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FT-IR studies of the NO adsorption on rare earth (Eu/Gd/Tb) exchanged new generation silicoaluminophosphate catalysts of chabazite type

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Abstract

Novel rare earth exchanged silicoaluminophosphate catalysts (small pore, 0.43 nm) of chabazite type have been prepared. The rare earth elements europium (Eu), gadolinium (Gd) and terbium (Tb) were used for preparing the cation exchanged chabazite type SAPO-18 catalysts. Routine and sophisticated instrumental techniques were used for the material characterisation. The FT-IR technique was used to study the in situ interaction of NO on the rare earth exchanged SAPO-18 catalysts. The adsorption of NO on the Eu-, Gd-, Tb-exchanged SAPO-18 samples led to the formation of nitrous oxide, mono- and dinitrosyl complexes of Eu, Gd and Tb, nitrogen dioxide and nitrate species. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: NO; Eu; Gd; Tb; Chabazite; SAPO-18; FT-IR

1. Introduction

Recently, a number of studies have been reported on air pollution control, environmental catalysis and catalytic materials. From the environmental catalysis point of view, the range of heterogenous catalysts utilised varied from noble metal to transition metal supported materials for decomposition of hazardous gases. So far utilisation of the copper exchanged zeolites/silicoaluminophosphate materials has been considered for preparing the stable and economical catalysts [1–7]. In the field of heterogenous catalysis, numerous studies have been reported on the potential of copper catalysts and their NO reduction ability, however, no studies on certain f block elements are reported. Nitric oxide adsorption on heterogenous catalysts is widely used to study the nature and properties of adsorption sites present on the catalyst surface, preferably by FT-IR spectroscopy. The infrared frequencies and changes in the frequencies of the stretching vibrations of the adsorbed molecule give information about the adsorption sites (viz. type of sites, the state of metal, the state and localisation of cations, etc.) [8]. In this work, we have studied the adsorption-interaction of typical probe molecule with active metal species on the Eu-, Gd-, Tb-exchanged novel silicoaluminophosphate of type 18.

2. Experimental

2.1. Catalyst preparation

The Eu-, Gd-, and Tb-exchanged SAPO-18 materials were prepared by a liquid ion-exchange method. The calcined SAPO-18 was ion-exchanged with Eu, Gd and Tb in 0.010 M rare earth nitrate solution at

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343 K for 2 h, then filtered, washed and dried. This procedure was repeated two times. The materials were dried overnight at 373 K. SAPO-18 was obtained by calcination of the as-synthesised SAPO-18. As-synthesised SAPO-18 was prepared by hydrothermal crystallisation of gel (molar composition: 1.6 $C_8H_{19}N$, 1.0 Al_2O_3, 0.4 SiO_2, 0.9 P_2O_5, 50 H_2O) in a Teflon autoclave at 443 K for 8 days [9]. The crystallisation product was filtered, thoroughly washed and dried in air at 343 K. The *N*,*N*-diisopropylethylamine template was removed by calcination in a muffle furnace at 773 K for 16 h. The chemicals used for the synthesis work were Catapal (aluminium oxyhydroxide, AlO(OH)), *o*-phosphoric acid (85%, Merck), Aerosil (fumed silica, SiO_2) and *N*,*N*-diisopropylethylamine (99%, Aldrich). The details of the material characterisation and FT-IR measurements are given elsewhere [4,8,10–12].

3. Results and discussion

3.1. Characterisation

Highly crystalline and pure SAPO-18 was used for the preparation of rare earth exchanged SAPO-18 catalysts. The characteristics of the Eu-, Gd-, and Tb-exchanged SAPO-18 catalysts are listed in Table 1. The XRD and BET investigations indicated that the rare earth exchanged SAPO-18 catalysts were of high purity. After exchange with Eu, Gd and Tb, the micropore volume of SAPO-18 decreased by 44, 48 and 60% from 0.25 to 0.14, 0.25 to 0.13 and 0.25 to 0.10 $cm^3\ g^{-1}$, respectively. The total surface area decreased by 40, 39 and 43% from 653 to 394 $m^2\ g^{-1}$ for Eu-SAPO-18, 653 to 401 $m^2\ g^{-1}$ for Gd-SAPO-18 and 653 to 374 $m^2\ g^{-1}$ for Tb-SAPO-18.

