

Infrared Study of the Interaction between Nitric Oxide and Magnesium Oxide Catalyst

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Abstract

The interaction between NO and MgO catalyst, such as NO adsorption and its reduction with H_2 , was studied by infrared spectroscopy. For NO adsorption onto MgO, rather complicated bands were observed at around 850 cm^{-1} , $1100\text{--}1250\text{ cm}^{-1}$, $1300\text{--}1600\text{ cm}^{-1}$, and $2190\text{--}2200\text{ cm}^{-1}$, which were tentatively assigned to NO^- , NO_2^- , NO_3^- and N_2 species. An exchange reaction between the oxygen of adsorbed NO_2^- species and the lattice oxygen of the MgO surface was observed. It seems that the formation of adsorbed NO_2^- species proceeds mainly via disproportionation of NO, and partly via surface reaction between NO and the lattice oxygen of the MgO surface. The main product of $NO + H_2$ reaction was N_2O (more than 90%) with small amount of N_2 . The IR spectra during the reaction were very similar to those of NO adsorption, and no hydrogen containing species such as NH_x could be detected. The mechanism of $NO + H_2$ reaction on MgO was explained as proceeding via adsorbed NO_2^- species.

1. Introduction

Much attention has been paid to the catalytic reduction of nitrogen oxide from the point of view of environmental problems. In this connection NO adsorption on various catalysts has been studied using various techniques. Infrared spectroscopy gives important information about the geometrical structures and reactivities of adsorbed species on catalysts (LITTLE, 1966; TAMARU *et al.*, 1975, for example). NO adsorption on MgO has been studied by electron paramagnetic resonance spectroscopy (EPR) (LUNSFORD, 1967) and IR (CERRUTI *et al.*, 1974). In the EPR study, two paramagnetic species were observed, which were attributed to NO_2^{2-} ion, formed by the reaction between NO and surface oxygen at room temperature, and to molecular NO at around -180°C . In the IR study, complicated bands were attributed to several surface species such as NO_2^- , NO^- , and $N_2O_2^{2-}$ coordinated to Mg^{2+} . On the other hand, KAGAMI *et al.* (1981) recently observed that ammonia

decomposes steadily on MgO to form nitrogen and hydrogen in gas phase. It seems consequently that MgO is an interesting catalyst to study for reactions containing nitrogen species. In this report, the adsorption of NO and its reduction with hydrogen on MgO has been studied by means of infrared spectroscopy.

2. Experimental

Magnesium oxide powder (about 50 mg) from Merck was pressed into a disk 20 mm in diameter at 500 kgf/cm². Two such disks were put into an infrared cell, and were used for both infrared and reaction measurements.

The apparatus used for this study was similar to that described previously (TAMARU *et al.*, 1975). The infrared cell was attached to a closed circulation system, of which the total dead space was approximately 380 cm³.

Pretreatment of the catalyst was carried out as follows. The catalyst was gradually heated under vacuum up to 450°C and maintained at this temperature for 1 hour. The catalyst was then oxidized with 75 Torr of oxygen at 450°C for several hours. After evacuating for 30 minutes at the same temperature it was reduced with 75 Torr of hydrogen for about 20 hours, followed by evacuation for 30 minutes. Absorption peaks due to carbonate almost disappeared after the hydrogen treatment. Prior to each experiment, the sample was treated with hydrogen (75 Torr) at 450°C for about 20 hours, and was evacuated at 450°C for 30 minutes.

A Fourier transform infrared spectrometer, JEOL JIR-10, was used in single-beam operation. The resolution was set at 2 cm⁻¹ and each spectrum was obtained by summing up 256 scans. Infrared measurements were carried out after the cell was cooled to room temperature. The reaction products were analyzed by gas chromatography and mass spectrometry.

