

Adsorption of NO and CO on silver-exchanged microporous materials

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Abstract

Investigations of nitric oxide (NO) and carbon monoxide (CO) adsorption were carried out on the silver-exchanged high silica pentasil zeolite and chabazite-type silico-aluminophosphate materials. Novel Ag-SAPO-34 and Ag-ZSM-5 catalysts were prepared and characterised using routine instrumental techniques. Detailed FTIR studies were carried out on the interaction of NO/CO over Ag-SAPO-34 and Ag-ZSM-5. FTIR spectra indicated the formation of various NO/CO complexes on the silver-exchanged materials. Influence of the NO/CO pressure and evacuation on the surface species have been studied. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Air pollution caused by release of nitric oxide (NO) and carbon monoxide (CO) from stationary or mobile sources could be effectively controlled using different types of heterogenous catalysts. The range of heterogenous catalysts utilised varies from noble metal to transition metal-supported materials. There has been considerable interest in the development of economical and stable catalysts particularly the copper-exchanged zeolites catalysts [1a,1b–5].

The Cu-exchanged ZSM-5 zeolite catalyst possesses high NO decomposition activity, greater than traditional catalysts and other metal-exchanged zeolites. However, the Cu–zeolite, despite exhibiting high and stable activities, has problems with catalytic activity at lower temperatures. In the field of heterogenous catalysis, numerous studies have been reported on the potential of copper catalysts and their NO reduction ability [1a,1b–8]; however, very few studies on the other Group 1B (Au or Ag) are reported [9,10]. NO or CO adsorption on heterogenous catalysts is widely used to study the nature and properties of adsorption sites present on the catalyst surface. IR spectroscopy is a technique commonly used to investigate NO/CO adsorption on the catalyst. The IR frequencies and changes in the frequencies of

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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.) [3,5, 11,12a,12b,13]. In this work, we have studied the adsorption interaction of typical probe molecules with active metal species on the silver-exchanged novel silico-aluminophosphate and aluminosilicate materials. The adsorption experiments of NO/CO on the Ag-SAPO-34 and Ag-ZSM-5 molecular sieves were carried out in order to investigate the type of silver metal species present on the Ag-SAPO-34 and Ag-ZSM-5 materials.

2. Experimental

2.1. Preparation of the silver-exchanged microporous materials

Ag-SAPO-34 and Ag-ZSM-5 were prepared by the liquid ion-exchange method. The calcined SAPO-34/ZSM-5 was ion-exchanged with 0.014 M silver nitrate solution at 348 K for 4 h, then filtered, washed and dried. This procedure was repeated thrice. Finally, the samples were heated at 793 K for 5 h. SAPO-34 was obtained by calcination of the as-synthesised SAPO-34. Thermal stability of SAPO-34 phase was studied using the XRD and BET techniques by calcining the material at 773 and 973 K. The SAPO-34 material is stable at higher temperatures and towards humidity. As-synthesised SAPO-34 [5] was prepared by hydrothermal crystallisation of the gel (molar composition: 2.5 TEOH 1.0 Al₂O₃ 0.82 P₂O₅ 0.42 SiO₂ 51 H₂O) in a Teflon autoclave initially at 423 K for 48 h and at 473 K for 58 h. The crystallisation product was filtered, thoroughly washed, dried and calcined at 793 K for 16 h. The chemicals used for the synthesis work were aluminium oxy hydroxide (Al O OH), *o*-phosphoric acid (85%, Merck), tetraethylammonium hydroxide (35 wt.%, Aldrich) and tetraethyl *or*-

tho-silicate (99%, Aldrich). Details of the ZSM-5 zeolite preparation and characterisation already have been reported [14].

2.2. Characterisation and FTIR measurements

The materials were characterised by elemental analysis, XRD, scanning electron microscope (SEM) and BET techniques. The X-ray powder diffraction pattern of the as-synthesised SAPO-34 and ZSM-5 obtained with a Siemens SIE 122D diffractometer indicated the high purity of the materials. The chemical composition of the samples was determined by ICP analysis. The details of characterisation techniques and instruments utilised for the chemical analysis and structure determination are reported earlier [5,14,15]. The surface area and pore volume of the materials were obtained by N₂-dynamic adsorption/desorption technique ($p/p_o = 0.3$) using a Micromeritics ASAP2000 Instrument. The morphology and crystal size of the materials were investigated using a JEOL JSM 35MF SEM. FTIR studies were performed on self-supported wafers (~ 15 mg, thickness 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 cell. All the precalcined samples were first activated at 623 K for 4 h and further in vacuum ($< 10^{-4}$ Torr) at the same temperature for 16 h. A high purity mixture of nitrogen (95%) and NO (5%) and high purity CO supplied by BOC, Australia was used as NO or CO source. Infrared spectra of the samples were obtained at 2 cm⁻¹ resolution using a Perkin-Elmer FT-IR 1725X spectrometer.

