Journal of Molecular Catalysis, 69 (1991) L7–L13

JOURNAL OF
MOLECULAR
CATALYSIS
Letter

Infrared study of the disproportionation reaction of nitric oxide on NiY zeolite

Huang Minming, Yuan Chunhua and **Chen Kunsong**
Department of Modern Chemistry, University of Science and Technology of China, Hefei 230026 (China)

(Received July 14, 1990; revised July 9, 1991)

Introduction

The disproportionation reaction of nitric oxide occurs on a series of zeolites [1]. A detailed infrared study of this reaction on Y-type zeolites has been reported by Chao and Lunsford [2], which shows that low temperature (195 K) is required for NaY and decationated Y, whereas CaY can catalyze the reaction at room temperature. Moreover, NiY zeolite has been characterized by many authors using IR techniques. It is accepted [1] that the adsorption of NO on NiY produces a single band which was first reported by Naccache and Ben Taarit [3], and even dehydration before adsorption is not necessary [4] because NO is a stronger ligand than water. However, the band location reported in the literature varies from 1890 [1] to 1910 cm^{-1} [5] depending on the reporting laboratories. The latter position is actually the same as one of the bands belonging to N_2O_3 produced from NO disproportionation. Therefore, an IR investigation has been carried out on NiY zeolite upon exposure to NO, in order to explore the disproportionation reaction and further confirm the band position for NO adsorption on NiY.

Experimental

The zeolite sample was prepared by aqueous ion exchange at 333 K from NaY and $Ni(NO_3)_2$ solution, with a degree of exchange of 60.7%. For the IR experiments, the sample was pressed into self-supporting wafers (ca. 10 mg cm^{-2}) and mounted in a conventional high vacuum IR cell (10^{-3} Pa). Normally, the wafers were dehydrated at different temperatures and then cooled in vacuum, followed by introduction of 50×10^2 Pa NO at 313 K. Spectra were recorded on a Nicolet 5DX FTIR spectrophotometer operating at 4 cm^{-1} resolution and generally one hundred 1-second scans of the region 4600–600 cm^{-1} were averaged.

0304-5102/91/$3.50
© Elsevier Sequoia/Printed in The Netherlands

Results and discussion

After dehydration at 723 K for 1 h, exposure to NO followed by brief evacuation produced one band at 1892 cm^{-1}, consistent with most of the literature data. Nevertheless, nitric oxide remaining in the IR cell exhibited completely different spectra, shown in Fig. 1. New peaks appeared at 1273, 1305, 1400(doublet), 1470, 1567, 1912, 2120, 2197 and 2236(shoulder) cm^{-1}, as well as the 1892 cm^{-1} band. All of these bands grew in intensity at different rates with time of exposure. The 1892 cm^{-1} band was certainly the fastest. Thus, after 90 min of exposure, the 1912 cm^{-1} band could not be distinguished from the line at 1892 cm^{-1}. Since the 1912, 1567 and