¹⁴N¹⁶O from Takachiho Chemical Co., Ltd. was purified by distillation under vacuum until residual nitrous oxide was not detected by both gas chromatography and infrared spectra. ¹⁵N¹⁶O (99.3 atom %) was obtained from Hikari Kogyo Co., Ltd. and used without further purification. ¹⁴N¹⁸O (96 atom %) was synthesized by discharging a mixture of ¹⁴N₂ and ¹⁸O₂. H₂ from Takachiho Chemical Co., Ltd. was purified by a Deoxo Pd tube and a liquid nitrogen cold trap.

3. Results and Discussion

3.1. Nitric oxide adsorption on MgO at room temperature

When NO was adsorbed on MgO at room temperature, rather complicated bands were observed in the infrared spectra. Fig. 1 shows the FT-IR spectra of ¹⁴N¹⁶O adsorbed on MgO at room temperature for various exposure times. In this system, the rate of adsorption was slow, and it took a long time to reach adsorption equilibrium as reported by CERRUTI *et al.* (1974). Even when MgO was exposed to NO for more than 20 hours, still changes in the IR bands were observed.

Figs. 2 and 3 show the FT-IR spectra of adsorbed ¹⁵N¹⁶O and ¹⁴N¹⁸O respectively.

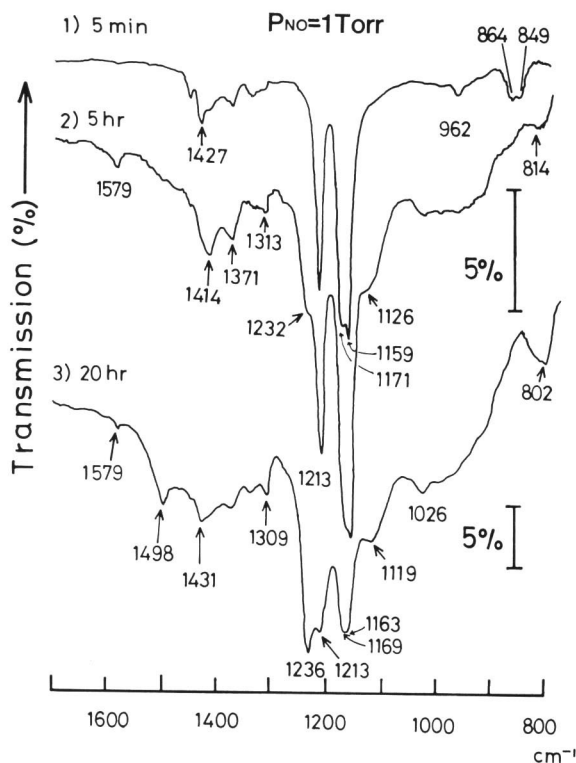


Fig. 1. FT-IR spectra of adsorbed species after $^{14}\text{N}^{16}\text{O}$ circulation on MgO at room temperature.

Each band between 800 and 1600 cm^{-1} showed isotope shifts for both $^{15}\text{N}^{16}\text{O}$ and $^{14}\text{N}^{18}\text{O}$, which suggests that these bands can be assigned to the species containing both nitrogen and oxygen. On the other hand, these bands were grouped by their behavior to evacuations and hydrogen treatments at various temperatures. The behavior of adsorbed $^{14}\text{N}^{18}\text{O}$ in H_2 treatment is shown in Fig. 4 for example. This behavior is essentially the same as that described in section 3.2 (see Fig. 7).

We tentatively assigned them according to the data of coordination compounds (NAKAMOTO, 1978) and the results of NO on MgO (CERRUTI *et al.*, 1974) and NO on CaO (LOW *et al.*, 1974). These results are summarized in Table 1, which are partly different from those reported by CERRUTI *et al.* (1974). They studied NO adsorption on high surface area MgO (previously degassed at 800°C) at room temperature by infrared spectroscopy, and observed quite complex bands at $800\text{--}900\text{ cm}^{-1}$, $1110\text{--}1250\text{ cm}^{-1}$ and $1350\text{--}1450\text{ cm}^{-1}$, which were assigned to NO_2^- ions with various configurations and NO^- and $\text{N}_2\text{O}_2^{2-}$ ions, coordinated to Mg^{2+} ions. For NO^- species, our results are in good agreement with them except the existence of two peaks separated about 10 cm^{-1} . In accordance with CERRUTI *et al.* (1974), we assigned these peaks to NO^- species adsorbed on Mg^{2+} in a bent form. The two peaks may come

