Mat. Res. Bull., Vol. 18, pp. 269-273, 1983. Printed in the USA.
0025-5408/83/030269-05$03.00/0 Copyright © 1983 Pergamon Press Ltd.

CATALYTIC ACTIVITY OF HY-TYPE ZEOLITE FOR THE DISPROPORTIONATION OF NITROGEN MONOXIDE

Yoshinori Kanno* and Hisao Imai**

* Government Industrial Research Institute,Nagoya
1,Hirate-cho,Kita-ku,Nagoya 462,Japan
** Research Laboratory of Engineering Materials,
Tokyo Institute of Technology; Nagatsuta-cho,
Midori-ku, Yokohama 227,Japan

(Received January 3, 1983; Communicated by J. B. Goodenough)

ABSTRACT

The disproportionation of NO on HY-type zeolite was carried out at 15°C by a pulsed microreactor. The catalytic activity began to appear at the pretreatment temperature 500°C and showed its maximum in the region of 600 to 700°C. The Lewis acid sites of HY-type zeolite seem to act as the active sites. TPD profiles after the reaction were composed of three peaks. The amount of peak β also showed its maximum at the pretreatment temperature ca. 600°C.

Introduction

The disproportionation of NO ($4NO = N_2O + N_2O_3$) on zeolites was first reported by Addison and Barrer(1). Although a few infrared studies(2,3) were made for elucidating the reaction mechanism, the nature of the active sites was not established. Later, the disproportionation of NO on MgHY-type zeolites with different degrees of ion exchange was carried out by a pulsed microreactor, and the concentration of the bare magnesium ions located in the Site II of the faujasite structure was determined by the measurement of CO chemisorption, which was the technique used by Egerton and Stone(4). The results indicated that the active sites for this reaction were magnesium ions located on Site II of the MgHY-type zeolites(5).

The disproportionation of NO on alkaline-earth metal oxides has been investigated by infrared spectroscopy(6) and by a pulsed microreactor(7). The results indicated that the disproportionation of NO was catalyzed not only by the zeolites exchanged with various metal ions, but also by alkaline-earth metal oxides. The activity sequence was obtained as follows: MgO > CaO > SrO > BaO. The disproportionation of NO on Y-type zeolites exchanged with various metal ions has also been investigated(8). The results indicated that alkaline-earth Y-type zeolites showed high activity, and the order of catalytic activity was obtained as follows: CaY > CdY > MgY > ZnY > LaY > BeY > NaY > LiY > KY > SrY > BaY, AgY, HgY, FeY, AlY = 0. The surface of an HY-type zeolite, if suitably activated, may possess both oxidizing and reducing properties, and catalytic activity appears on elevating the pretreatment temperature(9). The purpose of the present study was to see whether an HY-type zeolite shows catalytic activity for the disproportionation of NO.

Experimental

An NaY-type zeolite(SK-40) was ion-exchanged 16 times at 90°C in 10% solutions of ammonium nitrate. The resultant NH_4Y-type zeolite was washed 3 times by 0.1N ammonia solution and dried overnight at 110°C. Chemical analysis of the sample was done by flame spectrophotometry and gravimetry; it showed the unit-cell composition corresponding to $(NH_4)_{56.2}Na_{0.8}(AlO_2)_{57}(SiO_2)_{135}\,nH_2O$. The NH_4Y-type zeolite was pressed into tablets,crushed, and sized(32 ~ 60 mesh). The HY-type zeolite was prepared by removal of ammonia from the NH_4Y-type zeolite. The specific surface area of the HY-type zeolite was calculated to be 1032 m^2/g from the nitrogen adsorption isotherm. Measurement of catalytic activity and the TPD profile were carried out as described in the previous paper(8). The effluent gas of the TPD experiment was analyzed with gas chromatography with Porapak T and a Molecular Sieve 13X column kept at 50°C using He carrier gas.

Results and Discussion

Catalytic activity and pretreatment temperature

Fig. 1 shows the relationship between the catalytic activity for the disproportionation reaction $4NO = N_2O + N_2O_3$ and the pretreatment temperature. The catalyst treated at 400°C showed no activity, which coincided with the results obtained by Chao and Lunsford(3). The catalytic activity increased with pretreatment temperature from 500°C, to a broad maximum in the temperature region 600 to 700°C; it decreased gradually with a further increase in the pretreatment temperature, disappearing above 800 °C. X-ray examination showed that this decrease was due to the collapse of crystalline structure.

Flockhart et alii suggested that an ESR study of the redox properties of HY-type zeolites gave information about the nature of the

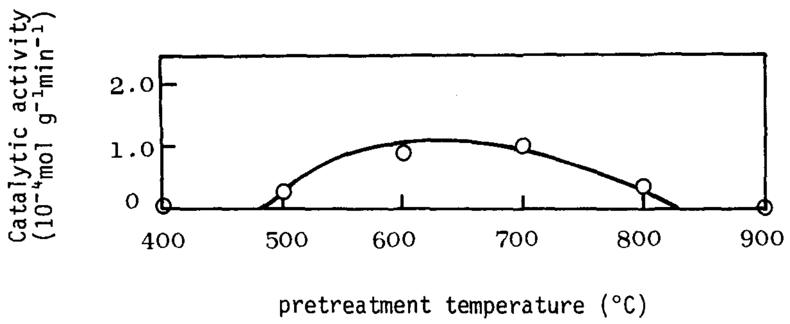

Fig.1 Catalytic activity plotted against pretreatment temperature

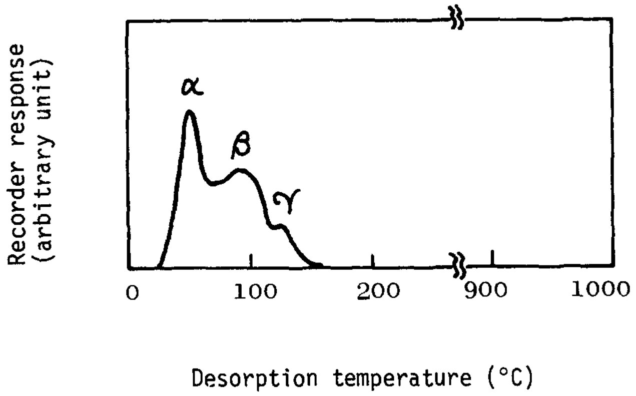

Fig.2 TPD spectra (pretreatment temp. 600°C)

