Reduction of NO over impregnated Cu/ZSM-5 in the presence of O_2

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Received 3 April 1992; accepted 26 May 1992

Cu/ZSM-5 catalysts prepared by impregnation of Cu acetate are active for NO reduction. In mixtures containing both NO and O_2, reductants such as CO or CH_4 preferentially react with O_2, but propane reacts preferentially with NO. Small amounts of O_2 actually increase the reduction of NO by C_3H_8. The N_2 yield reaches a maximum near an O_2/C_3H_8 ratio = 5, i.e. the stoichiometry of total C_3H_8 oxidation. At much higher than stoichiometric O_2 contents for total C_3H_8 oxidation the N_2 yield with C_3H_8 (54%) is still substantially higher than, for instance, with CO of the same or larger concentration. The hypothesis that an intermediate of C_3H_8 oxidation is responsible for the enhanced NO reduction is discussed. Temperature-programmed reduction shows that after reaction with $NO + C_3H_8$ and sub-stoichiometric amounts of O_2 Cu in the catalyst is mainly metallic, but CuO particles appear to be formed in the presence of an excess of O_2.

Keywords: NO_x abatement; Cu/ZSM-5; metal/zeolites

1. Introduction

The search continues for an effective nitrogen oxide (NO_x) abatement system for both automobile and power plant emissions. The detrimental effects of NO_x on the environment have imposed a new immediacy on the need to solve this problem. In the automotive industry the most effective catalysts that reduce NO_x in the exhaust gases require expensive and scarce noble metals such as rhodium (Rh) and platinum (Pt). The vanadium based catalysts now widely installed at power plants in Japan and Germany pose environmental problems due to poisonous, volatile vanadium compounds and the "slip" of ammonia (NH_3) during NO_x reduction.

Recently, zeolite catalysts have been shown to convert NO_x to nitrogen (N_2) [1–7]. Iwamoto et al. obtained a N_2 yield greater than 80% from NO decomposition with "excessively" ion-exchanged copper zeolites. With a Cu loading from

50 to 150% of the theoretical ion exchange level, the yield of N_2 increased from 20 to 85%. However, decomposition is inhibited by the presence of oxygen [4,8]. We observed that at low temperatures NO and O_2 swiftly combine to NO_2, which reacts with more NO to N_2O_3. This N_2O_3 is visible as a blue deposit on a cold trap maintained at 195 K. In the presence of reducing gases such as ethene, propane, or propene, Iwamoto and Held observed a selective reduction of NO in the presence of O_2 [9–11]. At low O_2 concentrations, O_2 actually enhanced the reduction of NO [12].

In this paper research is reported on Cu/ZSM-5 catalyst prepared by impregnation instead of ion exchange. The reduction of NO by CH_4, CO, and C_3H_8 was studied both in the absence and in the presence of O_2. Changes in the Cu valence state were examined by temperature programmed reduction (TPR) of the catalyst before and after the reactions.

2. Experimental

2.1. CATALYST PREPARATION

The H-ZSM-5 with Si/Al = 20 from UOP (Lot #13923-57C) was washed three times with a 0.04 M $NaNO_3$ solution (Aldrich Chemical Company, Lot #08407EX). It was impregnated by mixing 9.36×10^{-3} mol $(CH_3CO_2)_2Cu \cdot xH_2O$ 98% (Aldrich Chemical Company, Lot #03319AW) with 10 g washed zeolite in 250 ml de-ionized H_2O. The mixture was dried overnight at 303 K with a Büchi rotavap. The catalyst was calcined in flowing O_2 (180 ml/min) from 298 to 773 K at 0.66 K/min and held at 773 K for 2 h to remove organic ligands. The catalyst was cooled to room temperature in O_2. The chemical composition of the catalyst was determined by inductively coupled plasma (ICP) (Thermo Jarrel Ash Corp., Atomscan 25 spectrometer). The Cu content of the catalyst was 4.91 wt%.

