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Effect of supports on formation and reduction rate of stored nitrates on NSR catalysts as investigated by in situ FT/IR

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ABSTRACT

Surface dynamics of nitrates on NOx storage–reduction (NSR) catalysts are examined by means of in situ FT/IR. In the initial state of NOx storage, both nitrite and nitrates are formed on Pt–Ba/Al_2O_3 surface, and then nitrite become abundant with the increase of storage time. The initial rate of nitrate storage is faster in a flow of NO/O_2 mixture than in a flow of NO_2 without O_2. The presence of oxygen is found to be essential for the conversion of surface nitrite to nitrates. The rate and amount of nitrate formation are strongly affected by type of supports. The storage ability is in the order of $MgO > Al_2O_3 > ZrO_2 > SiO_2$, which is in accordance with that of basicity of the supports. On the other hand, the rate of nitrate reduction by H_2 is in the different order: $Al_2O_3 > ZrO_2 > SiO_2 > MgO$. The strong contribution of acid–base property of supports as a controlling factor is suggested.

1. Introduction

The demand for lean-burn gasoline and diesel engines in vehicles are expected to increase because there are strong efforts to reduce CO_2 emissions by improving fuel economy. Since air/fuel ratio is higher in lean-burn gasoline and diesel engines than in gasoline engines, three-way catalyst is not effective for these fuel economy vehicles. Especially, the reduction of NO and NO_2 (NOx), which cause photochemical smog formation and acid rain, is very difficult in such oxygen rich exhausts. On the three-way catalysts, NO is reduced to N_2 by unburned hydrocarbons (HC), CO, and H_2. However, undesired consumption of these reductants by combustion with excess O_2 occurs in such O_2 rich exhausts. To control these competitive reactions, new catalysis technology based on novel concepts is desired.

NOx storage–reduction (NSR) system, which was developed by Toyota Motor Company, is an effective technology to remove NOx from lean-burn engines [1–4]. The NSR system is performed with an engine operating alternatively under lean or rich conditions and an evolved three-way catalyst originally based on Pt–Ba/Al_2O_3. NOx is stored in the storage materials such as BaO as nitrates during lean conditions, and the stored NOx is released from the storage materials and reduced over noble metals by H_2, HC, and CO while turning the engine to rich conditions for a short period. In order to understand such complicated catalyst system, several investigations have been carried out to clarify the effect of each component, such as noble metals [5–7], storage materials [8–11], and supports [12,13]. Although the effect of supports other than Al_2O_3 has been studied mainly on storage capacity and NOx reduction activity [12,13], kinetics of stored nitrate under lean and rich conditions are not quantitatively examined.

In the present study, in order to clarify the effect of supports on the reaction steps under lean and rich conditions, a kinetic study of surface nitrates is carried out by means of in situ FT/IR under reaction conditions. The effect of oxygen in the rate of nitrates formation is also examined.

2. Experimental

Supports of SiO_2 and MgO were supplied by the Committee of Reference Catalysts, Catalysis Society of Japan (JRC-SIO-8 and JRC-MGO-1) [14,15]. Al_2O_3 and ZrO_2 were purchased. First, supported Pt catalysts were prepared by impregnating supports with an aqueous solution of platinum nitrate followed by evaporation to dryness at 353 K overnight and by calcination in air at 673 K for 3 h. Then, the obtained supported Pt catalysts was impregnated with an aqueous solution of barium acetate and further evaporated to dryness at 353 K overnight and by calcination in air at 673 K for 3 h. The contents of Pt and Ba are 1 wt% and 13 wt%, respectively.

The dispersion of Pt was estimated by the CO-pulse method [14,15]. A catalyst is first treated in an air flow at 673 K for 15 min followed by purge with He for 15 min, and then reduced in a flow of

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H_2 at 673 K for 15 min followed by purge with He for 15 min. Then the catalyst is cooled in a flow of He, and a series of CO pulses are injected with an interval of 2–3 min until the amount of exit CO pulses reaches a steady-state value. In the present study, in order to avoid oxidation of CO to CO_2 followed by adsorption on Ba site as carbonate, the sample cell was soaked in a dry ice/ethanol bath and the adsorption of CO was carried out at 208 K.