3. Results and discussion

The Ag-SAPO-34 and Ag-ZSM-5 catalysts were prepared from the highly crystalline SAPO-34 and ZSM-5 materials. The chemical composition, morphology and nitrogen sorption

Table 1
Properties of the silver exchanged microporous materials

SAPO-34	48.6 Al 40.0 P 11.4 Si
Ag-SAPO-34	8.1 Ag 44.5 Al 33.0 P 10.5 Si
SAPO-34 crystal shape	Irregular
Crystal size (μm)	< 3
N_2 sorption capacity at 78 K of SAPO-34 (mmol g^{-1})	6.33
Micropore volume of SAPO-34 ($\text{cm}^3 \text{g}^{-1}$)	0.25
N_2 sorption capacity at 78 K of Ag-SAPO-34 (mmol g^{-1})	3.25
Micropore volume of Ag-SAPO-34 ($\text{cm}^3 \text{g}^{-1}$)	0.14
ZSM-5	Si/Al = 16.8
Ag-ZSM-5	Si/Al = 17.2, Ag/Al = 0.78
Crystal shape	Hexagonal
Crystal size (μm)	4
N_2 sorption capacity at 78 K of ZSM-5 (mmol g^{-1})	5.3
Micropore volume of ZSM-5 ($\text{cm}^3 \text{g}^{-1}$)	0.15
N_2 sorption capacity at 78 K of Ag-ZSM-5 (mmol g^{-1})	3.5
Micropore volume of Ag-ZSM-5 ($\text{cm}^3 \text{g}^{-1}$)	0.09

capacity of the SAPO-34, Ag-SAPO-34, ZSM-5 and Ag-ZSM-5 catalysts are presented in Table 1. The characterisation of SAPO-34 and ZSM-5 materials using XRD, BET, SEM and ICP indicated the high material purity. The calcined SAPO-34 and ZSM-5 materials possess very high surface area, 606 and 495 $\text{m}^2 \text{g}^{-1}$, respectively. After silver exchange, decrease in the surface area, N_2 sorption capacity and micropore volume of SAPO-34 and ZSM-5 was observed (Table 1).

3.1. Adsorption of NO on the silver-exchanged microporous materials

Fig. 1 displays the FTIR spectra in the fundamental range of NO adsorbed on the Ag-SAPO-34 at 296 K and different pressures. Adsorption of NO on vacuum-dehydrated Ag-SAPO-34 produced bands in the region of 2500–1400 cm^{-1} . At the NO adsorption pressure of 12 Torr of adsorbed NO on the Ag-SAPO-34, the spectrum exhibits absorption bands at 2261–2230, 1908, 1847, 1734, 1623, 1557 and a doublet near 1456 cm^{-1} . Table 2 shows the NO absorption bands and their assignments on the Ag-SAPO-34. The IR bands are attributed to mono-nitrosyl [$\text{Ag}(\text{I})-(\text{NO})(1908 \text{ cm}^{-1})$], $\text{Ag}(\text{I})-(\text{NO})_2$ (1734

cm^{-1}), $\text{Ag}(\text{II})-\text{NO}_2$ (1620 cm^{-1}), N_2O (2261 cm^{-1}), N_2O_3 (1557 cm^{-1}), and $\text{Ag}-(\text{NO}_3)$ [(doublet, 1456, 1435 cm^{-1})]. Adsorption of NO at higher pressures (Fig. 1a–c) on the Ag-SAPO-34 leads to an increase in the intensities of a series of bands at 2240, 1908, and 1456

