Harnessing Pore Architecture and Functional Design in Metal-Organic Frameworks for High-efficiency Ammonia Separation

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Alumina-based metal–organic frameworks (Al-MOFs) were applied to ammonia (NH_3) synthesis for adsorptive separation of 1–5% NH_3 at 25–100 °C and 1 bar, potentially improving energy efficiency and reducing capital costs by simplifying downstream processing. Monte Carlo simulations and temperature-programmed analyses revealed that pore-surface functional groups and pore geometry play critical roles in NH_3 adsorption, beyond the conventional emphasis on surface area. Among the studied materials, CAU-10-OH showed high NH_3 uptake (3.6–1.8 mmol g_{-1} at 25–100 °C) and stable performance over 15 adsorption–desorption cycles (~180 h). Its adsorption capacity was comparable to that of microporous ZSM-5 zeolites and significantly higher than those of silica and activated carbon. The moderate NH_3 adsorption heat (~60 kJ mol^{-1}), associated with hydroxyl groups in cage-like pores (2.41 Å), enabled efficient low-concentration NH_3 separation under ambient conditions. Integration of CAU-10-OH downstream of Ru-catalyzed mild NH_3 synthesis demonstrated rapid NH_3 capture, highlighting its potential for practical synthesis–separation processes under mild conditions.

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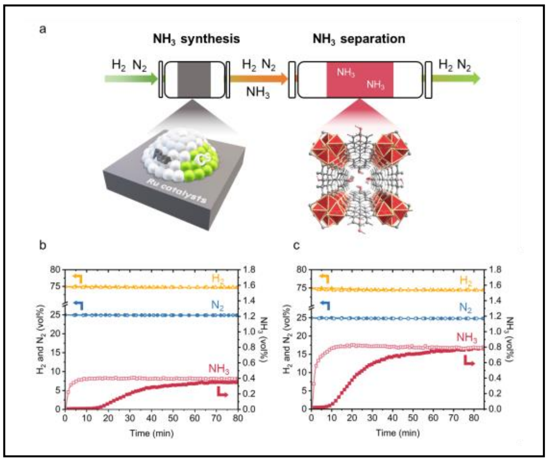

Figure 1. (a) Schematic of the integration of unit (ii) CAU-10-OH as an NH_3 adsorbent, with unit (i) mild NH_3 synthesis using (b) Cs-Ru/Al_2O_3, operated at 400 °C and 1 bar, and (c) Cs-Ru/SGCNT, operated at 350 °C and 1 bar, in comparison to systems without a CAU-10-OH adsorbent presented in empty symbols. A gas mixture containing H_2 and N_2 in a molar ratio of 3:1 (GHSV = 7344 h^{-1}) was supplied for NH_3 synthesis using a catalyst weight of 0.1 g. The product gas mixture containing H_2, N_2, and NH_3 was separated using 0.1 g of CAU-10-OH at 25 °C.