PILLARED CLAYS AS SUPERIOR CATALYSTS FOR SELECTIVE CATALYTIC REDUCTION OF NITRIC OXIDE

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Abstract

In the last annual reports, we reported Cu-exchanged pillared clays as superior selective catalytic reduction (SCR) catalysts. During the past year we explored the possibilities with MCM-41, a new class of molecular sieve. In this report, Rh exchanged Al-MCM-41 is studied for the SCR of NO by C_3H_6 in the presence of excess oxygen. It shows a high activity in converting NO to N_2 and N_2O at low temperatures. *In situ* FT-IR studies indicate that Rh-NO^+ species (1910-1898 cm^{-1}) is formed on the Rh-Al-MCM-41 catalyst in flowing NO/He, NO+O_2/He and NO+C_3H_6+O_2/He at 100-350 ^oC. This species is quite active in reacting with propylene and/or propylene adspecies (e.g., π-C_3H_5, polyene, etc.) at 250 ^oC in the presence/absence of oxygen, leading to the formation of the isocyanate species (Rh-NCO, at 2174 cm^{-1}), CO and CO_2. Rh-NCO is also detected under reaction conditions. A possible reaction pathway for reduction of NO by C_3H_6 is proposed. In the SCR reaction, Rh-NO^+ and propylene adspecies react to generate the Rh-NCO species, then Rh-NCO reacts with O_2 , NO and NO_2 to produce N_2, N_2O and CO_2. Rh-NO^+ and Rh-NCO species are two main intermediates for the SCR reaction on Rh-Al-MCM-41 catalyst.

Introduction

Removal of nitrogen oxides (NO_x, x = 1, 2) from exhaust gases has been a challenging problem in recent years. Selective catalytic reduction (SCR) of NO_x by hydrocarbons in the presence of excess oxygen has been extensively studied.[1,2] Supported Pt-group metals have been reported to be active at lower temperatures and are stable in the presence of water vapor and sulfur dioxide.[1-9] Platinum, iridium, palladium, rhodium and ruthenium supported on Al_2O_3, TiO_2, SiO_2, ZrO_2, and ZSM-5 have been studied.[3-8] More recently, MCM-41 as a support and ion-exchanged MCM-41 have been studied in our laboratory[9] for the SCR reaction. Both ZSM-5 and MCM-41 have channel-type pores, however, the pores are much bigger in the MCM-41 catalysts, i.e., 0.5-0.6 nm in ZSM-5 vs. 3-4 nm in MCM-41. Hence the mass transfer resistance is considerably lower in the MCM-41 catalysts. Among various noble metals doped on Al_2O_3, Pt was reported to be the most active and resistant to H_2O and SO_2, but it produces substantial amount of N_2O. By comparison, Rh/Al_2O_3 has the highest product selectivity for N_2.[5] These different behaviors may be related to the different characteristics of the two metals and thus two different reaction pathways in the SCR reaction. For Pt supported catalysts, e.g., Pt/Al_2O_3 and Pt/ZSM-5, the reaction mechanism has been studied by TAP (temporal analysis of

products) and FT-IR techniques.[8,10] It has been generally accepted that the reaction path for reduction of nitric oxide involves a two-step process in which the NO molecules are decomposed to N and O atoms on the reduced platinum sites, then the N atom combines another N atom or a NO molecule to produce N_2 or N_2O. The oxidized Pt sites are regenerated by reduction with hydrocarbons (e.g., C_3H_6).[8,10,11] However, few studies on SCR on Rh supported catalysts have been reported and the mechanism for NO reduction on Rh catalysts is still unclear.[2,7,12].

In this work, we first report the activities and product selectivities of Rh-exchanged Al-MCM-41 for SCR of NO by propylene in the presence of excess oxygen. The mechanism was studied by focusing on the surface adspecies of the catalyst by *in situ* FT-IR spectroscopy under reaction conditions. MCM-41 was chosen for this study because it has high thermal stability, high BET surface area and large pore volume. It has already attracted considerable interests in resent years. It has been studied as catalysts, support and sorbents.[13-16] In our previous study, platinum doped MCM-41 catalyst showed higher specific activity than Pt/Al_2O_3 for the SCR reaction.[9] The present study shows that the Rh-exchanged Al-MCM-41 catalyst is more active and selective for N_2 than the Pt doped MCM-41 catalyst. It is also shown that N_2 and N_2O originate mainly from the reaction between $Rh\text{-}NO^+$ and propylene adspecies.

Experimental Section

Catalyst Preparation and Characterization. Al-MCM-41 (Si/Al=10) was synthesized according to the procedure given by Borade and Clearfield.[17] Fumed silica (99.8%, Aldrich), tetramethylammonium hydroxide pentahydrate (TMAOH, 97%, Aldrich), 25 wt.% cetyltrimethylammonium chloride (CTMACl) in water (Aldrich), $Al[C_2H_5CH(CH_3)O]_3$ (97%, Aldrich) and NaOH (98.1%, Fisher) were used as source materials for preparing Al-MCM-41. Solution A was prepared by dissolving 1.325 g TMAOH in 100 ml deionized water and then adding 5 g fumed silica. Solution B was obtained by dissolving 0.72 g NaOH in deionized water and adding 25 ml CTMACl followed by adding 2.19 ml $Al[C_2H_5CH(CH_3)O]_3$ at room temperature. The two solutions were stirred for 10-15 min, then solution A was added to solution B. The reaction mixture had the following chemical composition $1SiO_2$-$0.05Al_2O_3$-0.23CTMACl-$0.11Na_2O$-0.089TMAOH-$125H_2O$. After being stirred for 15 min, the mixture was transferred into a 250 ml three-neck flask and was then heated at 100 °C for 48 h. After filtering, the solid was washed, dried and calcined at 560 °C for 10 h in a flow of air (150 ml/min). The XRD pattern of Al-MCM-41 (Fig. 1) was consistent with that reported previously for Al-MCM-

41 molecular sieve[13,17] and all XRD peaks could be indexed on a hexagonal lattice with d_{100} = 3.9 nm.