2.2. REACTION STUDIES

The reduction experiments were conducted in a flow reactor made of stainless steel tubes and a quartz reactor containing 250 mg catalyst supported on a 25–50 μm porous frit, 10 mm in diameter. The bed depth was approximately 1 mm. The catalyst was reduced in flowing H_2 (30 ml/min) while heating from 298 to 773 K and held for 2 h at 773 K. Then the catalyst was purged for 0.5 h in flowing He (30 ml/min) before the reaction was started. All reactions were conducted at 773 K. The gas flow rates were regulated by mass flow controllers, and the total gas flow rate was maintained at 100 ml/min. The NO concentration was 4000 ppm, and the N_2 yield was quantified by gas chromatography with an Alltech 13x molecular sieve column. The reactor was equipped with sealable teflon valves, so the catalyst could be moved to the TPR apparatus without exposing to air.

2.3. TEMPERATURE-PROGRAMMED REDUCTION (TPR)

The apparatus used for the TPR experiments was described by Tzou et al. [13]. The sample was purged with Ar (30 ml/min) for 0.5 h at 298 K and the system was cooled in flowing Ar to 193 K. Then the sample was heated in 5% H_2 in Ar (30 ml/min) at 8 K/min while H_2 consumption was recorded.

3. Results and discussion

Our results in figs. 1 and 2 show that the reduction of NO strongly depends on the nature of the reducing molecule and the oxygen content of the gas mixture. With CH_4 the yield decreases precipitously and remains below 15% for all mixtures containing $\geqslant 1\%$ O_2 (fig. 1). Without O_2, the N_2 yield reaches 46%. Previously Iwamoto and Hamada [12] had classified reductants into two groups, selective (C_2H_4, C_3H_6, C_3H_8, C_4H_8) and non-selective (H_2, CO, CH_4, C_2H_6) for NO abatement in the presence of O_2. Similar results had been obtained by Truex et al. [14].

Selective reduction of NO by C_3H_8 is illustrated in fig. 2. The highest yield (94%) was observed in the presence of O_2 at 773 K and $W/F = 0.15$ g s cm^{-3}. At O_2 concentrations below that necessary for complete combustion of C_3H_8,

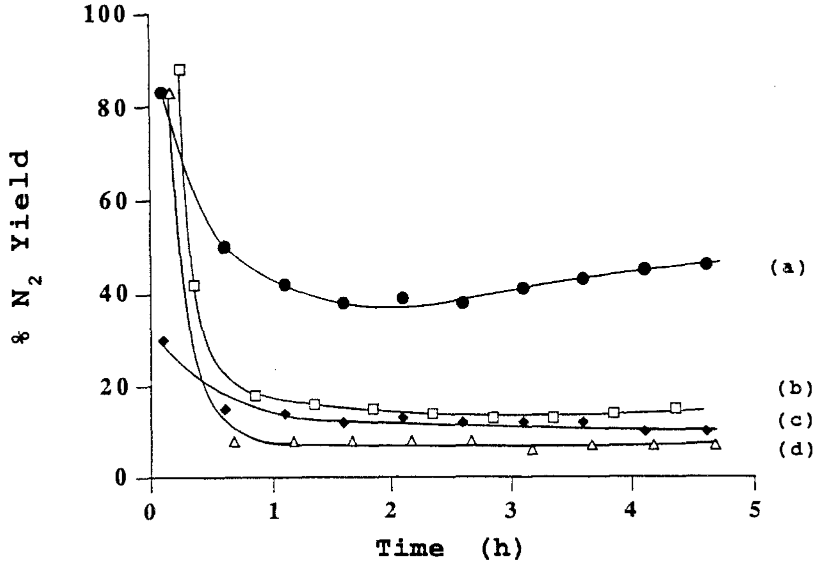

Fig. 1. Effect of O_2 on NO reduction with CH_4. (a) 0% O_2, (b) 1% O_2, (c) 6% O_2, and (d) 10% O_2. Temperature 773 K, 4000 ppm NO, 4000 ppm CH_4, $W/F = 0.15$ g s cm^{-3}.

