Direct synthesis amine-functionalized mesoporous silica for CO$_2$ adsorption

Zhihui Hu, Donghui Zhang, Li Zhou
School of chemical engineering and technology, Tianjin University

Abstract
Carbon dioxide is a key global warming gas and its capture and sequesteration is an important issue that has drawn global attention. Especially when Kyoto Protocol take effect, it has became a global issue of common concern.

There are many technologies for CO$_2$ capture, included absorption, adsorption, membranes and so on$^{[1-2]}$. In the industry, it has been always used organic ammonia solution to absorb CO$_2$, but organic ammonia solution brings serious corrosion and is difficult to regenerate, entailing high costs$^{[3]}$. In order to decrease the cost for separating CO$_2$ and N$_2$, researchers look for some solid sorbents without corrosion, some common solid sorbents were used, for example: zeolite$^{[5]}$, carbon$^{[4]}$, silica gel$^{[6]}$ and so on. Although some of them have big adsorption capacity of CO$_2$, the adsorption selectivity of CO$_2$ and N$_2$ is small.

Since periodic mesoporous silicas discovered by Mobil researchers in 1992$^{[7]}$, various methods for synthesizing mesoporous silica were invented, such as FUD silica$^{[8]}$, AMS silica$^{[9]}$ and so on. Owning to mesoporous silicas have ordinal structure, uniform meso-sized channels, researchers find that amine-functionalized mesoporous silica was used to adsorb CO$_2$, which has big adsorption selectivity of CO$_2$ and N$_2$. Two methods were used to synthesize amine-functionalized mesoporous silica, impregnating and post-synthetic graft. For example, Diethanolamine was used to impregnate into MCM-41$^{[10-11]}$, Tetraethylenepentamine was used to impregnate into SBA-15, but the amine function is easy to escape from the silica; γ-Aminopropyltriethoxysilane(APTES) and [N-(2-aminoethyl)-3-aminopropyl]trimethoxysilane are used to graft on the SBA-15$^{[12-13]}$. Amine-grafted SBA-15 has big adsorption selectivity of CO$_2$ and N$_2$. But most of reactions between SBA-15 and organic silane occurred in the region of hole edge by grafting amine on the mesoporous silica, and within the deep hole there are little amine groups, which lead to low adsorption capacity of CO$_2$ for the mesoporous silica. In order to increase the quantity of amine on the silica and enhance its adsorption capacity of CO$_2$, we synthesize amine-functionalized mesoporous silica via the SN$^+$ – I$^-$ mechanism, as described in Scheme 1. In this case, with Isobutyric Acid as a structure-directing agent (SDA), APTES functions as a co-structure directing agent (CSDA), the force for forming the silicamicelle by direct electrostatic interaction between the positively charged amino groups in APTES and the negatively charged head groups in the isobutyric acid. The surfactant in the as-synthesized mesoporous silica (AMS) were removed by using monoethanolamine and ethanol.
Scheme 1. Synthesis principles of amine-functionalized mesoporous silica

Chuang et al\textsuperscript{[21]} utilize APTES synthesis amine-functionalized SBA-15 by post-synthetic, the CO\textsubscript{2} capacity of it is about 0.4 mmol/g, but we use APTES to direct synthesize AMS, that adsorption capacity of CO\textsubscript{2} is about 0.64 mmol/g.

References