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Promotion of the $NO + O_2$ reaction by Ba–Y, FAU zeolite at 25 °C

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A remarkably high inferred initial rate of NO oxidation by O_2 has been observed over Ba–Y, FAU zeolite at 25 °C in simple flow-reactor experiments. The rate of reaction at steady state was found to be lower, but still an order of magnitude greater than over alumina-supported Pt, also at 25 °C.

KEY WORDS: NO oxidation; Ba–Y.

1. Introduction

NO oxidation is believed to be an essential step in the overall reaction that leads to NO_x storage in the lean NO_x trap [1]. It is also necessary for achieving maximum efficiency of selective catalytic reduction of NO_x, based on urea [2], and critical to the operation of the continuously regenerating diesel particulate filter [3]. Generally, Pt is used to catalyze NO oxidation, although non-thermal plasma has also been employed for this purpose in recent work where various ion-exchanged-Y, FAU zeolites were considered as catalysts for NO_x reduction in diesel exhaust [4]. Here, we report our observation that one of these zeolites, Ba–Y, can itself promote the $NO + O_2$ reaction at an initial rate exceeding that in the gas phase by several orders of magnitude at 25 °C. Further, under steady-state conditions, it is an order of magnitude more active than alumina-supported Pt, also at 25 °C. These results, which cast new light on a technologically important reaction, are interesting since NO interacts rather weakly with Ba–Y.

2. Experimental details

Experiments were conducted with a U-tube quartz reactor (1/4″ o.d.) packed with between 0.15 and 0.20 g catalyst powder. The catalyst sample was always dehydrated at 500 °C in He, 1% H_2 in He, or 6% O_2 in He (all of which yielded equivalent results) for 30 min, then cooled to 25 °C in He prior to testing. Testing consisted of exposing the sample to one of three gas compositions, 500 ppm NO in He, 500 ppm $NO + 6\%$ O_2 in He, or 390 ppm NO_2 in He while alternately monitoring NO and NO_2 (NO_x – NO) with a Rosemont Model 951 chemiluminescence analyzer as a function of time. Total gas flow was 500 ml/min.

The Ba–Y sample, provided by PNNL, has been described previously [4]. Briefly, it was prepared by twice exchanging Ba for Na ions in Na–Y from Zeolyst (CBV100 with SiO_2/Al_2O_3 of 5.1) using a barium acetate solution with calcination steps at 500 °C after each exchange. An alumina-supported Pt catalyst (2wt%) was made following the standard incipient wetness procedure, using platinum tetra-amine nitrate as precursor.

3. Results

As shown in figure 1(a), NO passes relatively freely over dehydrated Ba–Y at 25 °C. With the addition of O_2, however, NO completely disappears from the exiting gas stream for several minutes, eventually reappearing with about 13% having been converted to NO_2, as shown in figure 1(b). When NO_2 is passed over the Ba–Y, all of it is adsorbed initially, as shown in figure 1(c). These results suggest that the Ba–Y promotes the reaction of NO with O_2 to form NO_2, which adsorbs initially. Further evidence comes from temperature-programmed desorption results, shown in figure 2, where the NO_x (95% of which is NO_2) desorption profile of the Ba–Y exposed to $NO + O_2$ closely matches that of the Ba–Y exposed to NO_2. The ratio of desorbed NO_x to Ba was found to be about 0.8 in both cases. It should be noted that the results shown in figures 1(b) and (c) were completely reproducible following desorption of NO_2.

This behavior was only observed at 25 °C, however. At a temperature of 15 °C, where NO_2 can still strongly adsorb on dehydrated Ba–Y, the addition of O_2 to NO had no effect. Further, corresponding experiments with Na–Y and alumina-supported baria indicate that the observed behavior cannot be solely due to properties of

