Evidence for the formation, isomerization and decomposition of organo-nitrite and -nitro species during the NO_x reduction by C_3H_6 on Ag/Al_2O_3

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Abstract

The formation of organo-nitrite and -nitro species ($R-ONO$ and $R-NO_2$) as intermediates during the selective catalytic reduction (SCR) of NO_x by C_3H_6 over Ag/Al_2O_3 was investigated by temperature-programmed desorption (TPD) and in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). The addition of KBr to Ag/Al_2O_3 catalyses the isomerization of $R-NO_2$ to $R-ONO$ on $KBr-Ag/Al_2O_3$, which confirms the presence of $R-NO_2$ on Ag/Al_2O_3.
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1. Introduction

After about two decades of intensive academic and industrial research, many of the fundamental questions relating to the selective catalytic reduction (SCR) of NO_x by hydrocarbons (HC) have been addressed, however, there is still some debate about the mechanism of NO_x reduction. Numerous intermediates have been reported to take part in the NO_x reduction over non-zeolitic oxides catalysts, such as alumina supported silver (Ag/Al_2O_3) and the mechanism are rather complicated, which can be simply described as below [1–6]:
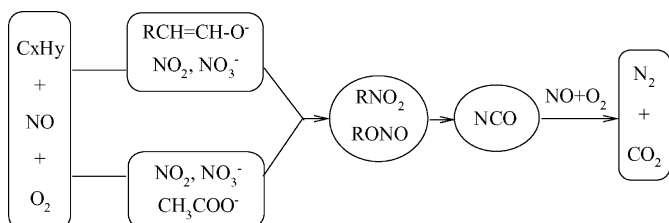
Infra-red (IR) spectra and temperature-programmed desorption (TPD) results have shown that large amounts of adsorbed nitrates (NO_3^-) were formed in $NO + O_2$ during the SCR of NO_x on Al_2O_3 or Ag/Al_2O_3 [7–10]. Furthermore, it has been shown that the nitrate species were converted to N_2 during exposure to the reductant, at rates that were similar to those of the steady state reduction of NO_x [7–10]. These results strongly support the conclusions reached by many research teams on the role of nitrate species as true reaction intermediates in the SCR process over oxides. Similarly to the case of NO, most authors have proposed the formation of partial oxidation productions ($C_xH_yO_z$) as the first reaction step in the reaction of the hydrocarbon with O_2. Acetate surface species, as a partial oxidation production of hydrocarbon, was commonly observed during the NO_x reduction over Al_2O_3, Ag/Al_2O_3 and Cu/Al_2O_3, and was consumed at rates similar to that of the NO_x reduction [7–12]. Thus, acetate is also a true intermediate in the NO_x reduction by hydrocarbon and plays a key role in this process. More recently, we observed a novel enolic species ($RCH=CH-O^-$) and found that this species has high activity to react with $NO + O_2$ during the NO_x reduction over Ag/Al_2O_3 [5,6].

It is well known that isocyanate species (–NCO) species is a vital intermediate for the SCR of NO_x over Ag/Al_2O_3 catalyst [1–6,13], and its high productivity indicates a high efficiency of NO_x reduction by ethanol or hydrocarbons [14–17].

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Up to now, however, organo-nitrite and -nitro species (R-ONO and R-NO$_2$), as true intermediates in the SCR of NO$_x$ by hydrocarbons, are still a matter of debate. The decomposition of organo-nitrite and -nitro species yields –NCO species [16,18], whereas these organic nitrogen species are not readily detected on Ag/TiO$_2$-ZrO$_2$, Ag/Al$_2$O$_3$, Al$_2$O$_3$, Pt/SiO$_2$, and *M*-ZSM-5 (*M* = Cu, Co, Ce, Na, H) catalysts during the NO$_x$ reduction [2,3,18–22]. In the case of R-ONO, IR study in a vacuum system suggested this species is a key intermediate for the SCR of NO$_x$ [2,3]. Under a real flow catalytic reaction condition, however, such information is barely obtained in situ. For R-NO$_2$, its IR peaks is located at 1580–1530 and 1410–1370 cm^{-1}, where many peaks, due to different species, appear in the two ranges [2,16,18,19], and therefore there is no direct evidence supporting the presence of R-NO$_2$ during the SCR of NO$_x$. In addition, actual NO$_2$ yields and thermo-dynamically predicted yields of NO$_2$ suggest that the formation of NO$_2$ during the C$_3$H$_6$-SCR of NO over γ-Al$_2$O$_3$ may not be formed by the direct oxidation of NO with O$_2$. Consequently, R-ONO followed by its decomposition or oxidation was suggested to be the main route for the formation of NO$_2$ [4,23,24], which can be regarded as an indirect evidence of the presence of organo-nitrogen species during the SCR of NO$_x$.

