

HYDROGENATION OF BUTYRONITRILE
ON PROMOTED RANEY NICKEL CATALYSTS

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ABSTRACT

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The basic purpose of this research was to develop a catalyst with improved characteristics for nitrile hydrogenation. An important commercial application is the hydrogenation of adiponitrile to hexamethylenediamine. The optimal catalyst would have a high activity and selectivity to primary amine even in the absence of hydroxyl ions.

Hydrogenation of butyronitrile to butylamine (BA) was used as a test reaction. Room temperature, 1 atmosphere, liquid phase batch reactions (methanol-water solvent) were carried out in order to evaluate catalyst performance.

An Fe-Cr doubly-promoted catalyst had the highest activity while the unpromoted catalyst had the lowest activity. Iron promoted catalysts had intermediate activities. All of the catalysts had similar selectivities under the conditions studied. Sodium hydroxide addition dramatically increased the selectivities.

Adsorption and reaction studies were done in the presence and absence of base and at various BA concentrations to show the relationship between BA adsorption and the rate of condensation. BA was found to adsorb on two different types of sites, one which is blocked by hydroxyl ions and one which is not. The hydroxyl blocked sites made up about 40 % of the total BA adsorption sites. Total BA uptake on the unpromoted catalyst was 0.35 compared to 0.1 mmol/g for the doubly-promoted catalyst.

A simple analytical model was developed which accounts for many of the general trends observed in liquid phase hydrogenation of nitriles over Raney® nickel catalysts. The model helps to explain changes in catalyst activity and selectivity under a variety of amine and nitrile concentrations, solvent conditions, and hydrogen pressures. According to the model, promoters increase catalyst activity by increasing the rate of nitrile

adsorption. The model also accounts for selectivity enhancement by hydroxyl ion, ammonia, and tertiary amine addition.

For the first time, sponge nickel catalysts were prepared from Mn-Ni alloys. Leaching a 14 at. % nickel alloy produced a catalyst with similar activity but slightly lower selectivity compared to the unpromoted Ni-Al catalyst. Leaching a 28 at. % nickel alloy produced a novel microporous crystalline alloy catalyst. The microstructure was characterized before and after leaching by optical microscopy and x-ray diffraction.