

Continuous Al migration from binder or supported aluminum into zeolite framework structure during methanol-to-propylene reaction

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Abstract: TPAOH templated all-silica MFI (TPAOH-S-1) was inactive in MTP reaction, however, rapid methanol conversion growth from 41% to 98% was received after extrusion with Al₂O₃ and acid washing (TPAOH-S-1-Ex-HCl); it kept 99% methanol conversion and 52.5% propylene selectivity for 400 h; besides it showed a higher Propylene/Ethylene ratio of 11.3. 1.5 wt% Al impregnated TPAOH-S-1 also showed similar catalytic performance as TPAOH-S-1-Ex-HCl. Several regenerated AlCl₃/TPAOH-S-1 samples after various reaction time were characterized by NH₃-TPD and ²⁷Al MAS NMR, which pointed toward gradual aluminum insertion into TPAOH-S-1 framework. A superior MTP catalyst with 960 h lifetime and 53.2% propylene selectivity was designed by combining hierarchical structure and gradual Al migration.

Keywords: MTP, Al migration, hierarchical structure.

1. Introduction

Zeolites have been widely used in the refinery and petrochemical industries that benefits from its special pore structure and intrinsic acidity. Acidity, including acid density¹, acid strength, acid distribution² and acid accessibility, is an important factor that affects catalysts activity, stability and selectivity, especially in methanol conversion reactions. Numerous work has been reported on flexible tuning acidity by in-suit synthesis, metal modification, hydro-thermal treatment or acid washing, by contrast, there has been relatively less research on Al insertion into silica-rich zeolite to adjust the acidity for catalytic property improvement. To our best knowledge, few studies have focused on in-suit Al migration for catalysts during high-temperature reaction. A superior catalysts were firstly designed by continuous aluminum migration from Al₂O₃ binder or supported aluminum compounds into all-silica MFI framework during reaction.

2. Experimental

TPAOH-S-1 was received with a clear gel (TPAOH-TEOS-H₂O), F-S-1 was synthesized with additional NH₄F. Extrusion was performed in a homemade apparatus with 40wt% pseudo-boehmite (dry mass of powder zeolites). AlCl₃/TPAOH-S-1 was received by incipient impregnation method. All of the samples were characterized by Ar adsorption, NH₃-TPD, FT-IR, ²⁷Al NMR MAS, and TEM results. Reaction temperature was 773 K, methanol WHSV was 3 h⁻¹, H₂O/CH₃OH molar ratio was 1.

3. Results and discussion

As shown in Fig. 1a, extruded F-S-1-Ex, F-S-1-Ex-HCl (with additional HCl washing) and TPAOH-S-1-Ex were all inactive for MTP reaction that was similar with powder S-1. It was interesting that TPAOH-S-1-Ex-HCl exhibited much higher initial methanol conversion of 41%, and it reached above 90% after 20 hours' reaction, then kept 99% methanol conversion for 400 hours; it showed higher propylene selectivity of 52.2%, and lower methane and ethylene selectivity of 0.4% and 4.6%, respectively, finally leading to higher P/E ratio of 11.3.

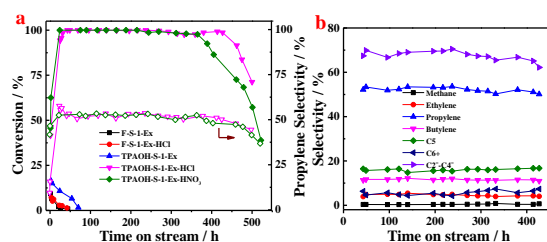


Figure 1. Catalytic performance of extruded catalysts with or without acid washing: methanol conversion and propylene selectivity (a) and product selectivity over TPAOH-S-1-Ex-HCl versus time on stream (b).

