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# $NO_x$ abatement over VPO catalysts

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Vanadium phosphorus oxide ($P/V = 1.1$) was found to be active for NO reduction by butane to $N_2$ at 766–816 K. The conversion increased with increasing butane concentration, increasing temperature, and decreasing NO concentration. The activity per surface vanadium ion compared favorably with other active catalytic systems, but was low in the absence of butane. Propane was also effective in reducing NO over this catalyst.

**Keywords:** $NO_x$ reduction by butane; vanadium phosphorus oxide catalyst

## 1. Introduction

The current laws governing the emission standard of toxic gases are becoming more stringent due to the continuing deterioration of the environment. In order to meet the new challenge there is a need to explore novel catalytic systems for pollution control. NO is a serious pollutant. It causes acid rain, and $NO_x$ abatement is an urgent priority. Catalytic decomposition of NO is the most attractive method for its removal. Otherwise, catalytic reduction of NO with an environmentally benign reductant is also an acceptable alternative.

Cu-ZSM5 is the best known NO decomposition catalyst to date [1]. However, its activity is still too low for commercial application [2]. Recently it has been demonstrated that on Cu-zeolite, alkane can reduce NO selectively to $N_2$ [2,3]. Alkanes are relatively inert molecules and can be easily disposed by burning in excess air.

The objective of our research is to examine the role of low valent vanadium cations in NO decomposition and reduction. Literature results have shown that $N_2$ formation from NO on $V_2O_5$ pre-reduced with $NH_3$ was possible [4]. Pulse reaction of NO over $V_2O_4$ also showed $N_2$ formation from NO [5]. Accompanying $N_2$ production in these reactions oxidation of the $V^{4+}$ ion to $V^{5+}$ occurred. These results suggested that $V^{4+}$ ions stabilized against oxidation might be effective in NO decomposition. VPO catalysts, in which vanadyl pyrophosphate is the only identifiable bulk phase, have been shown to contain vanadium in a stabilized 4+ oxidation state [6] and thus may possess the ability to decompose NO. Furthermore

VPO catalysts are active in the activation of alkanes [7]. Thus they may be able to effect the selective reduction of NO. This paper reports the results of catalytic reactions of NO on a VPO catalyst.

## 2. Experimental

VPO catalyst with a P/V ratio of 1.1/1 was prepared as in ref. [8]. The hemihydrate was activated in a flow of $O_2$/butane/He = 10/1/39 at 673 K for 14 h to form the active catalyst. Before each subsequent experiment, the catalyst was treated in $O_2$/butane at 658 K for 10 min.

The NO reduction experiments were conducted in a reaction system constructed with 1/8″ stainless steel tubing. The reactor was constructed of quartz. For experiments of NO reduction with alkane the catalyst was treated in $O_2$/butane at 658 K for 10 min and then heated in pure He to the reaction temperature. Butane and NO at the desired ratio was then introduced. The products were analyzed with gas chromatography. Hydrocarbon and $CO_2$ products were analyzed using a 10 ft Porapak Q (Alltech) column. CO, NO and $N_2$ were analyzed using a column composed of a $1\frac{1}{2}$ ft Carbosphere (Alltech) column and a $1\frac{1}{2}$ ft molecular sieve 5A column linked in series. The BET area of the catalyst was 17.6 $m^2$/g. X-ray diffraction of the catalyst after activation showed only the $(VO)_2P_2O_7$ phase.

## 3. Results and discussion

Fig. 1 shows the change in the activity at 762 K for NO reduction with butane on a fresh catalyst (one that was just formed from the hemihydrate), using a NO/butane ratio of 22. The activity for $N_2$ production was very low initially, but increased over the next 8 h before attaining the maximum activity, which was about ten times the initial activity. The selectivity of reduction of NO to $N_2$ was >95% at 766 K. CO and $CO_2$ were also produced. As shown in the figure, the production rate of $CO_x$ decreased gradually over the course of the experiment. The initial rate of $CO_x$ production exceeded that which could be accounted for by the rate of butane reaction. That is, there was more carbon in the exit stream of the reactor than in the feed. This could be explained by the deposition of carbonaceous compounds during the transformation of the catalyst in the $C_4H_{10}/O_2$ mixture from the hemihydrate form to the vanadyl pyrophosphate phase. These deposits were slowly burnt off when NO was introduced, thus exposing more active sites for the reduction of NO. At point A in the figure, the catalyst was cooled down in He to room temperature and left overnight. It was then exposed to a feed of $O_2$/butane/He of 10/1/39 for 10 min at 673 K as in the start of a new experiment. This brief exposure to $O_2$/butane again caused a transient depression in $N_2$ yield, confirming that the low activity was due to the butane/$O_2$ treatment. The duration of this tran-

