



ELSEVIER

Journal of Molecular Catalysis A: Chemical 171 (2001) 243–249

C JOURNAL OF
MOLECULAR
CATALYSIS
A: CHEMICAL

www.elsevier.com/locate/molcata

Effects of air pollutants on the cerium exchanged high silica zeolite catalyst: a Fourier transform infrared study

Chis Kladis^a, Suresh K. Bhargava^{a,*}, Karl Foger^b, Deepak B. Akolekar^a

^a Materials Research Group, Department of Applied Chemistry, RMIT University, City campus, Melbourne, Vic. 3001, Australia

^b Ceramic Fuel Cells Limited, 170 Browns Road, Noble Park, Vic. 3174, Australia

Received 25 September 2000; received in revised form 18 January 2001; accepted 19 February 2001

Abstract

The interaction of air pollutants such as nitric oxide (NO) and carbon monoxide (CO) gases on the cerium exchanged ZSM-5 material was studied by FT-IR spectroscopy. Highly crystalline and pure H-ZSM-5 was used for preparing the cerium exchanged material. The cerium exchanged ZSM-5 material was characterised by conventional techniques such as ICP-OES, nitrogen sorption capacity (BET), XRD and XPS. X-ray photoelectron spectroscopy identified the presence of both Ce^{III} and Ce^{IV} species on the surface of the prepared catalysts. The in situ interaction of NO and CO on the cerium exchanged ZSM-5 was studied using an FT-IR Pyrex/quartz cell. The adsorption of NO gas led to the formation of nitrous oxide, mono- and dinitrosyl complexes of cerium, nitrogen dioxide and nitrate species. The adsorption of CO gas led to the formation of mono-, di- and tricarbonyl complexes of cerium and carbon dioxide and carbonate species. The types of NO and CO sites on the Ce-ZSM-5 catalyst are similar to those observed on copper exchanged catalysts, in particular Cu-SAPO-34 and Cu-ZSM-5. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: NO; CO; Cerium; Ce-ZSM-5; FT-IR; Pentasil zeolite; Air pollutants

1. Introduction

At the present time, noble metals such as Rh, Pt and Pd are used for the catalytic decomposition of toxic gases like NO, CO and SO₂ released into the atmosphere from industrial and automobile exhaust sources. With an increase in global air pollution, efforts are being made to obtain more effective catalytic materials such as transition metal oxides — zeolites [1,2]. The potential applications of zeolitic microporous materials in a variety of chemical

reactions and separation processes has resulted in the rapid development of new generation molecular sieves with different structures and compositions. The chemical composition and extra-framework cations of the zeolite significantly affect the molecular adsorption-interaction with the zeolitic active sites, thus strongly influencing the catalytic properties of the zeolitic material [3–8]. The interaction of molecular species with active metal sites is usually studied with nitric oxide [9–11] or carbon monoxide [12,13] probe molecules using the FT-IR technique. In the present paper, the adsorption-interaction of typical probe molecules with the active cerium species on the highly crystalline ZSM-5 catalyst was investigated.

* Corresponding author. Tel.: +61-3-9925-3365;
fax: +61-3-9925-3365.
E-mail address: suresh.bhargava@rmit.edu.au (S.K. Bhargava).

2. Experimental

2.1. Catalyst preparation

Ce-ZSM-5 was prepared by a liquid ion-exchange method. The calcined ZSM-5 was ion-exchanged with Ce in 0.010 M cerium nitrate solution at 343 K for 2 h, then filtered, washed and dried. This procedure was repeated twice. The samples were dried overnight at 373 K. Details of the H-ZSM-5 zeolite preparation and characterisation have already been reported [14].

2.2. Characterisation

The Ce-ZSM-5 material was characterised by ICP-OES, BET, XRD and XPS techniques. The chemical composition of the samples was determined by ICP-OES analysis using a Perkin-Elmer Optima 3000 DV instrument. Surface area and pore volume of the material was obtained by the N₂-dynamic adsorption/desorption technique using a Micromeritics ASAP2000 instrument. X-ray powder diffraction patterns were obtained with a Philips PA2000 diffractometer using a Ni- α filtered Cu K α X-ray source. The XRD pattern of the H-ZSM-5 was similar to the accepted pattern. XPS surface analysis was conducted for determining the surface concentration and binding energy of O 1s, Si 2p, Al 2p and Ce 3d using a Fisons Microlab 310F instrument operating in the constant pass energy mode [10]. All spectra were referenced to C 1s (285 eV).

