopore volume is V_{total} minus V_{micro}.

Sample	Si/Al ICP-MS	NH_3 capacity (mmol/g)	S_{BET} (m^2/g)	V_{total} (mL/g)	V_{micro} (mL/g)
PARENT	46	0.35	313	0.28	0.09
Treated with 0.05 M NaOH	39	0.37	372	0.39	0.09
Treated with 0.20 M NaOH	27	0.36	419	0.37	0.10

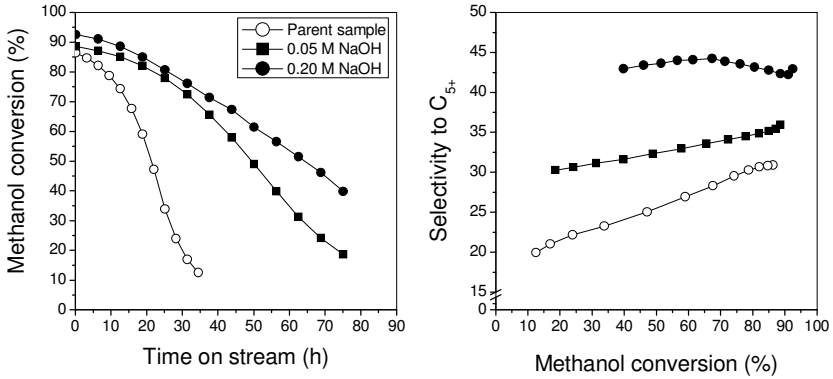

Figure 1. Left panel: Conversion of methanol/DME into hydrocarbons as a function of time on stream at 370 °C and WHSV = 8 $gg^{-1}h^{-1}$. Right panel: Selectivity towards C_{5+} as a function of conversion for the three catalyst samples.

Significance

Desilication of H-ZSM-5 with NaOH solution constitutes an effective and simple post synthesis technique leading to substantial catalyst improvement in the methanol to gasoline reaction, both with respect to catalyst lifetime and selectivity towards the desired C_{5+} product fraction

References

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