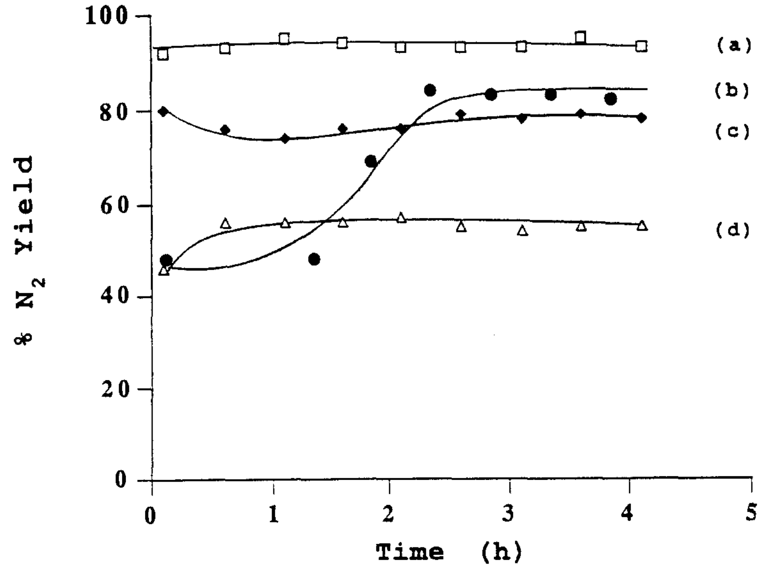

Fig. 2. Effect of O_2 on NO reduction with C_3H_8. (a) 1% O_2, (b) 0% O_2, (c) 6% O_2, and (d) 10% O_2. Temperature 773 K, 4000 ppm NO, 4000 ppm C_3H_8, W/F = 0.15 g s cm^{-3}.

i.e. $O_2/C_3H_8 = 5/1$ (2% O_2), the N_2 yield increases (fig. 3). This suggests that a partial oxidation product of the $C_3H_8 + O_2$ reaction is instrumental in reducing NO, as suggested by Truex et al. [14]. The present finding that the N_2 yield

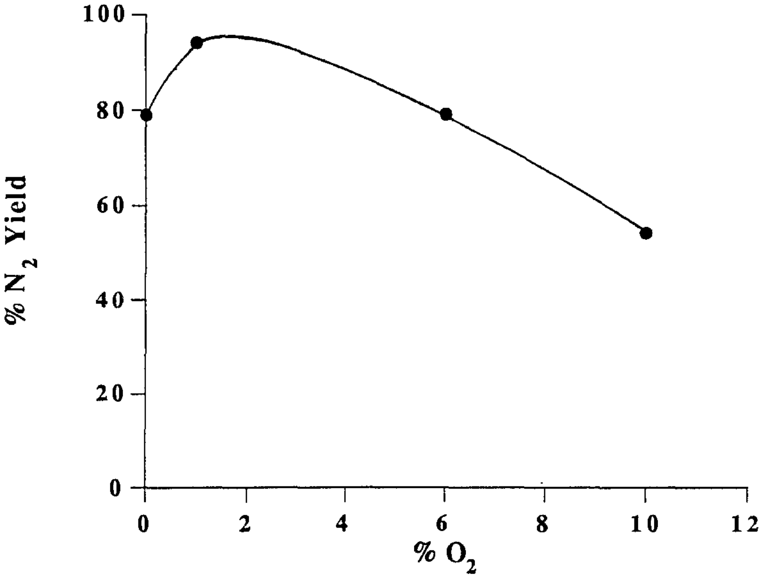

Fig. 3. Combined effects of O_2 and C_3H_8 on N_2 yield. Temperature 773 K, 4000 ppm NO, 4000 ppm C_3H_8, W/F = 0.15 g s cm^{-3}.

increases with O_2 concentration below the stoichiometry of total combustion of C_3H_8 to $3CO_2 + 4H_2O$ gives further credence to this hypothesis. However, with propene as the reductant and an excessively ion-exchanged Cu/ZSM-5 catalyst Iwamoto observed a broad maximum in N_2 yield for O_2/C_3H_6 ratios between 8 and 20 instead of the stoichiometric ratio of 4.5 [9].

In the present work a 10% O_2 concentration, i.e. an O_2/C_3H_8 ratio of 25, still gave a N_2 yield greater than 50%. The problem has, therefore, been addressed whether incomplete combustion of C_3H_8 to CO and subsequent interaction of CO with NO might be an essential mechanism. We tested mixtures of NO, CO, and O_2 and compared these results with the test of NO, C_3H_8 and O_2. In the region where the N_2 yield increases with O_2 concentration each C_3H_8 molecule was replaced with three CO molecules and a N_2 yield of less than 20% was obtained. This suggests that the N_2 yield enhancement by C_3H_8 is not attributed to CO resulting from oxidation of C_3H_8. In mixtures of NO with O_2 concentrations greater than 2% and a larger excess of CO the N_2 yield is less than 16%. It therefore follows that the high efficiency of C_3H_8 at large O_2 concentrations must be due to either a partial oxidation product other than CO or to some specific effect of C_3H_8 on its reaction intermediates on the nature of the Cu sites.