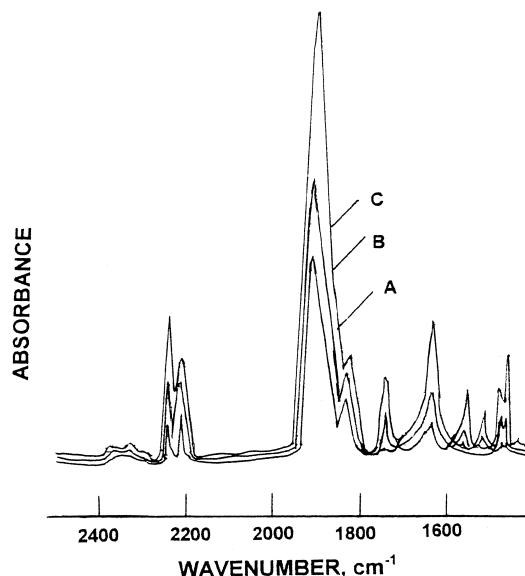


Fig. 1. FTIR spectra of NO adsorbed over the dehydrated silver exchanged silico-aluminophosphate molecular sieve (temperature 296 K, NO pressure a = 12 Torr; b = 22 Torr; c = 61 Torr).

Table 2

Nitric oxide/carbon monoxide adsorption on silver exchanged microporous materials

Ag-SAPO-34		Ag-ZSM-5	
Assignment	Wavenumber (cm ⁻¹)	Assignment	Wavenumber (cm ⁻¹)
N ₂ O adsorbed	2240, 2209 ^a	N ₂ O adsorbed	2261–2130 ^a
Ag(I)–(NO)	1907 ^b	Chemisorbed NO ₂	2130 ^a
Ag(I)–(NO) ₂ asymmetric	1734 ^a	Ag(I)–(NO)	1908 ^b
Ag(II)–NO ₂	1623 ^a	Ag(I)–(NO) ₂ asymmetric	1744 ^{a,c}
N ₂ O ₃	1557 ^a	Ag(II)–NO ₂	1620 ^a
Ag–NO ₃	1456, 1434 ^a	N ₂ O ₃	1557 ^a
Physi-sorbed CO ₂	2348 ^{a,d}	Ag–NO ₃	1456 ^a , 1435 ^a
Ag ⁺ –CO complex	2184 ^b	Physi-sorbed CO ₂	2361 ^a , 2338 ^a
CO species adsorbed on Ag metal	2132 ^{a,e}	Ag ⁺ –CO complex	2190 ^b
		CO species adsorbed on Ag metal	2140 ^{a,e}

^a Minor.^b Major.^c Observed above the NO pressure of 61 Torr.^d Appears above the CO pressure of 12 Torr.^e Shoulder.

cm⁻¹ and a decrease in the intensities of bands at 1623 and 1557 cm⁻¹. Analysis of the FTIR results indicate rise in the concentration of N₂O, Ag(I)–NO and Ag–(NO₃) species, and decline in the Ag(II)–(NO₂) concentration with the increase in NO surface coverage. Among the species, the concentration of Ag(I)–NO is significantly increased. After evacuation of NO gas phase at 296 K (vacuum < 10⁻⁴ Torr, 30 min), the concentration of N₂O (2240 cm⁻¹) and Ag(I)–NO (1908 cm⁻¹) species decreased while the concentration of Ag(II)–NO₂ (1623 cm⁻¹) was unaffected.

FTIR spectra of NO adsorption on the Ag-ZSM-5 at 296 K and different pressures are shown in Fig. 2. Adsorption of NO on the activated Ag-ZSM-5 produced three strong bands and three weak bands in the region of 2500–1400 cm⁻¹. In the presence of 12 Torr of adsorbed NO on the Ag-ZSM-5, the spectrum exhibits absorption bands at 2261–2230, 2130, 1908, 1620, 1557 and 1456 cm⁻¹ (Table 2). The three strong bands are attributed to the chemisorbed NO₂ (2130 cm⁻¹), mono-nitrosyl [Ag(I)–(NO) (1908 cm⁻¹)] and Ag(II)–NO₂ (1620 cm⁻¹) species and the three weak bands correspond to N₂O (2261 cm⁻¹), N₂O₃ (1557