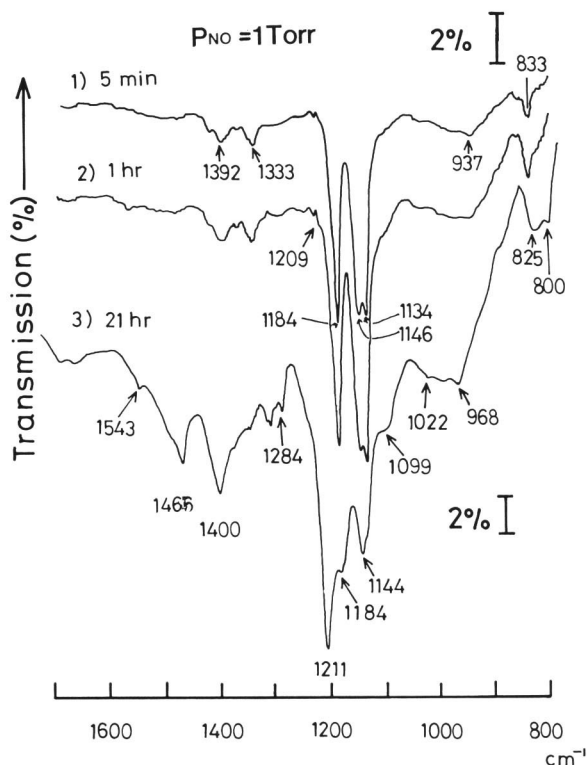


Fig. 2. FT-IR spectra of adsorbed species after $^{15}\text{N}^{16}\text{O}$ circulation on MgO at room temperature.

from sites of slightly different nature.

In Table 1, adsorbed N_2 species are also listed. These bands are detectable after heating above 150°C . Low *et al.* (1974) observed the 2175 cm^{-1} band after degassing above 300°C in the case of NO adsorption on CaO. They attributed it to NO^+ species on CaO, which is very similar to those around 2200 cm^{-1} observed in this study. These bands observed in this study exhibited reasonable isotope shift when $^{15}\text{N}^{16}\text{O}$ was adsorbed, but did not when $^{14}\text{N}^{18}\text{O}$ was adsorbed, which suggests that they are not due to oxygen containing species. We assigned them to adsorbed N_2 species in accordance with the case of NH_3 decomposition on MgO (KAGAMI *et al.*, 1981). It should be noted that as for NH_3 decomposition on MgO, a broad band at 2080 cm^{-1} was also observed and was assigned to adsorbed N_2 species. However, for NO adsorption and $\text{NO} + \text{H}_2$ reaction (see section 3.2) on MgO, that broad band was not observed. This difference will be discussed in section 3.2.

It seems that NO_2^- species are mainly produced by the disproportionation of NO, because an appreciable amount of N_2O was observed in the gas phase at the initial stage of NO adsorption. But there is some experimental evidence that the lattice oxygen of MgO surface seems to be involved in the formation of adsorbed NO_2^-