Fig. 2a showed methanol conversion for Al impregnated samples. $\text{AlCl}_3/\text{TPAOH-S-1}$ displayed higher initial conversion of 60.0%, and it increased to 100% in 8 h. Obviously decrease of methanol conversion appeared after 180 h. Fig. 2b showed acid properties of regenerated $\text{AlCl}_3/\text{TPAOH-S-1}$ samples after various reaction time. Fresh $\text{AlCl}_3/\text{TPAOH-S-1}$ (Fresh) showed only one NH_3 desorption peak at 480 K that belonged to weak acid sites. For regenerated $\text{AlCl}_3/\text{TPAOH-S-1}$ after 2 hours' reaction (Re-2h), another peak at higher temperature appeared that belonged to strong acid sites, Re-8h showed larger peak at higher temperature, both of the weak and strong acidity increased with prolonging reaction time. It could be speculated that enhanced activity was attributed to increasing strong acidity. ^{27}Al MAS NMR spectra of regenerated samples over various reaction time in Fig. 2c were used to directly demonstrate gradual Al insertion during reaction. A little sharp signal at 55 ppm appeared for Re-2h that corresponded to framework tetrahedral Al, besides, the signal representing six-coordinated Al species reduced. Largest signal at 55 ppm and smallest signal at 0 ppm were observed for Re-313h.

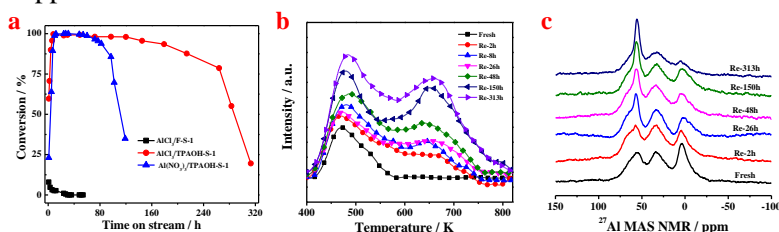


Figure 2. Methanol conversion versus time on stream (a) over Al impregnated samples. Catalytic performance; NH_3 -TPD profiles (b) and ^{27}Al MAS NMR spectra (c) of samples before or after reaction for AlCl_3 impregnated TPAOH-S-1 samples.

A superior catalyst was received by combining gradual Al migration and hierarchical structure. AT2 samples with uniform mesoporous structure was received by NaOH treatment of parent B-S-1 with additional TPAOH (TEM results in Fig. 3c,3d). Parent B-S-1, AT1 and AT2 samples were extruded, acid washed and evaluated in MTP reaction. Parent-Ex-HCl kept 100% methanol conversion for 300 h, AT1-Ex-HCl showed much higher stability of about 775 h that was attributed to enhanced diffusion rate of nano debris after NaOH treatment. Further improvement of lifetime to 960 h was received for AT2-Ex-HCl sample with mesoporous structure. To our best knowledge, it is the most stable catalyst under this harsh reaction conditions up to now, besides, it also showed higher propylene selectivity of 53.2%.

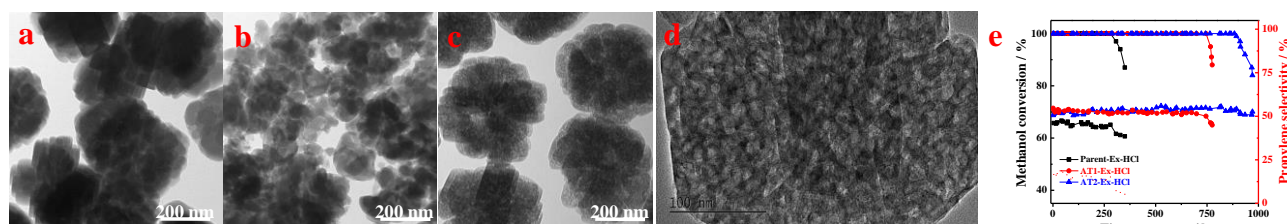


Figure 3. TEM results of B-S-1 (Parent, a), NaOH treated B-S-1 (AT1, b), and NaOH+TPAOH treated B-S-1 (AT2, c,d); and catalytic performance of extruded and acid treated B-S-1 (Parent-Ex-HCl), AT1-Ex-HCl and AT2-Ex-HCl (e).

4. Conclusions

Gradual Al insertion into zeolite framework of Al impregnated TPAOH-S-1 was demonstrated by NH_3 -TPD and ^{27}Al MAS NMR results. Shaping TPAOH-S-1-Ex with gradual Al insertion into zeolite framework during reaction showed higher lifetime of 400 h, propylene selectivity of 52.2% and P/E ratio of 11.3. Further improvement of catalytic performance was received by combining continuous Al migration and hierarchical structure, AT2-Ex-HCl showed longest lifetime of 960 h, and it also showed higher propylene selectivity of 53.2%. The present work brings a great method for designing and preparing superior catalysts by taking advantage of in-suit Al migration during reaction.

References

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