

Interaction of Acetonitrile with Cobalt-Containing Aluminophosphates: An X-ray Absorption Investigation

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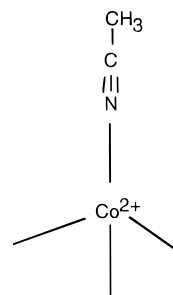
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XAFS data have been collected on reduced cobalt-containing aluminophosphate molecular sieves, both before and after sorption of the probe molecule, acetonitrile. Data are reported for CoAlPO-5, CoAlPO-18, CoAPSO-44, and cobalt-exchanged SAPO-18. Analysis of both the XANES and EXAFS reveals three different types of species: in the first the acetonitrile is coordinated linearly to the Co^{2+} in the framework (Brønsted acid) center; in the second, a nonlinear structure is suggested in which the nitrogen of the acetonitrile occupies an oxygen vacancy, thereby coordinating to Co^{2+} Lewis acid sites. In the third, two or more of the probe molecules coordinate to extraframework Co^{2+} ions. The results are consistent with the models proposed for Brønsted and Lewis acid centers in these systems in a previous EXAFS study.

Introduction

Substitution of lower valent metal ions in microporous materials, including zeolites and aluminophosphates, is known to produce strong acid catalysts possessing either Brønsted or Lewis or both types of acid centers. To assist the understanding of the catalytic properties of microporous solids, it is important to elucidate the structure, strength, and type of the acid centers.¹ Greater understanding of the structure and particularly local structural information around the heteroatom responsible for generation of the acid centers has been gained from NMR, computational methods, and more recently X-ray absorption spectroscopy.^{2–6} Acid strength is commonly determined by temperature-programmed desorption and calorimetric methods,^{7–10} with the type of acid centers (both Brønsted and Lewis acid centers) usually determined by infrared spectroscopy either with or without a probe molecule (see ref 11 and references and therein). There are advantages in using small- and medium-sized probe molecules such as CO, H_2O , NO, NH_3 , acetonitrile, and pyridine for the routine determination of the type of acid centers in the internal pores and external surfaces of microporous solids,^{7,11–16} whereas large molecules such as quinoline¹⁷ are conveniently used to investigate the acidity of external surfaces. Of these molecules, acetonitrile is extensively used to differentiate the various types of acid centers in many small-pore microporous systems.^{7,15,18,19} Although it has been shown that this molecule interacts with protons associated with the Brønsted acid sites of zeolites,^{18,19} it is also considered to interact directly with the heteroatom in divalent ion-substituted aluminophosphates^{7,15} rather than the proton as in the case of aluminosilicates. In particular, recent IR studies¹⁵ of cobalt- as well as magnesium-substituted aluminophosphates led to the proposition that the acetonitrile interacts directly with the heteroatom as shown in Chart 1. Although this kind of model is plausible from the interpretation of IR data alone, more direct structural information can be obtained from X-ray absorption spectroscopy (XAS) by probing the local structure around the metal ion responsible for the acidity. Indeed, the use of this technique is particularly appropriate in this case since it is atom specific and

CHART 1



is known to be highly sensitive to linear coordination geometries. The presence of such a geometry, for example, in metal cyanide complexes,^{20–22} results in an enhancement of both the main absorption edge intensity (the so-called white line)²⁰ and the EXAFS amplitude (as discussed in, for example, ref 21). Thus, by virtue of acetonitrile being a linear molecule, it is possible to determine from XAS whether it forms a linear complex with the metal ion centers.

In the present paper, we therefore report a systematic Co K-edge XAS study of the interaction of acetonitrile with various cobalt-substituted aluminophosphates of the type AlPO-18, APSO-44, AlPO-5. Cobalt-substituted AlPO-18 and APSO-44 catalysts, both of which are related to the chabazite structure, are known to exhibit Brønsted acidity.^{4,23} The local structure of the Brønsted acid center, which has a distorted tetrahedral coordination, together with the redox capability of these materials have been discussed in detail in a recent study.⁶ In contrast, CoAlPO-5 has been found to possess predominantly Lewis acid centers that have been shown to have a different local structure. Furthermore, IR and TPD studies indicated that probe molecules (ammonia or acetonitrile) interact strongly with the acid centers in this catalyst.⁷ Our present results reveal that acetonitrile interacts linearly with the Co(II) ions in the case of CoAlPO-18 and CoAPSO-44, whereas a bridging (Co-N-P) geometry is proposed for CoAlPO-5.