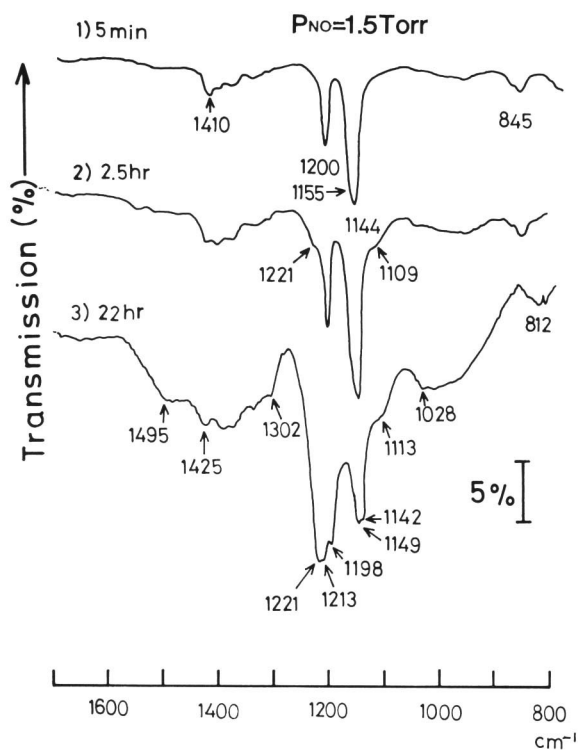


Fig. 3. FT-IR spectra of adsorbed species after $^{14}\text{N}^{18}\text{O}$ circulation on MgO at room temperature.

species, as described below. Fig. 3 shows the time dependence of adsorbed $^{14}\text{N}^{18}\text{O}$ on MgO. At first, the bands at 1200 and 1221 cm^{-1} were observed, which could be attributed to adsorbed $\text{N}^{18}\text{O}_2^-$ and $\text{N}^{18}\text{O}_3^-$ respectively. But in 22 hours, another band at 1213 cm^{-1} appeared between these two bands, which was similar to that of $\text{N}^{16}\text{O}_2^-$ species in the case of $^{14}\text{N}^{16}\text{O}$ adsorption, and may be attributed to NO_2^- species containing ^{16}O . Therefore, it seems likely that lattice oxygen would partly participate in the formation of adsorbed NO_2^- species.

After MgO was exposed to $^{14}\text{N}^{18}\text{O}$ at room temperature for 22 hours, 50 Torr of hydrogen was circulated over the catalyst at various temperatures. These results are shown in Fig. 4. The change in the spectra up to 200°C is similar to the case of $^{14}\text{N}^{16}\text{O}$ and $^{15}\text{N}^{16}\text{O}$ adsorption. Above 300°C , however, the band at 1221 cm^{-1} , which had almost disappeared at 200°C , came back again. The 1221 cm^{-1} band at room temperature is assigned to $\text{N}^{18}\text{O}_3^-$ species, but NO_3^- on MgO is unstable so that it decreases immediately above 200°C . Therefore the 1221 cm^{-1} band above 300°C cannot be assigned to $\text{N}^{18}\text{O}_3^-$. But the wavenumber of that band is the same as the $\text{N}^{16}\text{O}_2^-$ species in the case of N^{16}O adsorption, which remains even above 300°C . Consequently, the 1221 cm^{-1} band above 300°C may be assigned to $\text{N}^{16}\text{O}_2^-$ or $^{16}\text{ON}^{18}\text{O}^-$.