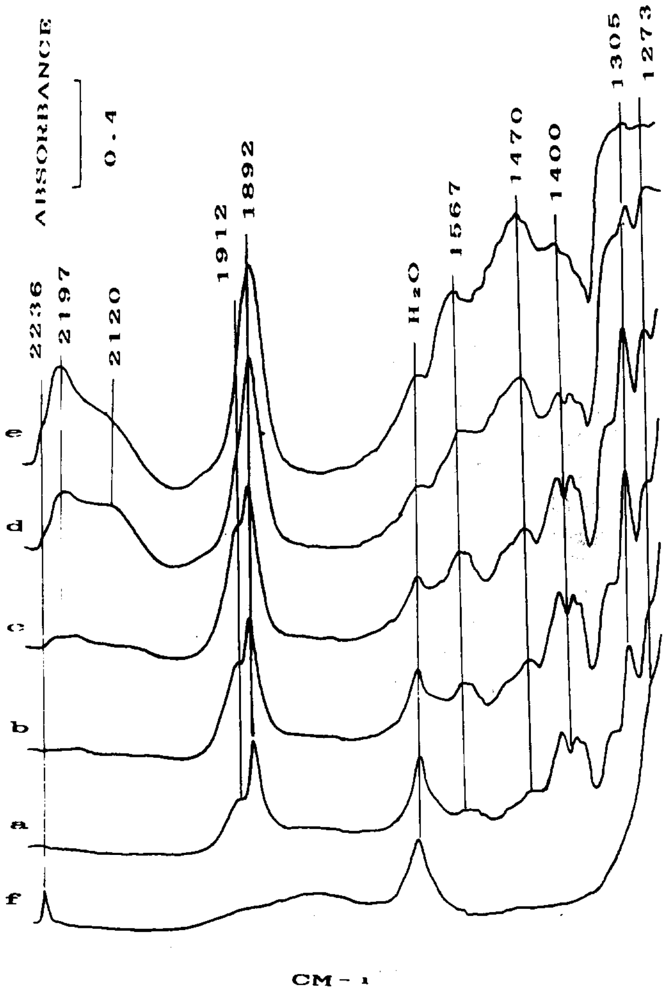

Fig. 1. IR spectra of NiY dehydrated at 723 K for 1 h followed by exposure to 5000 Pa NO at 313 K for (a) 5 min, (b) 15 min, (c) 30 min, (d) 60 min, (e) 120 min, (f) spectrum obtained after adsorption of 500 Pa N_2O at room temperature on a partially dehydrated NiY sample.

1305 cm^{-1} bands always changed simultaneously and their positions were very close to those observed on NaY, in agreement with Chao and Lunsford [2], these bands were assigned to adsorbed N_2O_3. It was also reported [2] that the adsorption of N_2O on Y-type zeolites produces a major peak around 2250 cm^{-1}, however, this band was weak and broad at room temperature [6]. In order to establish the identity of IR absorption of N_2O on NiY, 500 Pa pure N_2O was added at room temperature, and peaks at 2236 as well as 1273 cm^{-1} (very weak) appeared (Fig. 1f). Therefore, it is understood that the shoulder at 2236 cm^{-1} (masked by the 2197 cm^{-1} band) and part of the 1273 cm^{-1} peak in Fig. 1a–1e were due to adsorbed N_2O. The presence of both N_2O_3 and N_2O then suggested that the disproportionation of NO (eqn. (1)) occurred on NiY even at room temperature with low NO pressure.

$$4NO \longrightarrow N_2O_3 + N_2O \tag{1}$$

Another part of the 1273 cm^{-1} band was attributed to nitrite ions [7] present in zeolites under various conditions [2]. In this work the nitrite ions originated from the hydrolysis of nitrosonium ion, which will be commented on later. All other bands were basically the same as those found in the NO–NaY system [2] when the disproportionation reaction occurred. Consequently, the 2197 and 2120 cm^{-1} bands are assigned to adsorbed $NO_2{}^+$, which also arose from the disproportionation, the 1470 cm^{-1} band was due to a nitrito complex, and a doublet at 1400 cm^{-1} was assigned to adsorbed $NO_3{}^-$ which is produced from the decomposition of N_2O_3. Apparently, the above-mentioned argument is mainly based on the convincing work on Y zeolites carried out by Chao and Lunsford [2], the new contribution here merely that the 1912 cm^{-1} band on NiY indicates the disproportionation reaction, which would be easily overlooked because of the close proximity of the 1912 and 1892 cm^{-1} bands.

