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Effects of zeolite structure and aluminum content on thiophene adsorption, desorption, and surface reactions

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Abstract

The adsorption and desorption of thiophene and the reactions of thiophene-derived adsorbed species in He, H_2, and O_2 were examined on H-ZSM5, H-Beta, and H-Y with varying Si/Al ratios. Thiophene adsorption uptakes (per Al) were independent of Al content, but were above unity and influenced by zeolite structure (1.7, 2.2, and 2.9 on H-ZSM5, H-Beta, and H-Y). These data indicate that thiophene oligomers form during adsorption and that their size depends on spatial constraints within zeolite channels. Adsorption and oligomerization occur on Brønsted acid sites at 363 K. Thiophene/toluene adsorption from their mixtures show significant thiophene selectivity ratios (10.3, 7.9, and 6.4, for H-ZSM5, H-Beta, and H-Y zeolites), which exceed those expected from van der Waals interactions and reflect specific interactions with Brønsted acid sites and formation of toluene–thiophene reaction products. Treatment of thiophene-derived adsorbed species above 363 K in He or H_2 led to depolymerization of thiophene oligomers and to the formation of unsaturated adsorbed species with a 1:1 thiophene/Al stoichiometry on all zeolites and at all Si/Al ratios. These unsaturated species desorb as stable molecules, such as H_2S, hydrocarbons, and larger organosulfur compounds, formed via ring opening and hydrogen transfer from H_2 or co-adsorbed species, and also form stranded unsaturated organic deposits. Smaller channels and higher Al contents preferentially formed H_2S, benzotiophenes, and arene products during treatment in He or H_2, as a result of diffusion-enhanced of secondary reactions of desorbed thiophene molecules with adsorbed thiophene-derived species. Only oxidative regeneration treatments led to full recovery of thiophene uptake capacities. A preceding treatment in H_2, however, led to the partial recovery of thiophene-derived carbon atoms as useful hydrocarbons and decreased the amount of CO_2 and SO_2 formed during subsequent oxidative treatments required for regeneration.

Keywords: Thiophene; Zeolites; Adsorption; Desorption; Oligomerization; Regeneration

1. Introduction

Organosulfur compounds in fuels cause toxic emissions and inefficient performance of exhaust catalysts [1–3]; thus, processes for their removal have been widely explored [4–20]. Selective adsorption [21–31] can be carried out at low temperatures; they avoid saturation of alkenes and arenes, which prevail during hydrodesulfurization catalysis, but available materials show limited adsorption capacities and selectivities. Thiophene, benzothiophene, and their alkyl derivatives are the most abundant organosulfur compounds in gasoline; more reactive sulfides, disulfides, and mercaptans are present as minor components. Thiophene represents a particular challenge, because it resembles abundant arenes and alkenes in electron density and basicity, thus making chemical specificity difficult during adsorption and catalysis. The crystalline framework structure, high specific area, and structural and compositional flexibility make zeolites potential candidates for thiophene adsorption [32]. Thiophene adsorbs on H-ZSM5 [28] with modest selectivity relative to benzene; samples with high Al-content showed high adsorption capacities for thiophene and alkyl-thiophenes, indicating specific interactions with Al sites and possible acid-catalysed alkylation reactions with alkenes or other components to form larger organosulfur compounds [31]. Y-zeolites exchanged with Cu or Ag cations selectively adsorb thiophene from benzene via specific π-interactions [25,33,34].

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We recently reported a detailed study of thiophene adsorption and reactions on H-ZSM5, including reactions of thiophene-derived adsorbed species O_2, He, H_2, and C_3H_8 [35]. Acid sites were partially restored with H_2 or C_3H_8 treatments to recover most thiophene-derived carbons as useful hydrocarbons.