In this paper, the formation of organo-nitrogen species during the SCR of NO$_x$ by C$_3$H$_6$ over Ag/Al$_2$O$_3$ was investigated by TPD and in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). In addition, we found that the addition of KBr to Ag/Al$_2$O$_3$ is beneficial for detection of the DRIFTS peaks of R-ONO and R-NO$_2$ during the SCR of NO$_x$ by C$_3$H$_6$ over Ag/Al$_2$O$_3$. It must be emphasized that the KBr dilution technique is not suitable for studying NO$_x$ containing system such as the SCR of NO$_x$ by IR. However, this KBr dilution technique demonstrates the presence of R-NO$_2$, as a real intermediate in the NO$_x$ reduction by C$_3$H$_6$ over Ag/Al$_2$O$_3$.

2. Experimental

An Ag/Al$_2$O$_3$ (5 wt%) catalyst was prepared by an impregnation method as follows: Al$_2$O$_3$ powder (200 m^2/g) was introduced into an appropriate amount of silver nitrate aqueous solution. The sample was dried at 393 K for 3 h and calcined at 873 K for 3 h in air.

Temperature-programmed desorption (TPD) was performed in a catalytic reactor. This reactor consisted of a 1.2-cm-OD quartz tube with a 0.5-mm-OD thermocouple placed in the center of a bed of 40–80 mesh catalyst particles (0.5 g). The thermocouple measured the temperature and provided feedback to the temperature programmer, which regulated heating of the electric furnace. An Aglient quadrupole mass spectrometer (5973 N) detected products immediately downstream of the reactor as they were desorbed from the catalyst, and a computer allowed multiple signals and the thermocouple output to be recorded, simultaneously. After exposing the catalyst to the fed gas for 60 min at 473 K, the catalyst was cooled to room temperature in He (30 ml/min) flow, and then the temperature was ramped at 60 K/min in the flow of He while the temperature and desorption products were recorded.

In situ DRIFTS spectra were recorded on a Nexus 670 (Thermo Nicolet) FTIR, equipped with an in situ diffuse reflection chamber and a high sensitivity MCT/A detector. An Ag/Al$_2$O$_3$ catalyst with or without KBr addition for the in situ DRIFTS studies was finely ground and placed into a ceramic crucible in the in situ chamber. Mass flow controllers and a sample temperature controller were used to simulate the real reaction conditions, such as mixture of gases, pressure and sample temperature. Prior to recording each DRIFTS spectrum, the Ag/Al$_2$O$_3$ catalyst was heated in situ in 10% O$_2$/N$_2$ flow at 873 K for 1 h, then cooled to the desired temperature for taking a reference spectrum. All gas mixtures were fed at a flow rate of 100 ml/min. All spectra were measured with a resolution of 4 cm^{-1} and with an accumulation of 100 scans.

3. Results and discussion

3.1. TPD study

Fig. 1 shows TPD spectra of Ag/Al$_2$O$_3$ after exposing to NO (800 ppm) + O$_2$ (10%) at 473 K for 60 min. The observed species were NO (m/z = 30), NO$_2$ (m/z = 46), and O$_2$ (m/z = 32). No peaks attributable to N$_2$O were observed. Two desorption peaks of NO were observed at 582 and 806 K. Furthermore, the latter was accompanied by desorption of O$_2$ and small amount of NO$_2$ at the same temperature. Similar result was reported by other research group, in which they suggested that these peaks are derived from the decomposition of unidentate nitrate on Ag/Al$_2$O$_3$ [25]. The NO desorption peak at 582 K is possibly originated from bridging or bidentate nitrate [25].