It was noticed that the spectra shown in Fig. 1 still exhibited a water band at 1635 cm^{-1}. Therefore, further experiments were performed in two extreme cases: (1) exposure to NO on a hydrated sample (after evacuation at room temperature), and (2) the sample was strongly dehydrated at 773 K for 2 h to eliminate water completely. In the former case the band at 1892 cm^{-1} appeared but the other bands due to disproportionation disappeared except for a weak band at 1273 cm^{-1} (Fig. 2a). Moreover, the 1892 cm^{-1} band did not increase but decreased in intensity with time of exposure (Fig. 2b), while the band at 1273 cm^{-1} increased slightly. Kasai [4] assigned the 1892 cm^{-1} to species Ni^{1+}–NO and concluded that the Ni^{2+} ions in hydrated NiY were reduced to Ni^+ by NO, due to the hydrolysis reaction following the reduction:

$$Ni^{2+} + NO \longrightarrow Ni^{1+}{-}NO^+ \xrightarrow{+NO} Ni^{1+}{-}NO + NO^+ \tag{2}$$

$$NO^+ + H_2O \longrightarrow H^+ + HNO_2 \tag{3}$$

The appearance of the 1273 cm^{-1} band was consistent with the product HNO_2; on the other hand, the formation of protons could not be confirmed in the IR hydroxyl region due to masking caused by the presence of water.

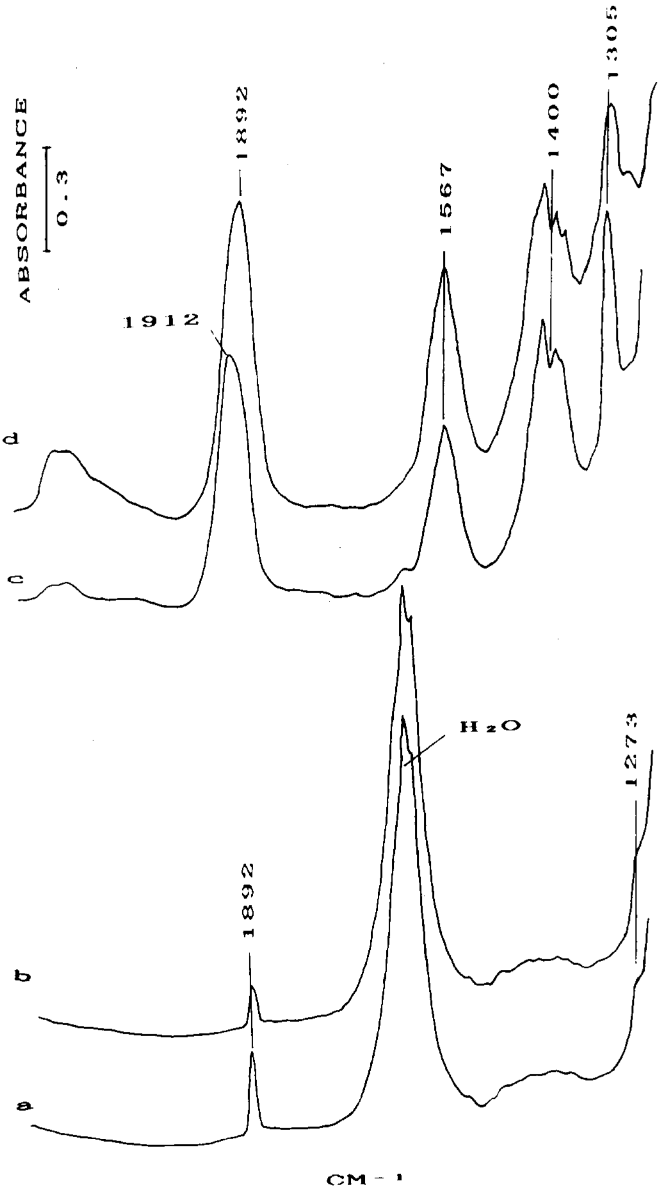

Fig. 2. IR spectra of hydrated NiY after exposure to 5000 Pa NO at 313 K for (a) 5 min, (b) 20 min; and spectra of NiY dehydrated at 773 K for 2 h followed by exposure to 5000 Pa NO at 313 K for (c) 10 min, (d) 20 min.