Rh-exchanged Al-MCM-41 was prepared by using conventional ion exchange procedure. 1 g Al-MCM-41 sample was added to 200 ml 10^{-3} M $Rh(NO_3)_3$ solution at 70 ^oC with constant stirring. The pH value of the solution was adjusted to 6 with NaOH solution in order to maximize the rhodium ion-exchange capacity. A low pH is not favorable for ion exchange because of competition from H^+ and the fact that Rh exists as Rh^{3+}. At high pH Rh would precipitate as $Rh(OH)_3$. The exchange process was carried out for 6 h and repeated three times. After that, the mixture was filtered and washed 5 times with deionized water. The obtained solid sample was first dried at 120 ^oC in air for 12 h, then heated at 400 ^oC for 6 h in a flow of 5.34%H_2/N_2. The rhodium content in the Rh-Al-MCM-41 sample was analyzed by neutron activation analysis and was 3.14% (i.e., 61.7% ion exchange). The Rh dispersion was determined by CO chemisorption[9] and was 93%. The BET surface area, pore volume and average pore size of the Rh-Al-MCM-41 sample measured by N_2 adsorption at -196 ^oC with a Micromeritics ASAP 2010 micropore size analyzer were 952 m^2/g, 1.22 cm^3/g and 4.5 nm, respectively.

Catalytic Performance Measurement. The SCR activity measurement was carried out in a fixed-bed quartz reactor.[9] 0.1 g sample, as particles of 60-100 mesh, was used in this work without any pretreatment. The activity was measured after reaching a "steady state." The typical reactant gas composition was as follows: 1000 ppm NO, 1000 ppm C_3H_6, 2% O_2 and balance He. The total flow rate was 250 ml/min (ambient conditions). The premixed gases (1.01% NO in He and 1.00% C_3H_6 in He) were supplied by Matheson Company. The NO_x concentration was continuously monitored by a chemiluminescent NO/NO_x analyzer (Thermo Electro Corporation, Model 10). The other effluent gases were analyzed by a gas chromatograph (Shimadzu, 14A) at 50 °C with a 5A molecular sieve column for O_2 , N_2 and CO, and a Porapak Q column for CO_2, N_2O and C_3H_6.

FT-IR Study. Infrared spectra were recorded on a Nicolet Impact 400 FT-IR spectrometer with a TGS detector. Self-supporting wafers of 1.3 cm diameter were prepared by pressing 10 mg samples and were loaded into a high temperature IR cell with BaF_2 windows. The wafers could be pretreated *in situ* in the IR cell. The wafers were first treated at 400 ^oC in a flow of He (99.9998%) for 30 min, and then cooled to desired temperatures, i.e., 350, 300, 250, 200, 100 ^oC. At each temperature, the background

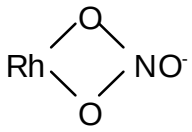
spectrum was recorded in flowing He and was subtracted from the sample spectrum that was obtained at the same temperature. Thus the IR absorption features that originated from the structural vibrations of the catalyst were eliminated from the sample spectra. Unless otherwise stated, a standard pretreatment procedure at 350 ^{o}C was performed before gas adsorption. The procedure consisted of oxidizing the sample in flowing O_2 for 10 min followed by purging with He for 15 min, then reducing the sample by H_2 for 10 min and finally flushing in He for 15 min. In the experiment, the IR spectra were recorded by accumulating 100 or 8 scans at a spectral resolution of 4 cm^{-1}. The gas mixtures (i.e., NO/He, C_3H_6/He, NO+O_2/He, C_3H_6+O_2/He, NO+C_3H_6+O_2/He, etc.) had the same concentrations as that used in the activity measurements, i.e., 1000 ppm NO (when used), 1000 ppm C_3H_6 (when used), 2% O_2 (when used) and balance of He. The total gas flow rate was 250 ml/min.

Results and Discussion

Catalytic Performance for SCR Reaction. For pure Al-MCM-41, no NO conversion to N_2 or N_2O was obtained at 200-400 ^{o}C under the reaction conditions (0.1 g sample, 1000 ppm NO, 1000 ppm C_3H_6, 2% O_2 and 250 ml/min of total flow rate).

Whereas, as shown in Table 1, Rh-Al-MCM-41 was active for the SCR reaction. With increasing temperature, the NO conversion increased first, passing through a maximum, then decreased at higher temperatures. The maximum NO conversion appeared at the temperature at which C_3H_6 conversion reached 100%. At high temperatures, the decrease in NO conversion was due to the combustion of C_3H_6 by O_2. Carbon dioxide was the only product (besides water) of propylene oxidation. The nitrogen balance was above 95% in this work. The product selectivity for N_2 was between 60% and 78%. The maximum NO conversion on Rh-Al-MCM-41 catalyst was slightly higher than that on Pt/MCM-41 catalyst (68.2% at 300 ^oC vs. 63.6% at 250 ^oC)[9] under the same reaction conditions. The former also had much higher product selectivities for N_2 than the latter, which is in agreement with the previous result that Rh doped catalysts have higher N_2 selectivities than Pt catalysts.[2] Since Al-MCM-41 was inactive in the SCR reaction, it is clear that rhodium acted as active sites for NO reduction on the Rh-Al-MCM-41 catalyst. The high activity on the catalyst may be attributable to the high rhodium dispersion (93%, obtained by CO chemisorption). It is known that ion exchange can be used to prepare highly dispersed Rh in NaY zeolite.[18]

IR Spectra of NO and NO_2 Adsorption on Rh-Al-MCM-41 Catalyst. The adsorption of NO and NO_2 was studied at 250 ^oC on both oxidized and reduced Rh-Al-MCM-41 by FT-IR spectroscopy. The oxidized Rh-Al-MCM-41 was obtained by calcining the sample at 350 ^oC in a flow of O_2 for 10 min followed by purging with He for 15 min. After the sample was exposed to a flowing NO/He for 10 min at 250 ^oC, three IR bands were observed at 1900, 1634 and 1534 cm^{-1} (Fig. 2a). The band at around 1900 cm^{-1} was always observed on NO adsorbed Rh catalysts. It is attributable to NO adsorbed on the partially oxidized Rh sites, i.e., $Rh\text{-}NO^+$ [7,19-21], which is generated by the donation of the unpaired electron from the $2p\ ^*$ antibonding orbital of the NO molecule to the 4d orbital of rhodium. This results in an increase in the strength of N-O bond and hence the NO molecule associated with Rh^+ sites is more difficult to decompose to N and O atoms than the free NO molecule. The band at 1534 cm^{-1} is due to the ν (N=O) vibration of the bidentate nitrato species: [19]