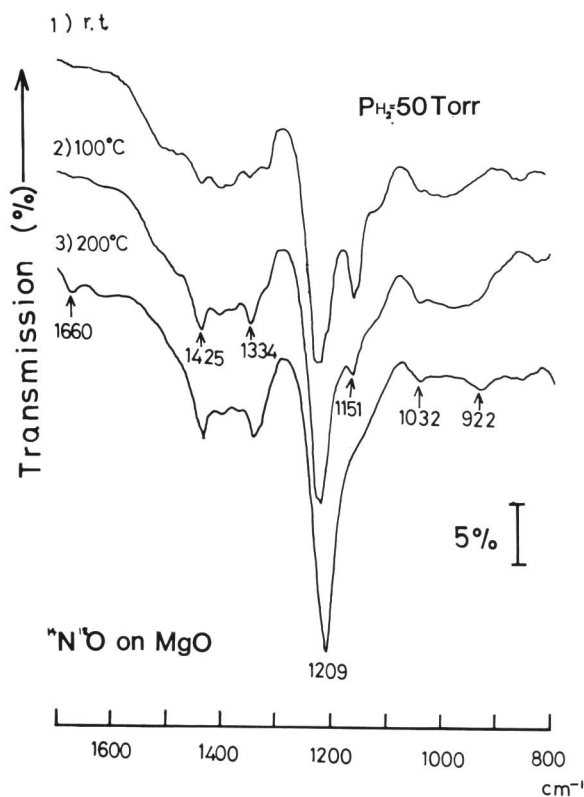
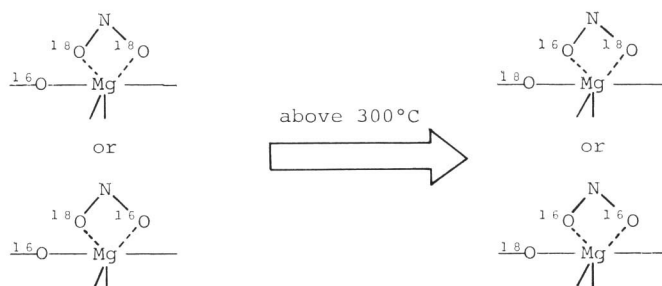


Fig. 4-1

species. The 1211 cm^{-1} band of $\text{N}^{18}\text{O}_2^-$ had almost disappeared at 400°C , and bands at 1433 and 1221 cm^{-1} , which were similar to those in the case of N^{16}O adsorption, were observed. Therefore it seems that NO_2^- species containing ^{18}O can exchange its oxygen with the lattice oxygen of MgO surface to form $\text{N}^{16}\text{O}_2^-$ or $^{16}\text{ON}^{18}\text{O}^-$ species above 300°C as follows:



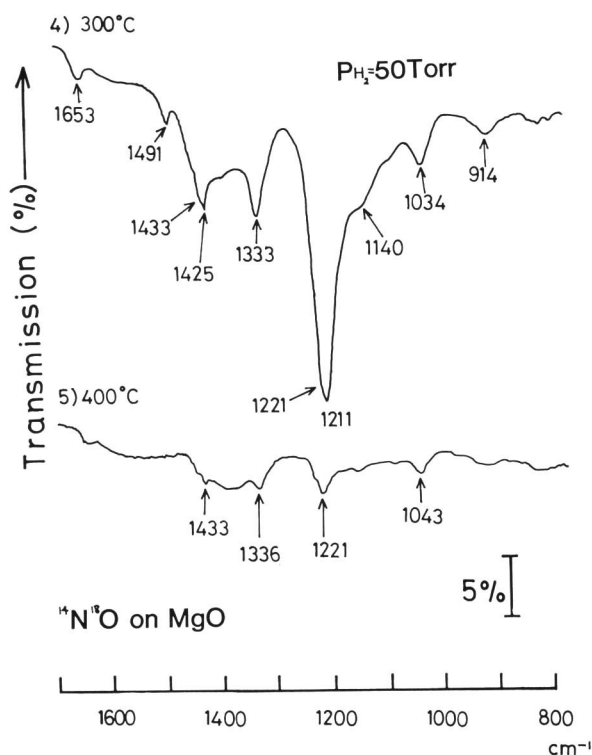


Fig. 4-2

Fig. 4. FT-IR spectra of adsorbed species after H_2 treatment at various temperatures. Initial MgO surface was exposed to $^{14}N^{18}O$ at room temperature for 22 hours (see Fig. 3).

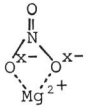
3.2. Nitric oxide reduction with hydrogen on MgO

A gas mixture of 50 Torr of NO and 50 Torr of H_2 was circulated over MgO catalyst. The reaction proceeded above $250^\circ C$, and evidently above $350^\circ C$. The products of this reaction were N_2O , N_2 , and H_2O . The selectivity for N_2O ($N_2O/(N_2+N_2O)$) was more than 90%.

