

Novel nanoporous superacids with ordered porous structure for fine chemical synthesis

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Nanoporous silica materials have received considerable attention in recent years owing to their astounding properties such as high specific surface areas and large specific pore volumes. However, these materials have several disadvantages, including neutral amorphous framework, poor water stability, and weak acidity, which limit their applications, especially in catalysis and adsorption. These problems can be overcome by introducing hetero-atoms into the silica framework of these nanoporous silica materials. However, it is very difficult to incorporate the metal atoms in the silica framework because the preparation of these materials requires a highly acidic medium where the solubility of the metal source is very high and a large quantity of toxic acids such as HCl or HF is required to introduce the acidic medium as it controls the self-assembly process and the rate of condensation of the silica precursors. These requirements make the existing methodology highly toxic, corrosive, expensive, and environmentally unfriendly. Here we introduce a novel superacid assisted self-assembly process wherein non-ionic polymeric surfactants are used as templates together with the inorganic precursors and a small amount of super acids (SAs) such as amidosulfamic acid or triflic acid for the preparation of nanoporous metallosilicates (NSA). Interestingly, the prepared materials exhibit super-acidic property, well-ordered structure with excellent textural parameters including high specific surface area, and large pore volume, and high stability. The formation of highly ordered structure with a high acidity is mainly due to the fact that the addition SAs increase the rate of condensation of the inorganic precursors and assist the self-assembly of organic structure directing agent to obtain well-ordered mesostructure. In addition, SAs facilitate a high content of di or trivalent metal incorporation in the silica framework which is critical to obtain high acidity and further bonds strongly within the wall structure that ultimately introduces super-acidity to the NSA materials. This novel concept of superacid assisted strategy has never been previously attempted and NSA materials fabricated using this approach exhibit not only the super-acidic functionalities but also excellent morphology. The nitrogen adsorption results revealed that the samples exhibit a large pore diameter (13.4 nm) and pore volume (1.54 cm³/g). The acidity of the NSA materials was found to be 20 times higher than that of nanoporous aluminosilicates prepared via HCl assisted routes. The acidity of NSA materials can be tuned from 1.5 to 6.1 mmol of ammonia per gram (Fig. 1 inset) by increasing the amount of SAs and the metal precursor added to the synthesis mixture. Finally, NSA materials are used as catalysts for the production of jasminaldehyde (α -pentyl cinnamaldehyde), a natural fragrance chemical, through aldol condensation of 1-heptanal with benzaldehyde in liquid phase. NSA materials showed excellent catalytic activity with 90% 1-heptanal conversion and 100% selectivity towards jasminaldehyde. The super-acidic functionality of NSA catalyst makes them highly active even at reaction temperatures as low as 40°C.

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