This species was also observed on the NO adsorbed Rh/SiO_2 catalyst by Srinivas et al.[20] The weaker band at 1634 cm^{-1} may be assigned to NO_2 adsorbed on Rh sites.[7,20] NO was also adsorbed on a reduced sample. Rh-Al-MCM-41 was reduced by H_2 at 350 ^oC for 10

min followed by purging with He for 15 min. NO was then adsorbed at 250 ^{o}C for 10 min. The Rh-NO^{+} band was stronger and appeared at a lower wavenumbers (1895 cm^{-1}) as compared to that on the oxidized sample (Fig. 2b), indicating that more Rh^{+} sites were produced on the reduced catalyst. In addition, two weak bands were seen at 1776 and 1644 cm^{-1}. The 1776 cm^{-1} band can be assigned to Rh-NO^{-}.[20-23] The NO^{-} species with a weakened N-O bond would be easier to dissociate. It is known that NO molecules could be decomposed to N and O atoms on reduced Rh sites and thus oxidize the Rh sites.[21] While the assignment of the band at 1644 cm^{-1} is complicated, Xin et al. [10] and Tanaka et al. [23] assigned the band around 1657 cm^{-1} on Pt catalyst to ν(ONO), but the wavenumbers of nitrito complexes generally fall in the range of 1485-1400 cm^{-1} and 1110-1050 cm^{-1}, as shown by Nakamoto.[22] Therefore this band could also be due to Rh-NO^{-} at different sites on the Rh catalyst , as suggested by Srinivas et al. [20] The IR spectrum of NO+O_2/He adsorbed on Rh-Al-MCM-41 was similar to that of NO adsorbed on the oxidized sample, i.e., Rh-NO^{+} (1904 cm^{-1}), Rh-NO_2 (1634 cm^{-1}) and a bidentate nitrato species (1541 cm^{-1}) were observed (Fig. 2c). When Rh-Al-MCM-41 was treated in a flow of NO_2/He, Rh-NO^{+} (1910 cm^{-1}), Rh-NO_2 (1627 and 1602 cm^{-1}) and a bidentate nitrato species (1554 cm^{-1}) were formed, with Rh-NO_2 as the dominant species (Fig. 2d). The formation of Rh-NO^{+} indicates that NO_2 molecules were partly decomposed to NO molecules on Rh sites.

IR Spectra of adsorbed $NO+O_2$ at Different Temperatures. Fig. 3 shows a series of spectra of Rh-Al-MCM-41 in flowing $NO+O_2$/He at different temperatures. After the sample was treated by $NO+O_2$/He at 100 ^oC for 10 min, Rh-NO^+ (1910 cm^{-1}), Rh-NO_2 (1634 cm^{-1}) and bidentate nitrato species (1543 cm^{-1}) were formed (Fig. 3a). In addition, a small peak was observed at 1315 cm^{-1}. This peak was also seen on the NO_2 adsorbed Rh-Al-MCM-41, but not observed on the NO adsorbed sample that was pretreated by H_2. This peak was most likely due to adsorbed NO_2^- species.[22] This species disappeared at 200 ^oC (Fig. 3b). With an increase in temperature, the Rh-NO^+ band (1910 cm^{-1}) grew to a maximum intensity at 250 ^oC, and then declined at higher temperatures. Rh-NO^+ was the dominant species at temperatures below 300 ^oC. By comparison, increasing the temperature from 100 to 350 ^oC resulted in an increase in the bidentate nitrato species (1543 cm^{-1}), but a decrease in the Rh-NO_2 species (1634 cm^{-1}) (Fig. 3). The bidentate nitrato species became the dominant adspecies at 350 ^oC due to oxidation of rhodium. Because NO molecules are easily decomposed to N and O atoms and thus oxidizing the pre-reduced Rh sites to form [$Rh(O_2)^-$], other NO molecules can adsorb on the oxidized Rh sites [$Rh(O_2)^-$] to form RhO_2NO, i.e., bidentate nitrato species. At high temperatures,

most of the Rh surface was covered by oxygen atoms, and many Rh sites were oxidized to [$Rh(O_2)^-$] sites, so bidentate nitrato became the dominant species.

IR Spectra of Rh-Al-MCM-41 in a Flow of $C_3H_6+O_2$/He. When Rh-Al-MCM-41 was exposed to flowing $C_3H_6+O_2$/He at 100 ^oC, a series of IR bands were observed (Fig. 4a). The weak peaks between 3084 and 2924 cm^{-1} resulted from asymmetric or symmetric C-H stretching vibrations of $=CH_2$ and $-CH_3$ groups of gaseous or weakly adsorbed C_3H_6.[24,25] They disappeared after the sample was purged by He for 15 min. The stronger bands at 1675 and 1430 cm^{-1} can be assigned to acrolein and carboxylate adspecies, respectively.[21,24-26] The appearance of the band at 1594 cm^{-1} indicates the formation of polyene species.[21] The shoulders at 1490 and 1372 cm^{-1} are due to π-allyl complex (π-C_3H_5) and allylic species, respectively.[21,26] The assignments of these bands are summarized in Table 2. These results indicate that oxidation of C_3H_6 took place on the Rh-Al-MCM-41 catalyst at 100 ^oC. With an increase in temperature, the intensity of the carboxylate species (1430 cm^{-1}) grew to a maximum at 250 ^oC and then declined, and it disappeared completely at 350 ^oC. The other adspecies, i.e., allylic, π-C_3H_5, polyene and acrolein, decreased with the increase in temperature and vanished at 300 ^oC. Moreover, four new bands at 2363, 2335, 2103 and 2046 cm^{-1} appeared at 200 ^oC (Fig. 4b). The

bands at 2363 and 2335 cm^{-1} can be assigned to gaseous or weakly adsorbed CO_2 species, while the other two bands are attributed to carbon monoxide adsorbed linearly on two different rhodium sites.[20,21] Increasing temperature resulted in an increase of CO_2 bands but a decrease of CO adspecies bands. The oxidation reaction of propylene has been intensively studied on various catalysts and the mechanism is understood.[21] The above results suggests that the reaction route between C_3H_6 and O_2 on the Rh-Al-MCM-41 catalyst is in agreement with the previous mechanism, i.e., propylene molecules are first adsorbed on the active sites (Rh sites) to produce allylic and π-C_3H_5 species, which can further dehydrogenate to form a polyene species or react with oxygen species to produce acrolein and carboxylate species. They are finally oxidized to CO and CO_2 by oxygen.