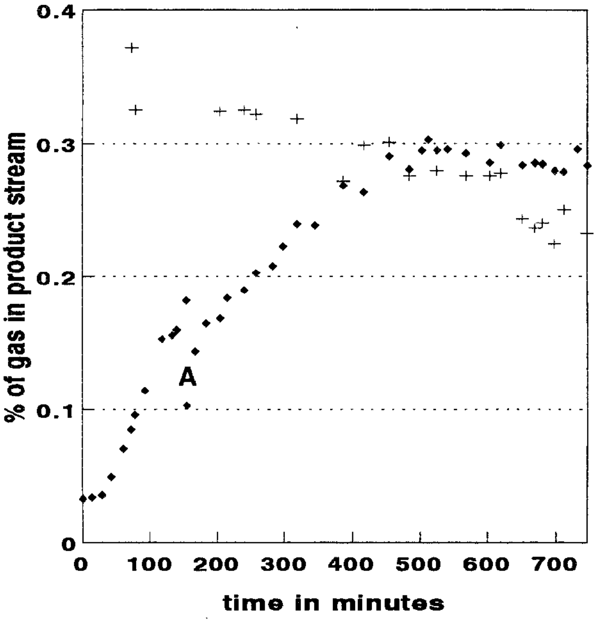


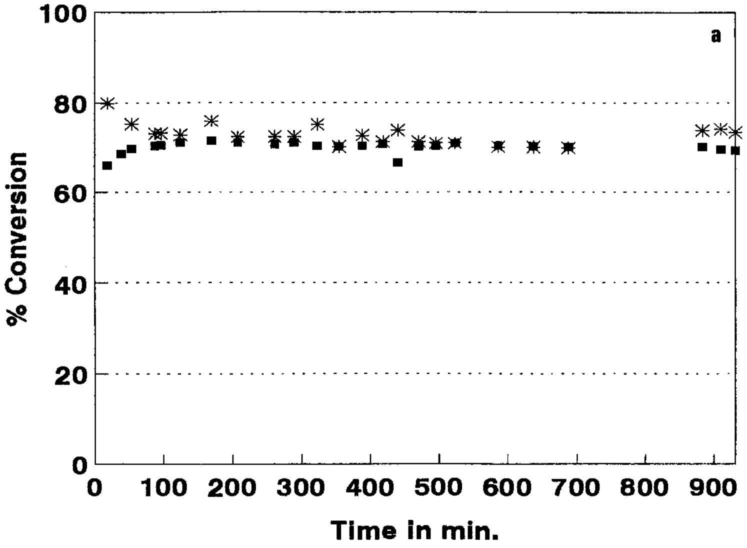
Fig. 1. Amounts of $N_2$ and $CO_x$ in the product stream as a function of time on stream. Feed conditions: NO = 1.7%, $C_4H_{10}$ = 0.08%, $W/F = 0.15$ g min/cm$^3$; 762 K. (◆) $N_2$, +$CO_x$. The data were collected after the catalyst was activated in a $C_4H_{10}/O_2$ mixture for 14 h at 673 K. At point A, the catalyst was re-exposed to $C_4H_{10}/O_2$ for 10 min at 673 K.

sient was dependent on the butane concentration during the subsequent NO reduction experiment and became insignificant at higher butane concentrations such as those used in fig. 2.

The dependence of the activity on the time on stream was investigated for two different temperatures, and the results are shown in figs. 2a and 2b. The activity was constant at 816 K. However, at 766 K there was a 24% decrease in activity over a 24 h period. The activity was higher at the higher temperature. This is different from the behavior of a Cu-ZSM5 catalyst for NO decomposition which showed that the activity decreased with increasing temperature in this temperature range [2,3].

Table 1
Dependence of conversion on NO concentration at 766 K

| [butane] (%) | [NO] (%) | NO/butane | $W/F$(g min/cm$^3$) | NO conversion (%) |
|---|---|---|---|---|
| 0.11 | 1.71 | 15.6 | 0.11 | 39.6 |
| 0.10 | 0.44 | 4.4 | 0.06 | 61.4 |
| 0.11 | 0.24 | 2.2 | 0.06 | 87.0 |
| 0.05 | 0.11 | 2.2 | 0.03 | 80.7 |



