Presence of two close protons as key factor for propene oligomerization over H-ZSM-5 zeolites

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Abstract: *Two sets of H-ZSM-5 zeolites differing in the occurrence of Al pairs (AlSiSiAl in 6MRs) or distant Al atoms were employed to analyze the effect of the proton proximity on the adsorption, desorption and reaction steps of propene oligomerization. Propene adsorption and the formation of oligomeric alkoxides is faster over isolated protons, while the proton proximity results in faster olefin(s) release from H-bonded propene and oligomeric alkoxides. The rates of the propene oligomerization over close protons exceed 3 – 9 fold the rates over isolated proton. Thus, the Al atom distribution represents a new parameter in evaluating acid-catalyzed reactions over H-zeolites.*

Keywords: H-MFI, Al distribution, propene oligomerization.

1. Introduction

H-ZSM-5 zeolites represent key catalysts for acid-catalyzed reactions of hydrocarbons in oil processing, petrochemistry and fine chemicals. There is a question if, beside the Al concentration and 3D pore volume, the location and proximity of framework Al atoms and thus of attached protonic sites in H-MFI affect acid-catalyzed processes. The distribution of the Al atoms in the framework T(Si, Al$^-$) sites of ZSM-5 and high-silica zeolites is not random and not controlled by statistical rules [1]. The Al atoms in ZSM-5 with Si/Al > 12 occur in AlSiSiAl sequences (Al pairs, Al_{2Al}) in 6MRs and as far distant single Al atoms (Al_{1Al}) located in different rings (Figure 1); AlSiAl arrangements are not present [1]. We developed synthesis methods providing H-ZSM-5 with predominant population either of Al_{2Al} or Al_{1Al} [2]. This progress enabled investigation of the contribution of close H$^+$ (adjacent to AlSiSiAl) and far distant protons to the acid-catalyzed transformations of hydrocarbons, specifically here to individual steps of the process of oligomerization of propene, in "a nanoscale reactor" of a void volume of the channel intersection.

2. Experimental

Two series of H-ZSM-5 with Si/Al molar ration 13-30 containing 80 - 90 % of Al atoms located in 6 MRs as Al pairs (H-ZSM-5_{2Al}) or single Al atoms (H-ZSM-5_{1Al}) (Figure 1) were prepared by hydrothermal synthesis [2]. The arrangement of Al atoms in ZSM-5 framework was controlled by tuning the synthesis conditions by using appropriate Si and Al sources, Na$^+$ ions and accompanying anions, and order of addition of particular substrates. Presence and concentration of 2Al or 1Al sequences in H-ZSM-5 was analyzed using Vis analysis of Co exchange ZSM-5 and ^{27}Al 3Q MAS NMR 11.7 T spectrometer. Propene oligomerization over H-ZSM-5 (22 % C_3H_6 in He, 3 $mol_{C3}mol_{Al}^{-1}\ min^{-1}$) was carried out from 473 to 533 K. The development of reaction intermediates and oligomers desorption was followed by the time-resolved fast "in situ" FTIR spectroscopy using a Nicolet 6700 spectrometer.

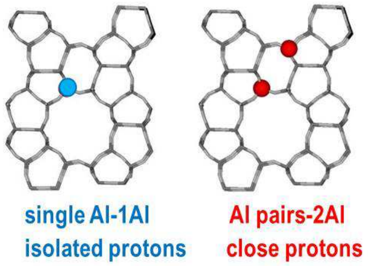

Figure 1. Schematic siting of Al atoms in H-ZSM-5 framework [1,2].

3. Results and discussion

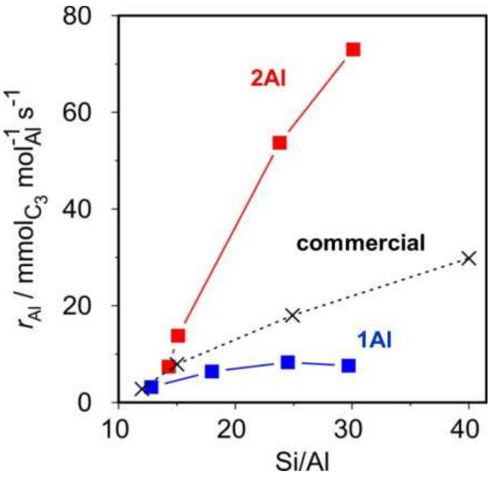

Figure 2. Reaction rate of C_3H_6 oligomerization over H-ZSM-5_{2Al}, H-ZSM-5_{1Al}, and commercial samples depending on the Si/Al ratio [2].