Experimental Section

Co K-edge X-ray absorption spectra of the as-prepared, calcined, reduced, and acetonitrile-adsorbed catalysts were

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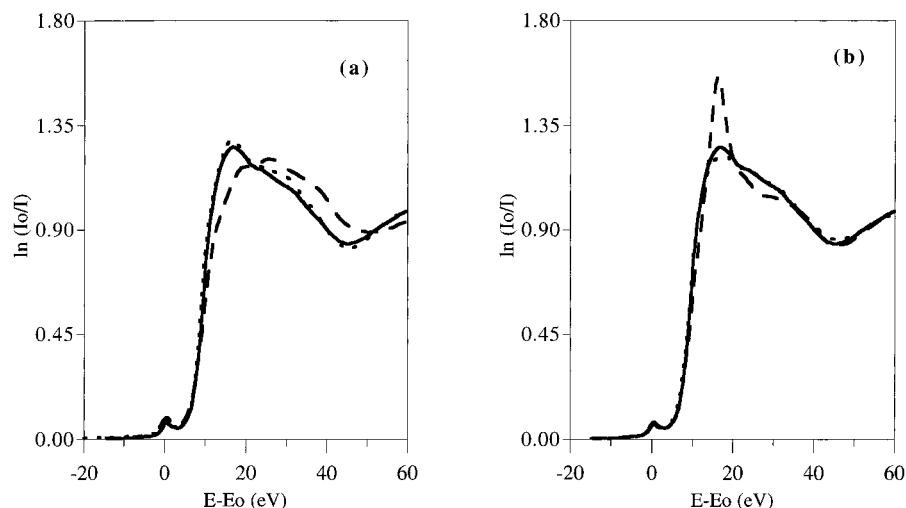


Figure 1. Comparison of the Co K-edge XANES of (a) as-prepared (solid line), calcined (long dash curve), and reduced (short dash curve) CoAlPO-18 catalyst. Part b shows reduced (solid line), acetonitrile adsorbed (long dash curve), and desorbed (short dash curve) catalyst.

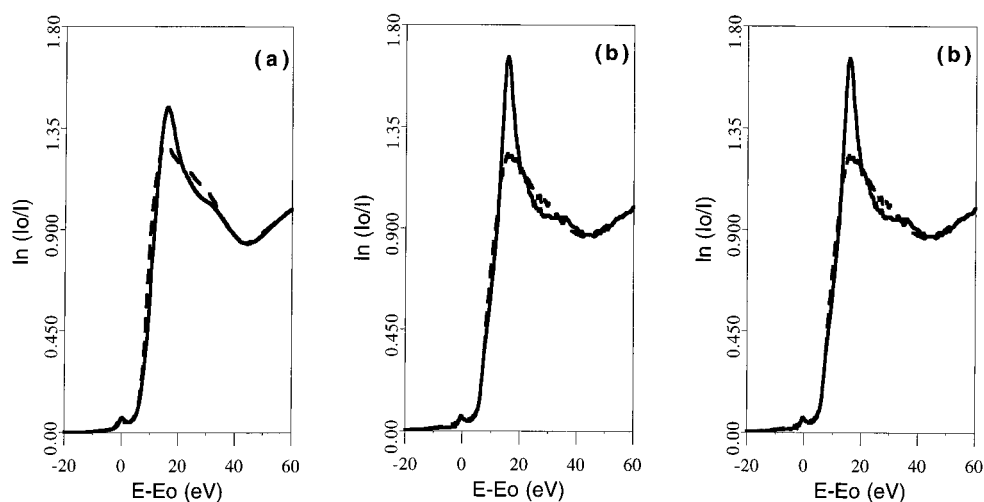


Figure 2. Comparison of the Co K-edge XANES of reduced (dashed curve) or dehydrated in the case of cobalt-exchanged SAPO-18 and acetonitrile-adsorbed (solid line) (a) CoAlPO-5, (b) cobalt-exchanged SAPO-18, and (c) CoAPSO-44 catalyst.