cm⁻¹), and Ag–(NO₃) (doublet, 1456, 1435 cm⁻¹). For the silver-exchanged high silica pentasil material, NO adsorption experiments at different pressures were carried out in order to study the influence of NO gas pressure on the Ag–NO complexes. FTIR results related to the different catalyst surface coverage (at different pressures) on the Ag-ZSM-5 samples are shown in Fig. 2a–d. For Ag-ZSM-5, the pressure exhibits significant influence on formation of the NO complexes. The formation of Ag (I)–(NO)₂(asymmetric) is observed at 1744 cm⁻¹ above the NO pressure of 61 Torr. With an increase in the NO pressures, the concentration of species, such as Ag (I)–(NO), N₂O, Ag(I)–(NO)₂ (asymmetric) and Ag–(NO₃) species, increased, while a decline in the concentration of chemisorbed NO₂ and Ag(II)–NO₂ species is observed. Ag(I)–(NO) seemed to be the most abundant species compared with the other species. During evacuation of the sample at 303 K (10⁻⁵ Torr) for 30 min, the bands at 2261–2230, 2130, 1908 and 1557 cm⁻¹ decreased in intensity while the bands at 1620, 1456 and 1540 cm⁻¹ increased in intensity, indicating that the Ag–(NO₂) and Ag–(NO₃) are the most surface stable species.

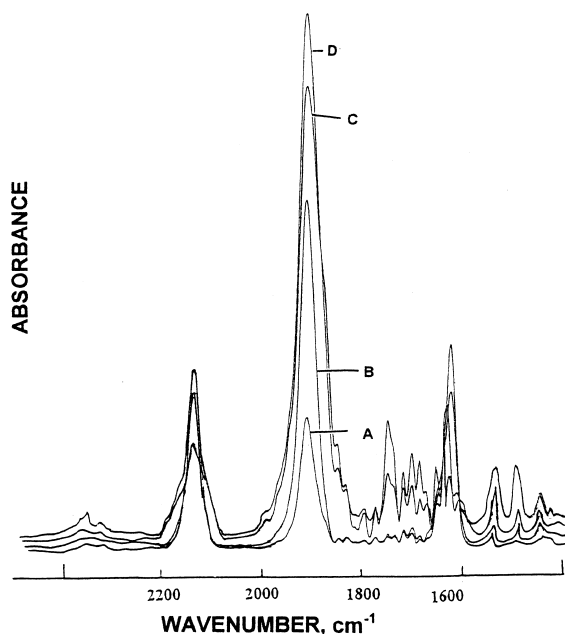


Fig. 2. FTIR spectra of NO adsorbed over the dehydrated silver exchanged high silica pentasil zeolite (temperature 296 K, NO pressure a = 12 Torr; b = 22 Torr; c = 61 Torr; d = 103 Torr).

NO adsorption on the Cu-ZSM-5, Cu-SAPO-34 catalysts [1a,1b,3,5] or on the Au-catalysts [10] leads to the formation of Cu(I)-NO, Cu(II)-NO, Cu(I)-(NO)₂ (asymmetric) and N₂O, Au(I)NO, Au-(NO₃), etc., species, respectively. The pressure of NO and evacuation strongly influences the concentration of these species. The assignments of infrared bands for NO adsorption over the silver-exchanged microporous materials are consistent with most of the literature [3,5,10,13,16–18]. The NO adsorption trend and mechanism for NO conversion over the silver-exchanged materials is expected to follow a similar path to the conversion over transition metal-exchanged microporous materials [3,5]. The formation of N₂O and NO₃ on the silver-exchanged ZSM-5 and SAPO-34 materials occur in a similar way to that of gold-exchanged NaY zeolite [10]. N₂O and NO₃ species formation on the Ag-catalyst could be explained by following scheme:



3.2. Adsorption of CO on the silver-exchanged microporous materials

CO adsorption on the zeolites gives information about the oxidation and coordination state of the charge balancing cations as well as the concentration of surface species. CO adsorption is a widely used method for analysis of active sites on ion-exchanged zeolites because of its ability to act as a weak σ -donor and as a π -acceptor, sensitivity towards the electrostatic fields surrounding transition metal cations in the zeolites and interaction with cationic Lewis acid sites.

Fig. 3 shows CO-FTIR spectra of the Ag-exchanged SAPO-34 catalyst. CO adsorption studies were carried out at different CO pressures and temperatures. The IR frequencies of the different bands observed over the Ag-exchanged SAPO-34 catalyst are compiled in Table 2. Adsorption of CO (equilibrium pressure at 6 Torr) on the activated Ag-SAPO-34 samples led to the appearance of bands at 2184 (s, strong),

