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COADSORPTION OF NITRILES AND CO ON Cu-ZSM-5: AN IN SITU FTIR SPECTROSCOPIC STUDY

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ABSTRACT

The coadsorption of acetonitrile (ACN) or deuterated acetonitrile (dACN) with CO at Cu-ZSM-5 reveals several interesting features concerning the partial valency of Cu. Specifically, CO binds at Cu^{+1} and Cu^0 centers (in the absence of preadsorbed ACN) and exhibits C-O stretching frequencies of 2157 cm^{-1} and 2112 cm^{-1} , respectively. Carbon monoxide readily adsorbs at an ACN (or dACN) saturated Cu-ZSM-5 and exhibits a C-O stretch of 2122 cm^{-1} , a value more consistent with a partially reduced Cu^{+1} center. Furthermore, the IR cross section for the CN stretch in a number of nitriles (ACN, dACN, and benzonitrile) coadsorbed with CO displays interesting effects attributed to rehybridization and changes in CN dipole moment.

INTRODUCTION

The catalytic opportunity that Cu-ZSM-5 has for potentially reducing NO_x emission through reduction by hydrocarbons has prompted an enormous international examination of this material and the chemical properties it displays [1-6 and references contained therein]. Attendant with the study of this catalytic material there have been an ever expanding number of postulated mechanisms regarding how the Cu center in this material reacts with NO , O_2 and hydrocarbon molecules [1-6]. Regardless of how the active metal center reacts with these gaseous species it is fairly certain that the Cu center itself undergoes substantial coordination geometry and partial valence changes. In this work we highlight a very ready demonstration of how coadsorbed gaseous species used in model studies of NO_x reduction indirectly probe the local valence of Cu species in solid state exchanged ZSM-5 through changes in vibrational frequencies of coadsorbed species. The implication of how adsorption and coadsorbates alter valence changes at the active metal site has obvious practical implications in understanding how these materials operate mechanistically.

EXPERIMENT

All experiments were performed in a turbomolecularly pumped chamber derived from a 2.75" conflat six-way cross mounted vertically in the sample compartment of a Mattson Cygnus 100 FTIR spectrometer. Measurements were performed in the transmission mode at a typical frequency resolution of either 2 or 4 cm^{-1} . Infrared specific components included an MCT detector, a KBr beam splitter, and CaF or KBr vacuum windows. Samples were powders pressed into tungsten wire mesh that was resistively heated using the methodology of Ref. 7. Sample temperatures (95 - 1000K) were monitored using a type K thermocouple spot-welded to the center of the tungsten mesh. The sample meshes were supported on specially designed stainless steel mounts attached to a metal to ceramic feed-through mounted on a double wall (1.00" outside diameter) sample manipulator rod. The sample rod was mounted onto a linear motion translator that enabled it to be positioned above and at (in and out of the IR beam) the center portion of the six-way cross. Vacuum integrity was achieved by passing the rod through fixed spring-loaded teflon seals. A complete gas flow manifold with provisions for cleaning of gases and/or mass flow control of gaseous reactants are also attached to the experimental chamber.

Acetonitrile, deuterated acetonitrile, and benzonitrile were all obtained from Aldrich Chemical and were degassed using several freeze-pump-thawed cycles prior to use. The CO used in these experiments was research purity from Matheson and it was stored in a glass bulb kept under liquid nitrogen to ensure the removal of metal-carbonyl (mainly Fe and Ni) impurities present in research grade CO stored in metal cylinders. The zeolite sample was transferred into the IR beam, cooled and IR spectra were collected with gradually increasing sample temperature.