After exposing Ag/Al$_2$O$_3$ to C$_3$H$_6$ (1714 ppm) + O$_2$ (10%) at 473 K for 60 min, a TPD experiment was performed in He and the results were also shown in Fig. 1. A strong C$_3$H$_6$ desorption peak (m/z = 41) was observed at 468 K. Three peaks
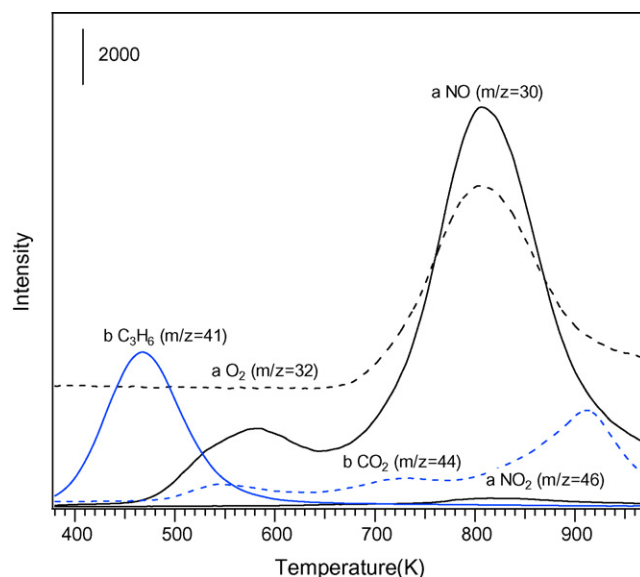

Fig. 1. TPD spectra of Ag/Al$_2$O$_3$ after exposing to (a) NO (800 ppm) + O$_2$ (10%)/N$_2$ and (b) C$_3$H$_6$ (1714 ppm) + O$_2$ (10%)/N$_2$ at 473 K for 60 min.

were observed for CO_2 ($m/z = 44$) at elevated temperatures: 545, 732 and 913 K.

The same TPD experiment was performed after exposing the catalyst to a flow of NO (800 ppm) + C_3H_6 (1714 ppm) + O_2 (10%) at 473 K for 60 min, whereas different results were observed. As shown in Fig. 2, three NO desorption peaks were observed at 506, 692 and 826 K. Compared to Fig. 1, the NO and O_2 peaks originated from the decomposition of unidentate nitrate were also observed at 826 K, while the peak at 582 K assignable to bridging or bidentate nitrate was no longer detected. It should be noted that two new NO desorption peaks at 506 and 692 K (Fig. 2) were both accompanied by CO_2 desorption. Meanwhile, the temperatures in which the CO_2 desorption occurred were quite different if compared with Fig. 1, also indicating that different intermediates were formed during this process. Consequently, we think that these peaks should be derived from the decomposition of nitrogen- and oxygen-containing compounds. During the SCR of NO_x by C_3H_6 over Ag/Al_2O_3, the possible nitrogen- and oxygen-containing compounds are R-NO_2, R-ONO, –NCO and –CN [4,6].

3.2. DRIFTS study

DRIFTS experiments were carried out to confirm the presence of organo-nitrite and -nitro species as true intermediates in the SCR of NO_x by C_3H_6 over Ag/Al_2O_3 [16,18]. Fig. 3(a) shows the in situ DRIFTS spectra of Ag/Al_2O_3 in a flow of NO + O_2 + C_3H_6 at different temperatures. Peaks at 1614, 1585, 1556 and 1304 cm^{-1} were observed, and assigned to unidentate (1556 cm^{-1}), bidentate (1585 and 1304 cm^{-1}) and bridging (1614 cm^{-1}) nitrate, respectively [8,25]. Peaks at 1572 and 1466 cm^{-1} are attributed to ν_{as}(OCO) and ν_s(OCO) of adsorbed acetate, respectively [8,9,11,12]. Peak at 1377 cm^{-1} is due to δ_s(CH$_3$) [16]. According to our earlier papers [5,6,26–29], peaks at 1633, 1416 and 1336 cm^{-1} are assigned to a novel