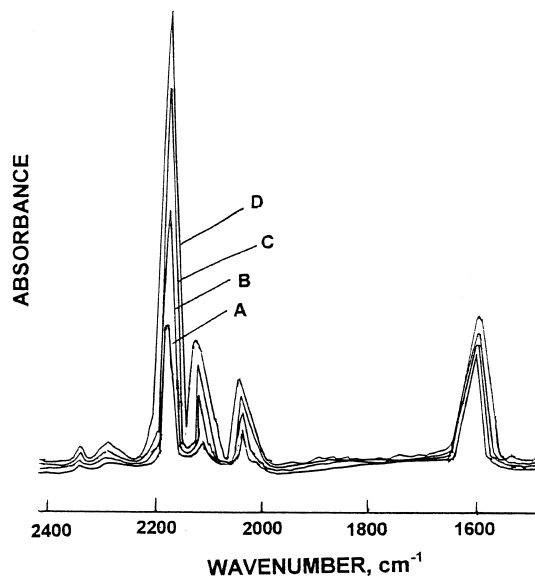


Fig. 3. FTIR spectra of CO adsorbed over the dehydrated silver exchanged silico-aluminophosphate molecular sieve (temperature 296 K, CO pressure a = 6 Torr; b = 12 Torr; c = 22; d = 61 Torr).

2132 (w, weak, shoulder) and 1623 (w) cm^{-1} . The IR spectra at the CO pressure of 12, 22, and 61 Torr are shown in Fig. 3b–c. At the CO pressure of 12 Torr and above, a weak band appears at 2348 cm^{-1} . Analysis of the FTIR results (Table 2) shows that the weak band at 2348 cm^{-1} developed during the CO adsorption on Ag-SAPO-34 has been attributed to the ν_3 vibration of physisorbed CO_2 , linearly bound to the cation by ion-induced dipole interaction [13,19,20]. The band at 2348 cm^{-1} is an indication of CO_2 formation during the adsorption of CO on the silver-exchanged SAPO-34 catalyst. CO adsorption on the Ag-SAPO-34 catalysts leads to formation of CO complexes and weakly bound carbon dioxide. These results are in agreement with the results reported elsewhere [13]. The IR bands at 2184 cm^{-1} for the Ag-SAPO-34 assigned to the Ag^+-CO complex. The negligible small peak at 2132 cm^{-1} is attributed to CO species adsorbed on Ag metal. The slight formation of Ag metal from Ag^+ occurs via the auto-reductive process. The weak band at 1623 cm^{-1} is attributed to the CO and CO_2 entrapped in the structure [21].

The increase of CO equilibrium pressure from 6 to 61 Torr leads to a shift from 2184 to 2181 cm^{-1} and increase in the concentration of CO species chemisorbed on the Ag cationic sites as evidenced by increase in the intensity of 2184 cm^{-1} bands. The intensity of 2132 cm^{-1} band increases with the CO equilibrium pressure, indicating increase in the concentration of carbonyl species on Ag metal due further reduction of Ag^+ to Ag^0 . It follows from the FTIR results that the Ag-SAPO-34 contains substantial number of Ag(I) centers with a small fraction of Ag metal centers. In previous studies [12a,12b,22], it has been reported that adsorption of CO on the Cu-catalysts indicates the formation of mono- and di-carbonyl species and the presence of the isolated Cu^+ sites and the associated Cu^+ cation sites. After CO adsorption, the evacuation experiment was carried out in order to explore the behaviour of Ag and CO species on the SAPO-34 catalyst surface. After evacua-

tion of CO gas at 296 K (vacuum $< 10^{-4}$ Torr, 50 min), the intensity of bands at 2184 and 2132 cm^{-1} decreased, whereas the intensity of the 2348 cm^{-1} band increased. After evacuation, the concentration of Ag^+-CO species is relatively higher than that of the other species suggesting that the carbonyl species is strongly held by the Ag(I) sites and dependence of the stability of Ag(I) centers.

Fig. 4 shows IR spectra of CO over the dehydrated Ag-ZSM-5 catalyst. The adsorption of CO at 299 K resulted in the appearance of one main band at 2190 and four weak bands at 2361, 2338, 2140 and 1640 cm^{-1} are also detected. The surface species formed on the Ag-ZSM-5 are similar to that of the Ag-SAPO-34. Upon increasing the CO pressure (Fig. 4a–d), the bands at 2190 and 2140 cm^{-1} rises in intensity and shift to 2186 and 2136 cm^{-1} . The CO surface coverage strongly affects the formation of mono-carbonyl and carbon dioxide species on the Ag-ZSM-5. Evacuation leads to decrease in the concentration of mono-carbonyls