Therefore, after evacuation at 433 K, pyridine vapour was introduced at the same temperature. It was found that the characteristic band for pyridinium at 1543 as well as 1490 cm^{-1} became much stronger (nearly double), while the 1452 (Lewis acid) and 1441 cm^{-1} (attached to Na$^+$) bands were almost unchanged in this case, compared with those obtained on a hydrated sample without previous NO adsorption and measured under the same conditions. Thus the decline of the 1892 cm^{-1} band with time seems to offer further evidence for Kasai's suggestion.

In contrast, the adsorption of NO on the strongly dehydrated sample produced very intense bands belonging to the disproportionation products. Initially the 1912 cm^{-1} band was so strong that it completely obscured the 1892 cm^{-1} band (Fig. 2c). The subsequent change in intensity was quite similar to that shown in Fig. 1, that is, lengthy exposure also caused an increase in all bands and clear appearance of the 1892 cm^{-1} band. However, the 1273 cm^{-1} band could not be clearly detected in this case. Therefore it is concluded that the disproportionation of NO on NiY is facile but strongly depends on the existence of 'bare' Ni^{2+}, which probably has no water ligand. In contrast, the species $Ni^{+}-NO$ is relatively stable and the hydrolysis of nitrosonium ion, which formed during the reduction of Ni^{2+}, is relatively slow and strongly depends on the presence of water. It must be pointed out that disproportionation is increasingly facile at lower temperature. For example, even a partially dehydrated NiY also showed a very strong 1912 cm^{-1} band which obscured the 1892 cm^{-1} band after exposure to NO at 273 K.

After adsorption of NO on a dehydrated sample, degassing at room temperature for a long time usually left the doublet centered at 1400 cm^{-1}. However, subsequent readsorption of NO at room temperature could not produce IR bands belonging to disproportionation products, except for a strong band at 1892 cm^{-1}. Furthermore, in this case the spectrum remained unchanged with time of exposure. Similarly, the readsorption of NO on a hydrated and adsorbed–degassed sample also produced an intense 1892 cm^{-1} band unchanged with time of exposure. Keeping in mind that the 1892 cm^{-1} band is indicative of the $Ni^{1+}-NO$ species and that Ni^{2+} is necessary for both the disproportionation and the formation of NO^{+}, then the suppression of these two reactions could be explained by the consumption of Ni^{2+} during reaction (2).

In search of further evidence for this interpretation, the NiY sample was first reduced at 573 K in 5×10^{4} Pa H_2 for 1 h after dehydration. This special treatment [8] was employed in order to reduce most Ni^{2+} to Ni^{1+}. Subsequent admission of NO produced the 1892 cm^{-1} band without the accompanying bands due to N_2O_3 (Fig. 3a). However, a new band appeared at 1725 cm^{-1} which declined quickly with time of exposure and vanished completely after 50 min exposure. Concomitantly, the bands due to N_2O_3 appeared and gradually increased. The 1725 cm^{-1} band occurs in the stretching frequency region of the NO group observed in nitrosyl metal complexes [9]. For example, $Cr(NO)_4$ exhibited this band [10] at 1721 cm^{-1} and a series of nitrosyl–Ir complexes had this band [11] at 1715, 1720 and 1780 cm^{-1}. Thus, a reasonable assignment of this band in our case would be to the formation of a nitrosyl complex of nickel. The rapid disappearance of this band demonstrated the instability of the complex and its subsequent decomposition, which resulted in a partial oxidation of nickel to Ni^{2+} indicated by the