2.3. FT-IR measurements

FT-IR studies were performed on self-supported wafers (ca. 20 mg, thickness of 10.0 mg cm⁻²). A self-supported wafer was fixed to a stainless steel holder located in the sample holder of a Pyrex/quartz FT-IR cell. All samples were first activated under vacuum (<10⁻⁴ Torr) at 573 K for 16 h. A high purity mixture of nitrogen (95%) and nitric oxide (5%) and carbon monoxide (99.95%) supplied by Linde, Australia, were used as the NO or CO source. FT-IR spectra of the samples were obtained at 2 cm⁻¹ resolution using a Perkin-Elmer System 2000 or 1725 \times FT-IR spectrometer. The spectrum of the dehydrated sample was used as a background from which the

adsorbed spectrum was subtracted and necessary background subtractions were concluded for all the spectra. The FT-IR spectra were collected at room temperature and at different gas pressure depending upon the experimental conditions.

3. Results and discussion

3.1. Characterisation

Highly crystalline and pure ZSM-5 was used for preparation of the Ce-ZSM-5 catalyst. The characteristics of the Ce-ZSM-5 catalyst are listed in Table 1. After exchange with cerium, the micropore volume of ZSM-5 decreased by 44% from 0.18 to 0.10 cm³ g⁻¹. The total surface area after exchange with cerium decreased by 27% from 429 to 315 m² g⁻¹ for ZSM-5. After dehydration, the ZSM-5 material is a crystalline solid permeated by micropores. Ion-exchange with Ce can lead to micropore blockage in the material's structure which in turn causes the volume and shape of the ZSM-5 micropores to be reduced and/or distorted [8].

The surface concentration of the elements and the binding energy data for the Ce exchanged ZSM-5 was determined by XPS analysis (Table 1). Bulk chemical and XPS surface analysis for the Ce-ZSM-5 material indicates that the levels of silicon and aluminium were slightly higher in the bulk than on the surface. The higher surface Ce/Al ratio indicates that most of the Ce metal ions are present on the surface of the ZSM-5

Table 1
Properties of the cerium exchanged high silica zeolite catalyst

Product composition (mol%)	
ZSM-5 (calcined)	Si, 99.3; Al, 0.7
Ce-ZSM-5	Ce, 0.7; Si, 98.6; Al, 0.7
Surface area, micropore volume	
H-ZSM-5 (m ² g ⁻¹)	429
H-ZSM-5 (cm ³ g ⁻¹)	0.18
Ce-ZSM-5 (m ² g ⁻¹)	315
Ce-ZSM-5 (cm ³ g ⁻¹)	0.10
Ce-ZSM-5: XPS analysis	
Surface composition (at.%)	Ce 3d 1.9, Si 2p 28.9, Al 2p 1.0, O 1s 57.6, C 1s 10.6
E _b (eV) (FWHM (eV)) ^a	Ce 3d 883.5, Si 2p 103.6, Al 2p 74.7, O 1s 533.2

^a Referenced to C 1s (285 eV).

