

## Effects of Ammonia and Amines on Propylene Disproportionation over a Tungsten Oxide Silica Catalyst

### INTRODUCTION

The reaction of propylene disproportionation on a tungsten oxide silica catalyst has been a subject of considerable research activity aimed at clarifying its mechanism (1-8). The interest in this catalytic reaction system has stemmed from two experimental observations: (1) The catalyst requires a prolonged break-in period (6) and (2) the catalyst exhibits an anomalous gas-phase mass transfer effect (3, 4). It has been shown (6) that, in part, the induction period is due to reduction of the promotor ( $\text{WO}_3$  to  $\text{WO}_{2.9}$ ). Various theories have been proposed for the portion of the induction period which cannot be attributed to simple reduction (9).

The anomalous mass transfer effects were first reported by Moffat *et al.* (3, 4). Their results indicated that these mass transfer effects could not be eliminated no matter how high the flow rate or how low the promoter concentration. They have postulated that the reaction is limited by site-localized diffusional effects. In later studies, however, it was found that it was possible to eliminate these mass transfer effects by using feed rates about an order of magnitude higher than those predicted to be necessary by classical calculations (3, 8).

Recently Pennella *et al.* (7, 9) have discussed a molecular orbital approach to propylene disproportionation on tungsten oxide silica catalysts. They have postulated that this reaction occurs through promotion

of electrons from molecular orbitals comprising metal d orbitals and olefin  $\pi$  orbitals to levels comprising metal d orbitals and olefin antibonding  $\pi$  orbitals. According to the Pennella view, at steady-state activity only a certain number of sites are active. To increase the activity of the catalyst, the inactive sites must somehow be modified. One way to accomplish this is to add ligands capable of decreasing the energy levels in question. They have supported this view experimentally by dosing the propylene feed continuously with small amounts of polyenes (e.g., 1,5-cyclooctadiene), and a significant increase in catalytic activity resulted.

We have observed that dosing with ammonia and certain amines dramatically increases catalytic activity in the  $\text{WO}_3$ - $\text{SiO}_2$  system promoting propylene disproportionation. These increases are observed during break-in as well as with fully active catalysts. The effects, though temporary, are of significant duration and are similar to the results obtained by Pennella *et al.* (7) with polyolefins.

### METHODS

The experimental apparatus was a near-differential flow system and has been described elsewhere (5, 6). A 10%  $\text{WO}_3$  on  $\text{SiO}_2$  catalyst with a BET surface area of 223  $\text{m}^2/\text{g}$  obtained from Davidson Chemical Co. was used in all tests. The product gas analysis was done using glc (5, 6).

The apparatus was modified slightly to enable injection of controllable amounts of gases or liquids into the propylene feed. A standard gas-sampling valve with a 13-cm<sup>3</sup> sample loop was used to inject gases into the propylene feed stream. The liquid injection into the propylene feed was accomplished using syringe injection (amounts varying from 3  $\mu$ l to 0.1 cm<sup>3</sup>) using a heated injection port.

### RESULTS

The effect of ammonia on the catalytic disproportionation activity was studied both during the break-in period ( $\delta$ ) and during the steady-state regime. In all cases the catalyst activity is taken to be proportional to the observed conversion level. The results for ammonia injection are shown in Fig. 1. The experimental points are shown while the solid curve is the break-in rate predicted from the data of Luckner *et al.* ( $\delta$ ) using a first-order rate constant of 0.00351 min<sup>-1</sup>.

As can be seen from Fig. 1, a rapid and dramatic though temporary increase in activity is seen immediately following each ammonia injection throughout the break-in period. However, the normal break-in behavior appears to be occurring independently with the temporary effect of the ammonia injection superimposed. As

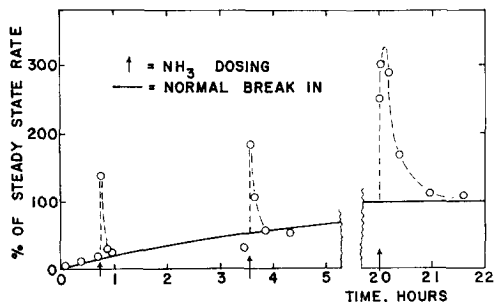


FIG. 1. The effect of NH<sub>3</sub> dosing on catalytic activity during break-in. 428°C; propylene flow rate, 2 cm<sup>3</sup>/s; 0.94 atm; 0.3 g of catalyst. —, expected break-in; ---, enhanced activity following NH<sub>3</sub> dosing.