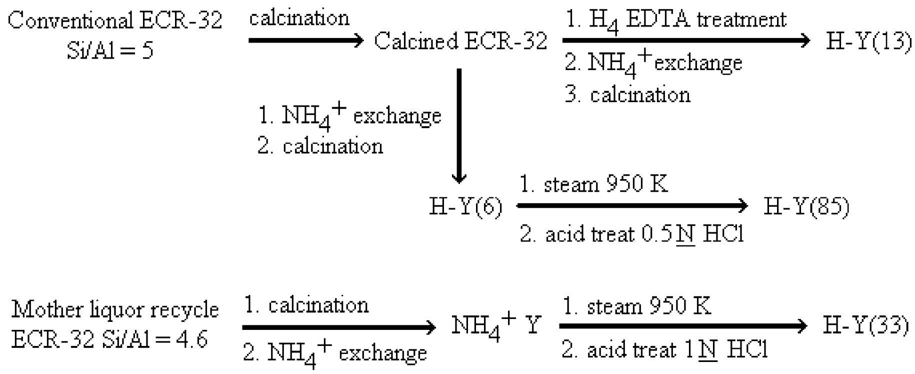
The structure and Al content of zeolites influence both adsorption capacity and regeneration pathways during thiophene adsorption processes [36–41]. Here, we examine the effects of zeolite channel size and crystal structure on the adsorption and subsequent reactions of thiophene using MFI, BEA, and FAU zeolites with similar Al content (Si/Al = 13); we also probe the effects of Al content in FAU structures (Si/Al = 6, 13, 33, and 85). Finally, we report thiophene adsorption stoichiometries on MFI, BEA, and FAU zeolites during adsorption, which are consistent with reversible oligomerization reactions during adsorption and thermal treatment, and the rates and selectivities in reactions of adsorbed thiophene-derived species during thermal treatments in He and H_2 streams.

2. Experimental methods

2.1. Zeolite-based adsorbents

Faujasite zeolites with three-dimensional 12-ring channels were used in their acid form. H-Y samples [H-Y(6) (Si/Al = 6, MC-5879), H-Y(13) (Si/Al = 13, MC-5876), H-Y(33) (Si/Al = 33, MC-5877), and H-Y(85) (Si/Al = 85, MC-58798)] were prepared by dealumination of high-silica ECR-32 with H_4EDTA and by sequential steaming and acid treatments using previously reported methods [42,43]. ECR was first prepared from a starting gel of composition, 9.6 TPAOH:1.6 Na_2O:Al_2O_3:24 SiO_2:350 H_2O:0.72 Na_2SO_4, where tetrapropylammonium hydroxide (TPAOH) and 10% of the alumina came from a seed solution with a SiO_2:Al_2O_3 ratio of 17.5. The recovered solids had a Si/Al atomic ratio of 5.1 and were calcined in dry air for 3 h at 873 K to remove organic template. One portion (100 g) was placed in refluxing H_2O (1500 g) for 20 h within a Soxhlet extractor, while slowly adding H_4EDTA (30.3 g) [43]. The product was recovered by filtration and washed with distilled H_2O. This dealuminated sample was converted to its proton form by four sequential 1 h exchanges with 10% NH_4Br solutions at 333 K. After the second and third exchanges, samples were treated in dry air at 623 K for 3 h. This sample gave a Si/Al ratio of 13 (by ICP-AES) and is denoted as H-Y(13). A second portion of the calcined ECR-32 was converted to its proton form by the procedure described above. After the second and third exchanges, samples were treated in dry air at 573 K for 3 h, a procedure that led to a Si/Al ratio of 6; this sample is denoted as H-Y(6). One portion of this second sample was then treated (175 g) with water vapor at 1 bar and 950 K for 5 h and then contacted with 0.5N HCl (2.63 L) under reflux for 3 h. The product was recovered by filtration and washed with distilled H_2O to give a sample with a Si/Al ratio of 85 [H-Y(85)].

A sample similar to H-Y(85) was prepared using a material prepared from a mother liquor recycle synthesis of ECR-32 as the starting material [44]. After treatment in dry air at 573 K for 3 h, this sample was exchanged with NH_4^+ and steamed by the same procedure as H-Y(85). The sample (10 g) was then treated in 150 cm^3 1.0N HCl under reflux for 4.5 h. The product was recovered by filtration and washed with distilled H_2O to give a Si/Al ratio of 33 [H-Y(33)]. A schematic description of the synthesis protocols is presented below.



Two H-Beta samples [H-Beta(13) (Si/Al = 13, CP814E) and H-Beta(38) (Si/Al = 38, CP811E)] were obtained from Zeolyst Corp. in NH_4^+ and H^+ forms, respectively. H-ZSM5(13) (Si/Al = 13, Lot 97EB-6197) was obtained from AlSi-Penta Corp. in NH_4^+ form. H-ZSM(40) (Si/Al = 40, CBV-5014) was obtained from Zeolyst Corp. in H^+ form. NH_4^+ zeolites were converted into their respective H^+ form by treatment in flowing dry air at 773 K for 3 h (Airgas, C.P. $> 99.9\%$, 1.7 $cm^3\ s^{-1}$). Chemical compositions, crystallite sizes, and pore volumes for H-Beta and H-ZSM5 zeolites are shown in Table 1; these data were provided by Zeolyst Corp. and AlSi-Penta Corp., respectively. Pore volumes of H-Y zeolites were measured from *n*-hexane