FT-IR spectra of adsorbed species during the $NO+H_2$ reaction at $250^\circ C$ are shown in Fig. 5. These spectra are very similar to those of NO adsorption. $NO+D_2$ reaction was carried out over MgO surface pretreated with D_2 . The results are shown in Fig. 6. The spectra are almost the same as those of $NO+H_2$ reaction except for the bands of surface OD group at around 2762 cm^{-1} , which leads to the conclusion that no hydrogen containing adsorbed species, such as NH_x , could be detected.

In this case, bands at 2220, 2200, and 2193 cm^{-1} were observed as in the case of NO adsorption at higher temperatures, and can be attributed to adsorbed N_2 species on MgO. KAGAMI *et al.* (1981) studied the NH_3 decomposition on MgO using in-

Table 1. Assignments of Adsorbed Species on MgO

Species	Frequency (cm ⁻¹)		
	¹⁴ N ¹⁶ O	¹⁵ N ¹⁶ O	¹⁴ N ¹⁸ O
N ₂	2210	2204	2210
	2200	2193	2202
	2193	2177	2193
	1213	1184	1200
	1126	1099	1113
	1309	1284	1302
	1232	1209	1221
	(a) 1171	1146	1155
	(b) 1161	1134	1144
	1435	1392	1425
	1342	1315	1333

frared spectroscopy, and observed sharp bands at 2220 and 2195 cm⁻¹, and a broad band at 2080 cm⁻¹. They attributed these bands to adsorbed N₂ species. The former two bands are very similar to those observed in this work, but the latter was not observed in this work. When hydrogen was introduced onto the MgO surface on which only adsorbed N₂ species had been formed by NH₃ decomposition, a band of adsorbed NH₂ species was formed with a decrease of adsorbed N₂ bands (KAGAMI *et al.*, 1981). When the catalyst was heated at 500°C in H₂, the bands of adsorbed N₂ species disappeared completely and NH₃ was produced in gas phase. But in this work, the production of NH₃ was not observed by hydrogen treatment at 500°C. Therefore, it seems that the adsorbed N₂ species, which is characterized by a broad band at 2080 cm⁻¹, takes part in the production of NH₃.

In order to study the dynamic behavior of each of the adsorbed species, the MgO surface, on which a gas mixture of NO and H₂ had been circulated at 250°C, was treated with hydrogen. After NO+H₂ reaction, H₂ was circulated at various temperatures for 30 minutes and the changes in each of the adsorbed species were examined by IR spectroscopy. These are shown in Fig. 7. The bands at 1232 and 1315 cm⁻¹ readily decreased at 250°C and completely disappeared at 400°C. On the other hand, the band at about 1210 cm⁻¹ was more inert and decreased above 300°C, where NO+H₂ reaction proceeds steadily and where the adsorbed NO₂⁻ species easily exchanges its oxygen with the lattice oxygen of MgO. Therefore, it seems that the adsorbed NO₂⁻ species starts to react above 300°C and takes part in the NO+H₂ reaction to form N₂O and N₂ in the gas phase.