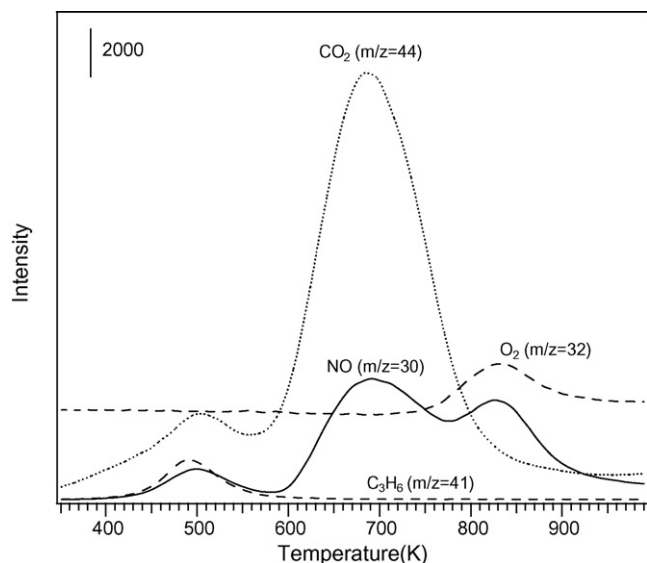Fig. 2. TPD spectra of Ag/Al_2O_3 after exposing to NO (800 ppm) + C_3H_6 (1714 ppm) + O_2 (10%)/N_2 at 473 K for 60 min.
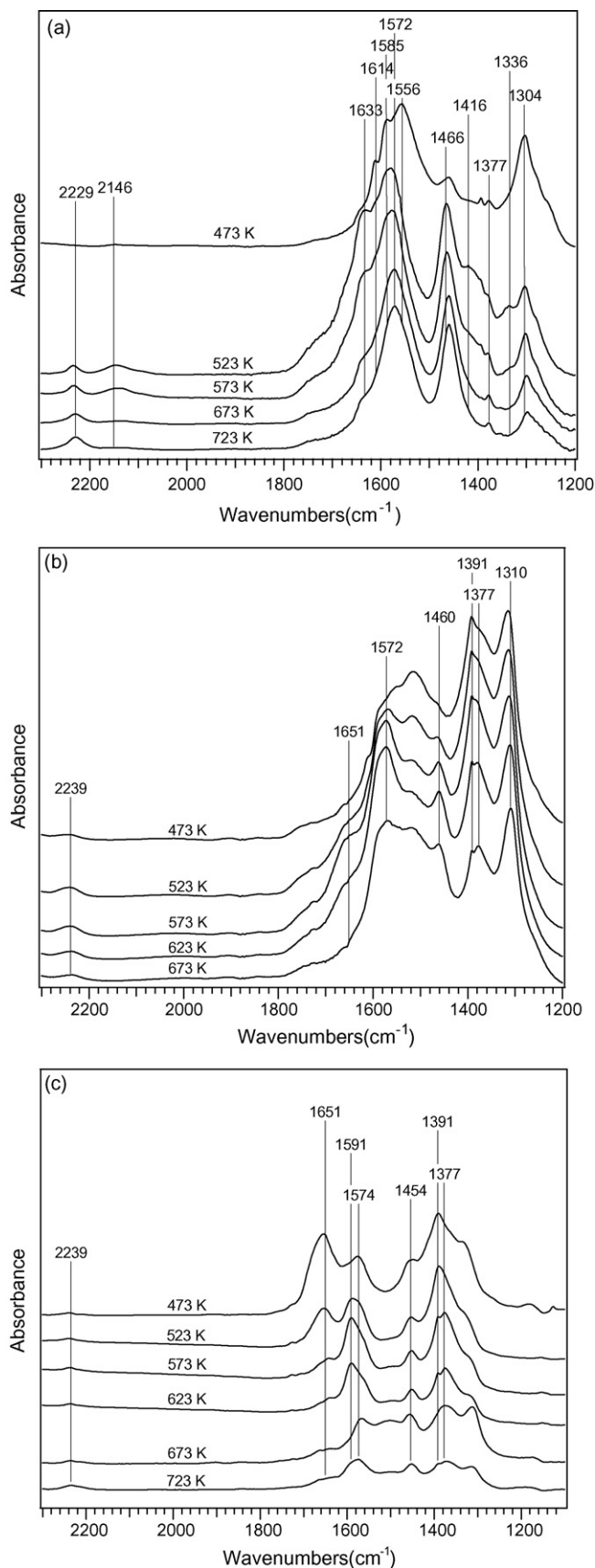