The in situ IR spectra were recorded using a JASCO FT/IR-620 equipped with a quartz IR cell connected to a conventional flow reaction system, which was used in our previous studies [16,17]. The sample was pressed into a 0.05-g self-supporting wafer and mounted into a quartz IR cell with CaF_2 windows. The spectra were measured by accumulating 20 scans at a resolution of 2 cm^{-1}. A reference spectrum of the catalyst wafer in flowing He was taken at 348 K, and was subtracted from each spectrum under the reaction conditions. The catalyst wafer was first exposed in a flow of $NO/O_2/He$ = 200 ppm/3%/balance, and then the flowing gas was switched to H_2/He = 0.2%/balance at a rate of 100 $cm^3\ min^{-1}$. The nitrate bands in transmission spectra were integrated and the amount of adsorbed nitrates were estimated by using extinction coefficient of $\varepsilon = 19.435\ abs/10^{-6}$ mol. The extinction coefficient was determined from a calibration line between the integrated intensity of nitrates in IR spectra and the stored NOx on typical catalysts (Pt–Ba/Al_2O_3 and Pt–Ba/ZrO_2). The stored NOx was estimated from the balance of injected and leaked NOx detected by NOx analyzer.

3. Results and discussion

3.1. Catalyst characterization

The XRD patterns of the catalysts after preparation are shown in Fig. 1. For all the catalysts, the lines assignable to $BaCO_3$ are observed. The other lines are due to the supports. The lines assignable to Pt metal were not observed. Comparing intensity and width of the lines of $BaCO_3$, it was suggested that there is not so much difference in dispersion of Ba species.

The dispersion of Pt was quantitatively estimated by the CO-adsorption. As shown in Table 1, the dispersion of Pt was affected by the supports in the following order: $Al_2O_3 > MgO > ZrO_2 \gg SiO_2$. Moderate dispersion of Pt was observed on Al_2O_3, MgO, and ZrO_2 supports, while that was very low on SiO_2 surface.

3.2. Effect of feed gas in storage of nitrate on Pt–Ba/Al_2O_3

Fig. 2 shows in situ FT/IR spectra of adsorbed species on Pt–Ba/Al_2O_3. In a flow of NO/O_2 mixture, strong absorption bands are observed at 1320, 1420, and 1540 cm^{-1}, which are assignable to bidentate (1320 and 1540 cm^{-1}) and monodentate (1420 cm^{-1}) nitrates, respectively [18,19]. In the initial stage of adsorption, weak band assignable to nitrite was also observed at 1200 cm^{-1}. The intensity of the bands assignable to nitrates gradually increased with the increase of storage time. While the band assignable to nitrite gradually decreased, indicating conversion of nitrite to nitrate. The similar results were obtained in flowing NO_2/O_2 and NO_2. In a flow of NO, on the other hand, a part of nitrite still remained even after 1800 s. Although the bands of nitrates in NO gradually increased with time-on-stream, the final intensity at 1800 s was smaller than that in NO/O_2.

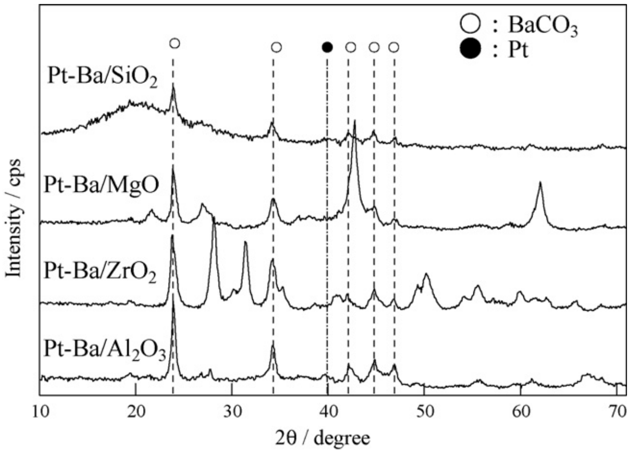

Fig. 1. XRD patterns of supported Pt–Ba catalysts.