TABLE 1

Effect of Amines on Steady-State Activity<sup>a</sup>

Amine	Initial activity change (percentage of initial activity)	Amount of liquid injected
<i>n</i> -Butylamine	+283	0.1 cm <sup>3</sup>
Hexyl amine	+233	0.1 cm <sup>3</sup>
Aniline	+510	3 $\mu$ l
Di- <i>n</i> -Butylamine	+310	3 $\mu$ l
Triethylamine	- 84	0.1 cm <sup>3</sup>
Pyridine	- 43	3 $\mu$ l

<sup>a</sup> Propylene flow rate, 2 cm<sup>3</sup>/s; 428°C; 3 g of catalyst.

can be seen, the effect is reversible and lasts about 15–60 min.

Table 1 shows the effect of various amines on the steady state activity of the catalyst.

In Fig. 1 and Table 1 the relative activity of the catalyst is reported, and this is taken to be the observed conversion level divided by the steady-state conversion level multiplied by 100.

The effect of ammonia injection was entirely reversible. Protracted injection of amines led to some deterioration in steady-state activity. A color change in the catalyst from blue to bluish black was observed following these injections.

The amines studied could be divided into two groups: the ones which increased disproportionation activity, and the ones which inhibited the reaction. A point of interest is that amines with no N–H bonds (pyridine and triethylamine) inhibited disproportionation activity. In contrast, all amines with one or more N–H bonds increased disproportionation activity of the catalyst.

### DISCUSSION

According to the Pennella model (see Introduction), inactive disproportionation sites can be quickly activated by modifications of the orbital energy levels by addition of suitable chelating ligands such as 1,5-

cyclooctadiene to the feed. In this paper we have shown that ammonia and many amines have a similar effect on the disproportionation reaction.

$\text{NH}_3$  has been found to be a particularly suitable compound for quickly increasing disproportionation activity with no damaging effect to the catalyst, but the ammonia effect is temporary and continuous ammonia additions would be necessary to maintain high activity.

The amines were tried because of their similarity to ammonia. As expected, various amines were also shown to accelerate the disproportionation reaction, although these compounds are less suitable because of their deteriorating effect on the catalyst. Amines with no N-H bonds, e.g., pyridine and triethylamine were found to decrease disproportionation activity.

While dosing of the feed quickly brings the catalyst to a higher level of activity, normal break-in appears to be unaltered by the dosing experiments. However, the initial state of the catalyst does appear to play a role in the dosing experiments with the greatest activity enhancement observed with a fully broken-in catalyst and the least with a catalyst at only about 15% of its steady-state activity. This suggests that the dosing is affecting the sites created by normal break-in rather than creating new sites.

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#### REFERENCES

1. Heckelsberg, L. F., Banks, R. L., and Bailey, G. C., *Ind. Eng. Chem. Prod. Res. Develop.* **7**, 29 (1968).
2. Heckelsberg, L. F., Banks, R. L., and Bailey, G. C., *Ind. Eng. Chem. Prod. Res. Develop.* **8**, 259 (1968).
3. Moffat, A. J., Clark, A., and Johnson, M. M., *J. Catal.* **18**, 345 (1970).
4. Moffat, A. J., Clark, A., and Johnson, M. M., *J. Catal.* **22**, 379 (1970).
5. Luckner, R. C., McConchie, G. E., and Wills, G. B., *J. Catal.* **28**, 63 (1973).
6. Luckner, R. C., and Wills, G. B., *J. Catal.* **28**, 83 (1973).
7. Pennella, F., and Banks, R. L., *J. Catal.* **31**, 304 (1973).
8. Hattikudur, U. R., and Thodos, G., in "Chemical Reaction Engineering II" (H. M. Hulbert, Ed.), p. 80. American Chemical Society, Washington, D. C., 1974.
9. Pennella, F., Regier, R. B., and Banks, R. L., *J. Catal.* **34**, 52 (1974).

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