IR Spectra of Reaction Between C_3H_6 and NO_x Adspecies. Rh-Al-MCM-41 was first treated with $NO+O_2$/He followed by He purge at 250 ^oC. C_3H_6/He was then introduced and the IR spectra were recorded as a function of time (Fig. 5). As noted above, Rh-NO^+ (1898 cm^{-1}), Rh-NO_2 (1629 cm^{-1}) and bidentate nitrato species (1536 cm^{-1}) were formed after Rh-Al-MCM-41 was treated with $NO+O_2$/He (Fig. 5a) and their IR bands did not decrease in flowing He for 5 min. After C_3H_6/He was passed over the sample for 15 seconds, the bands due to Rh-NO^+ (1898 cm^{-1}) and bidentate nitrato species

(1536 cm^{-1}) declined rapidly, while CO_2 (2363 and 2335 cm^{-1}) and Rh-CO (2025 cm^{-1})[20,21] species were formed (Fig. 5b). In addition, a new weak band at 2174 cm^{-1} was also observed, suggesting the formation of an isocyanate complex (Rh-NCO).[7,20,21,27-29] The Rh-NCO species was detected by many researchers when investigating the interaction of NO and CO on supported rhodium catalysts. For example, Hecker and Bell[27,28] studied the formation of -NCO by *in situ* IR spectroscopy on Rh/SiO_2. They assigned the band at 2300 cm^{-1} to Si-NCO and that at 2190-2170 cm^{-1} to Rh-NCO based on a comparison with the spectra of isocyanate complex over transition metals. The Rh-NCO species at 2172 cm^{-1} was also identified by isotope exchange experiment.[29] The decrease of the IR bands due to $Rh\text{-}NO^+$ and bidentate nitrato species as well as the formation of CO_2, Rh-CO and Rh-NCO species clearly indicated that C_3H_6 reacted with these nitrogen oxides adspecies. Decrease of the 1629 cm^{-1} band was not apparent. This is probably due to the fact that the product H_2O, resulting from oxidation of propylene, also has an IR band near 1629 cm^{-1}. The bands at 1629 and 1536 cm^{-1} vanished in 30 seconds (Fig. 5c). After the sample was treated in a flow of C_3H_6/He for 60 seconds, the $Rh\text{-}NO^+$ and Rh-NCO bands also disappeared and the CO adspecies became dominant on the surface, with a linear CO band at 2004 cm^{-1} and a bridged CO band at 1830 cm^{-1}.[20]

IR Spectra of Reaction Between $C_3H_6+O_2$ and Adsorbed NO_x. Figure 6 shows the IR spectra observed during the reaction between $C_3H_6+O_2$/He and nitrogen oxides adspecies at 250 ^oC. As $C_3H_6+O_2$/He was passed over the $NO+O_2$ adsorbed Rh-Al-MCM-41, there was a gradual decrease in the Rh-NO^+ band (1898 cm^{-1}) and the bidentate nitrato band (1536 cm^{-1}), and simultaneous formation of CO_2 (2363 and 2335 cm^{-1}). Meanwhile, Rh-NCO (2174 cm^{-1}) and Rh-CO (2103 and 2047 cm^{-1}) were progressively formed. On the other hand, some features that were assigned to acrolein (1670 cm^{-1}), polyene (1594 cm^{-1}), π-C_3H_5 (1492 cm^{-1}) and carboxylate species (1427 cm^{-1}) [21,24-26] also appeared. After 5 min, only a trace of Rh-NO^+ and Rh-NCO were detected, and the other IR features were similar to that of the fresh Rh-Al-MCM-41 catalyst exposed in flowing $C_3H_6+O_2$/He at 250 ^oC (as shown in Fig. 4c). These results indicate that C_3H_6 could also reduce the nitrogen oxides adspecies in the presence of excess oxygen, but the disappearance of nitrogen oxides adspecies required a longer time (> 5 min vs. 1 min) as compared with that in the absence of oxygen (compare Fig. 5 and Fig. 6). This is attributable to the competitive consumption of C_3H_6 by O_2. Besides, CO_2, not CO, was the main product of propylene oxidation in the reaction between $C_3H_6+O_2$ and nitrogen oxides adspecies.

IR Spectra of Rh-Al-MCM-41 in a Flow of NO+C_3H_6+O_2/He. To identify the species present on the catalyst under reaction conditions, IR spectra were recorded in a flow of NO+C_3H_6+O_2/He when Rh-Al-MCM-41 was heated from 100 to 350 ^oC. As shown in Fig. 7a, a series of IR bands were observed at 3084-2924, 1899, 1730, 1675, 1635, 1600, 1507, 1428 and 1373 cm^{-1} at 100 ^oC. These bands were also detected on the sample in flowing NO/He, NO+O_2/He and C_3H_6+O_2/He (Figs. 2, 3 and 4). As indicated above, the weak bands between 3084 and 2924 cm^{-1} are due to the C-H stretching vibration of C_3H_6; the bands at 1899 and 1730 cm^{-1} are attributable to Rh-NO^+ and Rh-NO^- species, respectively. The shoulders at 1675, 1600 cm^{-1} and the weak bands at 1507, 1428 and 1373 cm^{-1} can be assigned to acrolein, polyene, π-C_3H_5, carboxylate and allylic species, respectively.[20-26] The band at 1635 cm^{-1}, assigned to Rh-NO_2 species above, was probably also due to H_2O here because oxidation of C_3H_6 took place at 100 ^oC. When the temperature was raised to 200 ^oC, the IR bands attributed to Rh-NO^+ (1899 cm^{-1}), π-C_3H_5 (1507 cm^{-1}) and carboxylate (1428 cm^{-1}) increased (Fig. 7b). Moreover, two new peaks at 2174 and 1777 cm^{-1} appeared, which can be assigned to Rh-NCO and Rh-NO^- species, respectively.[20-22,27-29] The formation of Rh-NCO indicates that the reaction between NO and C_3H_6 occurred at 200 ^oC. At 250 ^oC, the IR bands due to CO_2 at 2363 and 2335 cm^{-1} were detected. In addition, a very small peak at 2241 cm^{-1} was also observed, suggesting

the formation of gaseous N_2O [20]. The IR bands of these adspecies were changed with an increase in temperature. Rh-NCO and carboxylate species grew to a maximum at 250 ^oC, and then decreased at higher temperatures. The maximum of Rh-NO^+ species appeared at 300 ^oC. At 350 ^oC, besides CO_2, Rh-NO^+ and Rh-NO_2, a new band at 1541 cm^{-1} was detected, which is attributable to the bidentate nitrato species.[19,20] It is noted that propylene was consumed by oxygen and nitric oxide at this temperature. No adsorbed or gaseous CO species was observed during the reaction at 100-350 ^oC.

