Active Catalysts for Production of Hydroxylamine in the HPO™ Process

Jaime R. Blanton[1*], Takuma Hara[2], Konrad Möbus[3] and Baoshu Chen[3]
[1]*Degussa Corporation,5150 Gilbertsville Highway, Calvert City, KY 42029 (USA)*
[2] *Degussa Japan, Tsukuba Minami Daiichi Kogyo Danchi, 21 Kasuminosato Ami-machi, Inashiki-gun Ibaraki-ken 300-0315 (Japan)*
[3] *Degussa Ag,Rodenbacher Chaussee 4, 63457 Hanau-Wolfgang (Germany)*
*jaime.blanton@degussa.com

Introduction

The production of nylon-6 is one of the large industrial processes globally. Nylon-6 is used for carpet, textile and industrial fiber applications as well as for engineering plastics. Caprolactam is a feedstock for nylon-6 [1]. There are several technologies available for the manufacture of caprolactam. Each process yields varying amounts of byproduct ammonium sulfate (AS), a low cost fertilizer.

Caprolactam is formed in four steps in the HPO™ process. First cyclohexane is oxidized to cyclohexanone. Next ammonia is oxidized in air over a noble metal and the nitrate ions are reduced to give hydroxylamine (hyam). Oximation followed by the Beckmann Rearrangement lead to the desired caprolactam product. Degussa has done extensive work to develop Pd/C catalysts with superior activity for the production of hyam (Equation 1).

$$NO_3^- + 3H_2 + 2H^+ \xrightarrow{Pd/C} NH_3OH^+ + 2H_2O \quad \textbf{Equation 1}$$

Many parameters influence the performance of a catalyst. In this case the preparation method, carbon support, metals and metal loading were investigated to see what the influence of each is on the manufacture of hydroxylamine.

Materials and Methods

Six catalysts available from Degussa were tested initially (Catalysts A-F). These catalysts were prepared by the same proprietary procedure and each contains 10% Pd except D which contains 9% Pd. In a typical test 750 mg of catalyst was added to a continuous stirred tank reactor (1500 rpm) containing the nitrate ions in 1L of phosphate buffer solution. The amount of hyam formed and selectivity after 90 min at 30°C were measured by titration [2]. Catalysts A and C were also chosen for studying the effect of Pd loading and Pt addition.

Catalyst filtration rates were measured by passing a slurry of buffer solution containing 5 g (dry) catalyst through a filter cloth at 0.1 MPa N_2 pressure.

Results and Discussion

Several catalysts were prepared and tested for their hyam activity. Numerous preparation methods were investigated. Catalysts prepared using the method that provided the most active catalysts were used in this study. Our aim was to see how varying the carbon support, Pd loading and Pt addition would affect the activity, selectivity and filterability of the catalyst in hopes of identifying the optimal catalyst for the hyam reaction (activity greater than 25 g hyam/g Pd, selectivity > 90% and fast filtration rate).

Of the catalysts prepared on different activated carbon supports, Catalyst A was found to be the most active and most selective catalyst for the hyam reaction. However, this catalyst had the poorest filterability of the catalysts evaluated. Catalyst F had good activity, but the lowest in this study, and had excellent filtration properties. A direct correlation between hyam activity and filtration rate was found (Figure 1). Hence, the particle size of the support is very important to the activity of the catalyst.

Figure 1. Hyam activity vs. filtration of catalysts

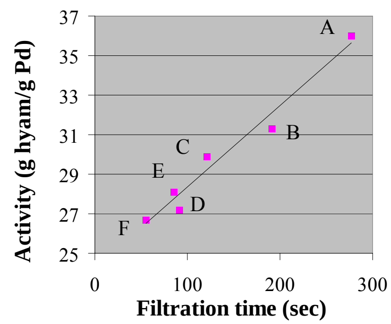

Table 1: Activity (g hyam/g Pd) and selectivity for bimetallic catalysts and catalysts of varying Pd loadings

Cat. Type	% Pd	% Pt	Activity	Selectivity
A	9	0	37.2	100
A	10	0	36.0	95.7
A	12	0	32.7	94.6
A	15	0	28.9	98.0
C	12	0	27.7	93.2
C	12	0.1	30.7	92.3
A	12	0.1	35.0	93.3
A	8	2	57.3	86.0

Catalyst metal loadings as well as bimetallic catalysts were also investigated. In one study the Pd content was varied from 9% to 15%. It was found that the catalyst efficiency increased with decreasing Pd loading (Table 1). In another study the performance of Pd + Pt bimetallic catalysts was compared with that of the monometallic catalysts. It is known that the addition of Pt enhances the activity of hyam catalysts while sacrificing selectivity [3]. By fine tuning the Pd and Pt concentrations, bimetallic catalysts were developed that matched the selectivity of Pd only catalysts with a boost in activity (Table 1).

Significance

Several highly active hyam catalysts have been developed for the HPO™ process. Depending on which performance indicator is most important (activity, selectivity or filterability) one can select the best Degussa catalyst for their application.

References

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