The surface concentration of the elements and the binding energy data for the rare earth exchanged SAPO-18 catalysts were determined by XPS analysis (Table 1). Bulk chemical and XPS surface analysis for the rare earth exchanged SAPO-18 materials indicated that the levels of Eu and Gd were lower in the bulk of SAPO-18 than on the surface, however, the levels of Tb were higher in the bulk than on the surface. The binding energies (Table 1) of the other elements (Al_{2p}, Si_{2p}, P_{2p}) are close to those for tetrahedrally coordinated elements in metal substituted aluminophosphates [10] and low silica zeolites [11].

3.2. NO adsorbed rare earth exchanged SAPO-18

The interaction between NO and rare earth exchanged SAPO-18 is depicted in Figs. 1–6. After dehydration of the rare earth exchanged SAPO-18 in vacuo at 573 K for 16 h, exposure to NO produced up to five strong bands attributed to the formation of nitrous oxide, nitrogen dioxide, nitrate, mono- and dinitrosyl species. The bands at ∼1910, ∼1845, ∼1630, ∼1570 and ∼2250–2150 cm^{-1} are assigned to M–NO, M–$(NO)_2$ (symmetrical), M–NO_2, M–NO_3 and N_2O adsorbed species, respectively. The assignment of bands is consistent with most of the literature data [4,6,10,12–15]. The nitrosyl rare earth complexes and intermediates resulting from surface reaction between nitric oxide and rare earth exchanged SAPO-18 are summarised in Table 2.

NO adsorption experiments at various pressures and temperatures were carried out in order to study the influence of nitric oxide gas pressure on the rare earth–nitric oxide complexes. FT-IR results pertaining to the pressure changes of NO on the rare earth exchanged SAPO-18 are presented in Figs. 1, 3 and 5. For the rare earth exchanged SAPO-18 catalysts, the intensity of the mononitrosyl (M–NO) band at 1910 cm^{-1} initially increases with increasing NO pressure before decreasing. In addition, the intensity of the dinitrosyl [M–$(NO)_2$] symmetric band at 1845 cm^{-1} decreases with an increase in NO pressure. The dinitrosyl complex subsequently is oxidised and converts to an unstable complex with N_2O and O^- adsorbed species (2250–2150 cm^{-1}). Further reaction with NO sees the conversion of the unstable N_2O and O^- complex to an M–NO_2 complex (1630 cm^{-1}). Even further reaction with NO results in the formation of an M–NO_3 complex (1570 cm^{-1}), possibly via an unstable NO_2 and O^- complex. Evacuation of the FT-IR cell at 10^{-4} Torr for 20 min sees the removal of all rare earth–nitric oxide complexes adsorbed by the catalyst.

The decomposition of adsorbed NO species at different temperatures and constant pressure over the dehydrated rare earth exchanged SAPO-18 catalysts is shown in Figs. 2, 4 and 6. Experiments were undertaken at constant NO pressure of 22 Torr and temper-