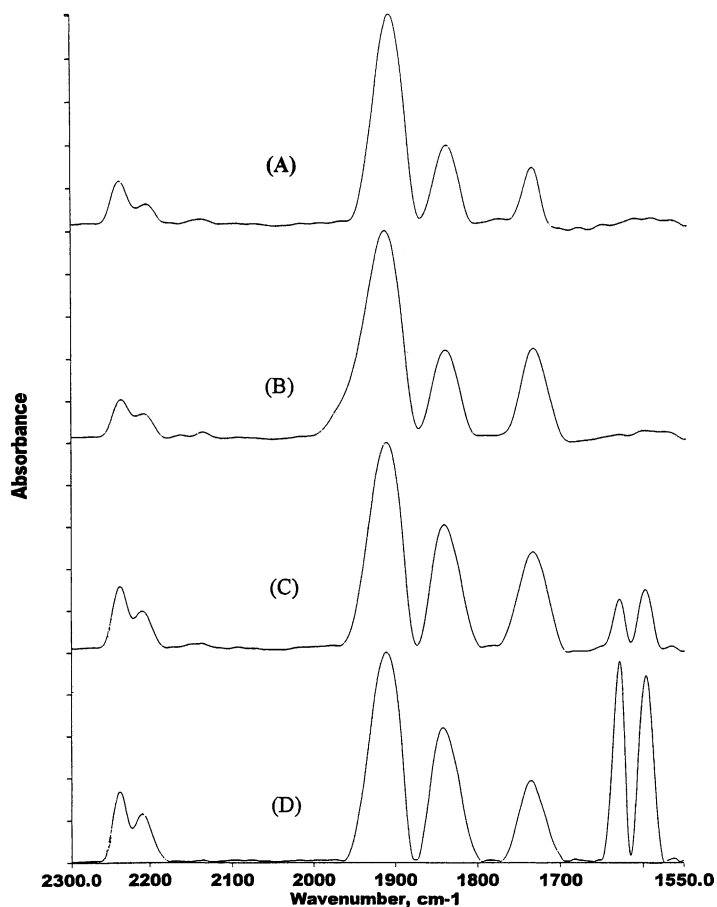


Fig. 1. FTIR spectra of NO adsorbed at various pressures over the dehydrated Ce-ZSM-5 catalyst: (A) 12 Torr, (B) 22 Torr, (C) 61 Torr and (D) 72 Torr.

molecular sieve and not in the bulk. The observed binding energies 883 and 886 eV indicated the presence of both the Ce^{III} and Ce^{IV} species on the ZSM-5 catalyst. The binding energies (Table 1) of the other elements (Al 2p, Si 2p and O 1s) are close to those for tetrahedrally co-ordinated elements in the zeolite molecular sieves [15,16].

3.2. NO adsorbed cerium exchanged ZSM-5

The interaction between NO and Ce exchanged ZSM-5 is depicted in Figs. 1 and 2. After dehydration of Ce-ZSM-5 in vacuo at 573 K for 16 h, exposure to NO produced up to four strong bands attributed to the formation of nitrous oxide, nitrogen dioxide,

mono- and dinitrosyl species. The bands at 1912, 1843, 1735, 1630 and 2250–2150 cm^{-1} are assigned to $\text{Ce}^{\text{III}}\text{-NO}$, $\text{Ce}^{\text{III}}\text{-(NO)}_2$, $\text{Ce}^{\text{III}}\text{-(NO)}_2$ (asymmetric), $\text{(Ce}^{\text{IV}}\text{-NO}_2)$, and $\text{Ce}^{\text{IV}}\text{-N}_2\text{O}$ adsorbed species, respectively. The assignment of bands is consistent with most of the literature data [9–12,17–22]. The nitrosyl complexes and intermediates resulting from surface reaction between nitric oxide and Ce-ZSM-5 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 cerium–nitric oxide complexes. FT-IR results pertaining to the pressure changes of NO on the Ce-ZSM-5 are presented in Fig. 1. At increasing NO pressure,