recorded at room temperature (rt). In a typical experiment, 100 mg of the catalyst was pressed into a disk and loaded into the in situ cell, described elsewhere.⁶ The catalyst was calcined in an oxygen flow, to remove the occluded organic template, at 550 °C and reduced at 400 °C in a H_2/N_2 mixture (10% H_2) prior to EXAFS measurement and acetonitrile adsorption. Here, we have used the deuterated form of acetonitrile to maintain consistency with an earlier IR study.¹⁵ The in situ cell containing the reduced catalyst was connected to a conventional vacuum system, and the cell was evacuated to about 2×10^{-4} Torr before 40 Torr of acetonitrile was admitted. Room-temperature EXAFS data were recorded at station 7.1 of the Synchrotron Radiation Source at Daresbury Laboratory, which operates at 2 GeV, with a typical current in the range of 130 to 250 mA. In the case of cobalt-exchanged SAPO-18, where the cobalt concentration is ca. 1 wt %, the fluorescence data collection mode was employed using a 13 element Canberra fluorescence detector. (In this case, three scans were recorded and averaged to improve the signal-to-noise ratio.) The experimental stations 7.1 and 8.1 were equipped with a Si(111) double-crystal monochromator and Si(220) monochromators, respectively. Both these stations were provided with ion chambers for measuring the I_0 (incident beam intensity) and I_t (transmitted beam intensity). A 50% harmonic rejection was used to avoid higher harmonic contributions.

The suite of programs available at the Daresbury laboratory, EXCALIB (to convert the raw data to energy vs. absorption coefficient), EXBROOK (for pre- and post-edge background subtraction), and EXCURV92²⁴ (for detailed curve fitting analysis of the EXAFS data), were used. Preedge subtracted and normalized XANES data were obtained from the EXBROOK program. Curved wave theory and multiple scattering calculations were employed to analyze all the EXAFS data without Fourier filtering. A typical data range of $3.0\text{--}11.0 \text{ \AA}^{-1}$ was used in all cases. The restrained analysis procedure employed for the analysis of the EXAFS data is described below where we present and discuss the results. $CoAl_2O_4$ ²⁵ and $DAF-2$ ²⁶ were used as the model compounds to extract the amplitude reduction factor (denoted AFAC in EXCURV92 program), and the value obtained of 0.81 was fixed for the analysis of the other systems studied here.

Results and Discussion

We discuss first the XANES results and then those for the EXAFS. The information yielded by the XANES and EXAFS are complementary and should unambiguously identify the nature of the coordination (either linear or bent) and reveal any changes in the coordination number.

XANES. As noted earlier, XANES is as equally sensitive as EXAFS to multiple scattering, generated due to the presence

TABLE 1: Structural Parameters (N = Coordination Number, R = Atom Pair Distance, and $2\sigma^2$ = Debye–Waller Factor) Obtained from the Analysis of the Co K-Edge EXAFS Data