Table 1
Properties of the rare earth metal exchanged SAPO-18 catalysts

Product composition (mol%)	
SAPO-18 (calcined)	Si, 17.7; Al, 42.9; P, 39.4
Rare earth-SAPO-18 (after ion-exchange)	Rare earth, 5.5; Si, 16.7; Al, 40.6; P, 37.2
Surface area of H-SAPO-18 ($m^2 g^{-1}$)	653
Micropore volume of H-SAPO-18 ($cm^3 g^{-1}$)	0.25
Surface area of Eu-SAPO-18 ($m^2 g^{-1}$)	394
Micropore volume of Eu-SAPO-18 ($cm^3 g^{-1}$)	0.14
Surface area of Gd-SAPO-18 ($m^2 g^{-1}$)	401
Micropore volume of Gd-SAPO-18 ($cm^3 g^{-1}$)	0.13
Surface area of Tb-SAPO-18 ($m^2 g^{-1}$)	374
Micropore volume of Tb-SAPO-18 ($cm^3 g^{-1}$)	0.10
Eu-SAPO-18: XPS analysis	
Surface composition (at.%)	Eu_{3d} 4.2, Si_{2p} 4.9, Al_{2p} 9.5, P_{2p} 20.4, O_{1s} 56.3, C_{1s} 4.7
E_b (eV) (FWHM (eV))[a]	Eu_{3d} 1137.1, Si_{2p} 103.8, Al_{2p} 74.6, P_{2p} 192.9, O_{1s} 533.4
Gd-SAPO-18: XPS analysis	
Surface composition (at.%)	Gd_{3d} 5.5, Si_{2p} 5.5, Al_{2p} 10.8, P_{2p} 13.1, O_{1s} 58.6, C_{1s} 6.5
E_b (eV) (FWHM (eV))[a]	Gd_{3d} 1187.9, Si_{2p} 102.3, Al_{2p} 74.9, P_{2p} 134.0, O_{1s} 531.9
Tb-SAPO-18: XPS analysis	
Surface composition (at.%)	Tb_{3d} 6.2, Si_{2p} 2.9, Al_{2p} 7.8, P_{2p} 11.4, O_{1s} 55.5, C_{1s} 16.2
E_b (eV) (FWHM (eV))[a]	Tb_{3d} 1243.0, Si_{2p} 100.5, Al_{2p} 74.8, P_{2p} 133.8, O_{1s} 532.0

[a] Referenced to C_{1s} (285 eV).

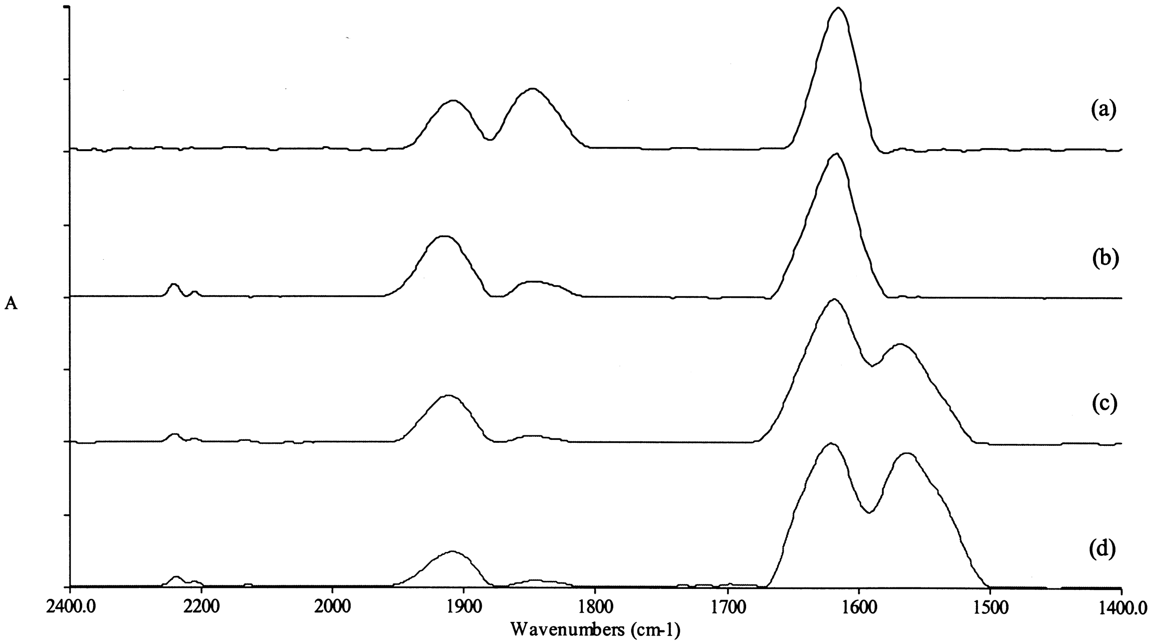

Fig. 1. FT-IR spectra of NO adsorbed at various pressures over the dehydrated Eu-SAPO-18 catalyst: (a) 12 Torr; (b) 22 Torr; (c) 61 Torr; (d) 72 Torr.

