Removal of Thiophene Impurities from Benzene by Selective Adsorption in Zeolite ZSM-5

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Thiophene impurities can be removed from benzene by selective adsorption in zeolite ZSM-5 either in the gaseous or in the liquid phase; the adsorbed thiophene can be almost completely recovered by conventional desorption techniques.

One major source of benzene is high-temperature coal pyrolysis.[1] The benzene produced in this process contains impurities, especially thiophene, which must be removed for most technical applications. Currently, two industrial purification processes are in use for this purpose,[1] *viz.* sulphuric acid treatment and catalytic hydrotreating. One feature that both processes have in common is that thiophene is chemically converted and, hence, lost. As an alternative, one could envisage removal of thiophene by selective adsorption. Indeed, Cu^{2+}-exchanged Y-type zeolites have been shown to act as selective adsorbents for this application.[2] Again, however, thiophene cannot be recovered because it is too strongly held and/or chemically converted by CuY. The only way to regenerate the zeolite is to burn off the adsorbate which, inevitably, brings about an undesired emission of SO_x. We have now discovered that various forms of zeolite ZSM-5 act as selective adsorbents for the removal of thiophene impurities from benzene. Compared to CuY, they offer the advantage that the adsorbed thiophene can be recovered as such, *e.g.* by thermal desorption.

Most of the adsorption experiments were conducted in a flow-type apparatus with a fixed bed adsorber. In a multicomponent saturator,[3] the carrier gas (nitrogen) was simultaneously loaded with vapours of benzene (p_{Bz} = 23.3 kPa) and thiophene (p_{Th} = 0.18 kPa). The adsorber effluent was analysed periodically (typically every 4 min, which is short compared to the breakthrough time of thiophene) by on-line capillary gas chromatography (Carbowax 20 M column, stationary phase: polyethylene glycol, length 50 m, held isothermally at 65 °C). This way, the breakthrough curves for benzene and thiophene were obtained. Samples of zeolite ZSM-5 with different Si/Al ratios were synthesized, calcined at 540 °C in air and used as adsorbents without further ion exchange in the mixed H–Na forms. To explore whether

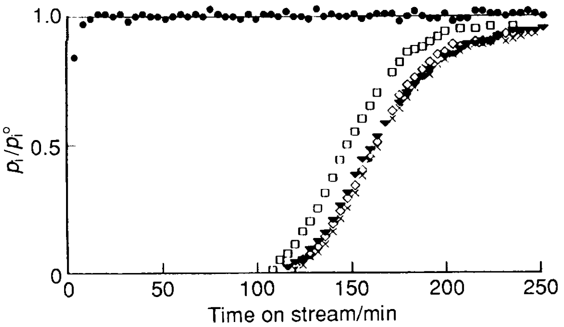

Fig. 1 Breakthrough curves for benzene and thiophene in the gas-phase adsorption on H, Na-ZSM-5 (n_{Si}/n_{Al} = 20). Temperature: 50 °C, mass of dry adsorbent: 3 g, flow of carrier gas: 32 cm^3. ● Benzene; × thiophene (1st cycle); ▼ thiophene (2nd cycle); □ thiophene (3rd cycle); ◇ thiophene (4th cycle).

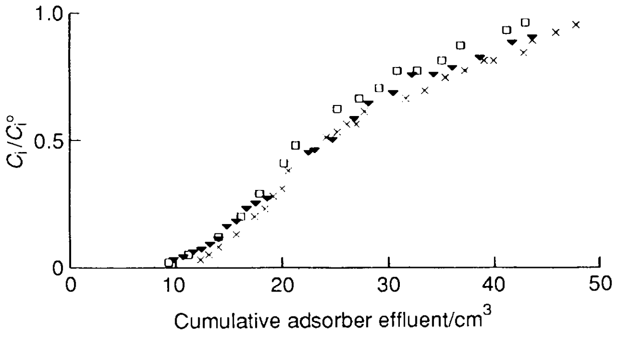

Fig. 2 Breakthrough curves for the liquid-phase adsorption of coke-oven benzene on silicalite **I**. Adsorption temperature: 25 °C, mass of dry adsorbent: 6 g, flow of feed mixture: 7.5 cm^3 h^{-1}; × 1st cycle; ▼ 2nd cycle; □ 3rd cycle.

thiophene can be removed in the liquid phase as well, either a mixture of 0.5 wt.% thiophene and 99.5 wt.% benzene or a real coke-oven benzene was pumped through a column filled with the adsorbent. Desorption experiments were performed by flushing the adsorbent with nitrogen while slowly increasing the temperature from 50 to 350 °C within two to three hours and keeping the final temperature for an additional three hours. The desorbing components were collected in a cold trap and analysed by gas chromatography.

Typical results obtained in four successive adsorption/desorption cycles are presented in Fig. 1. Since the breakthrough curves for benzene do not differ from cycle to cycle, only one curve is plotted for the sake of clarity. Almost immediately after the beginning of an experiment, benzene reaches its initial partial pressure, whereas thiophene is completely retained by the zeolite for more than 100 min. After this time, the partial pressure of thiophene at the adsorber outlet slowly increases until it approaches the value at the adsorber inlet ($p_{Th}/p_{Th}^{\circ} = 1$). Integration of the breakthrough curves yields final thiophene loadings (mass of thiophene adsorbed per mass of dry zeolite) of 15 to 17 mg per g. Approximately 80 to 90% of the adsorbed thiophene can be recovered by thermal desorption in a purge of nitrogen. The remaining portion, however, leads to a slow diminution of the adsorption capacity (*cf.* Fig. 1, third adsorption cycle). The initial capacity can be restored by purging the heated adsorbent in an oxidizing atmosphere. In the present series of experiments (Fig. 1), this was done between the third and the fourth adsorption cycle.

The potential of a variety of other zeolites with different pore widths and pore geometries for the thiophene/benzene separation was subsequently investigated. However, zeolites, such as, ZSM-12, ZSM-22, ZSM-23, ZSM-35, ZSM-48, EU-1 or Beta proved to be almost unselective. It was only with zeolite ZSM-11, which is structurally related to ZSM-5 (both belong to the pentasil family) that comparable adsorption selectivities were observed. This suggests that structural features of the zeolitic channel system play an important role in this separation.

So far, the best results were achieved with silicalite **I**. Its adsorption capacity for thiophene amounted to 22 mg g^{-1}, of which more than 90% could be recovered in the desorption step. In principle, the same promising results were obtained in the liquid phase with a real coke-oven benzene as feed (*cf.* Fig. 2). The only difference was that the concentration of thiophene in the adsorber effluent increased more slowly than in the gas-phase experiments. This could be due, at least in part, to the somewhat lower adsorption temperature (25 instead of 50 °C) in the liquid-phase experiments.

As a whole, the removal of thiophene impurities from benzene by selective adsorption in zeolite ZSM-5 or silicalite **I** appears to be a promising alternative to the conventional purification processes. Further work is underway in our laboratory to elucidate the reasons for the excellent separation selectivities observed in the thiophene/benzene adsorption on pentasil-type zeolites.

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