

# ENVIRONMENTAL CATALYSIS

A research team is synthesizing structured materials for use in heterogeneous catalysis.

**Principal Investigator:** Harold Kung

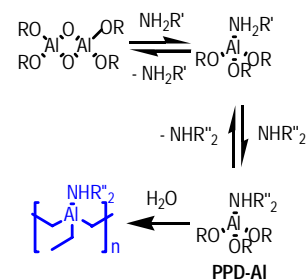
**Collaborator:** Mayfair Kung

**Objective:** Aluminum chloride and aluminum alkoxides are common Lewis acids that are used as catalysts and cocatalysts in a liquid or supported liquid phase to catalyze various chemical reactions including Friedel-Craft, dehydration of alcohol, aminolysis, and polymerization. A solid alumina ( $\text{Al}_2\text{O}_3$ ) catalyst is a more environmentally friendly alternative to the soluble aluminum compounds because of the ease of its separation from the reaction mixture for further reuse. Ordinarily, Lewis acidity of alumina, which is required for catalysis, is generated by dehydroxylation (calcination) of surface-bound hydroxyl groups to create coordinatively unsaturated aluminum ions. The Kung group has developed a new method of preparation of alumina, which produces a much higher concentration of active Lewis acid sites – and hence higher catalysis rates – than conventional alumina without calcination.

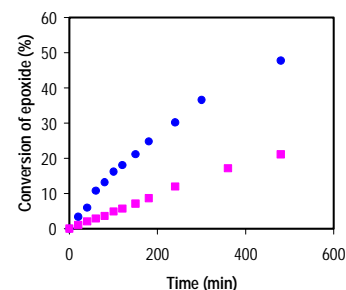
**Approach:** Throughout the synthesis, coordinative unsaturation of aluminum ions is protected with amines (strong Lewis bases) by converting dimeric aluminum precursors (*e.g.*, aluminum alkoxides) into monomeric amine-alumina adducts. In the end, piperidine-Al (PPD-Al) adducts are hydrolyzed to yield a solid catalyst with a low concentration of hydroxyl groups and a significant amount of bound piperidines. The structures of the intermediates are elucidated by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy, while the final product is analyzed by solid-state  $^{27}\text{Al}$  MAS NMR spectroscopy and DRIFT spectrometry. Significantly, the piperidines bound to the catalyst can be exchanged with other Lewis bases making the Lewis acid sites of aluminum accessible for catalysis.

**Results:** The researchers have demonstrated that alumina prepared by the controlled hydrolysis of the PPD-Al monomeric complex is a more active catalyst for epoxide aminolysis than traditional sol-gel alumina (SG-Al) prepared by the hydrolysis of aluminum alkoxide. The much higher activity of PPD-Al than the SG-Al suggests that the former catalyst has a significantly higher density of surface Lewis acid sites than the latter one. Assuming that calcination of SG-Al at  $500\text{ }^\circ\text{C}$  removes about  $\frac{1}{2}$  of the surface hydroxyl groups and one surface Lewis acid is formed from condensation of two hydroxyls, about  $\frac{1}{4}$  of the surface Al ions on SG-Al are then available as Lewis acid sites. Since PPD-Al is about five times more active than SG-Al, every Al ion on the surface of PPD-Al must be an active Lewis acid site. These calculations are consistent with the model, in which most, if not all of the surface Al ions in PPD-Al, are coordinated to piperidine molecules.

**Publications:** Xue WM, Jung MC, Kozlov AI, Popp KE, Kung HH, *Appl. Catal. A: Gen., submitted*; Kozlov AI, Kung MC, Xue WM, Kung HH, *Angew. Chem. Int. Ed.* **2003**, *in print*.



$\text{Al}_2\text{O}_3$  with a high density of Lewis acidic Al surface ions (shown in blue) is prepared by the hydrolysis of amine-Al adducts. The amines located on Al can be readily exchanged with other Lewis bases thus effecting the catalyst activity.



Comparison of the rates of cyclopentane oxide aminolysis by PPD-Al (blue trace) and SG-Al (magenta trace).