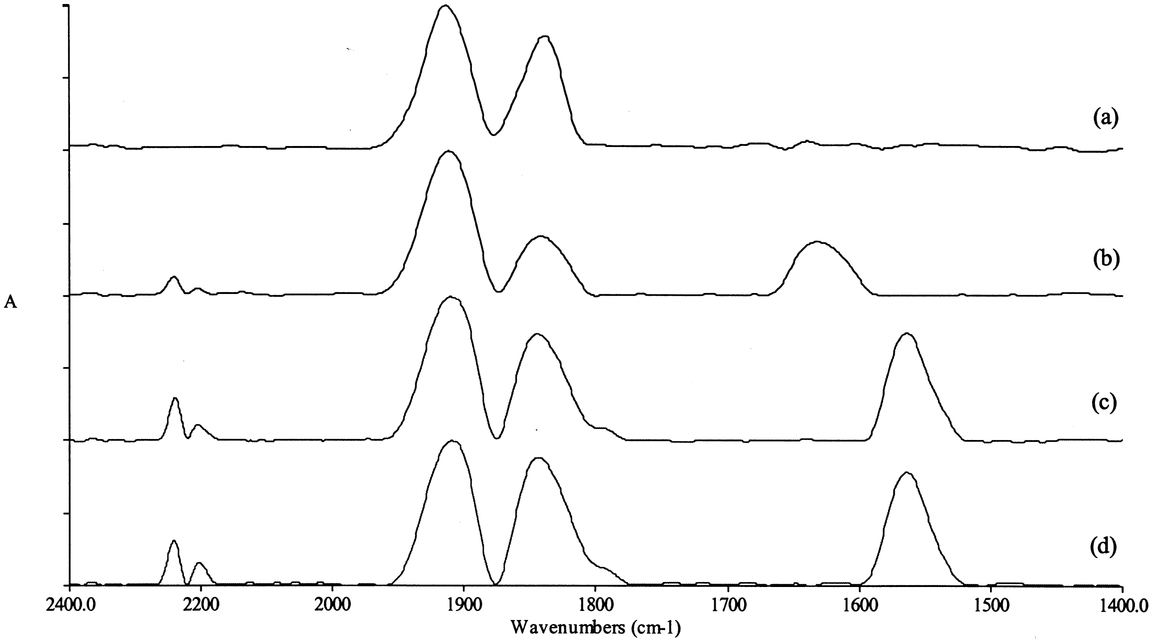

Fig. 2. FT-IR spectra of NO adsorbed at various pressures and temperatures over the dehydrated Eu-SAPO-18 catalyst: (a) 12 Torr; (b) 22 Torr; (c) 373 K; (d) 473 K.

