

Supporting Information

Toluene Methylation by Methyl Mercaptan and Methanol over Zeolites – A Comparative Study

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Catalyst

NH₄-ZSM5-15 (CBV 3024E) was purchased by Zeolyst International. Prior to reaction, the catalysts were calcined in reactor at 550 °C for 8 h, and thus NH₄-ZSM5-15 was transformed into HZSM5-15 catalyst.

Catalyst characterisation

N₂ isotherms used to determine the apparent surface area (BET approach) were obtained by N₂ sorption. The experiments were conducted at - 196 °C using a Micromeritics ASAP 2010 sorptometer. Before experiments, the samples were desorbed under vacuum at 300 °C for 8 h.

The number of acid sites was evaluated by temperature programmed desorption (TPD) of ammonia using a Micromeritics AUTOCHEM 2910 apparatus. The sample (around 0.1 g) was first heated at 600 °C in air flow for 6 h. Then it was saturated with NH₃ by flowing a 5% (v) NH₃/He mixture at 100 °C during 30 min. After that, the sample was purged for 2 h in a He flow to eliminate loosely bonded NH₃. Finally it was heated at a constant temperature ramp-up of 10 K min⁻¹ up between 175 and 600 °C in He flow (30 ml min⁻¹). The NH₃ concentration evolving from the sample during the last heating step was continuously measured by a thermal conductivity detector (TCD).

Catalytic activity measurements

The reaction between toluene and CH₃SH (or CH₃OH) has been carried out in a fixed bed flow microreactor (i.d. = 4 mm) with 100 mg of HZSM-5 catalyst (grain size of 150-250 µm), in a continuous nitrogen flow (30 mLmin⁻¹) and atmospheric pressure. Each catalytic test (duration of 4h) has been performed at a constant temperature (250, 350, 450 or 550 °C) with a fresh catalyst sample using a T/CH₃SH(CH₃OH) molar ratio of 1/1. The toluene weight hourly space velocity (WHSV) was 4 h⁻¹. Catalyst performance was measured at 120 min after feeding of the reactants started. The products were analyzed online by gas chromatography (Shimadzu, GC 2014) using an auto-sampling valve. The GC was connected to a dual detector device, flame ionization detector (FID) and flame photometric detector (FPD). Calibration curves were obtained using pure compounds or mixture with known concentrations.

Table S1. Composition of the aromatic fraction

Reagents	T (°C)	Aromatics (mol%) ^a			
		T	B	X	TMB
T + CH ₃ SH	250	98.0	0	1.8	0.2
	350	79.0	1.2	14.9	4.9
	450	31.5	1.2	55.3	12.0
	550	52.6	13.1	32.2	2.1
T + CH ₃ OH	250	89.5	0	9.2	1.3
	350	56.9	2.1	37.5	3.5
	450	55.9	4.6	34.6	3.9
	550	49.5	14.9	31.1	4.5

^a T = toluene, B = benzene, X = xylene, TMB = tri-methylbenzenes

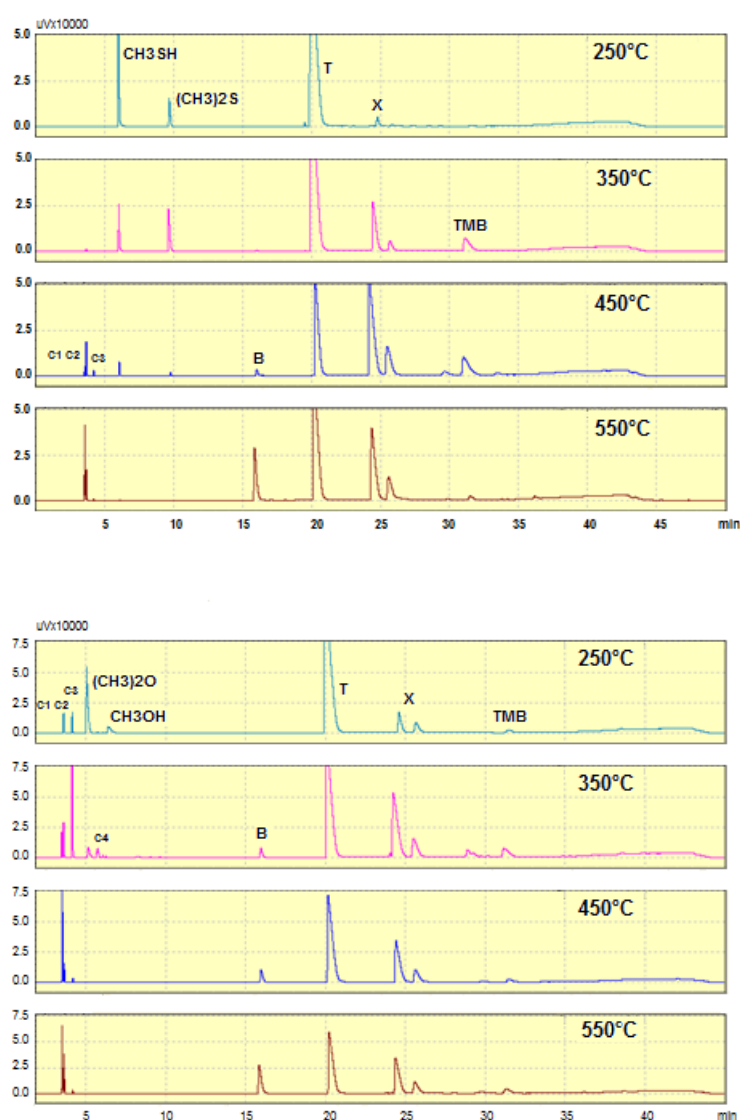


Figure S1. GC-FID chromatograms for the reaction T + CH₃SH (up) and T + CH₃OH (bottom) at various temperatures, after 120 min on stream. Reaction conditions: weight of catalyst = 100 mg; nitrogen flow = 30 mLmin⁻¹; WHSV (toluene) = 4 h⁻¹.

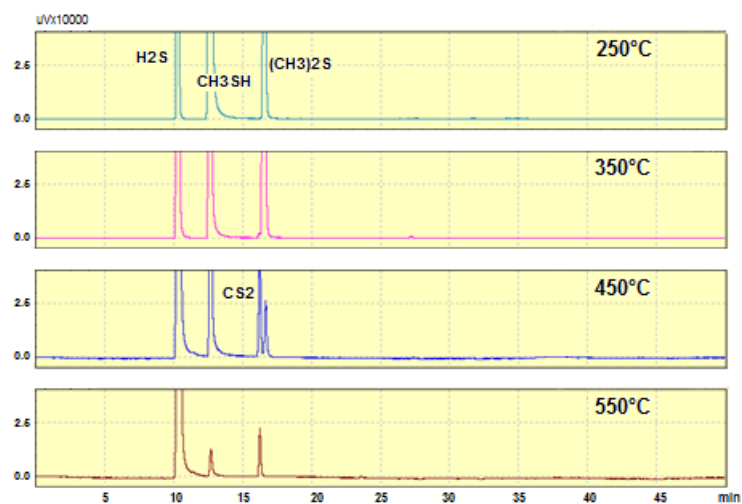


Figure S2. GC-FPD chromatograms for the reaction T + CH₃SH at various temperatures, after 120 min on stream. Reaction conditions: weight of catalyst = 100 mg; nitrogen flow = 30 mLmin⁻¹; WHSV (toluene) = 4 h⁻¹