Reaction Mechanism of NO Reduction by C_3H_6 in the Presence of O_2. As indicated above, when NO was introduced to the oxidized Rh-Al-MCM-41 or NO+O_2 was passed over the reduced sample at 250 ^oC, Rh-NO^+, bidentate nitrato species and a small amount of Rh-NO_2 were observed. Rh-NO^+ was the dominant species on the surface. It was also observed on Rh-Al-MCM-41 in the presence of NO+C_3H_6+O_2/He at 100-350 ^oC (Fig. 7). The nitrogen oxides adspecies were quite reactive towards C_3H_6 at 250 ^oC in the absence or presence of excess oxygen, leading to the formation of Rh-NCO, CO and CO_2 (Figs. 5, 6). However, under reaction conditions, the bidentate nitrato species was not detected until C_3H_6 was totally consumed at 350 ^oC (Fig. 7). It can not be a reaction intermediate in the SCR reaction. It is also unclear if Rh-NO_2 species existed on

the catalyst under reaction conditions due to its overlap with the H_2O band. Considering that the concentration of Rh-NO_2 was always much lower than that of Rh-NO^+ on the NO adsorbed Rh-Al-MCM-41 catalyst (Figs. 2,3), its contribution to the production of N_2 and N_2O would be small as compared with that by Rh-NO^+, even if it is formed under reaction conditions. Therefore, Rh-NO^+ may be the main primary intermediate species for the reduction of NO by C_3H_6.

When C_3H_6 and C_3H_6+O_2 reacted with the nitrogen oxides adspecies on the Rh-Al-MCM-41 catalyst, Rh-NCO was produced (Fig. 5 and 6). This species was also observed on the catalyst under reaction conditions (Fig. 7). In the study of NO + CO reaction, Rh-NCO was detected on the rhodium doped catalysts and attracted considerable interests.[19] It was considered to be formed from the reaction between CO and Rh-N resulting from the dissociation of NO on the reduced Rh sites. However, in the SCR reaction, we did not detect any gaseous or adsorbed CO species on Rh-Al-MCM-41 (Fig. 7). Hence the Rh-NCO species was most probably formed from reduction of Rh-NO^+ by C_3H_6. The Rh-NCO species was reported to be active in reacting with O_2 and NO to form N_2 and N_2O on the Rh/Al_2O_3 catalyst.[30] Rh-NCO may also be another intermediate during the SCR reaction.

As $NO+C_3H_6+O_2$/He was passed over Rh-Al-MCM-41 at 100 ^oC, besides $Rh\text{-}NO^+$ and $Rh\text{-}NO^-$, acrolein, polyene, $\pi\text{-}C_3H_5$, carboxylate and allylic species were formed (Fig. 7). This suggests that partial oxidization of C_3H_6 took place at 100 ^oC. The reactions between the nitrogen oxides adspecies with propylene took place at above 200 ^oC, as identified by the formation of Rh-NCO, N_2O and CO_2 species. Since the propylene adspecies (polyene, $\pi\text{-}C_3H_5$, allylic species, etc.) are strong reductants, they can also reduce the nitrogen oxides adspecies at high temperatures. Based on the above results, a possible mechanism for the reduction of NO by C_3H_6 in the presence of excess O_2 on the Rh-Al-MCM-41 catalyst is present as follows:

$$Rh^+ + NO \leftrightarrow Rh\text{-}NO^+ \quad (1)$$

$$C_3H_{6\,(g)} \rightarrow C_3H_{6\,(a)}\ (+[O]) \rightarrow \text{-}C_3H_5, \pi\text{-}C_3H_5, \text{polyene, ...} \quad (2)$$

$$Rh\text{-}NO^+ + C_3H_{6\,(a)}, \text{-}C_3H_5, \pi\text{-}C_3H_5, \text{polyene, ...} \rightarrow \ ... \rightarrow Rh\text{-}NCO \quad (3)$$

$$Rh\text{-}NCO + 1/2\ O_2 \rightarrow \ Rh + 1/2\ N_2 + CO_2 \quad (4)$$

$$Rh\text{-}NCO + NO \rightarrow Rh + N_2 + CO_2 \quad (5)$$

$$NO + 1/2\ O_2 \rightarrow NO_2 \quad (6)$$

$$Rh\text{-}NCO + NO_2 \rightarrow Rh + N_2O + CO_2 \quad (7)$$

$$Rh + 1/4\ O_2 \rightarrow Rh^+ + 1/2\ O^{2-} \quad (8)$$

The reaction begins with the adsorption of NO molecules on the partially oxidized Rh^+ sites to form Rh-NO^+ (reaction 1) and the adsorption of C_3H_6 on the catalyst to form propylene adspecies, such as allylic species, π-C_3H_5, polyene, etc. (reaction 2). The Rh-NO^+ and the adjacent propylene adspecies form the Rh-NCO species (reaction 3). The Rh-NCO then reacts with O_2 , NO and NO_2 to produce N_2, N_2O and CO_2 (reaction 4-7). At the same time, Rh is oxidized back to Rh^+ ions (reaction 8) and thus a catalytic cycle for the SCR reaction is accomplished. Besides the major reaction path, some N_2 and N_2O may also come from NO dissociation because a small amount of Rh-NO^- species was also observed under reaction conditions (Fig. 7). It is known that reduced Rh metal is active for the decomposition of NO molecules.[21] The above reaction mechanism on the Rh-Al-MCM-41 catalyst is different from that on Pt doped catalysts [8,10,11] as well as Cu-ZSM-5 [1] , Co-ZSM-5 [31] and Mn-ZSM-5 catalysts [32] .

In addition to the SCR reaction, the propylene adspecies can also be oxidized by oxygen. The reaction path is as follows:

-C_3H_5, π-C_3H_5 (+[O]) → acrolein (+[O]) → carboxylate (+[O]) → CO_2 (9)

-C_3H_5, π-C_3H_5 (+[O]) → polyene (+[O]) → CO_2 (10)

The oxidation reaction competes with the SCR reaction for the consumption of propylene.