Fig. 3. DRIFTS spectra of Ag/Al_2O_3 at different temperatures in a flow of NO (800 ppm) + O_2 (10%) + C_3H_6 (1714 ppm)/N_2 (a) without KBr dilution; and the mass ratio of Ag/Al_2O_3 to KBr equals (b) 1:1 and (c) 1:4.

enolic species. In our TPD experiment, the desorption peaks resulted from the decomposition of enolic species were also detected, however, only trace of products were observed (results not shown). In the region of 2300–2100 cm^{-1}, –NCO and –CN peaks were observed at 2229 and 2146 cm^{-1}, respectively [3,13–17].

It should be noted that the peaks assignable to –NCO and –CN could not be observed at 473 K in Fig. 3(a). As described above, our TPD experiment was also performed after exposing Ag/Al$_2$O$_3$ catalyst to the flow of NO + O$_2$ + C$_3$H$_6$ at the same temperature, which indicates that the NO and CO$_2$ peaks at 506 and 692 K in Fig. 2 do not originated from the decomposition of –NCO and –CN. On the basis of this result and taking the stability of organo-nitrite and -nitro species into account [30], it is likely that the NO and CO$_2$ peaks at 506 and 692 K are originated from the decomposition of R-ONO and R-NO$_2$, respectively. On the other hand, it should be noted that no peaks attributable to R-ONO were observed in Fig. 3(a). Also, there is no evidence in favor of the presence of R-NO$_2$ as intermediate in this process, for its IR peaks locate at 1580–1530 and 1410–1370 cm^{-1}, where many peaks due to different species such as nitrates and acetate appear in the two ranges. As a result, we considered that the IR experimental conditions should be changed to detect the presence of R-ONO and R-NO$_2$ during the SCR of NO$_x$ by C$_3$H$_6$ over Ag/Al$_2$O$_3$, and we found that the addition of KBr to Ag/Al$_2$O$_3$ is benefit for this purpose.

After the Ag/Al$_2$O$_3$ catalyst was diluted in KBr (the Ag/Al$_2$O$_3$/KBr mass ratio was 1:1), the DRIFTS spectra of KBr-Ag/Al$_2$O$_3$ were measured in the flow of NO + O$_2$ + C$_3$H$_6$ at different temperatures. As shown in Fig. 3(b), the acetate (1572 and 1460 cm^{-1}) and nitrate (1310 cm^{-1}) were observed. Compared with Fig. 3(a) and (b), the obvious difference is the appearance of strong peaks at 1391 and 1377 cm^{-1} and a new weak peak at 1651 cm^{-1}. Further increasing the amount of KBr resulted in more drastic changes of DRIFTS spectra of KBr-Ag/Al$_2$O$_3$. When the ratio of Ag/Al$_2$O$_3$ to KBr was 1:4 (Fig. 3(c)), the peaks at 1574 and 1454 cm^{-1} attributed to acetate were similarly observed, while the peak at 1651 cm^{-1} becomes very strong at 473 K. According to our earlier research [3] and other group studies [2,16], the peak at 1651 cm^{-1} is assigned to ν(N=O) of R-ONO species. Whereas the strong peak at 1591 cm^{-1} in the temperature region of 523–623 K is difficult to assign due to the overlapping of the characteristic bands for different species, such as HCOO$^-$ and nitrates [8,18,25]. In addition, strong peaks at 1391 and 1377 cm^{-1} were also observed in Fig. 3(c).

To understand the appearance of strong peaks at 1391 and 1377 cm^{-1}, further investigation was carried out. Fig. 4 shows DRIFTS spectra of Ag/Al$_2$O$_3$ diluted in KBr (the mass ratio of catalyst to KBr was 1:4) in a flow of NO + O$_2$. Strong peak at around 1385–1373 cm^{-1} was observed together with two shoulder peaks at 1311 and 1491 cm^{-1}. These DRIFTS spectra are very similar to spectrum of KNO$_3$ powder, which is displayed as the top curve in Fig. 4. Thus, it is reasonable that adsorbed NO$_3^-$ species further reacts with KBr to form KNO$_3$ on KBr diluted Ag/Al$_2$O$_3$.