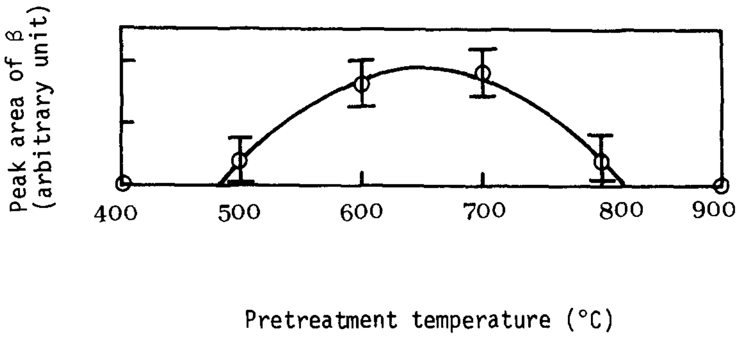

Fig.3 Peak area of β plotted against pretreatment temperature

sites responsible for oxidizing and reducing activities(10). They reported that Perylene adsorbed on an activated HY zeolite gave the nine-line spectrum attributed to the corresponding cation radical, the maximum radical concentration occurring at ca. 625°C. Since maximum reducing and oxidizing power in an HY-type zeolite requires activation temperatures around 600°C, dehydroxylation is necessary for the formation of the active centers. They also described that electron-transfer activities decrease with the collapse of its crystal structure at higher temperatures(11). It has also been reported that pretreatment at temperatures above 500°C results in dehydroxylation and formation of Lewis acid sites(12). It is ,therefore, reasonable to consider that Lewis acid sites have effects upon the disproportionation of NO.

TPD profile

TPD profiles were measured in order to get information about adsorbed species staying on the catalyst surface after the reaction. Fig. 2 shows the profile for a catalyst treated at 600 °C. The profile was composed of three peaks(α,β,γ) which agreed with that of Y-type zeolites exchanged with various metal ions(8). It turned out from the gas analysis that peaks α and β were mainly composed of NO and peak γ was N_2O.

The previous paper suggested that peak α was considered as the unreactive adsorbed NO and peak β seemed to be NO arising from the dissociation of N_2O_3 formed by the disproportionation: $N_2O_3 \rightarrow$ NO(peak β) + NO_2 (NO_2 was adsorbed in NaOH-packed column). Peak γ was regarded as the more strongly bonded N_2O(8). The amount of peak β, therefore, could be regarded as the index of N_2O_3 formed via disproportionation.

Fig. 3 shows the relationship between the peak area of β and the pretreatment temperature. It is clear, from figures 1 and 3, that the peak area of β corresponds well to the catalytic activity. In spite of the low resolution of the TPD peaks(α,β,γ), quantitative analysis of effluent gas of the catalyst treated at 600°C was made in order to determine the reaction stoichiometry. The results indicate that N_2O determined from pulse reaction is calculated to be 1.15×10^{-7} mol(a), N_2O contributing to peak γ is to be 1.9×10^{-8} mol(b), and N_2O_3 formed by the disproportionation is to be 1.1×10^{-7} mol(c). The algebraic sum of (a) and (b) nearly equals (c), which means that the amount of N_2O formed by this reaction is about equal to that of the N_2O_3 formed. Therefore, these results indicate that N_2O (in gas phase) and N_2O_3 (on catalyst surface) were formed by the disproportionation reaction $4NO = N_2O + N_2O_3$.

Conclusion

It was confirmed that the disproportionation of NO occurred on HY-type zeolite.

References

1. W.E.Addison and R.M.Barrer,J.Chem.Soc.,1955,757.
2. A.V.Alekseyev,V.N.Filimonov,and A.N.Terenin,DOK.Akad.Nauk. SSSR,147,1392(1962).
3. C-C.Chao and J.H.Lunsford,J.Am.Chem.Soc.,93,71(1971).
4. T.A.Egerton and F.S.Ston,J.Chem.Soc.,Farady Trans.I,69,22 (1973).
5. Y.Kanno and H.Imai,Nippon Kagaku Kaishi,1982,1559.
6. M.J.D.Low and R.T.Yang,J.Catal,34,479(1974).
7. Y.Kanno and H.Imai,Chem.Lett.,1982,723.
8. Y.Kanno and H.Imai,Mat.Res.Bull.,17,1161(1982).
9. J.Turkevich and Y.Ono,"Advances in Catalysis and Related Subjects",vol.20,p.135,Academic Press,(1969).
10. B.D.Flockhart,L.Mclonghlin and R.C.Pink,J.Catal.,25,305(1972)
11. B.D.Flockhart,M.C.Megarry and R.C.Pink,"Molecular Sieves", ACS,(1973),p.509.
12. J.W.Ward,J.Catal.,9,225,396(1967).