Conclusions

Rh-Al-MCM-41 was active for the reduction of NO by C_3H_6 in the presence of excess oxygen. The Rh-NO^+ species was observed by *in situ* FT-IR spectroscopy on the catalyst in flowing NO/He, NO+O_2/He and NO+C_3H_6+O_2/He. It could react with propylene and/or propylene adspecies (e.g., π-C_3H_5, polyene, etc.) at 250 ^oC in the presence or absence of oxygen. During the SCR reaction, an isocyanate species (Rh-NCO) was also detected. A main reaction path for the reduction of NO by C_3H_6 was proposed. In this path, Rh-NO^+ and propylene adspecies first form a Rh-NCO species, then the Rh-NCO species reacts with O_2 , NO and NO_2 to produce N_2, N_2O and CO_2.

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Table 1. Catalytic performance of Rh-Al-MCM-41 catalyst for SCR reaction

Temperature	NO Conversion	Selectivity (%)		C_3H_6 Conversion
(^oC)	(%)	N_2	N_2O	(%)
200	5.6	62.5	37.5	2.4
250	34.0	60.3	39.7	43.1
275	68.2	69.0	31.0	100
300	44.9	66.0	34.0	100
325	33.5	65.0	35.0	100
350	23.5	67.0	33.0	100
400	15.8	78.0	22.0	100

Reaction conditions: 0.1 g catalyst, [NO] = [C_3H_6] =1000 ppm, [O_2] = 2%, He = balance and total flow rate = 250 ml/min.

Table 2 Assignments of IR bands for the reaction $C_3H_6+O_2$ on Rh-Al-MCM-41

Bands (cm^{-1})	Assignments	References
3084	ν_{as} (=CH_2), C_3H_6	24, 25
2984	ν_s (=CH_2), C_3H_6	24, 25
2956	ν_{as} (-CH_3), C_3H_6	24, 25
2924	ν_s (-CH_3), C_3H_6	24, 25
2363, 2335	CO_2	20
2103, 2046	ν (CO), CO adsorbed on different Rh sites	20, 21
1675	ν_{as} (C=O), Acrolein	24-26
1594	Polyene species	21
1490-1510	π-allyl complex (π-C_3H_5)	21
1430	Surface carboxylate species	21
1372	Allylic species	26

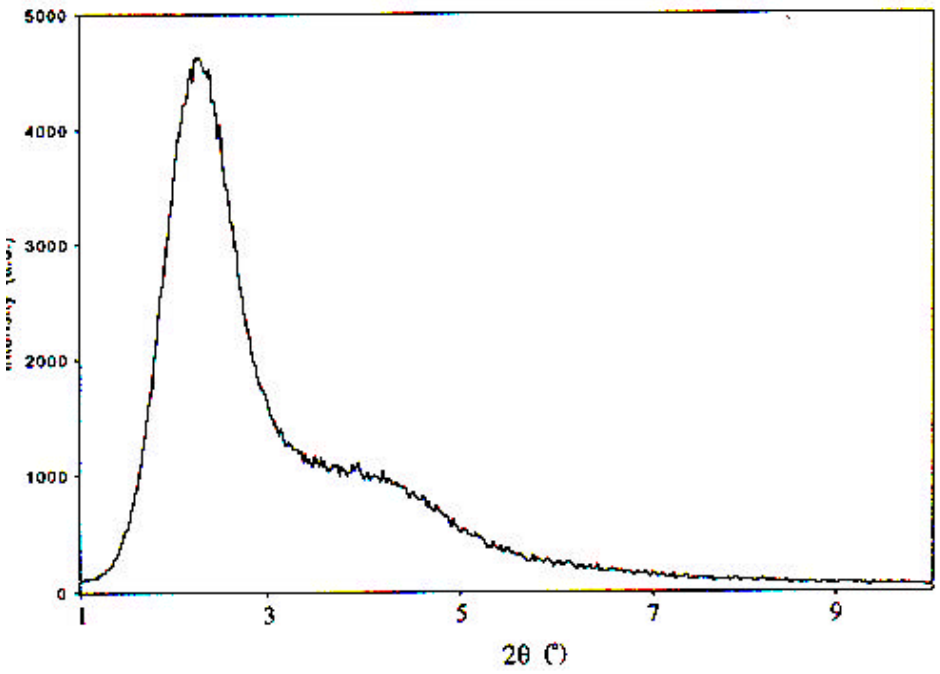

Fig. 1 XRD pattern of Al-MCM-41 sample.

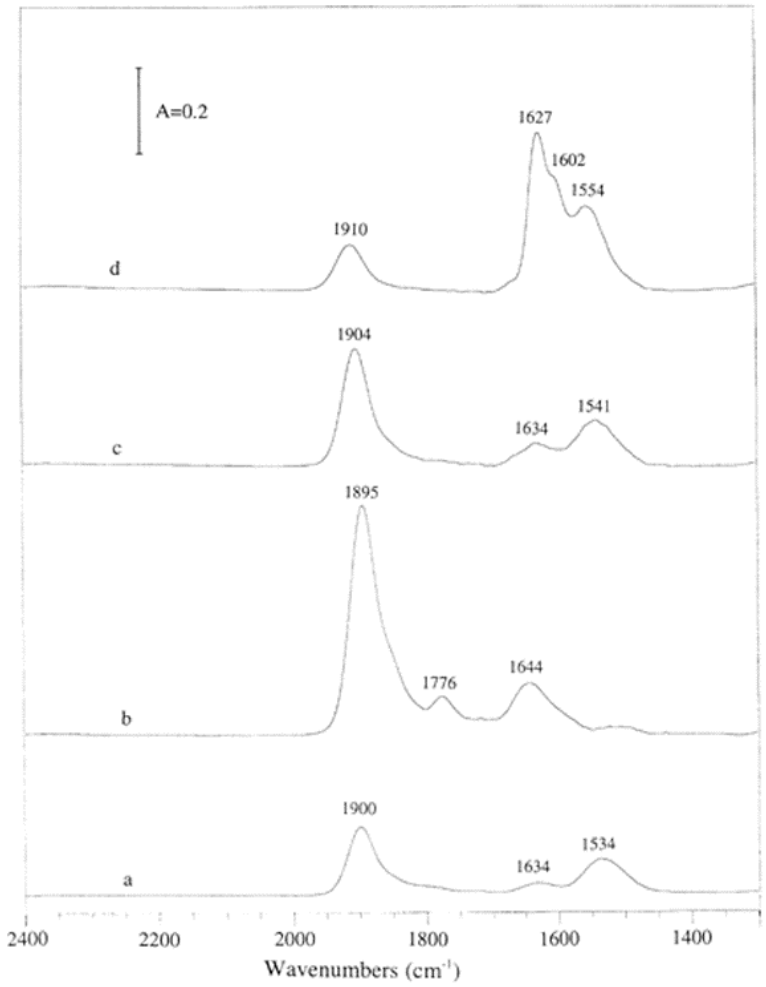

Fig. 2 IR spectra of (a) 1000 ppm NO adsorbed on Rh-Al-MCM-41 pretreated by O_2, (b) 1000 ppm NO adsorbed on Rh-Al-MCM-41 pretreated by H_2, (c) 1000 ppm NO + 2% O_2 adsorbed on Rh-Al-MCM-41 pretreated by H_2 and (d) 1000 ppm NO_2 adsorbed on Rh-Al-

MCM-41 pretreated by H_2. The spectra (100 scans) were collected after the gases were passed over the sample for 10 min at 250 ^{o}C.