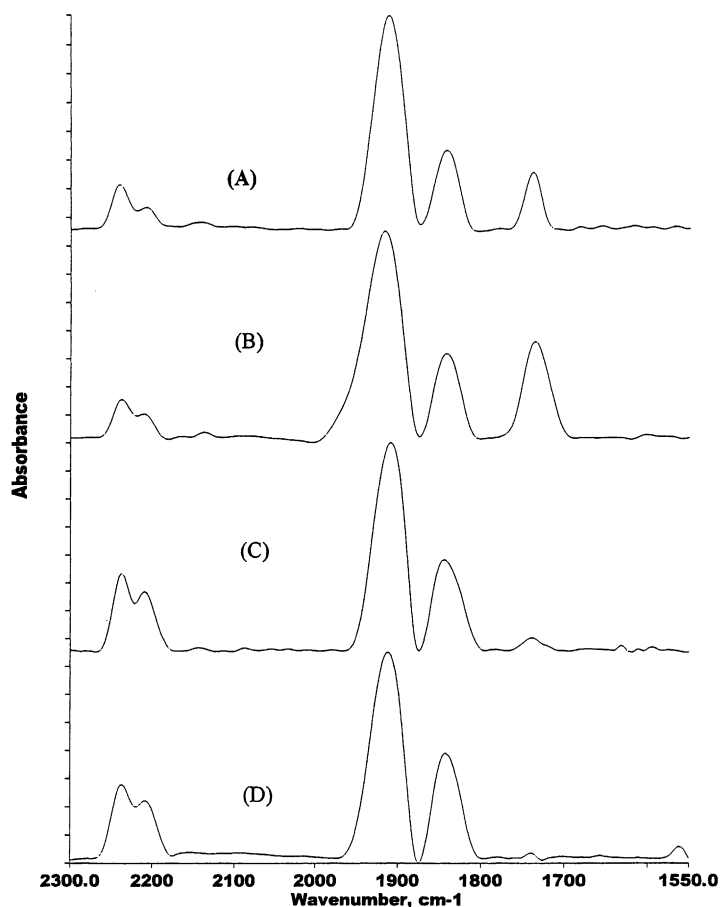


Fig. 2. FTIR spectra of NO adsorbed at various pressures and temperatures over the dehydrated Ce-ZSM-5 catalyst: (A) 12 Torr, (B) 22 Torr, (C) 373 K and (D) 473 K.

Table 2

Assignment of the type of species generated after the interaction of NO and CO with the cerium exchanged high silica zeolite catalyst

Species	Wave number (cm ⁻¹)
Ce ^{III} -NO	1912
Ce ^{III} -(NO) ₂ (symmetric)	1843
Ce ^{III} -(NO) ₂ (asymmetric)	1735
Ce ^{IV} -NO ₂	1630
Ce ^{IV} -N ₂ O	2250–2150
Ce ^{III} -CO	2117
Ce ^{III} -(CO) ₂ (symmetric)	2172
Ce ^{IV} -CO ₂	1630

the band at 1912 cm⁻¹ for Ce-ZSM-5 remains unchanged indicating the immediate saturation of the Ce^{III} sites of the catalyst with the mononitrosyl specie (Ce^{III}-NO). In addition, the conversion of the mononitrosyl to the dimer/dinitrosyl species increases with the NO pressure as indicated by the growth in the intensity of the symmetric band at 1843 cm⁻¹ (Ce^{III}-(NO)₂). The increase in the NO surface coverage exhibited the changes in the peak intensity of the other bands at 1735, 1639 and 2237–2150 cm⁻¹. The intensity of Ce^{IV}-NO₂ (1630 cm⁻¹) and Ce^{IV}-N₂O (2237–2150 cm⁻¹) bands increases significantly with the NO pressure. These results are consistent with those of copper exchanged zeolites [9,10,12]. The dinitrosyl cerium complex subsequently converts to