Table 1
List of catalysts examined in the present study

Catalyst	Pt content (wt%)	Ba content (wt%)	Pt dispersion (%)
Pt–Ba/Al_2O_3	1	13	52
Pt–Ba/ZrO_2	1	13	35
Pt–Ba/MgO	1	13	42
Pt–Ba/SiO_2	1	13	5.1

These nitrate bands were integrated, and the amount of adsorbed nitrates were estimated by using extinction coefficient of $\varepsilon = 19.435\ abs/10^{-6}$ mol. The integration was carried out in the range of 1650–1250 cm^{-1}, to neglect the contribution of the nitrite band. Fig. 3 shows time course of surface concentration of nitrates on Pt–Ba/Al_2O_3 in flowing NOx containing atmospheres. The rate and saturated amount of nitrates strongly depended on the atmospheres. An induction period was slightly observed in flowing NO/O_2 and NO_2/O_2, which may be due to the conversion of nitrite to nitrates at the initial stage of storage. From the maximum slope of the time dependence curve, the initial rates of nitrate formation were determined and summarized in Table 2. As shown in the table, the rate of nitrate storage was strongly affected by the atmospheres. Interestingly, the rate of nitrate storage was higher in the presence of O_2. Even in a flow of NO_2, the storage rate was lower than in a flow of NO/O_2. Since it is reported that nitrate storage starts from the oxidation of NO to NO_2 followed by adsorption of NO_2 on Ba site as shown in Eq. (1), one may expect that the first oxidation of NO to NO_2 plays an important role in the rate of nitrate storage [3]. However, the formation of nitrates was slower in a flow of NO_2 than in that of NO/O_2. The storage rate was more affected by the presence of O_2. The fact suggests that O_2 plays very important role in the oxidation step after the adsorption of NOx, such as the conversion of nitrite to nitrates [19–21]. The results can be rationalized that the oxidation of surface nitrite to nitrates is the major pathway for the formation of nitrates than the direct adsorption of NO_2 to nitrates. Forzatti et al. [21] proposed that storage of nitrate starts from oxidation of NO to gaseous NO_2 and then proceeds two parallel routes: (1) NO_2 disproportion on Ba sites with evolution of gaseous NO and (2) direct storage of NO_2 as nitrites followed by oxidation to nitrates. In the present study, the importance of latter route is confirmed though the comparison of the reaction rates of surface nitrates.

$$NO + O_2 \xrightarrow[Pt]{} (NO_2^-)ad \rightarrow (NO_3^-)ad \qquad (1)$$

3.3. Reduction of stored nitrate by hydrogen

Then, the rate of nitrate reduction was examined by using H_2 as a reductant. To simplify the discussion, the reduction of nitrates was started after the nitrate storage in a flow of NO_2/O_2. Fig. 4 shows the change in IR spectra in a flow of H_2 at 573 K. The bands assignable to nitrates decreased with time-on-stream,

