

Improved Catalyst for Synthesis of Secondary Amines by Reductive Alkylation

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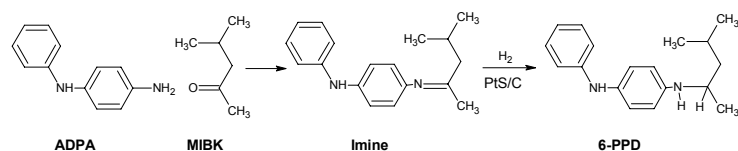
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Introduction

Reductive alkylation is an industrially important technique to synthesize secondary amines such as N-alkylarylamines which are used as antioxidants and antiozonants in polymers and rubber. The alkylation of an amine with a ketone is typically carried out in the liquid phase using a heterogeneous catalyst such as Pd, Pt, Rh, or Ru supported on carbon [1,2]. In a prior study, we showed that design of experiments could be used to optimize the Pt loading of a reductive alkylation catalyst [3]. In this study our focus was to improve the activity of Degussa's standard sulfided Pt/C catalyst used for the reductive alkylation without affecting the selectivity. This reduces the total Pt used per kg of product produced thereby making the process more economical. We chose the synthesis of N-(1,3-dimethylbutyl)-N-phenyl-p-phenylenediamine (6-PPD) by reductive alkylation of p-aminodiphenylamine (ADPA) with methyl isobutyl ketone (MIBK) over sulfur-promoted platinum catalysts as the model reaction.



The preparation of catalysts such as sulfided Pt/C is a complex process where both the type of raw material used and the catalyst preparation procedure can be tuned to improve the activity of the catalyst. A two-step procedure was adopted to arrive at an improved catalyst. The first step was to prepare a variety of 3% Pt/C catalysts and examine them using a probe reaction, hydrogenation of butenoic acid to butanoic acid, to select the most active catalysts. These catalysts were then promoted to form sulfided Pt/C which was tested under typical reductive alkylation conditions in an autoclave [3]. The resultant catalyst was found to be ~40% faster than the standard reductive alkylation catalyst.

Materials and Methods

The hydrogenation of butenoic acid over 3% Pt/C (200 mg) was conducted at 298K and atmospheric pressure in a 250 mL glass stirred tank reactor. The typical reaction consisted of hydrogenation a 10% solution butenoic acid (5.8 g) in ethanol and measuring the initial rate of hydrogen uptake. Testing of the sulfided catalyst was carried out in liquid phase in a well-stirred (1000 rpm) high-pressure reactor (Parr Instruments, 300 mL) at 30 bar and 150°C. The reaction mixture consisted of 61 g of ADPA (Acros Chemicals), 53 g MIBK (Acros Chemicals) and 370 mg of catalyst [3]. The reactor was operated at a constant pressure with

the liquid phase in batch mode and the hydrogen fed in at a rate proportional to its consumption. The reaction was monitored by hydrogen uptake and the product yield was determined from gas chromatographic (Agilent Technologies, 6890N) analysis. The selectivity to 6-PPD in all cases was >97% along with small amounts of unreacted imine.

Results and Discussion

Thirteen different Pt/C catalysts were tested for the hydrogenation of butenoic acid (Figure 1). Several catalysts were found to be more active than the standard catalyst (Catalyst F ~170 mL/g/min). Three of these catalysts (A, C, and E) were then selected to be sulfided and tested under typical reductive alkylation conditions described in the previous section. The time taken to achieve 95% conversion was noted in each case and compared to the standard catalyst.

Figure 1. Butenoic acid hydrogenation rate

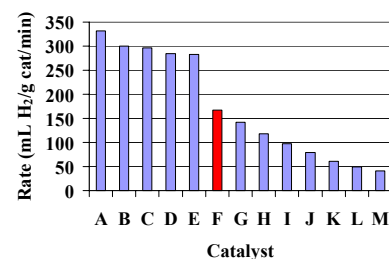
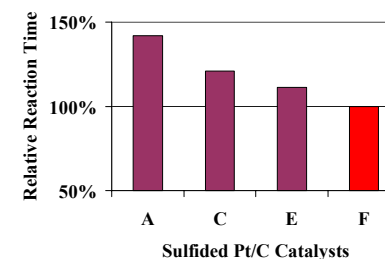


Figure 2. Relative reductive alkylation activity



The hydrogenation activity of C=C in butenoic acid was found to be a suitable predictor of the trend in hydrogenation activity of N=C in imine to 6-PPD. All three new catalysts were found to be more active than the standard catalyst for the synthesis of 6-PPD, with Catalyst A being the most active at ~40% shorter reaction time than the standard catalyst. Thus, the low pressure hydrogenation of butenoic acid can be considered as a suitable probe reaction for the sulfided Pt catalysts used for reductive alkylation. By varying the tunable parameters available during catalyst preparation, we were able to improve the performance of the catalyst by over 40%. Recyclability of this catalyst is yet to be assessed.

Significance

We were able to show that hydrogenation of butenoic acid is a suitable probe reaction for the sulfided Pt/C catalysts used in reductive alkylation. Using this, we developed a catalyst for the synthesis of the secondary amine 6-PPD that was over 40% faster than the standard catalyst.

References

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