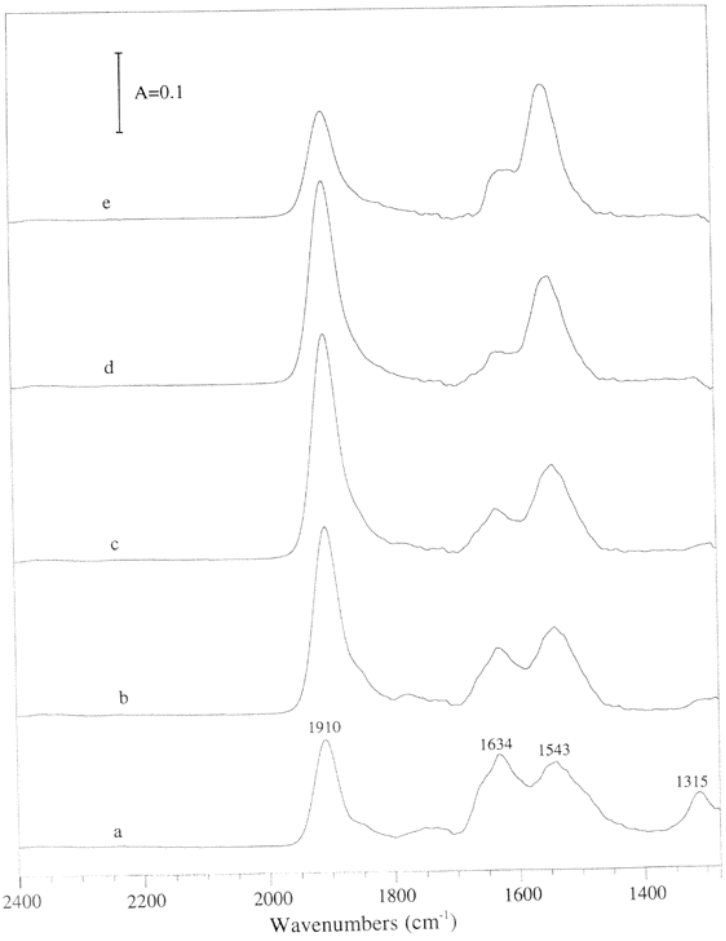

Fig. 3 IR spectra (100 scans) of Rh-Al-MCM-41 in a flow of 1000 ppm NO + 2% O_2/He at (a) 100, (b) 200, (c) 250, (d) 300 and (e) 350 ^{o}C.

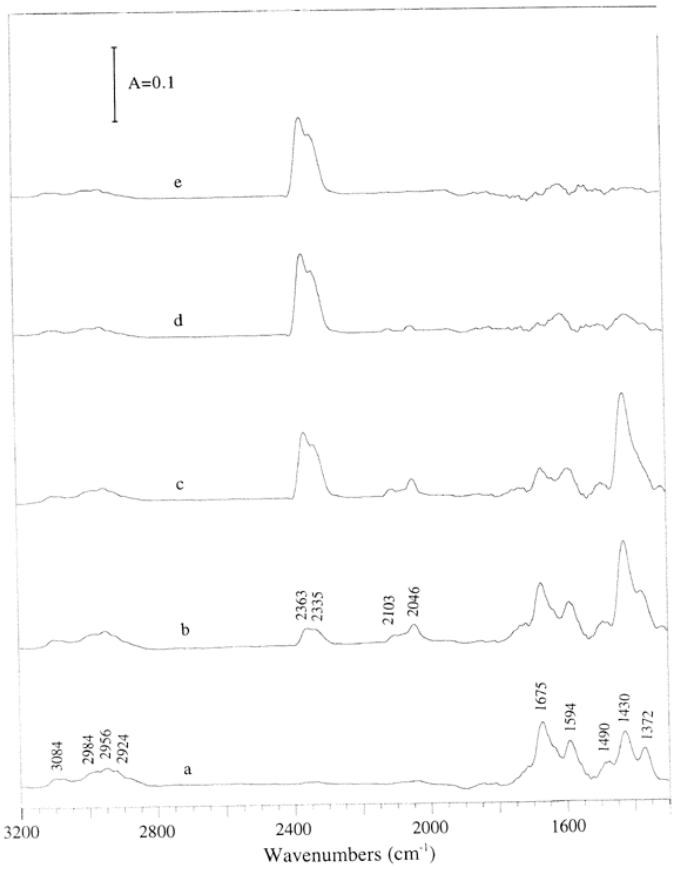

Fig. 4 IR spectra (100 scans) of Rh-Al-MCM-41 in a flow of 1000 ppm C_3H_6 + 2% O_2/He at (a) 100, (b) 200, (c) 250, (d) 300 and (e) 350 ^oC.