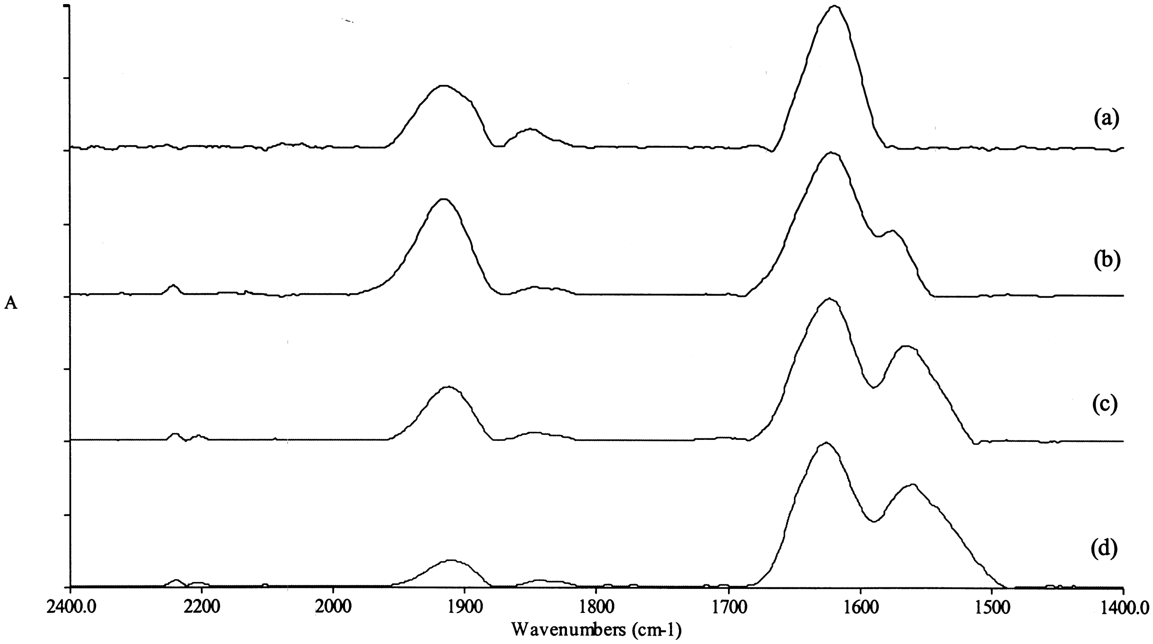

Fig. 3. FT-IR spectra of NO adsorbed at various pressures over the dehydrated Gd-SAPO-18 catalyst: (a) 12 Torr; (b) 22 Torr; (c) 61 Torr; (d) 72 Torr.