Temperature-programmed reduction showed that the oxidation state of the catalyst increased with increasing O_2 concentration (fig. 4). After reaction with NO, C_3H_8, and O_2 the catalyst had a reddish color for O_2 concentrations $\leqslant 1.7\%$, indicating the presence of metallic Cu. Temperature-programmed

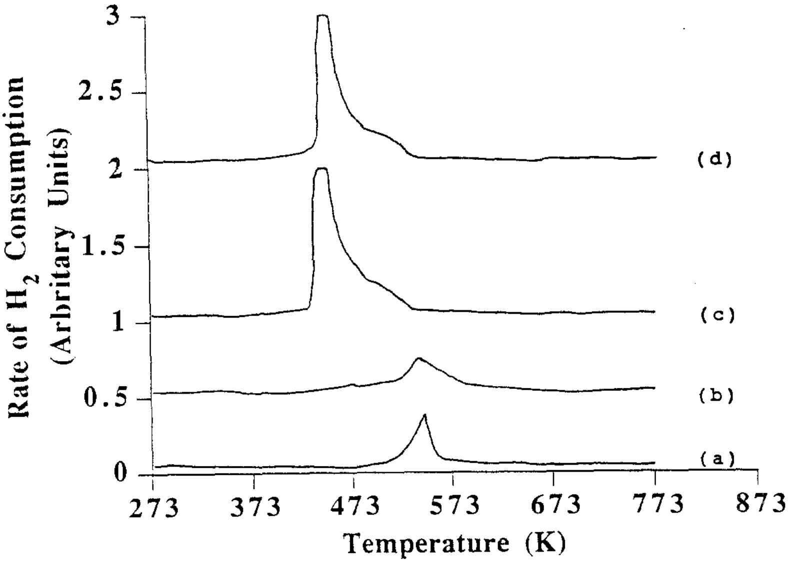

Fig. 4. Temperature-programmed reduction of Cu/ZSM-5 after reaction with C_3H_8 in the presence of various amounts of O_2. (a) 0% O_2, (b) 1.7% O_2, (c) 3.3% O_2, and (d) 4.1% O_2.

reduction revealed that more than 65% of the Cu was zero-valent (figs. 4a, 4b). At higher O_2 concentrations TPR showed that one species was reduced by H_2-TPR at 443 K (figs. 4c, 4d), the H_2 consumption corresponding to complete reduction of Cu^{2+} to Cu^0. The assignment of this TPR peak to CuO was confirmed by a second TPR after re-oxidizing with O_2 at 473 K; the same peak at 443 K was formed. Excessively exchanged Cu-ZSM-5 showed the presence of the same oxide with the same characteristic TPR peak at 443 K [15]. A TPR peak at 423 K was observed for Cu/Na Y [16]. It should be noted that the TPR peak ascribed to CuO occurs at a substantially lower temperature than that of bulk CuO. Moretti and Sachtler [16] suggested that well dispersed CuO particles on the zeolite could be reduced at a much lower temperature than larger CuO particles.

4. Conclusions

Impregnation is an effective technique for preparing Cu-ZSM-5 NO abatement catalysts. Impregnated Cu-ZSM-5 selectively reduces NO in the presence of C_3H_8 and excess O_2. With 4000 ppm NO and 4000 ppm C_3H_8, the yield of N_2 increases with O_2 concentration less than 2%. The position of this maximum corresponds to an O_2/C_3H_8 ratio sufficient for total combustion of C_3H_8. At higher O_2 concentrations the N_2 yield decreases, but remains substantially higher than that obtained with CH_4 and CO. TPR showed that Cu in the catalyst was oxidized to CuO. The data suggest that the combination of C_3H_8 and O_2 is due to a reaction intermediate of C_3H_8 oxidation which reacts strongly with NO, but CO has been eliminated as a potential candidate for this.

Acknowledgement

A grant in aid by the Mobil Corporation is gratefully acknowledged.

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