	atom pair	N	R (Å)	$2\sigma^2$ (Å ²)	bond angle (deg)	fit index ²⁵
CoAlPO-18 reduced	Co–O	3.0	1.90	0.011		27.58
	Co–O	1.0	2.03	0.013		
	Co–P	3.0	3.14	0.023	133 ^a	
	Co–P	1.0	3.34	0.024	141 ^a	
CoAlPO-18 with acetonitrile	Co–O	3.0	1.93	0.013		25.27
	Co–N	1.0	2.05	0.006		
	Co–C	1.0	3.15	0.010	180 ^b	
	Co–P	3.0	3.16	0.016	133 ^a	
CoAlPO-5 reduced	Co–O	4.0	1.93	0.014		25.05
	Co–P	3.0	3.13	0.018	130 ^a	
	Co–P	1.0	3.29	0.018	143 ^a	
	Co–O	3.5	1.96	0.014		
CoAlPO-5 with acetonitrile	Co–N	0.5	2.10	0.012		22.98
	Co–C	0.5	2.87	0.012	123 ^b	
	Co–P	3.0	3.12	0.018	129 ^a	
	Co–P	1.0	3.29	0.018	136 ^a	
Co-exchanged SAPO-18 dehydrated	Co–O	3.0	1.95	0.013		55.56
	Co–P	3.0	3.18	0.034	153 ^a	
	Co–O	2.8	1.97	0.010		
	Co–N	2.2	2.12	0.010		
Co-exchanged SAPO-18 with acetonitrile	Co–C	2.2	3.18	0.017	180 ^b	38.59
	Co–P	2.8	3.19	0.037	153 ^a	
	Co–O	3.0	1.91	0.016		
	Co–O	1.0	2.02	0.018		
CoAPSO-44 reduced	Co–P	3.0	3.17	0.022	136 ^a	18.78
	Co–P	1.0	3.44	0.022	155 ^a	
	Co–O	2.7	1.96	0.012		
	Co–N	1.7	2.12	0.008		
CoAPSO-44 with acetonitrile	Co–C	1.7	3.22	0.011	180 ^b	20.86
	Co–P	2.7	3.30	0.028	131 ^a	
	Co–O	3.0	1.91	0.016		
	Co–O	1.0	2.02	0.018		

^a Average bond angle corresponds to Co–O–P. ^b Average bond angle corresponds to Co–N–C.