A Cu-ZSM-5 sample with essentially no free hydroxyls was prepared by solid-state ion exchange of H-ZSM-5 with CuCl in a slight variation of a method described in Ref. [8]. The solid-state ion exchange was carried out in a quartz tube reactor attached to a vacuum line. The parent NH₄-ZSM-5 sample was first slowly heated up to 850 K and annealed at this temperature for 6 hrs. This treatment resulted initially in the slow, systematic dehydration followed by the deammoniation of the ammonium form ZSM-5. The sample then was cooled back to room temperature and removed from the reactor. Cuprous chloride in an amount larger than that needed for the quantitative ion exchange of protons for Cu⁺ ions was placed on the bottom of the quartz reactor. Then a thin layer of quartz wool was positioned on the top of the CuCl to prevent direct contact between CuCl and H-ZSM-5. The deammoniated H-ZSM-5 sample was then placed into the reactor and finally it was capped with a thick layer of quartz wool to protect the zeolite powder being sucked out of the vacuum line upon degassing and also to prevent to deposition of CuCl vapor in the vacuum line. The reactor prepared this way was first evacuated and then slowly heated up to about 400 K and kept at this temperature overnight to ensure the removal of adsorbed water from both the zeolite and the CuCl. Then the reactor temperature was raised to 700 K to provide a sufficient CuCl vapor pressure for the solid-state ion exchange. The reactor was kept at this temperature for 6 hrs and then it was heated up to 900 K to ensure the removal of all excess CuCl from the reaction zone.

Analytical characterization was accomplished using inductively coupled plasma mass spectroscopy and atomic emission spectroscopy. The elemental ratios for the Cu-ZSM-5 sample were: Si/Al= 27.9, Cu/Al=2.2.

RESULTS

A) CO/Cu-ZSM-5 and ACN (dACN)/Cu-ZSM-5: The adsorbates CO, ACN, and dACN were independently examined by IR as a function of sample temperature and partial pressure of the reactants. In this report we will focus on the fundamental vibration frequencies. For the sake of brevity; however, a more detailed description of all vibrational features for these adsorbates (and those also those observed for benzonitrile, trichloronitrile, and the C1 thru C3 nitroalkanes) will appear in another publication [9]. As reported previously [10] the C-O stretch was observed at 2157 cm⁻¹ for adsorption on Cu⁺ in ZSM-5. Catalyst pretreatment procedures such as oxidation and reduction cycles have been noted from in situ IR examination of adsorbed CO to produce several sites with the following respective C-O stretching frequencies at near saturation coverage: CO/Cu²⁺, 2195 cm⁻¹; and CO/Cu⁰, 2212 cm⁻¹ (gas phase CO, 2143 cm⁻¹). In the present study the Cu-ZSM-5 sample was exposed to ACN (and dACN) sufficient to populate one adsorbed molecule per Cu center. Although possible to force more ACN (dACN) onto Cu⁺ sites, it was provident to work in a coverage regime where only one ACN is located at each Cu⁺ site. Excess ACN (or dACN) was pumped away prior to CO admission. Adsorbed ACN was observed to have a C-N stretching frequency of 2298 and 2325 (the latter spectral signature arises from the Fermi resonance between a combination of $\delta_s(\text{CH}_3)$ plus $\nu(\text{C-C})$ and C-N stretches). The gas phase acetonitrile C-N stretch is seen at 2257 cm⁻¹. The C-N

stretch for adsorbed dACN also observed at 2298 cm^{-1} . In the following only dACN data will be shown.

B) CO/dACN(ACN)/Cu-ZSM-5 coadsorption: A stack plot covering the C-O stretching region is shown for CO dosed onto a dACN saturated Cu-ZSM-5 sample in Fig. 1A. Note that the primary C-O stretch is seen at 2122 cm^{-1} , approximately 35 cm^{-1} redshifted from the value observed for the same sample in the absence of dACN (or ACN). The low intensity features observed at 2110 cm^{-1} and 2250 cm^{-1} arise from the symmetric and asymmetric C-D stretches in the deuterated methyl group of the preadsorbed dACN. Note that for the C-O stretch no shift in the band position is observed as CO coverage is increased. However, the full width at half maximum (FWHM) is shown in Fig. 2 (after spectrally subtracting the C-D stretch component). Note that the FWHM is essentially constant until a relative coverage of 0.4 is reached at which point the width of the band linearly increases.