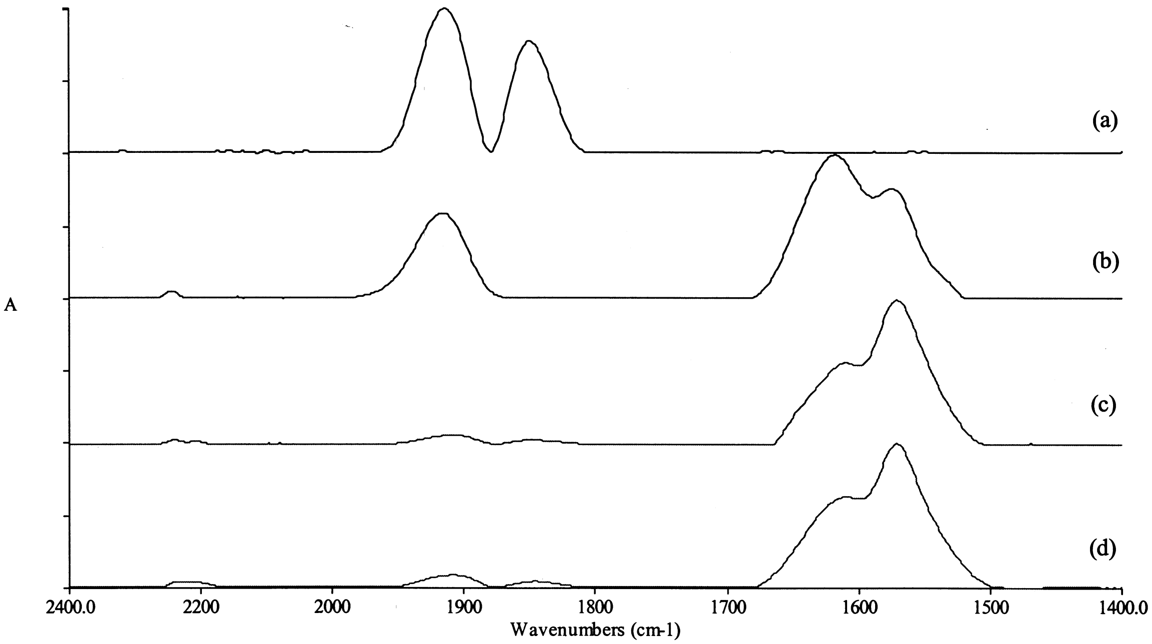

Fig. 4. FT-IR spectra of NO adsorbed at various pressures and temperatures over the dehydrated Gd-SAPO-18 catalyst: (a) 12 Torr; (b) 22 Torr; (c) 373 K; (d) 473 K.

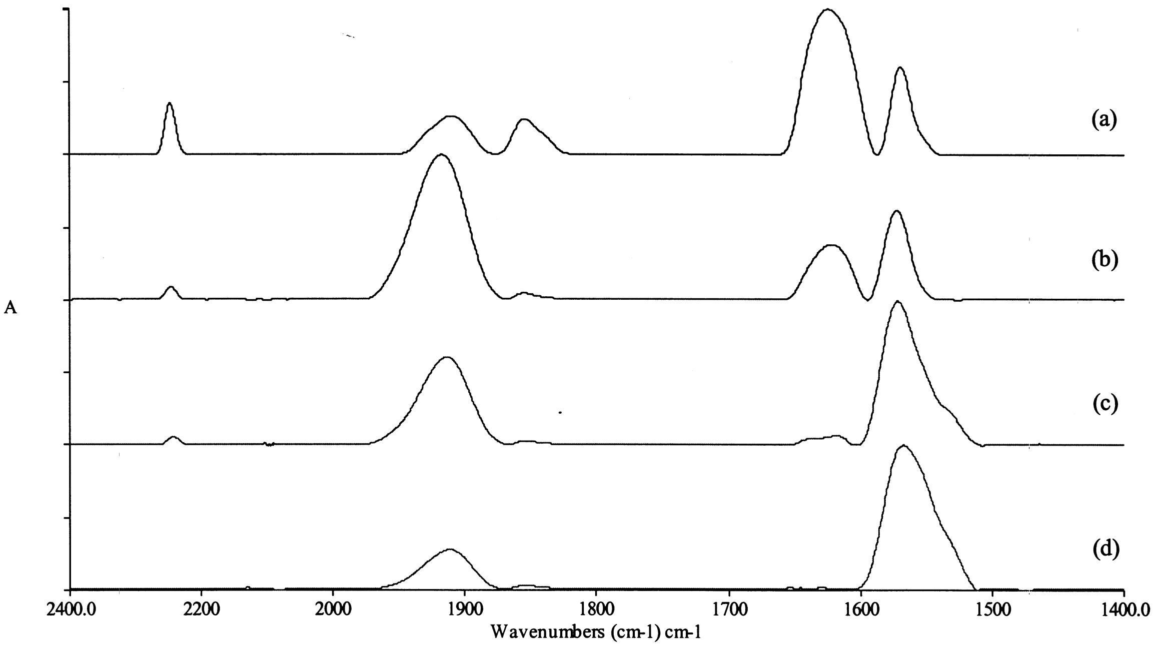

Fig. 5. FT-IR spectra of NO adsorbed at various pressures over the dehydrated Tb-SAPO-18 catalyst: (a) 12 Torr; (b) 22 Torr; (c) 61 Torr; (d) 72 Torr.