As described above, it seemed that the addition of KBr to Ag/Al$_2$O$_3$ would accelerate the formation of R-ONO on the

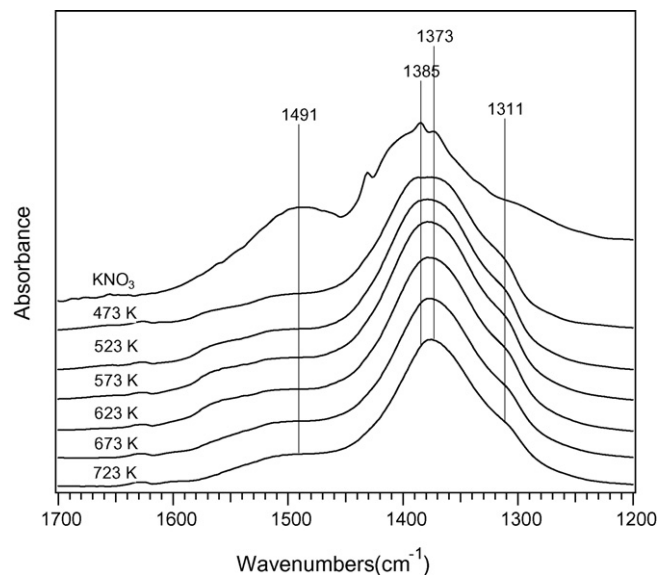Fig. 4. DRIFTS spectra of KBr-Ag/Al$_2$O$_3$ at different temperatures in a flow of NO (800 ppm) + O$_2$ (10%)/N$_2$. The mass ratio of Ag/Al$_2$O$_3$ to KBr equals 1:4.

catalyst in the flow of NO + O$_2$ + C$_3$H$_6$. In order to clarify our supposition, further investigation was carried out using CH$_3$NO$_2$ as a model of R-NO$_2$. Fig. 5(a) shows the DRIFTS spectra of Ag/Al$_2$O$_3$ without KBr addition in a flow of N$_2$ after exposing to CH$_3$NO$_2$ for 30 min at 298 K. Peaks at 1566, 1404 and 1381 cm^{-1} are assigned to ν_{as}(NO$_2$), ν_s(NO$_2$) and δ_s(CH$_3$) of adsorbed CH$_3$NO$_2$, respectively [16,18]. Peaks at 1595, 1392 and 1375 cm^{-1} are due to the adsorption of surface HCOO$^-$ [18]. In addition, –NCO and –CN peaks were observed at 2253–2229 and 2166–2148 cm^{-1}, respectively. Switching the fed gas to N$_2$ and heating the sample resulted in a disappearance of CH$_3$NO$_2$, accompanied by a sharp increase in the intensity of HCOO$^-$.

The same set of experiment was performed when the Ag/Al$_2$O$_3$ catalyst was diluted in KBr (the catalyst/KBr mass ratio of 1:4), and the spectra of CH$_3$NO$_2$ on KBr-Ag/Al$_2$O$_3$ were shown in Fig. 5(b). Compared with Fig. 5(a), a very strong peak at 1651 cm^{-1} was observed in the temperature range of 323–523 K. As shown in the top curve of Fig. 5(b), iso-amyl nitrite (i-C$_5$H$_{11}$-ONO), as a R-ONO model compound gives a strong peak for ν(N=O) of R-ONO at 1651 cm^{-1}, after exposing Ag/Al$_2$O$_3$ to iso-amyl nitrite at 298 K. Thus, the peak at 1651 cm^{-1} was attributed to CH$_3$-ONO species. It should be noted that an increase in the intensity of CH$_3$-ONO peak was accompanied by a drastic decrease in the intensity of CH$_3$NO$_2$ peaks at the temperature range of 323–473 K, indicating that the addition of KBr to Ag/Al$_2$O$_3$ catalyst enhances isomerization of CH$_3$NO$_2$ to CH$_3$-ONO. Similar isomerization of CH$_3$NO$_2$ to CH$_3$-ONO was also observed on the surface of Ag/Al$_2$O$_3$ in a vacuum system [16].