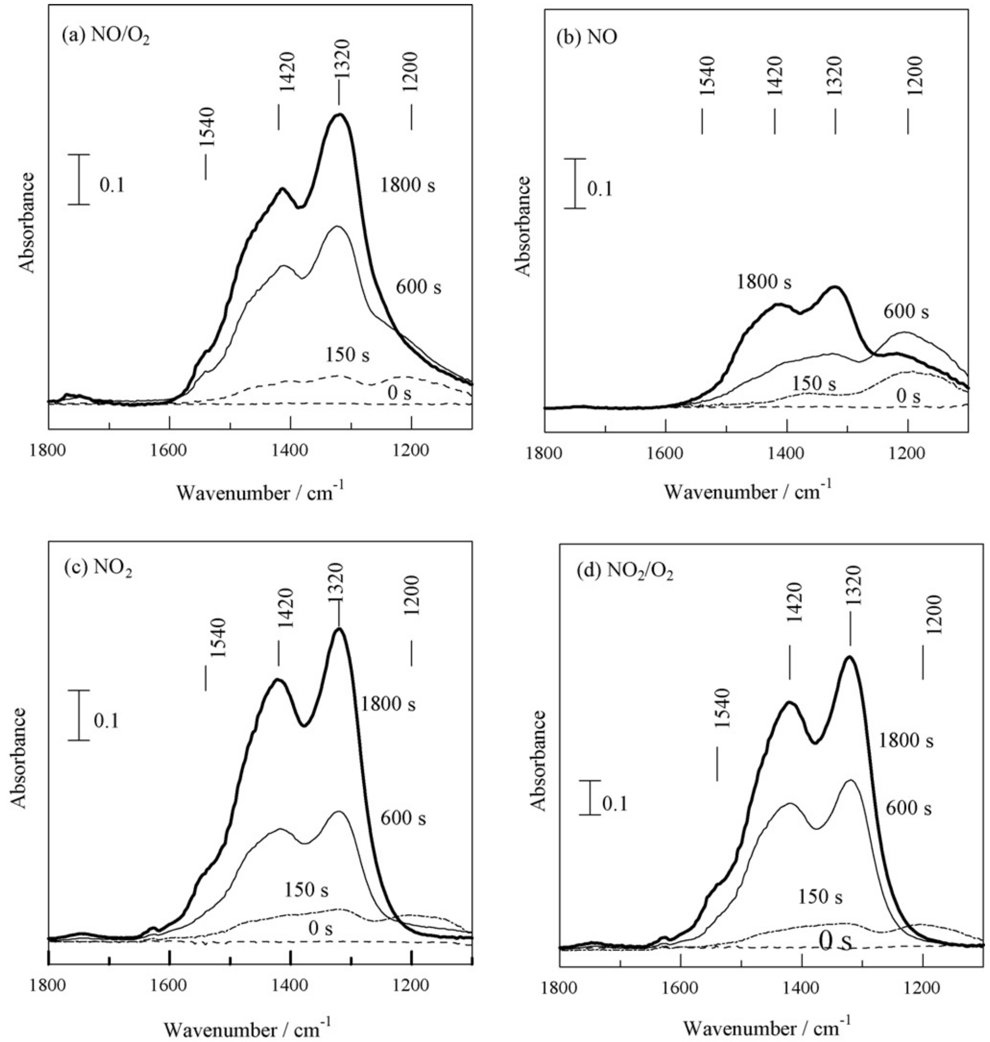

Fig. 2. In situ FT/IR spectra of adsorbed species on Pt–Ba/Al_2O_3 at 573 K in flowing (a) NO + O_2, (b) NO, (c) NO_2, and (d) NO_2/O_2. The concentration of NO, NO_2, and O_2 are 200 ppm, 200 ppm, and 3%, respectively.

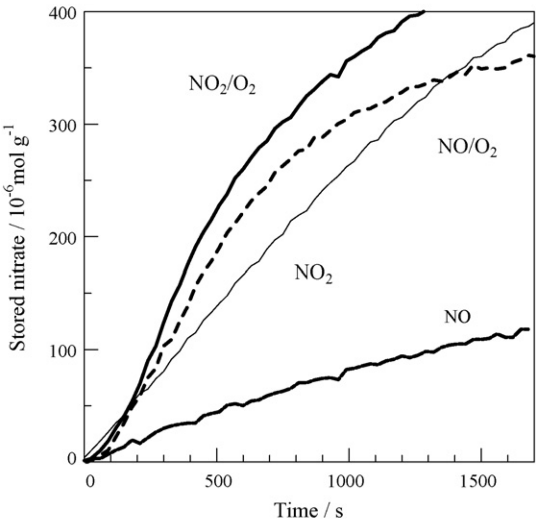

Fig. 3. Time course of stored nitrates on Pt–Ba/Al_2O_3 in a flow of NO/O_2, NO, and NO_2 at 573 K.

