

Characterization and development of catalysts for the synthesis of fatty nitriles at low temperature

Adrien Mekki-Berrada¹, Didier Grondin¹, Simona Bennici¹, Jean-Philippe Gillet², Jean-Luc Dubois² and Aline Auroux^{1,*}

¹CNRS UMR5256, Institut de Recherche sur la Catalyse et l'Environnement, Lyon, 69626, France

²ARKEMA, Centre de Recherches Rhône-Alpes, Pierre-Bénite, 69493, France

*Corresponding Author, e-mail: aline.auroux@ircelyon.univ-lyon1.fr

Introduction

Considering the impact of aviation fuels on greenhouse effect (still no low sulphur limitation) and the declining availability or increasing cost of non-renewable energies, less polluting and sustainable bio-fuels have been the focus of several studies in the last decade. Alcohols and nitriles appear as good replacement for alkanes, regarding their combustion energy (converging for increasing carbon number) [1, 2]. The batch process of conversion of fatty acids and ammonia into nitriles needs the action of a catalyst in order to perform the second dehydration, however the current catalysts need a high working temperature, which is the source of polymerization side reactions and energy loss. Our work has been focused on developing and characterizing by microcalorimetry improved catalysts in order to lower the operating temperature.

Experimental

Bulk metal oxide catalysts known for their almost amphoteric character (both acidic and basic sites in similar amounts such as ZnO, Al₂O₃, In₂O₃, ZrO₂, Ga₂O₃) were synthesized in order to enhance their surface dehydration properties and compared with commercial crystalline ones [3]. All samples were characterized by adsorption microcalorimetry (Setaram C80 Tian-Calvet microcalorimeter) of acidic (SO₂) and basic (NH₃) gas probes at 80°C. Amphoteric character was determined both from the irreversibly adsorbed volume of gas (V_{irrev} in $\mu\text{mol}\cdot\text{m}^{-2}$ of catalyst) and the adsorption energies (q_{diff} in $\text{kJ}\cdot\text{mol}^{-1}$) (Fig.1). The catalysts were then tested on a small pilote batch reactor of 170 g reactants (without solvent). The catalytic test consists of a 500 mL reactor heated to the operating temperature in which ammonia is bubbled so that at the end of the test two stoichiometric equivalents of the reactant have been added. 0.024mol% of catalyst (relative to the reactant) is added at the beginning of the experiment. Industrial oleic acid (70%) is used as a reactant. The evolution of the reaction is followed by acid-base titration and the final product is distilled in order to obtain the yield of nitrile

Results and Discussion

Figure 1 displays on the left side the chemisorbed amount of basic probe (NH₃) corresponding to the number of acidic sites and the amount of acidic probe (SO₂) corresponding to the number of basic sites. On the right side the differential heats of adsorption determined by microcalorimetry linked with volumetry for the crystalline indium oxide (squares) and the synthesized homologue (triangles) are shown as an example of the acid-base differences that can occur from this difference in preparation (higher basicity, similar acidity).

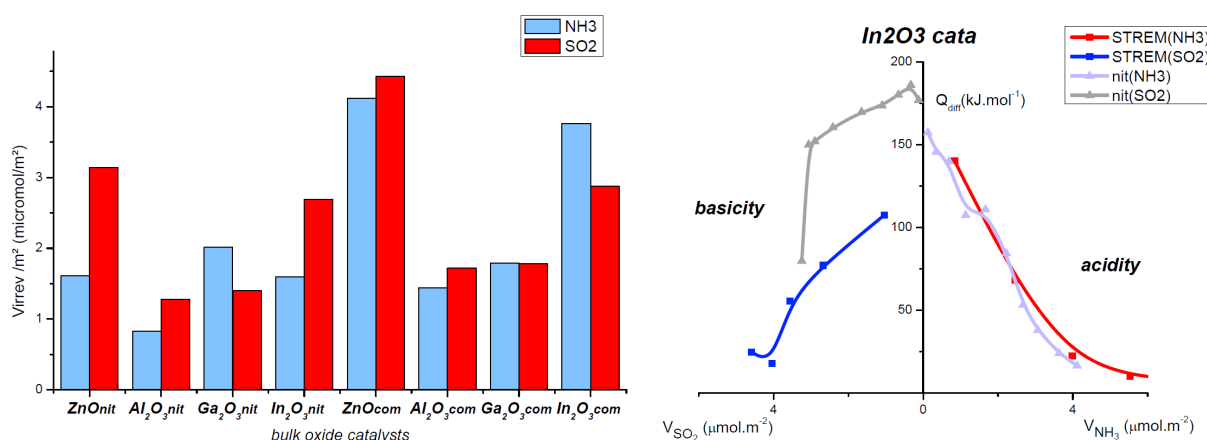


Figure 1. (left) irreversible adsorption volumes of NH₃ and SO₂ of commercial and synthesized ZnO, Al₂O₃, Ga₂O₃ and In₂O₃, and (right) the differential adsorption heats of indium oxides.

Catalysts presenting only acidic (tungstate) or basic (magnesium oxide) character display a poor catalytic behaviour already from the first dehydration step. Then, among amphoteric catalysts, the evolution of amide (intermediate species)

concentration is a better discrimination tool and presents a different evolution towards temperature and catalyst amount for every catalyst. GC-FID methods have been adapted to separate the main species (acids, amides, nitriles) and help to provide a better understanding of the mechanism. The influence of working temperature as well as the screening of mixed oxides or salt-type catalysts for conjugating benefits of different catalysts (on the first or second dehydration, on the decreasing of side-reactions) are also studied.

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