Based on this, we can clearly explain the sharp changes of DRIFTS spectra of Ag/Al$_2$O$_3$ when the catalyst was diluted in KBr (Fig. 3(c)). That is, the addition of KBr to Ag/Al$_2$O$_3$ leads to the formation of KNO$_3$ and catalyzes the isomerization of R-NO$_2$ to R-ONO during the SCR of NO$_x$ by C$_3$H$_6$ over Ag/
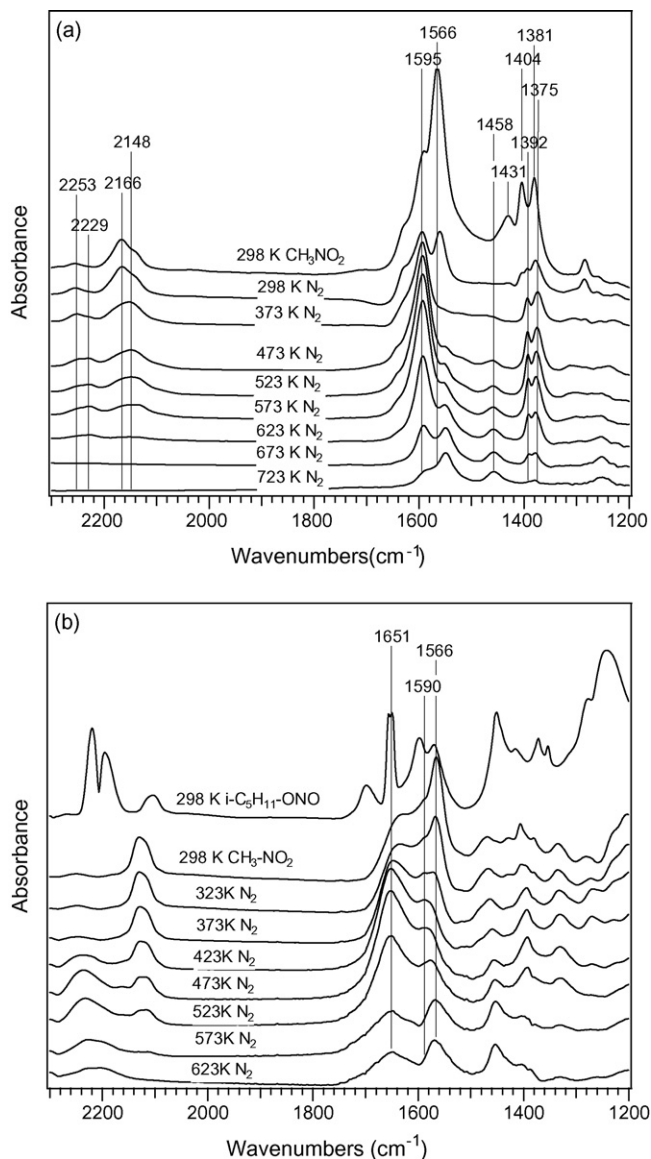
Fig. 5. DRIFTS spectra of Ag/Al$_2$O$_3$ at different temperatures in a flow of N$_2$ after exposing to CH$_3$NO$_2$ for 30 min at 298 K (a) without KBr addition; (b) KBr diluted Ag/Al$_2$O$_3$ and the mass ratio of Ag/Al$_2$O$_3$ to KBr equals 1:4.

Al$_2$O$_3$. In other words, large amounts of R-NO$_2$ formed on the surface of Ag/Al$_2$O$_3$ during the NO$_x$ reduction by C$_3$H$_6$.

4. Conclusions

Two evidences in favor of the presence of organo-nitrite and -nitro species (R-NO$_2$ and R-ONO) as true intermediates in the SCR of NO$_x$ by C$_3$H$_6$ were observed using TPD and DRIFTS methods. In general, KBr dilution technique is not suitable for studying the NO$_x$-containing system by IR method. In this case, however, the addition of KBr in Ag/Al$_2$O$_3$ provides an opportunity for observation of R-NO$_2$ and R-ONO, which are not readily detected under real reaction conditions during the SCR of NO$_x$. Further investigation demonstrates that the presence of KBr catalyses the isomerization reaction of R-NO$_2$ to R-ONO on the surface of KBr-Ag/Al$_2$O$_3$.

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