On the unusual stability of overexchanged FeZSM-5

Xiaobing Feng and W.K. Hall

Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260, USA

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It is the purpose of this Letter to announce the development of a zeolitic catalyst that is more active than CuZSM-5, durable, and free from poisoning by H_2O and/or SO_2. Therefore it may be of practical value in combustion catalysis. A preliminary report is given here; a more detailed one will follow shortly. The catalyst is an "overexchanged" FeZSM-5 made from NaZSM-5 in a special way to minimize H^+-bearing AlO_2^- sites.

Keywords: SCR; zeolite; FeZSM-5; NO_x catalyst; poison resistant SCR catalyst

1. Introduction

CuZSM-5 has been widely studied as a potential catalyst for the selective reduction (SCR) of NO_x to N_2 by hydrocarbons in the presence of excess O_2. Whereas in a "dry" gas stream it has sufficient activity, the most recent reviews [1,2] have pointed out that (a) it is severely poisoned by the H_2O that is unavoidably produced in the combustion process within the engine, and (b) undergoes dealumination and physical breakdown by severe steaming under reaction conditions. Grinsted et al. [3] found that an overexchanged CuZSM-5 with Si/Al = 40 made from HZSM-5 underwent dealumination accompanied by an activity that "decreased rapidly" when exposed to steam. Petunchi et al. [4] reported that in the absence of insufficient O_2, Cu^{2+} was reduced to Cu^0 with H^+ satisfying the base-exchange capacity and that it was these Brønsted sites that preferentially underwent dealumination. Monroe et al. [5] reported that their CuZSM-5 catalyst lost 80% of its initial activity in 4 h in a simulated engine test. Armor [1] has noted that CoZSM-5 "does appear to be much more hydrothermally stable" than CuZSM-5, but suggested that new catalyst compositions will be needed for practical applications. The durability of CoZSM-5 and CoFerrierite was tested [1]. A "substantial decrease" in NO conversion occurred when H_2O and SO_2 were added.

2. Experimental

The catalyst compositions are denoted by the principal base-exchange cation, the zeolite structure followed by the Si/Al ratio and the extent of exchange, e.g., FeZSM-5-20-183. (The last figure is calculated on the assumption that one Cu^{2+} replaces two Na^+. This assumption is untrue, but the convention is well established.) As noted many years ago [6], Fe^{2+} readily oxidizes to FeOOH in aqueous solutions so special techniques, even more stringent with ZSM-5 and ferrierite than with faujasite, are required to avoid this problem. These will be described in detail later. The parent zeolite used herein was NaZSM-5-20-100 furnished by Air Products and Chemicals Company.

Catalytic tests were carried out in the microreactor used in our recent work [4,7] slightly modified to permit introduction of H_2O and independently SO_2. This was accomplished by replacing a portion of the inert He stream with an equal volume of H_2O/He or H_2O/SO_2/He. Mixing with NO/He, O_2/He and i-C_4H_{10}/He occurred at the inlet of the reactor and in the 250 mg pure silica gel preheater ahead of the 50 mg of catalyst. The primary gas stream contained 2000 ppm NO, 2000 ppm i-C_4H_{10} and 3% O_2 with He to 1 atm. Since the total flow rate was 70 ml/min, the corresponding space velocity

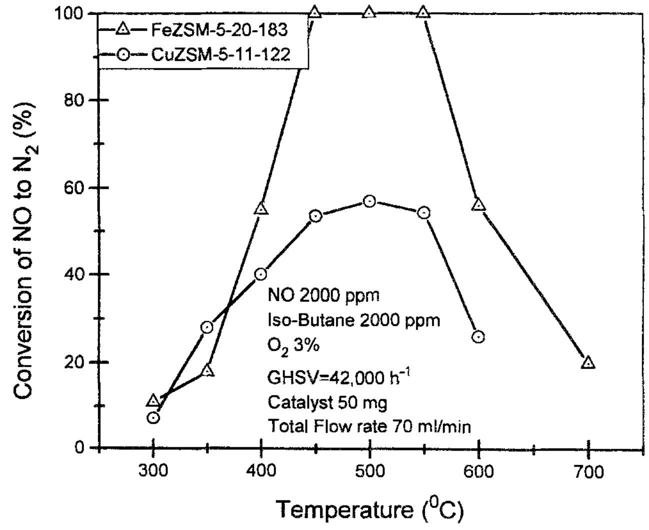

Fig. 1. Comparison of the conversion of NO into N_2 as a function of temperature for FeZSM-5 vs. CuZSM-5.

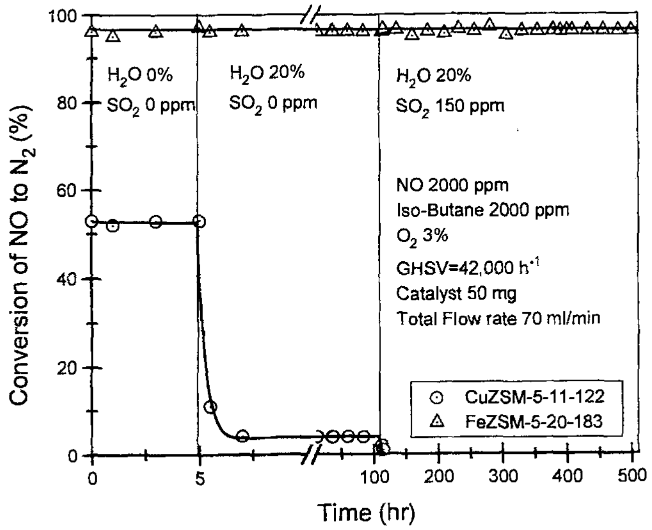

Fig. 2 Comparison of the effects of adding H_2O or H_2O and SO_2 to the same gas stream over FeZSM-5 vs. CuZSM-5 at 500°C. Percent conversion to N_2 is shown vs. time on stream.

was 42 000 h^{-1}. Product gases were determined by on-line GC as described elsewhere [8]. The reactor temperature was maintained constant at the desired value within ±1.0°C.

3. Results and discussion

The conversion of NO to N_2 at various temperatures over FeZSM-5-20-183 is compared with that for CuZSM-5-20-122 in fig. 1. It is seen that the former is about twice as active as the latter in the critical temperature range $450 < T < 550°C$ where 100% conversion was obtained with the FeZSM-5. This conveniently broad temperature range is sensitive, however, to space velocity and perhaps to other as yet unexplored variables, e.g., gas composition. These data were obtained with "dry" feed gas containing only the H_2O produced in the SCR reaction.

Fig. 2 shows the effects of added H_2O and/or SO_2 on the conversion to N_2. Whereas the CuZSM-5 became completely deactivated within the first 10–15 min, the FeZSM-5 catalyst was unaffected by either H_2O or SO_2 for extended periods. The present data showed no appreciable decrease in the 95% conversion to N_2 at 500°C in 20% H_2O plus 150 ppm of SO_2 for periods of up to 500 h. In earlier unpublished work, Segawa et al. [9] found no effect of 10% added H_2O for a period of 40 min at 300°C. Presently we are extending our data targeted at 2500 h (equivalent to the Federal mandate of 100 000 miles at 40 mph).

Acknowledgement

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