and the stored nitrates were almost consumed after 1800 s. During the reduction of nitrates by H_2, NO or NO_2 were not detected in the gas phase, indicating nitrate was reduced to N_2 or N_2O. It should be noted that the intensity of the bands was unchanged in a flow of only He at the same temperature even after 1800 s. This means that the rate of simple desorption is negligible at 573 K. Contribution of nitrite in the spectra was negligible. Above 2000 cm^{-1}, a broad O–H stretching bands were observed around 3600–3200 cm^{-1} during the reduction, while N–H band around 3000 cm^{-1} was not detected. The formation of NH_3 was not confirmed over the series of catalysts. From the time dependence of the integrated band intensity at 1650–1250 cm^{-1}, the rates of nitrate reduction were compared by using Pt–Ba catalyst supported on various metal oxides in the next section.

Table 2
Rate and amount of stored nitrates on Pt–Ba/Al_2O_3 at 573 K

	NO	NO_2	NO/O_2	NO_2/O_2
Rate of formation (μmol g^{-1} s^{-1})	0.13	0.24	0.52	0.59
Amount after 1800 s ($\times 10^{-6}$ mol g^{-1})	118	387	361	440

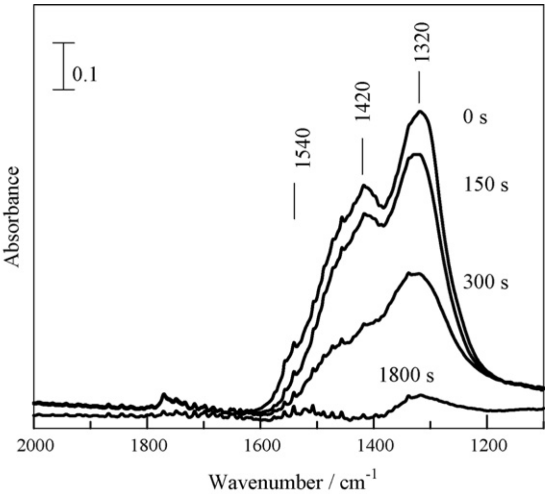

Fig. 4. In situ FT/IR spectra during the reduction of stored nitrates on Pt–Ba/Al_2O_3 in a flow of H_2 at 573 K.

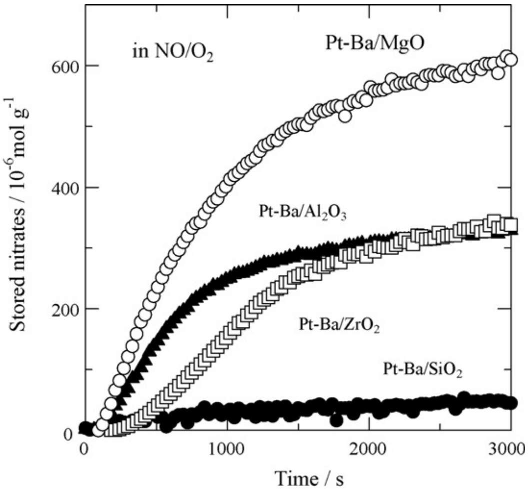

Fig. 6. Effect of supports on time courses of stored nitrates on supported Pt–Ba catalysts under the lean conditions (NO/O_2 = 200 ppm/3%) at 573 K.