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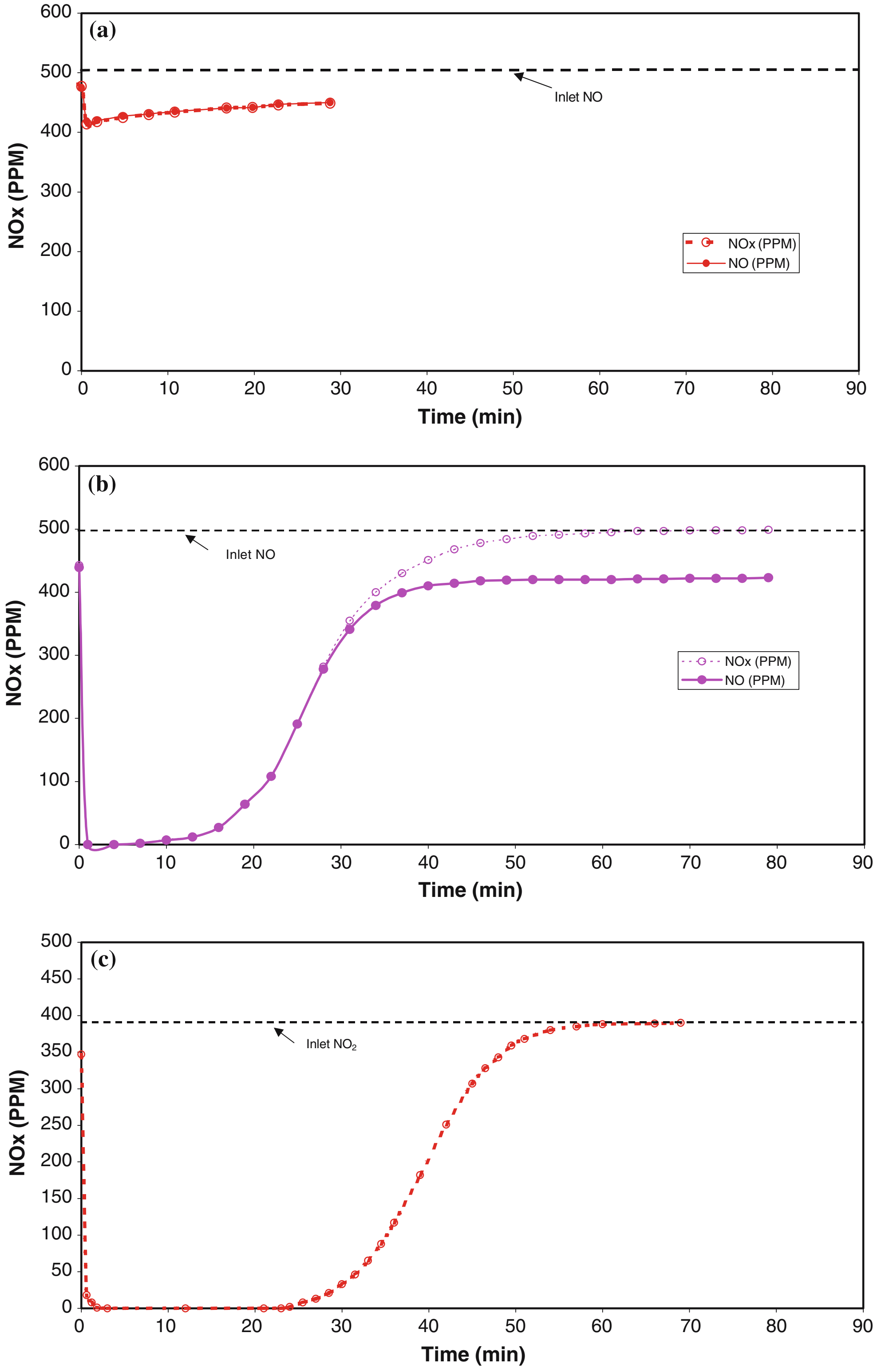

Figure 1. Reactor outlet NO_x as a function of time for 0.18 g of dehydrated Ba–Y at 25 °C exposed to NO (a), NO + O_2 (b), and NO_2 (c).

either the zeolite or baria. It is also worth noting at this point that the homogeneous reaction between NO and O_2 under these conditions (500 ppm NO, 6% O_2, and 25 °C) and space velocity would yield no more than about 0.005% over the empty reactor (or about 0.05% over the whole reactor plus gas mixing system) conversion [5], whereas the initial rate over the dehydrated Ba–Y is essentially 100%. In yet another comparison, the steady-state rate of NO_2 formation for the alumina-supported Pt (2wt%) catalyst was found to be about 1%

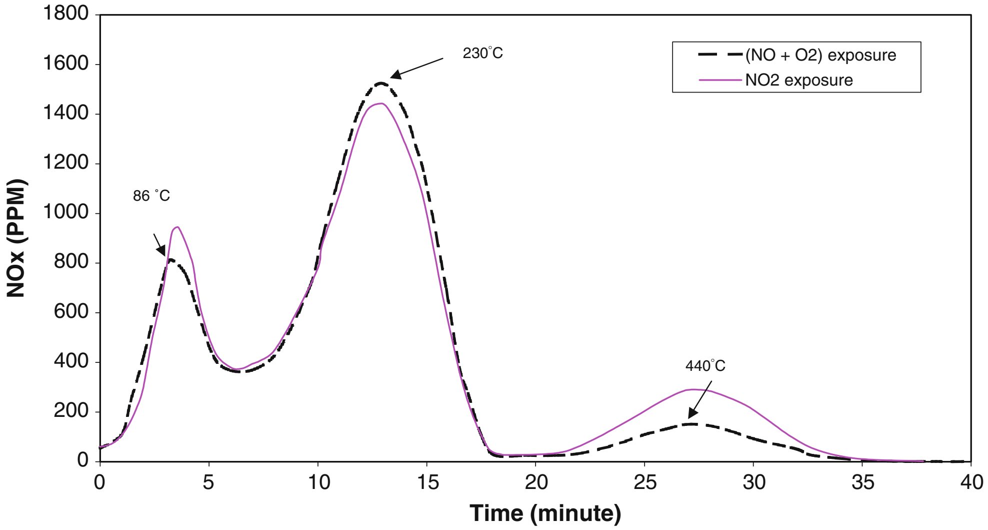

Figure 2. NO_x desorbed into a He flow during TPD following exposure of 0.18 g of dehydrated Ba–Y at 25 °C to either $NO + O_2$ or NO_2. Temperature ramp rate was ≈15 °C/min.

at 25 °C, about 15% at 150 °C, and about 80% (maximum attained) at 300 °C.

4. Discussion

The interaction of NO_x with a number of zeolites has been well studied, though the emphasis of much of this work has been on the identification of adsorbed species and likely adsorption mechanisms [6]. The interaction of NO with Na–Y, for example, is known to be weak [7], whereas that of NO_2 is much stronger (and stronger yet with Ba–Y) [8]. Less attention has been given to reaction rates, such as that of NO with O_2. In the present work, we provide evidence suggesting that this reaction is promoted by dehydrated Ba–Y, especially at low levels of NO_2 adsorption (relative to saturation), but only near room temperature. Dehydration of Ba–Y is also necessary. (In fact, exposure of Ba–Y containing a significant amount of water to NO_2 results in the accumulation of nitric acid which eventually destroys the zeolite structure.) It is hoped that these observations will stimulate additional efforts to further our understanding of NO oxidation.

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