

Purely Lewis Acidic Aluminosilicates with well-defined single sites

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ABSTRACT

While homogeneous catalysts are generally better understood than heterogeneous analogues, the latter are frequently preferred in large scale chemical industries due to ease of separation and recovery.¹ Despite this preference, a long standing challenge in heterogeneous catalysis has been the precise identification of the active sites responsible for catalysis. This challenge is exacerbated by the fact that traditional methods of creating surface active sites often lead to the formation of a number of similar sites, some of which show reduced activity or selectivity for the desired reaction. In this context, the advantages of well defined, single site catalysts are obvious.² Therefore there is an increased interest in the targeted synthesis of single site catalysts.³

The building block approach to creating solid matrices with arrays of identical active sites involves building the support structure out from around each site.^{4,5} Such strategies generally require three components. First, a molecule that is or can become the active site in the matrix is needed. Second, a molecule that is the precursor to the support matrix around the active site, and finally a coupling reaction that links the various components of the matrix together are required.

Herein we present a general building block synthetic strategy for targeting specific types of sites active in catalysis within a silicate matrix. In this contribution we focus on the preparation of atomically dispersed, well-defined, and purely Lewis acidic aluminum sites in silicate matrices. These amorphous matrices are composed of the sphaerosilicate cube (Si_8O_{20}) linked together by combinations of aluminum and siloxane groups. The use of rigid Si_8O_{20} units as building blocks to construct the support has several advantages - active sites in the matrix are easily isolated from one another and additionally, void volumes are developed within the growing network (i.e. porosity). Non-aqueous sol-gel reactions between the silicate cube and aluminum chloride precursor complexes are used to develop the support matrix around the Al active sites. The connectivity of the catalytically active aluminum centers to the surrounding silicate matrix can be varied by choice of aluminum precursor (Fig. 1). 3-connected Al $\leftarrow$ Py and Al $\leftarrow$ THF sites are obtained from the corresponding $\text{AlCl}_3\cdot\text{L}$ complexes and 4-connected sites are obtained from $\text{X}[\text{AlCl}_4]$ ($\text{X} = \text{Lutidinium}^+, \text{Bu}_4\text{N}^+$). The aluminum sites in these porous silicates are characterized by thermogravimetry (i.e. number of Cl atoms eliminated from Al site), IR and multinuclear SSNMR spectroscopies (Fig. 2), and by simple ligand exchange reactions (i.e. pyridine adsorption). The strength and quantity of acid sites is studied by TPD of ammonia.

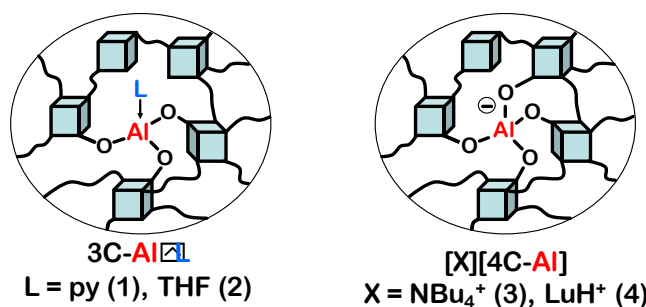


Fig. 1 3-connected and 4-connected aluminum(III) sites in the xerogels.

Their catalytic activities as Lewis acids are investigated for the aminolysis of styrene oxide by aniline. These single site aluminosilicate catalysts exhibit activities that are comparable to or better than analogous, well-known zeolite and amorphous aluminosilicate materials (e.g. β -zeolite, commercial silica-alumina). Their activities can actually be tuned by varying the preparation parameters so that the connectivity of aluminum to the surrounding silicate matrix as well as the length and flexibility of secondary linkers in the matrix can be modified. We believe that these novel aluminosilicate catalysts, containing targeted, well-defined aluminum sites, will play an important role in elucidating the roles of the active sites (Brønsted vs. Lewis) in many reactions of industrial importance such as olefin cracking,⁷ ethanol dehydration,⁸ etc.

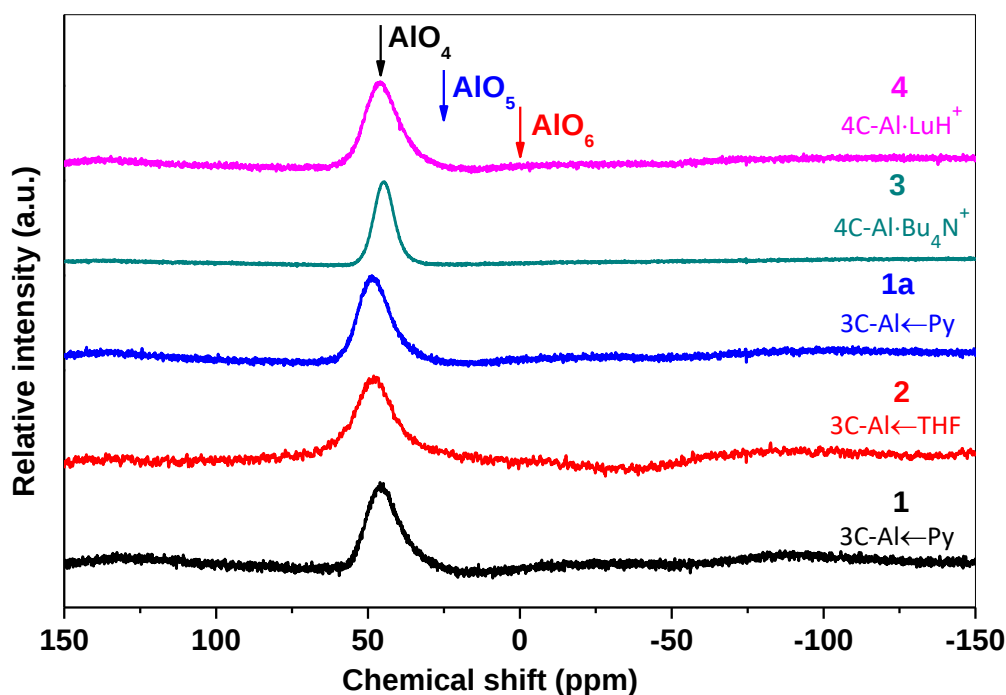


Fig. 2: ^{27}Al MAS NMR spectra. All samples contain Al in tetrahedral coordination only.

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