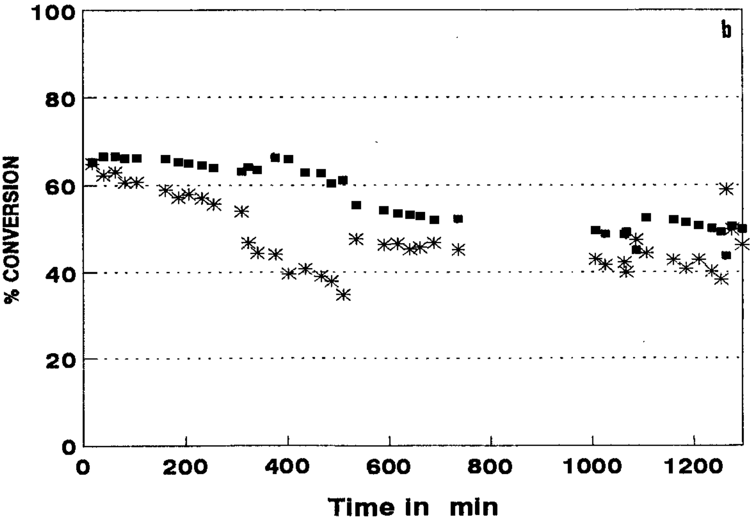


Fig. 2. Conversion of NO and butane at 766 and 816 K. (a) NO = 1.7%, $C_4H_{10}$ = 0.22%, $W/F$ = 0.12 g min/cm$^3$, 816 K and (b) NO = 1.7%, $C_4H_{10}$ = 0.24%, $W/F$ = 0.12 g min/cm$^3$, 766 K. (■) NO, (*) $C_4H_{10}$.

The dependence of the conversion of NO to $N_2$ on the NO concentration at a fixed butane concentration is shown by the first three experiments in table 1. The data showed that the NO conversion increased with decreasing NO concentration. The dependence of the activity on butane concentration is shown in fig. 3. At a fixed NO concentration, the rate of NO reduction increased with butane concentration. These experiments showed that the activity of the catalyst depended on the concentration of both NO and butane, and the conversion of NO was higher with

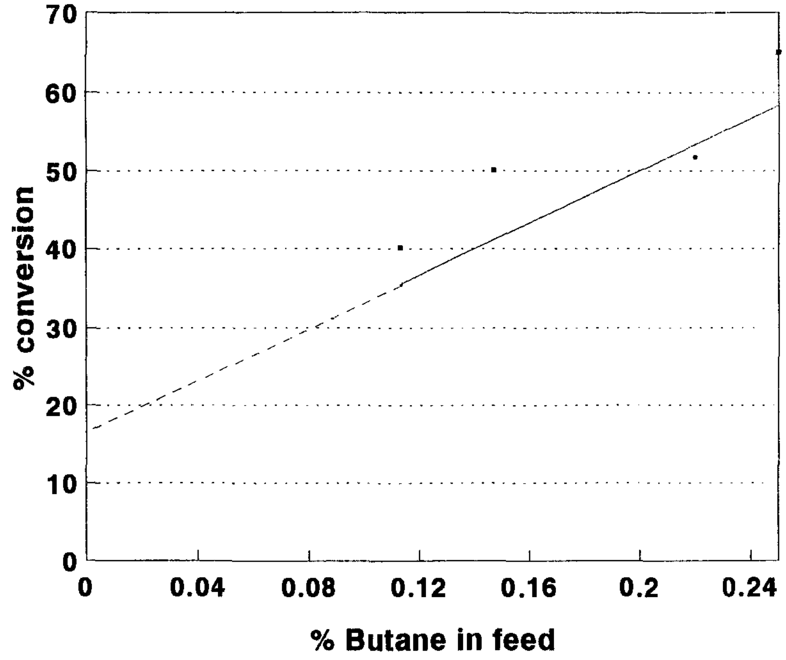


Fig. 3. Dependence of NO conversion to $N_2$ on butane concentration in the feed. NO = 1.7%, $W/F = 0.12$ g min/cm$^3$, 766 K. Results are the average of the data gathered in the first 3 h.

higher butane/NO ratios. The role of the alkane may be twofold. It may act as an oxygen scavenger to remove the oxygen deposited on the catalyst when NO decomposed, or it may directly react with the NO molecule.

When butane was removed from a reaction mixture of NO/butane/He of 1.7/0.19/98.1, the activity decreased by about 90% in 135 min at 816 K, as shown in fig. 4. If the sample was heated to 874 K at this point the activity was partially recovered to 36% of the value before deactivation, but fell again as a function of time on stream. The activity of the catalyst was higher at 874 K than 816 K after 140 min. The rate of decrease in the activity was strongly dependent on the history of the sample. If the feed was a NO/butane/He mixture of 2.1/6.5/91.4 (that is, a much higher concentration of butane), then the decrease in activity was much less rapid when butane was removed from the feed, and 66% of the original activity remained after 20 min at 766 K. In comparison, under the condition used in fig. 4, the activity would have dropped to only 20% of the initial activity.