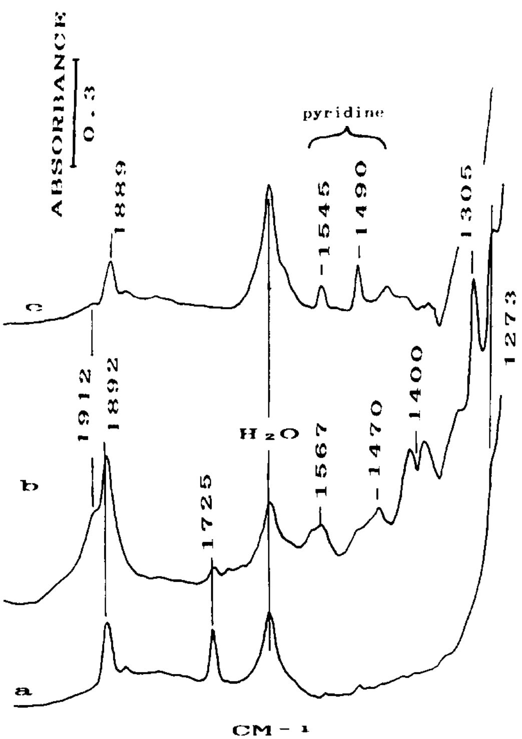

Fig. 3. IR spectra of NiY reduced with H_2 at 573 K for 1 h followed by exposure to 5000 Pa NO at 313 K for (a) 5 min, (b) 40 min, and (c) spectrum of dehydrated NiY after adsorption of trace pyridine followed by exposure to 5000 Pa NO at 313 K for 5 min.

reappearance of bands due to disproportionation products. In fact, the formation of Ni^{2+} was further evidenced by CO adsorption. Following the degassing in the above experiment, a new band appeared at 2214 cm^{-1} which is due to CO coordinated to Ni^{2+} located in supercages [12].

In another experiment, a trace of pyridine (under pressure <100 Pa) was first introduced after dehydration, and the subsequent exposure to NO resulted in a very weak 1912 cm^{-1} band (Fig. 3c) which also revealed a suppression of the disproportionation reaction. In fact, the change in band intensity was not very clear, and initially the band at 1892 cm^{-1} shifted to a lower frequency (1889 cm^{-1}). Since pyridine can only enter the supercages of Y zeolite, the suppression of the reaction revealed that the Ni^{2+} ions responsible for the disproportionation were located in the supercages.

In summary, we report here a facile disproportionation of NO on NiY zeolite. The active center for this reaction is the 'bare' Ni^{2+} located in the supercage. The hydrolysis of nitrosonium ion also accompanies the above reaction, provided water is present.

Acknowledgement

Financial support for this work was provided by the National Natural Scientific Research Council of China.

References

1 J. W. Ward, in J. A. Rabo (ed.), *Zeolite Chemistry and Catalysis* ACS Monograph No. 171, Washington D.C., 1976, p. 118.
2 C. C. Chao and J. H. Lunsford, *J. Am. Chem. Soc.*, *93* (1971) 71.
3 C. M. Naccache and Y. B. Taarit, *J. Chem. Soc., Faraday Trans. 1*, *63* (1973) 1475.
4 P. H. Kasai, R. J. Bishop and D. Mcleod, *J. Phys. Chem.*, *82* (1978) 279.
5 M. I. Vazquez, A. Corma and V. Fornes, *Zeolites*, *6* (1986) 271.
6 E. C. Delara and J. Vincent-Geisse, *J. Phys. Chem.*, *76* (1972) 945.
7 K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, Wiley, New York, 1963.
8 M. Kermarec, D. Ollvier, M. Richard, M. Che and F. Verduraz, *J. Phys. Chem.*, *86* (1982) 2818.
9 G. Socrates, *Infrared Characteristic Group Frequencies*, Wiley, Chichester, 1980, p. 145.
10 M. Herberhold and A. Razavi, *Angew. Chem. Int. Ed. Engl*, *11* (1972) 1092.
11 G. R. Clark, J. M. Waters and K. R. Whittle, *Inorg. Chem.*, *13* (1974) 1008.
12 C. L. Angell and P. C. Schaffer, *J. Phys. Chem.*, *70* (1966) 1413.