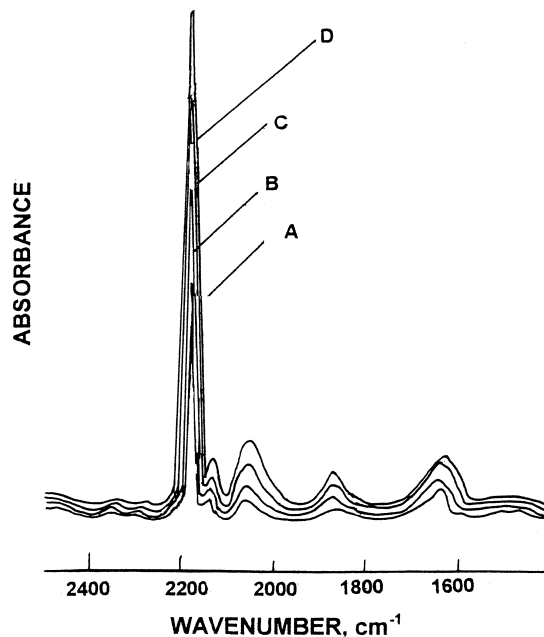


Fig. 4. FTIR spectra of CO adsorbed over the dehydrated silver exchanged high silica pentasil zeolite (temperature 296 K, CO pressure a = 12 Torr; b = 22 Torr; c = 61 Torr; d = 103 Torr).

and increase in the concentration of carbon dioxide species. The assignment of CO adsorption bands is in agreement with the previously reported ones [23,24].

Investigation on the CO adsorption on the Ag-exchanged NaA zeolite using different techniques has been reported [24]. The activation of the Ag-exchanged zeolite results into formation of the colour centres via an auto-reductive process. A process of auto-reduction occurs together with intense colouration of the sample, the former implies the appearance of Ag^0 atoms, the latter is indicative of covalent bond formation of silver. Similar colour centres are observed in the Ag-SAPO-34 and Ag-ZSM-5 samples after CO adsorption. Over these centres, one molecule of CO was chemisorbed per Ag ion available in the supercage of zeolite A. Formation of linear Ag_3^+ clusters upon activation was proposed. The CO adsorption-AgNaA study [23] shows that the amount of CO chemisorbed increases with the degree of Ag^+ for Na^+ . The total amount adsorbed also is enhanced by the presence of Ag^+ and increase linearly with the degree of exchange. At high degrees of exchange, $\text{Ag}^+-\text{Ag}^0-\text{Ag}^+$ species are formed. The isolated species and linear $\text{Ag}^+-\text{Ag}^0-\text{Ag}^+$ clusters are responsible for the chemisorption properties of the material. CO is chemisorbed on the Ag^+ ions available in the supercages (involved in the cluster formation or not). CO adsorption on the Ag-SAPO-34 and Ag-ZSM-5 shows the presence of similar Ag species.

4. Summary

NO adsorption on the silver-exchanged microporous materials resulted in the $\text{Ag(I)}-(\text{NO})$, $\text{Ag(I)}-(\text{NO})_2$, $\text{Ag(II)}-\text{NO}_2$, N_2O , N_2O_3 , and $\text{Ag}-(\text{NO}_3)$ complexes. The mono-nitrosyl species is the most abundant species on the Ag-SAPO-34 and Ag-ZSM-5 as compared with the other NO_x species. The frequencies for the NO_x complexes are slightly different for the

Ag-SAPO-34 and Ag-ZSM-5. With the increase in the NO surface coverage, an increase in the concentration of N_2O , $\text{Ag(I)}-\text{NO}$, $\text{Ag(I)}-(\text{NO})_2$ (only for Ag-ZSM-5) and $\text{Ag}-(\text{NO}_3)$ species and a decline in the $\text{Ag(II)}-(\text{NO}_2)$ concentration on the materials is observed. Evacuation experiments suggest that the silver nitrite and nitrate are the most stable surface species. Adsorption of CO on the Ag-SAPO-34 and Ag-ZSM-5 leads to mono-carbonyl and carbon dioxide species. The concentration of the mono-carbonyl and carbon dioxide species increases with increasing CO equilibrium pressure. In the case of NO or CO adsorption, the pressure strongly affects the concentration and distribution of the NO or CO complexes on the silver-exchanged microporous materials. The NO/CO FTIR results that indicates that substantial number of Ag(I) centers are present of the Ag-SAPO-34 and Ag-ZSM-5 materials.

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