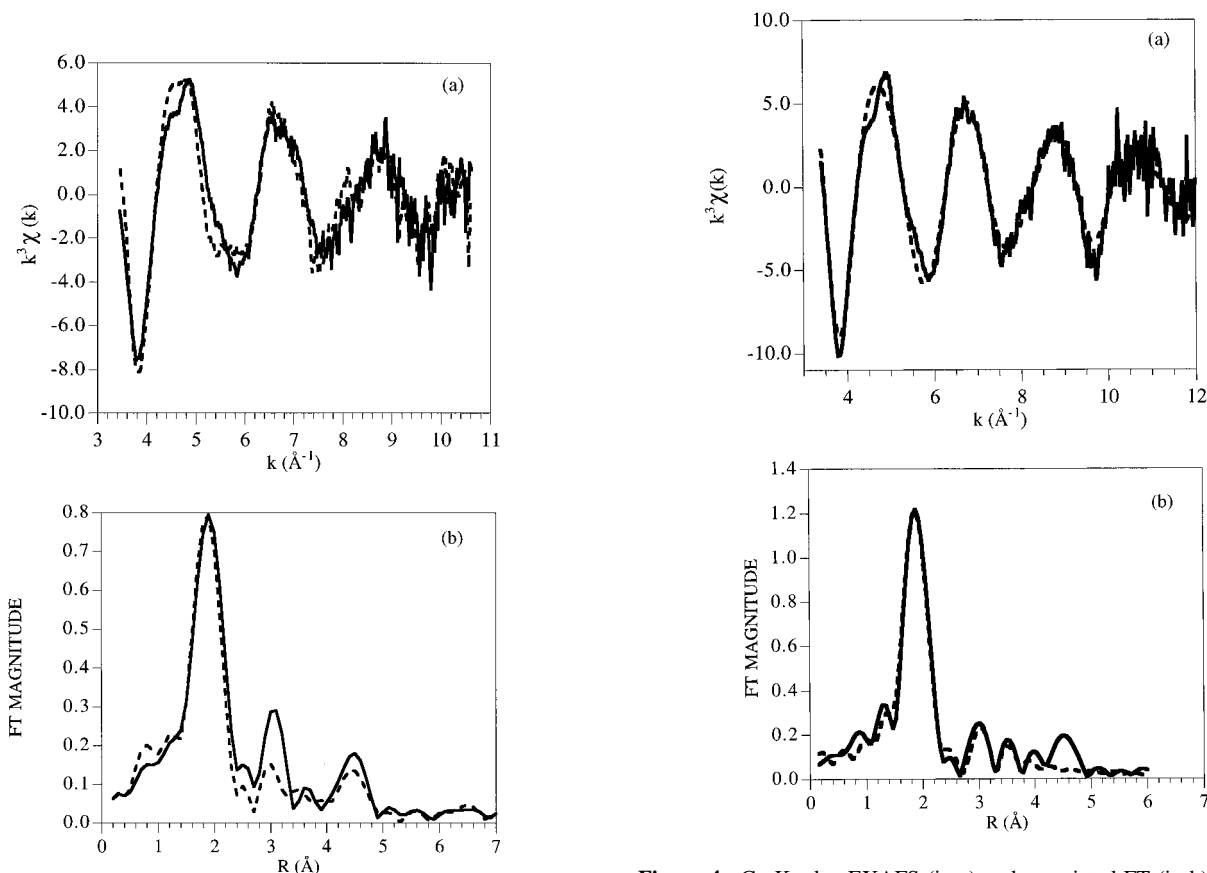


Figure 3. Comparison of the Co K-edge EXAFS data (in a) and the associated FT's (in b) of the reduced CoAlPO-18 (dashed curve) and the acetonitrile-adsorbed form (solid curve). Note that there is a distinct increase in magnitude of the FT at *ca.* 3.1 Å following the acetonitrile adsorption.

Figure 4. Co K-edge EXAFS (in a) and associated FT (in b) for the as-prepared CoAlPO-18. The solid line shows the experimental data and the dashed curve represents the best fit obtained using the multiple scattering approach. The derived Co–O distance with a coordination number of 4 is *ca.* 1.93 Å and the two Co–P distances are 3.18 and 3.31 Å with a Co–O–P bond angle of 132 and 144°.