3.4. Effect of various supports on nitrate storage and reduction by H_2

Fig. 5 shows in situ FT/IR spectra of adsorbed species on supported Pt–Ba catalysts in a flow of NO_2/H_2 at 573 K. For all the samples examined, the bands of nitrates were observed in the range of 1650–1250 cm^{-1} with basically the same ratio of bidentate and monodentate. In the case of Pt–Ba/SiO_2, the absorption band was not detected below 1280 cm^{-1} because of a strong background of SiO_2 absorption.

Fig. 6 shows time course of the amount of stored nitrates on supported Pt–Ba catalysts. The stored nitrates steeply increased with time, though the rate of nitrate formation was strongly affected by the supports. Pt–Ba/MgO showed the highest rate and amount of stored nitrates, while SiO_2 support is not effective for nitrate storage. Interestingly, an induction period was clearly observed in Pt–Ba/ZrO_2. The reduction rate of nitrates was also affected by the supports, as shown in Fig. 7. The stored nitrates were the most steeply reduced on Pt–Ba/Al_2O_3, while the reduction rates were low on Pt–Ba/MgO and Pt–Ba/SiO_2. An induction period for nitrate reduction was also observed clearly in Pt–Ba/ZrO_2, and slightly in Pt–Ba/Al_2O_3.

From the maximum slope in the time-on-stream, the initial rates of nitrate formation under the lean conditions are determined from Fig. 6, and are plotted in Fig. 8. The maximum rate of nitrate formation at 573 K is the highest on Pt–Ba/MgO, and in the order of $MgO > Al_2O_3 > ZrO_2 > SiO_2$. Since the saturation of nitrates took too long time at 573 K, the amount of stored nitrates was compared at 773 K. The saturated amount of stored nitrates at 773 K is almost in the same order, i.e., $MgO > ZrO_2 > Al_2O_3 > SiO_2$. This order is the opposite of the acid strength of the supports, which was estimated by titration of Hammett indicators [22]. This means that acid–base property is the critical controlling factor for the nitrate storage, and the NOx storage is more favorable on basic supports.

The rates of nitrate reduction were also estimated in the similar manner from Fig. 7, and are plotted in Fig. 9. Under the rich conditions, on the other hand, the rate of nitrates reduction showed different trend. The maximum rate of nitrate reduction is in the order of $Al_2O_3 > ZrO_2 > SiO_2 > MgO$. Taking the Pt dispersion into account, the reduction activity was compared as turnover frequency, i.e., the reduction rate per exposed Pt atom. The order of the turnover frequency was $SiO_2 > Al_2O_3 > ZrO_2 > MgO$. This trend was entirely opposite to the storage amount of nitrates, and in accordance with that of acid strength of the supports. Yazawa et al.

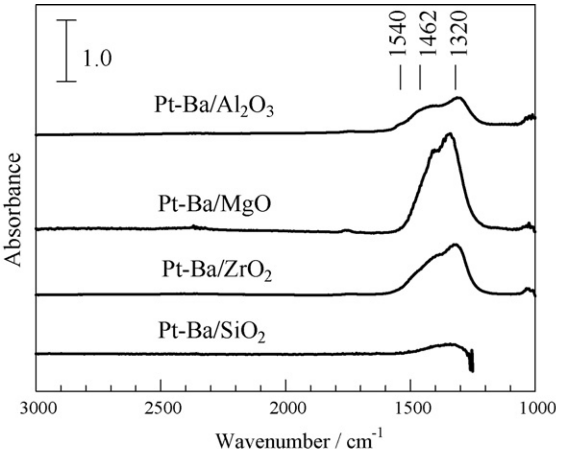

Fig. 5. In situ FT/IR spectra of adsorbed species on supported Pt–Ba catalysts in a flow of NO_2/O_2 at 573 K.