The concentrations of Al in Al_{2Al} in 6MRs was determined by the well-proven methodology [1, 3] using the $[Co(II)(H_2O)_6]^{2+}$ ion-exchange capacity of Na-ZSM-5 and the sum of concentrations of bare Co(II) ions coordinated in the α-, β- and γ-type framework rings in the dehydrated Co(II)-MFI obtained from their characteristic d-d transitions reflected in the UV-Vis spectra. The concentrations of the individual Co(II) ions correspond to half of those of Al atoms in Al_{2Al} in the respective rings. The concentration of Al_{1Al} atoms was calculated from the total Al atoms balance: $Al_{total} = Al_{2Al} + Al_{1Al}$. Al pairs were predominantly (60 – 80 %) located in β-6MRs at the channel intersections, less populated in Al pairs were located at the wall of the straight channels or in sinusoidal channels. H-ZSM-5 of prevailing Al_{1Al} also exhibited Al atoms mostly (55 – 90 %) at the channel intersections as obtained by the ^{27}Al MAS NMR study in [2]. Conversions of propene (at constant space time 3 mol$_{C3}$mol$_{Al}^{-1}$ min^{-1}) to C_4 – C_9 olefins (not aromatics) were much higher over H-ZSM-5_{2Al} than over H-ZSM-5_{1Al}. The selectivity to olefins and approx. equimolar formation of C_4 and C_5 olefins indicated oligomerization steps through C_6 to C_9 olefins, C_9 cracking, and the reaction of propene with C_4 to C_7 and C_5 to C_8 olefins. The rates of propene oligomerization over H-ZSM-5_{2Al} catalysts were 3 – 8 times higher than those over H-ZSM-5_{1Al}, and 2 – 5 times higher compared to those over commercial samples of comparable Al contents (Figure 2). While the rate of the overall oligomerization process was higher over H-ZSM-5_{2Al} compared to H-ZSM-5_{1Al}, the intrinsic rate of propene protonation and oligomerization over close protons was lower. Thus, the observed dramatic changes in the rate of propene oligomerization over close protons compared to single ones can be explain by combining the functionality of proton pairs and single protons in the intrinsic protonation/oligomerization activity and desorption/transport of oligomeric products. FTIR study of the interaction of propene with H-ZSM-5_{2Al} and H-ZSM-5_{1Al} at RT showed that the initial development of π-bonded propene (1632 and 1454 cm^{-1}) and mono-/oligomeric-carbocations (CH_2/CH_3 at 2936, 2859/2954 cm^{-1}) were at least of two orders faster over both types of samples compared to oligomers desorption. The formation of oligomeric carbocations was faster over H-ZSM-5_{1Al}, but the product desorption was faster over H-ZSM-5_{2Al}. This observation shows the lower stabilization energy of carbocations on close protons (H-ZSM-5_{2Al}) due to the charge repulsive forces. This also implies an easier desorption of oligomers from H-ZSM-5_{2Al} with close protons, which is reflected in catalytic performance of H-ZSM-5.

4. Conclusions

The defined proximity of Al atoms and thus of protons as the parameter significantly affecting intrinsic rate of olefin oligomerization and oligomers desorption. We found evidence that the rate of the overall oligomerization over H-ZSM-5_{2Al} greatly (3 – 8 times in TOF per Al(H^+)) exceeds H-ZSM-5_{1Al} under conditions when the rate determining step is oligomers desorption and activated transport from the pores. Employing H-ZSM-5 tailored to have a predominance of Al pairs in the framework (and thus of close protons) the rate of propene oligomerization per Al(H^+) is 2 – 5 times higher compared to commercial H-ZSM-5 samples.

References

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