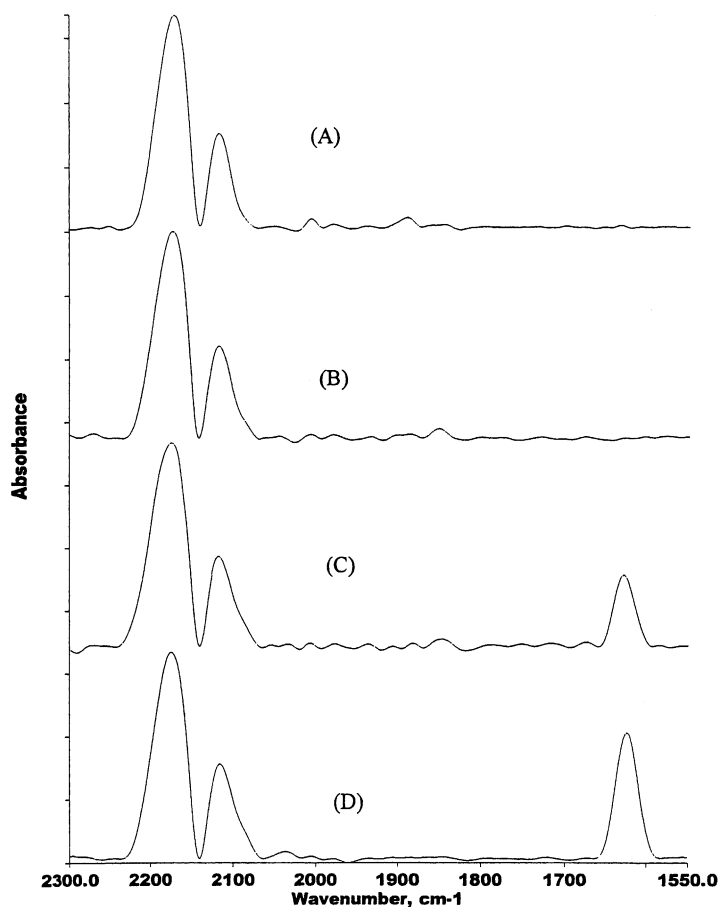


Fig. 3. FTIR spectra of CO adsorbed at various pressures over the dehydrated Ce-ZSM-5 catalyst: (A) 12 Torr, (B) 22 Torr, (C) 61 Torr and (D) 72 Torr.

an unstable Ce^{IV} complex with N_2O and O^- adsorbed species ($2250\text{--}2150\text{ cm}^{-1}$). Further reaction with NO leads the conversion of the unstable N_2O and O^- complex to a $\text{Ce}^{\text{IV}}\text{--NO}_2$ complex (1630 cm^{-1}).

The decomposition of adsorbed NO species at different temperatures and constant pressure over the dehydrated Ce-ZSM-5 catalyst is shown in Fig. 2. Experiments were undertaken at constant NO pressure of 22 Torr and temperatures of 373 and 473 K for 25–30 min. Heating a NO dosed Ce-ZSM-5 catalyst at 373 and 473 K caused the dinitrosyl band (1735 cm^{-1}) to decompose, eventually stripping it from the cerium active sites of the catalyst but had no effect on the other species present.

3.3. CO adsorbed cerium exchanged ZSM-5

The interaction between CO and Ce-exchanged ZSM-5 is depicted in Figs. 3 and 4. After dehydration of Ce-ZSM-5 in vacuo at 573 K for 16 h, exposure to CO produced up to three strong bands attributed to the formation of carbon dioxide, mono- and dicarbonyl species. The bands at 2172 (s, strong), 2117 (s), 2062 (shoulder) cm^{-1} are assigned dicarbonyls ($\text{Ce}^{\text{III}}\text{--}(\text{CO})_2$ (symmetric and asymmetric), $\text{Ce}^{\text{III}}\text{--CO}$) and the band at 1630 cm^{-1} (visible at higher pressures) is assigned to $\text{Ce}^{\text{IV}}\text{--CO}_2$ adsorbed species, respectively. The assignment of bands is consistent with most of the literature data

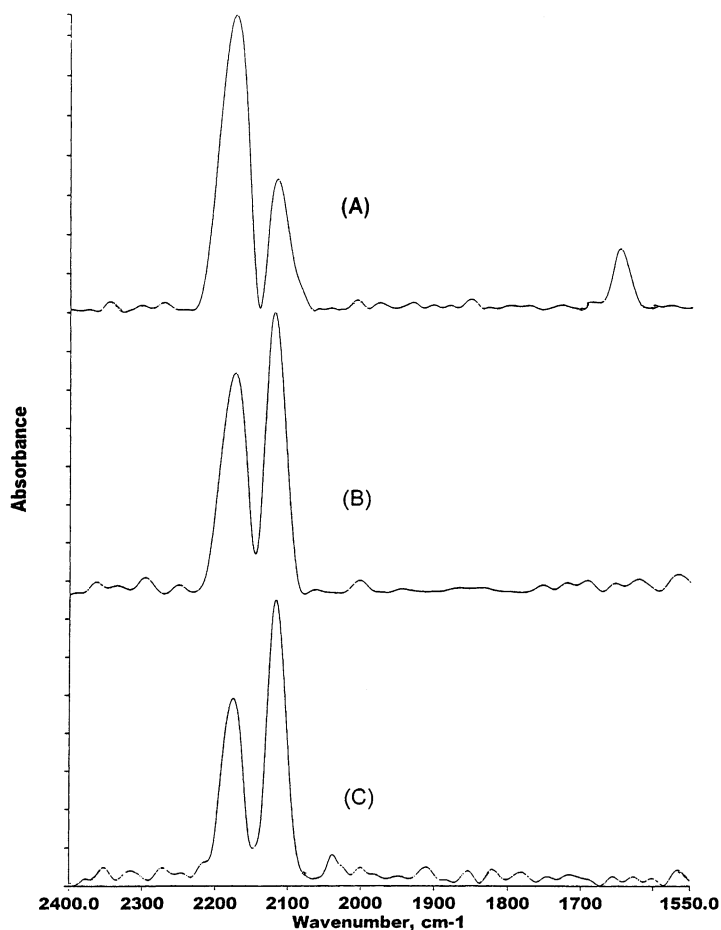


Fig. 4. FTIR spectra of CO adsorbed at various pressures and temperatures over the dehydrated Ce-ZSM-5 catalyst: (A) 29 Torr, 296 K (B) 373 K and (C) 473 K.