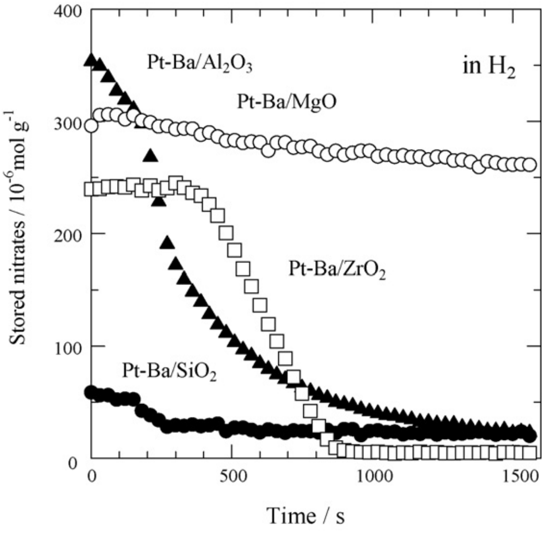

Fig. 7. Effect of supports on time courses of stored nitrates on supported Pt–Ba catalysts under the rich (H_2 = 0.2%) conditions at 573 K.

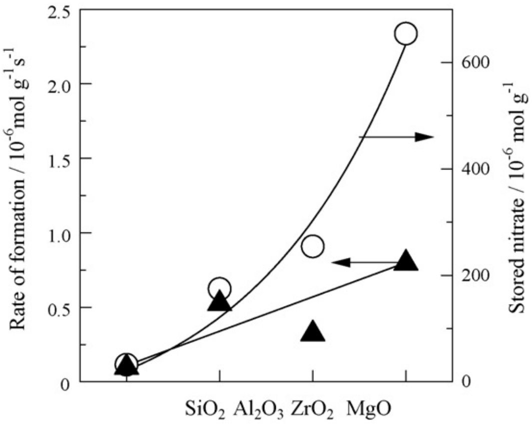

Fig. 8. Rate of nitrate formation at 573 K and saturated amount of stored nitrate at 773 K on supported Pt–Ba catalysts under the lean (NO/O_2 = 200 ppm/3%) conditions.

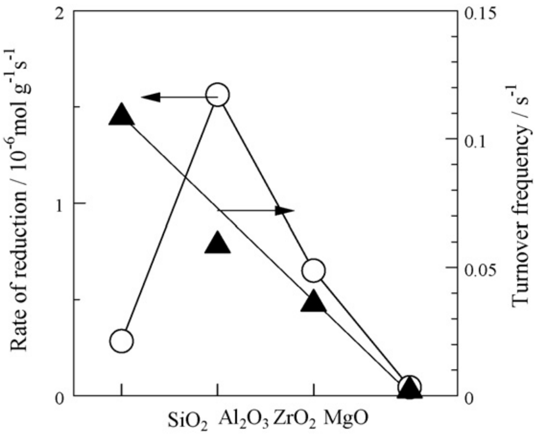

Fig. 9. Rate and turnover frequency of nitrate reduction in H_2 on supported Pt–Ba catalysts under the rich (H_2 = 0.2%) conditions at 573 K.

reported the same activity pattern on the total oxidation of propane [23]. Based on XANES spectra, they correlated the oxidation activity to the oxidation state of Pt. The supported Pt is in more reduced state on acidic supports, and thus shows higher activity on the total oxidation of propane. While, surface Pt is in oxidized state on basic supports such as MgO. In the case of the reduction of NOx, it is well known that the NOx reduction activity is strongly inhibited by surface adsorbed oxygen. The lower reduction activity of Pt–Ba/MgO may be attributed to the more oxidized Pt surface on MgO.

4. Conclusions

In situ analysis of surface dynamics of nitrates on Pt–Ba/Al_2O_3 catalyst revealed the importance of oxygen for the conversion of surface nitrite to nitrates. The rate and amount of nitrate formation are higher on Pt–Ba catalysts supported on more basic metal oxides. On the other hand, the turnover frequency of nitrate reduction by H_2 increased with the increase in the acid strength of supports. The importance of acid–base property of the supports on NSR catalysts is clearly demonstrated.

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