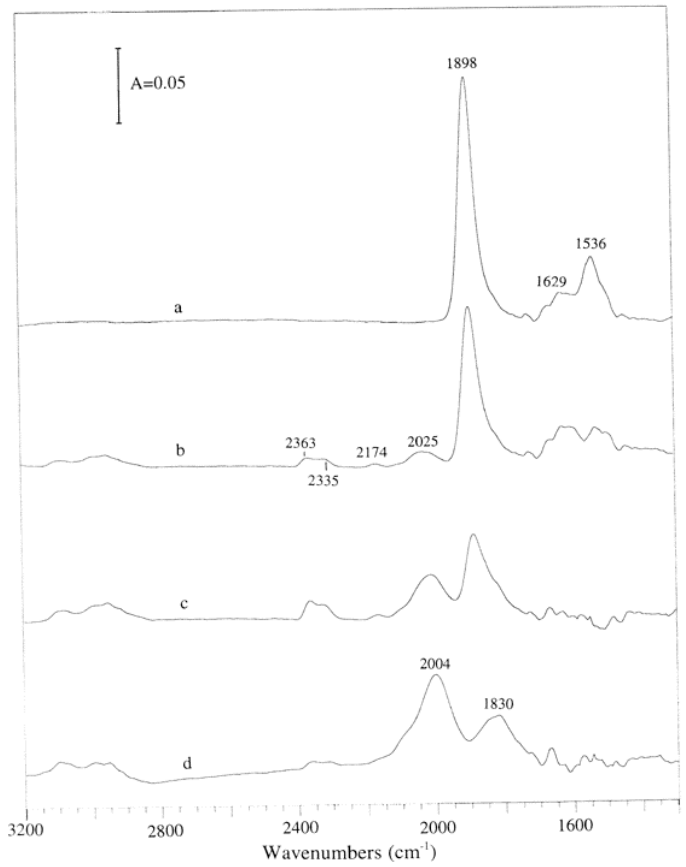
A=0.05
1898
1536
1629
a
b
2363
2335
2174
2025
c
2004
1830
d
3200
2800
2400
2000
1600
Wavenumbers (cm-1)

Fig. 5 IR spectra (8 scans) taken at 250 ^{o}C upon passing 1000 ppm C_3H_6/He over the $NO+O_2$ presorbed on Rh-Al-MCM-41 for (a) 0, (b) 15, (c) 30 and (d) 60 seconds.

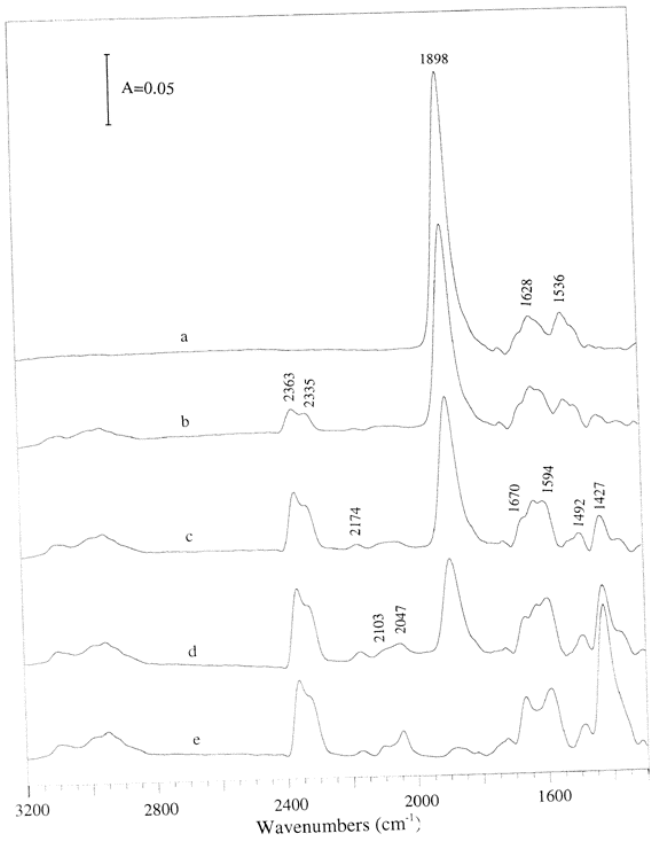

Fig. 6 IR spectra (8 scans) taken at 250 ^{o}C upon passing 1000 ppm C_3H_6 + 2% O_2/He over the NO+O_2 presorbed on Rh-Al-MCM-41 for (a) 0, (b) 15, (c) 30, (d) 60 and (e) 300 seconds.

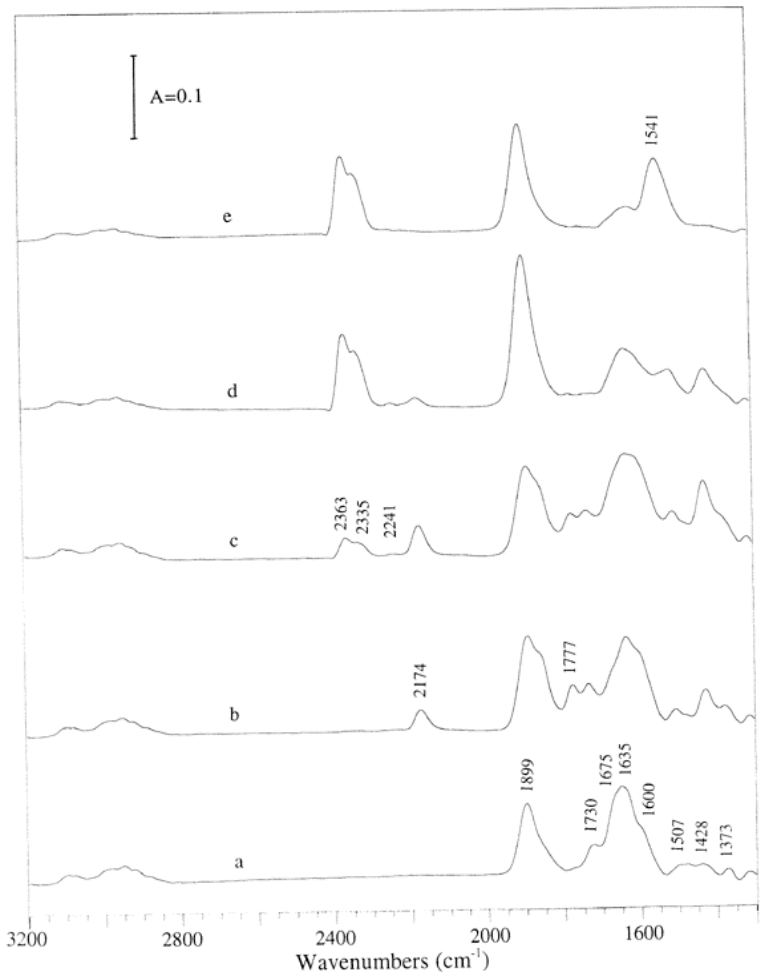

Fig. 7 IR spectra (100 scans) of Rh-Al-MCM-41 in a flow of 1000 ppm NO + 1000 ppm C_3H_6 + 2% O_2/He at (a) 100, (b) 200, (c) 250, (d) 300 and (e) 350 ^oC.