[13,19,23,24]. The carbonyl cerium complexes and intermediates resulting from surface reaction between carbon monoxide and Ce-ZSM-5 are summarised in Table 2.

CO adsorption experiments at constant pressures and temperatures were carried out in order to study the influence of carbon monoxide gas pressure on the cerium–carbon monoxide complexes. FT-IR results pertaining to the pressure changes of CO on the Ce-ZSM-5 are presented in Fig. 3. At increased CO pressure, only slight increase in intensity of the symmetric band at 2172 cm^{-1} ($\text{Ce}^{\text{III}}\text{-(CO)}_2$) and significant increase in the intensity of the monocarbonyl band at 2117 cm^{-1} ($\text{Ce}^{\text{III}}\text{-CO}$) was observed, indicating the

formation of cerium–carbonyl complexes on the active sites of the catalyst. The decomposition of adsorbed CO species at various temperatures and constant pressure over the dehydrated Ce-ZSM-5 catalyst is shown in Fig. 4. Experiments were undertaken at constant CO pressure of 29 Torr and temperatures of 373 and 613 K for 25–30 min. The FTIR results exhibits that the temperature significantly affected the distribution of the $\text{Ce}^{\text{III}}\text{-(CO)}_2$, $\text{Ce}^{\text{III}}\text{-CO}$ and $\text{Ce}^{\text{IV}}\text{-CO}_2$ species on the Ce-ZSM-5 catalyst.

The catalytic decomposition of adsorbed NO and CO over the dehydrated Ce-ZSM-5 catalyst at increased temperatures shows stable concentrations of $\text{Ce}^{\text{III}}\text{-NO}$ and $\text{Ce}^{\text{III}}\text{-CO}$ and increased concentrations

of $\text{Ce}^{\text{IV}}\text{-NO}_2$ and $\text{Ce}^{\text{IV}}\text{-CO}_2$ species. At temperatures above 373 K, the concentrations of $\text{Ce}^{\text{IV}}\text{-NO}_2$ and $\text{Ce}^{\text{IV}}\text{-CO}_2$ species decreases. On Ce-ZSM-5, the NO and CO sites are of similar type to those over the Cu-SAPO-34 and Cu-ZSM-5 catalysts. However, the observed site density or concentration of $\text{Ce}^{\text{III}}\text{-NO}$ and $\text{Ce}^{\text{III}}\text{-CO}$ species were higher over the Ce-ZSM-5 than the Cu-SAPO-34 and Cu-ZSM-5 catalysts. The higher site density explains the similar if not higher catalytic activity of Ce-ZSM-5 compared to Cu-SAPO-34 and Cu-ZSM-5 catalysts [9–13,25].

4. Conclusions

The adsorption of nitric oxide on the Ce-ZSM-5 catalyst resulted in the formation of $\text{Ce}^{\text{III}}\text{-NO}$, $\text{Ce}^{\text{III}}\text{-(NO)}_2$, dinitrosyl asymmetric, $\text{Ce}^{\text{III}}\text{-N}_2\text{O}$ and $\text{Ce}^{\text{IV}}\text{-NO}_2$ species. The pressure of nitric oxide affects the concentration and distribution of the NO complexes. Temperature, when applied to the catalyst, decomposed the $\text{Ce}^{\text{IV}}\text{-NO}_2$ complexes to the $\text{Ce}^{\text{III}}\text{-NO}$ and $\text{Ce}^{\text{III}}\text{-(NO)}_2$ complexes. The adsorption of carbon monoxide on the Ce-ZSM-5 catalyst resulted in the formation of $\text{Ce}^{\text{III}}\text{-CO}$, $\text{Ce}^{\text{III}}\text{-(CO)}_2$, $\text{Ce}^{\text{III}}\text{-(CO)}_3$, and $\text{Ce}^{\text{IV}}\text{-CO}_2$ species. The CO pressure and temperature affects the concentration, distribution and conversion of the CO complexes. At higher temperatures, the $\text{Ce}^{\text{IV}}\text{-CO}_2$ complexes decompose to the $\text{Ce}^{\text{III}}\text{-CO}$ and $\text{Ce}^{\text{III}}\text{-(CO)}_2$ complexes.