In addition to using butane, propane and CO were also tested as reductant. CO was not effective and the $N_2$ yield was low. Propane was a selective reductant of NO to $N_2$, but at 713 K twice as much propane as butane was needed to achieve the same nitrogen yield. Butane was not as active for NO reduction in the presence of oxygen (see table 2). The decrease in activity may be due to carbonaceous deposits resulted from the oxygen–butane reaction.

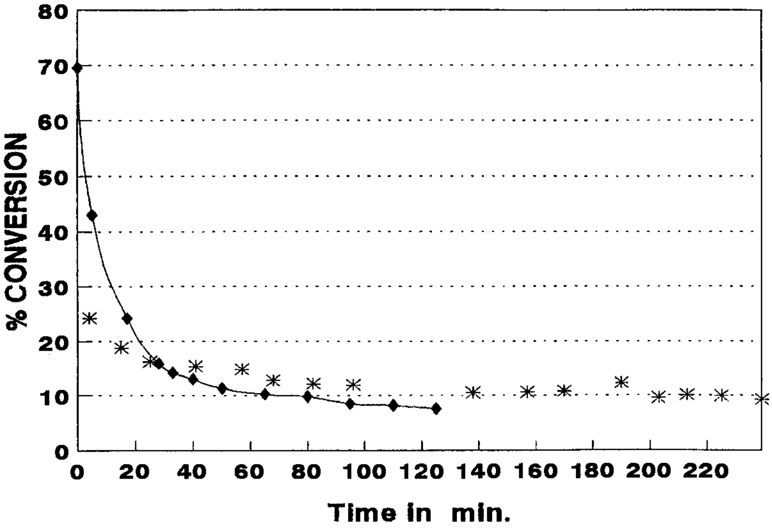


Fig. 4. Decrease in NO conversion to $N_2$ on VPO in the absence of butane. NO = 1.7%, $W/F = 0.12$ g min/cm$^3$. (◆) Time = 0 when butane was removed from feed at 766 K. (*) Time = 0 when sample first reached 874 K (see text).

The VPO catalyst used was a low surface area oxide and most of the vanadium cations were inaccessible to NO. In order to compare its activity with those of other catalysts, the number of surface vanadium ions on the catalyst was estimated assuming that the exposed surface was the (020) plane of vanadyl pyrophosphate [9]. The turnover frequencies (TOF), reported as moles of NO reacted (min·mole of exposed cation)$^{-1}$ for VPO, and as moles of NO reacted (min·mole cation)$^{-1}$ for the other samples, are shown in table 2 for three different reaction systems. It is interesting to note that under the conditions used for comparison, the activity of the VPO catalyst was comparable to the other systems. These results suggested that further study of the VPO system is warranted.

Table 2
Comparison of activities of different catalysts for NO reduction

| Catalysts | [NO] (%) | [reductant] (%) | | $[O_2]$(%) | TOF $(10^{-2})$[c] | Temp. (K) |
|---|---|---|---|---|---|---|
| 1.9% $V/TiO_2$[a] | 0.05 | $NH_3$ | (0.05) | 2 | 5 | 523 |
| Cu-ZSM5[b] | 0.1 | $C_2H_4$ | (0.025) | 2 | 2 | 625 |
| VPO | 0.11 | $C_4H_{10}$ | (0.053) | – | 0.9 | 766 |
| VPO | 0.46 | $C_4H_{10}$ | (0.1) | – | 1.2 | 766 |
| VPO | 0.46 | $C_4H_{10}$ | (0.1) | 0.43 | 0.6[d] | 766 |

[a] Ref. [10].

[b] Ref. [11].

[c] Moles NO reacted/mole cation · min.

[d] Activity was depressed with the introduction of $O_2$, but increased with time on stream and reached this level in 6 h.

## 4. Conclusion

It is shown here that a VPO catalyst was active in the reduction of NO by alkane. The activity of the catalyst in the absence of butane was low. In the presence of butane, the activity increased with increasing butane concentration. It also increased with increasing temperature. That the activity calculated per surface vanadium was comparable to that of vanadium supported on $TiO_2$ and Cu in Cu-ZSM5 indicated that further investigation of this system for selective reduction of NO by alkane may be promising.

## Acknowledgement

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