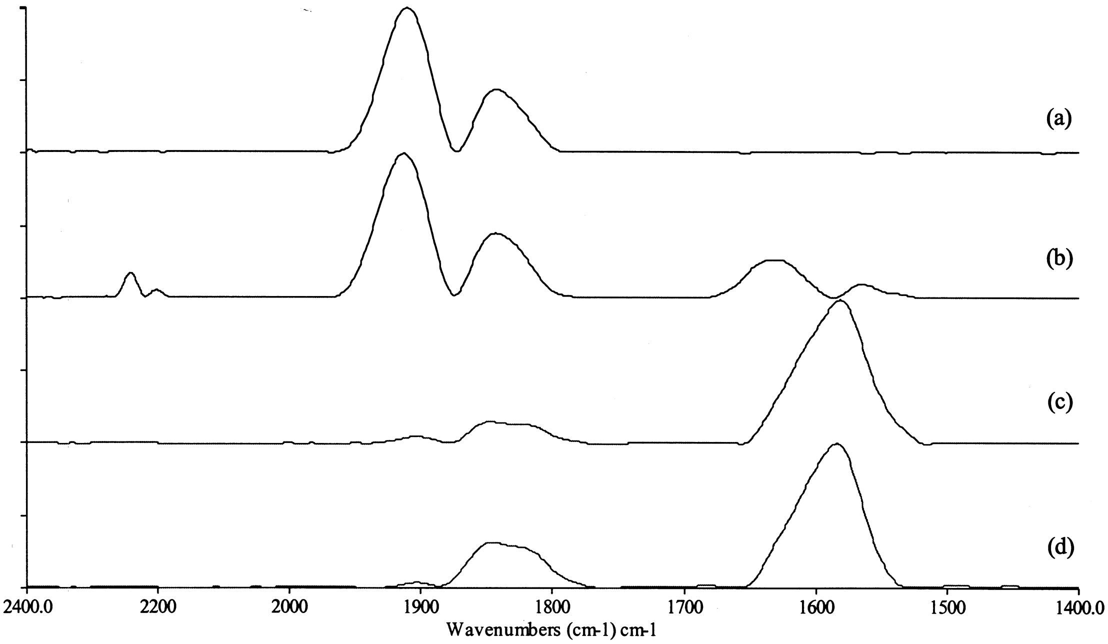

Fig. 6. FT-IR spectra of NO adsorbed at various pressures and temperatures over the dehydrated Tb-SAPO-18 catalyst: (a) 12 Torr; (b) 22 Torr; (c) 373 K; (d) 473 K.

atures of 373 and 473 K for 25–30 min. Heating a NO dosed rare earth exchanged SAPO-18 catalyst gave some interesting results. Heating the catalyst at 373 K decreased the intensity of the M–NO (1910 cm^{-1}) and [M–$(NO)_2$] (1845 cm^{-1}) bands to varying degrees. The intensity of the M–NO_2 band (1630 cm^{-1}) dramatically decreased and a new M–NO_3 complex is formed with a band present at 1570 cm^{-1}. Heating the rare earth exchanged SAPO-18 catalysts to 473 K saw the intensity of the M–NO_3 further increase while the M–NO_2 complex all but disappeared. The nitrous oxide, mono- and dinitrosyl bands all decreased. This would indicate that the M–NO_2 complex decomposed to an unstable NO_2 and O^- complex which could have been oxidised by NO (from the liberated M–$(NO)_2$ and M–NO species) to the M–NO_3.

Table 2
Assignment of the type of species generated after the interaction of NO with the rare earth metal exchanged SAPO-18 catalysts

Species	Wavenumber (cm^{-1})
M–NO	~1910
M–$(NO)_2$ (symmetrical)	~1845
M–NO_2	~1630
M–NO_3	~1570
M–N_2O	~2250–2150

4. Conclusions

The interaction of NO with Eu-, Gd- and Tb-exchanged SAPO-18 catalysts resulted in the formation of M–NO, M–$(NO)_2$, M–N_2O, M–NO_2 and M–NO_3 species. However, the concentration and distribution of these species is significantly affected by the type of rare earth elements (Eu/Gd/Tb). The catalyst temperature influences the decomposition of the M–NO_2 and M–NO_3 complexes to the M–NO and M–$(NO)_2$ complexes. The types of NO sites on the catalysts are similar to those observed on copper exchanged catalysts, in particular Cu-SAPO-34.

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