Acknowledgements

The authors would like to thank Dr. J. Gorman, Department of Applied Physics, RMIT, Melbourne, Australia, for assistance with the XPS analyses and Dr. C. Cunningham, Perkin-Elmer, Melbourne, Australia, for assistance with the ICP-OES analyses.

References

- [1] M. Iwamoto, *Stud. Surf. Sci. Catal.* 84 (1994) 1395.
- [2] H. Hosose, H. Yahiro, M. Mizuno, M. Iwamoto, *Chem. Lett.* (1991) 1859.
- [3] S.T. Wilson, B.M. Lock, E.M. Flanigen, US Patent 4310440 (1982).
- [4] D.B. Akolekar, *J. Catal.* 144 (1993) 148.
- [5] E.M. Flanigen, R.L. Patton, S.T. Wilson, *Stud. Surf. Sci. Catal.* 37 (1988) 13.
- [6] G.J. Gajda, R.T. Gajek, US Patent 5723710 (1996).
- [7] R.M. Barrer, *Zeolites and Clay Minerals*, Academic Press, London, 1978.
- [8] D.W. Breck, *Zeolite Molecular Sieves*, Wiley, New York, 1974.
- [9] T. Cheung, S.K. Bhargava, M. Hobday, K. Fogger, *J. Catal.* 158 (1996) 301.
- [10] D.B. Akolekar, S.K. Bhargava, K. Fogger, *J. Chem. Soc., Faraday Trans.* 94 (1998) 155.
- [11] C. Kladis, S.K. Bhargava, D.B. Akolekar, K. Fogger, *Catal. Today* 63 (2000) 297.
- [12] D.B. Akolekar, S.K. Bhargava, *Stud. Surf. Sci. Catal.* 105 (1998) 755.
- [13] K. Hadjiivanov, M. Kantcheva, D. Klissurski, *J. Chem. Soc., Faraday Trans.* 92 (1996) 4595.
- [14] D.B. Akolekar, *Sorption, Diffusion and catalytic reactions on zeolites and zeolite-like materials*, PhD Thesis, University of Poona, Poona, 1987.
- [15] D.B. Akolekar, *J. Catal.* 143 (1993) 227.
- [16] M. Huang, A. Adnot, S. Kaliaguine, *J. Catal.* 137 (1992) 322.
- [17] J. Valyou, W. Hall, *J. Catal.* 143 (1993) 520.
- [18] E. Shapiro, R.W. Joyner, W. Grunert, N.W. Haynes, M.R.H. Siddiqui, G.N. Baeva, *Stud. Surf. Sci. Catal.* 84 (1994) 1483.
- [19] L. Aparicio, W.K. Hall, S.-M. Fang, M.A. Ulla, W.S. Millman, J.A. Dumesic, *J. Catal.* 108 (1987) 233.
- [20] J. Anderson, G. Miller, C. Rochester, *J. Chem. Soc., Faraday Trans.* 86 (1990) 571.
- [21] E. Giamello, D. Murphy, G. Magnacca, C. Morterra, Y. Shioya, T. Nomura, M. Anpo, *J. Catal.* 136 (1992) 510.
- [22] T. Ishihara, M. Kagawa, F. Hadama, Y. Takita, *J. Catal.* 169 (1997) 93.
- [23] M. Iwamoto, H. Yahiro, N. Mizuno, W.-X. Zhang, Y. Mine, H. Furukawa, S. Kagawa, *J. Phys. Chem.* 96 (1992) 9360.
- [24] R. Keiski, M. Harkonen, A. Lahti, T. Maunula, A. Savimaki, T. Slotte, *Stud. Surf. Sci. Catal.* 96 (1995) 85.
- [25] T. Ishihara, M. Kagawa, F. Hadama, Y. Takita, *Stud. Surf. Sci. Catal.* 84 (1994) 1493.