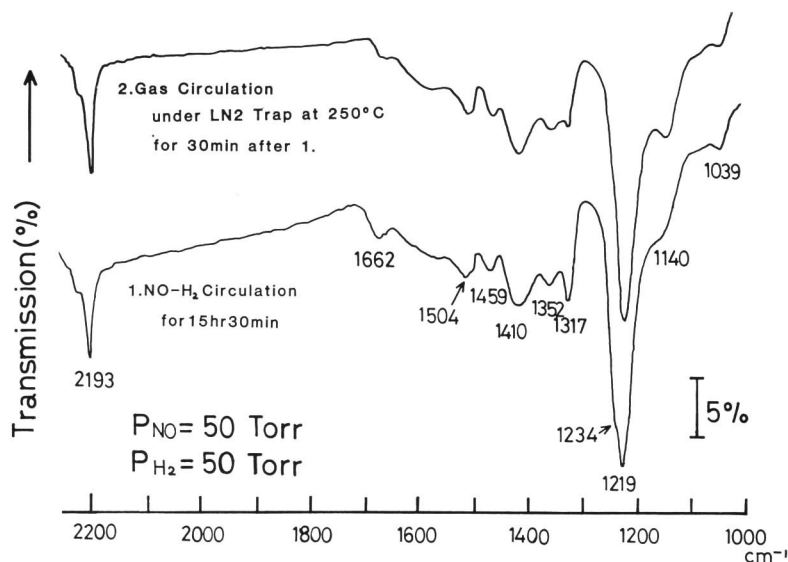


Fig. 5. FT-IR spectra of adsorbed species after NO+H₂ reaction on MgO at 250°C.

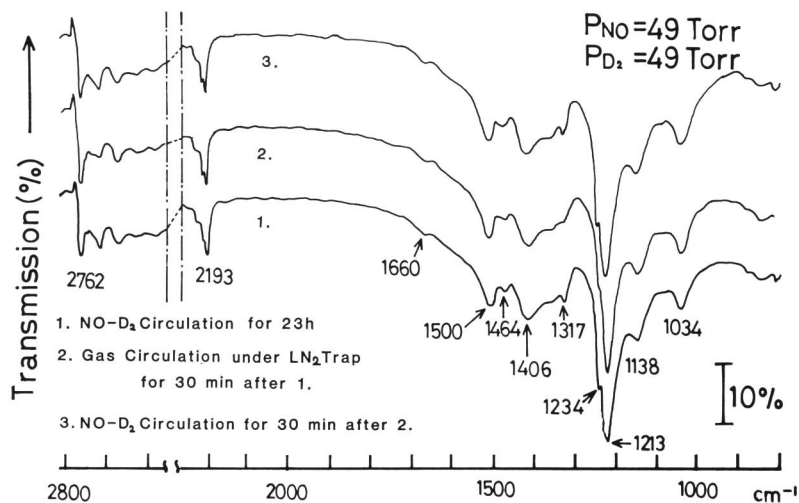


Fig. 6. FT-IR spectra of adsorbed species after NO+D₂ reaction on MgO at 250°C.

Further investigation is needed to elucidate completely the reaction mechanism of NO+H₂, but we tentatively summarize the features of NO adsorption and its reduction with H₂ on MgO in Fig. 8.

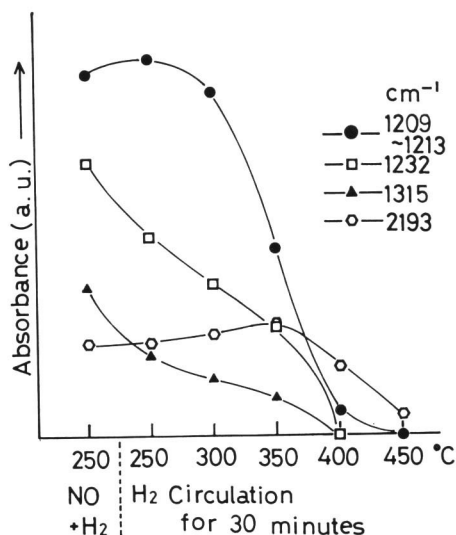


Fig. 7. Effect of H_2 treatment for adsorbed species on MgO. After a gas mixture of NO and H_2 had been circulated for about 20 hours at 250°C , H_2 was circulated for 30 minutes at various temperatures.

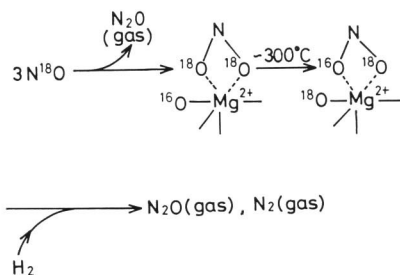


Fig. 8. Tentative scheme for NO adsorption and its reduction with H_2 on MgO.

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