In Fig. 1B the C-N stretch region is shown for the dACN/Cu-ZSM-5 sample as the relative coverage of CO increases (the data series is the same set as shown in Fig. 1A). Note that the C-N stretch is invariant in position until approximately 0.4 CO coverage is reached. Thereafter two features are very apparent in the spectra. First the C-N band center redshifts 9 cm^{-1} to 2290 cm^{-1} . Secondly, the absolute band C-N intensity increases approximately 100%. Although not readily transparent, careful spectral subtraction over the C-D region clearly indicates that no new dACN is being adsorbed. This was further confirmed in examining the C-H region of the CO/ACN/Cu-ZSM-5 system. An invariant integrated intensity of the C-H stretch region indicates that no new ACN is adsorbing on the sample (data not shown for brevity).

Fig. 1 A) C-O stretch region for various CO coverages at a dACN saturated Cu-ZSM-5;
B) C-N stretch region for dACN saturated Cu-ZSM-5 versus CO coverages of A.

Fig.2 FWHM of CO stretch as a function of relative coverage at a dACN saturated Cu-ZSM-5 sample.

DISCUSSION AND POSTULATED MODEL

Model: The interpretation of the interesting spectral shifts and intensity change in the C-N stretch of the coadsorbed dACN (ACN) is suggested from the coordination complex model shown in Fig. 4. From analogy to the coordination chemistry observed in

Fig. 4 Proposed Coordination Geometry in CO/ACN/Cu-ZSM-5 System (oxygen coordination to zeolite framework denoted by filled and unfilled triangles)

several inorganic ACN complexes [11,12] the ACN molecule is drawn with a linear N-C-C bond extending from the Cu^{+1} center. As CO adsorbs at the ACN/ Cu^{+1} sites they are suggested to initially fill with one ACN and one CO at each center. Note that during this initial adsorption, the C-O stretching frequency is observed at 2122 cm^{-1} , a value closer to a Cu^0 center than Cu^{+1} . With increased CO coverage two molecules eventually adsorb at each ACN/ Cu^{+1} site. The addition of the second CO weakens the ACN bonding to Cu^{+1} slightly such that the CN stretch is observed at a slightly lower energy and note (from Fig.

1B) that the dipole moment of the adsorbed ACN must also increase leading to an enhanced IR absorption cross section. To accomplish this latter rehybridization the Cu^{+1} center is suggested to give up some degree of coordination to the oxygen centers in the zeolite. To test of the viability of the aforementioned model and in particular the last point, DFT [13] calculations of CO and ACN adsorption on Cu-ZSM-5 are currently in progress. These theoretical studies should provide interesting structural and thermodynamic stability information with respect to the proposed intermediates suggested above. In describing a complex reaction scheme such as NO_x reduction, it is perhaps an oversimplified notion that Cu centers retain a rigid valence state even for chemisorption.

CONCLUSIONS

Coadsorbed CO and acetonitrile (or deuterated ACN) have been shown to be very sensitive to the electron density at the Cu^{+1} site when entrained in ZSM-5. The fundamental molecular stretching frequencies for C-O and C-N both shift in relation to the electron density changes at the Cu^{+1} site. Carbon monoxide coadsorbed at Cu^{+1} is seen at 2122 cm^{-1} , a value considerably lower than that observed in the absence of ACN (2157 cm^{-1}). The C-N stretch for ACN coadsorbed with CO is also observed to shift to lower values but is suggested to do so only upon coordination of a second CO molecule on the Cu^{+1} site as shown in Figure 4. The often noted valence changes in the literature of NO_x reduction indicate that subtle and interesting changes about the active metal site may play a very important role in its activity. In the present study, the coadsorption of common model compounds used in characterizing zeolite reactivity (e.g., ACN, CO) indicate that the adsorption process leads to a subtle valence redistribution at the adsorbate/metal center and potentially global site geometry changes within the zeolite host.

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