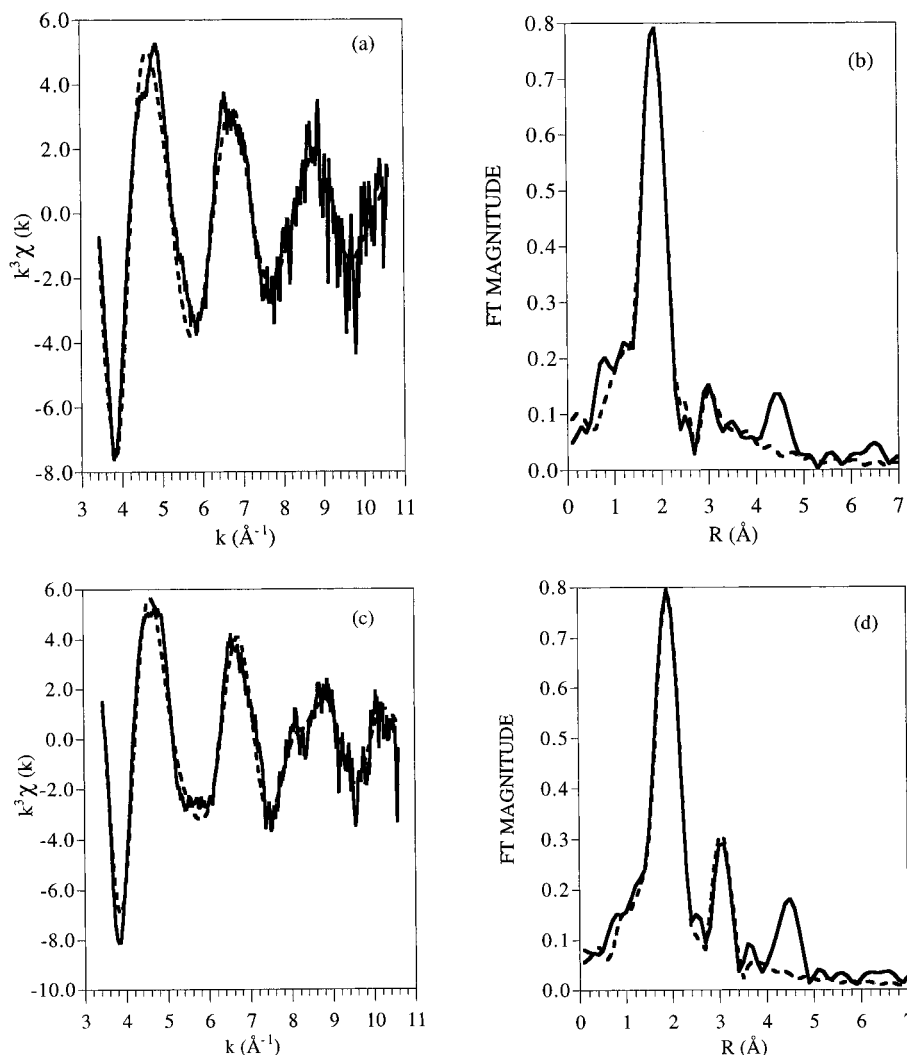


Figure 5. Co K-edge EXAFS and associated FT's for the reduced and subsequently acetonitrile adsorbed CoAlPO-18: (a) EXAFS of reduced CoAlPO-18; (b) associated FT for the reduced CoAlPO-18; (c) EXAFS of acetonitrile adsorbed on the reduced CoAlPO-18; (d) associated FT for the acetonitrile adsorbed on reduced CoAlPO-18. The solid curve shows the experimental data, and the dashed curve represents the best fit obtained using multiple-scattering approach.

of either octahedral coordination²⁷ or a coordinating linear molecule^{20,21} of the type studied here. Therefore, we compare first, in Figure 1a, the Co K-edge XANES spectra of CoAlPO-18 in the as-prepared, calcined, and reduced (acidic) form; second, we compare in Figure 1b XANES spectra of the reduced sample with the catalyst containing acetonitrile and after desorption at 300 °C. Although there are minor differences in the shape, edge, and intensity of the main absorption edge of the as-prepared, calcined, and reduced samples (Figure 1a), the most striking difference is seen between the sorbed and subsequently desorbed samples of the reduced catalyst containing acetonitrile (Figure 1b). The main absorption intensity, arising from the $1s \rightarrow 4p$ transition, is known to be sensitive to changes in coordination that result in increased multiple scattering for an octahedral coordination compared with the tetrahedral one.²⁷ A similar increase in intensity was also observed for metal complexes containing cyanide ligands resulting from increased multiple scattering contributions²¹ due to a linear coordination geometry. Therefore, our XANES observation strongly suggests that the acetonitrile interacts directly with the Co(II) centers of the reduced catalyst, thereby inducing strong multiple scattering effects; this type of coordination geometry corroborates our earlier model proposed on the basis of IR results.¹⁵ This intensity decreases markedly upon desorbing the acetonitrile at 300 °C (see Figure 1b), confirming

that the changes are directly related to the coordination of the acetonitrile molecule.

Similar striking effects are not seen in the case of acetonitrile adsorbed onto the reduced CoAlPO-5 catalyst (Figure 2a). It is known that CoAlPO-5 catalyst possess predominantly Lewis-type and considerably less Brønsted acid sites.^{6,28} The minimal changes in the white line intensity suggest that there is a different type of acetonitrile interaction (other than linear) with Co(II) centers associated with Lewis acid sites; but, the small increase in the white line intensity may be attributable to the interaction of acetonitrile with the Co(II) centers associated with the available Brønsted acid centers. Our earlier study⁶ suggested that the source of Lewis acidity was the formation of anion vacancies by dehydroxylation with coordinatively unsaturated cobalt (i.e., with a coordination number of less than 4); however, extraframework cobalt species have also been proposed^{29–31} to be the source of Lewis acidity. To investigate the latter possibility in CoAlPO-5, a cobalt-exchanged SAPO-18 sample (containing extraframework cobalt) was used as a model system. The Co K-edge XANES of the acetonitrile adsorbed on to a dehydrated cobalt-exchanged SAPO-18 shows a pronounced increase in white line intensity (see Figure 2b), suggesting the presence of higher concentrations of linear coordination when compared with both CoAlPO-5 and CoAlPO-18 samples; the

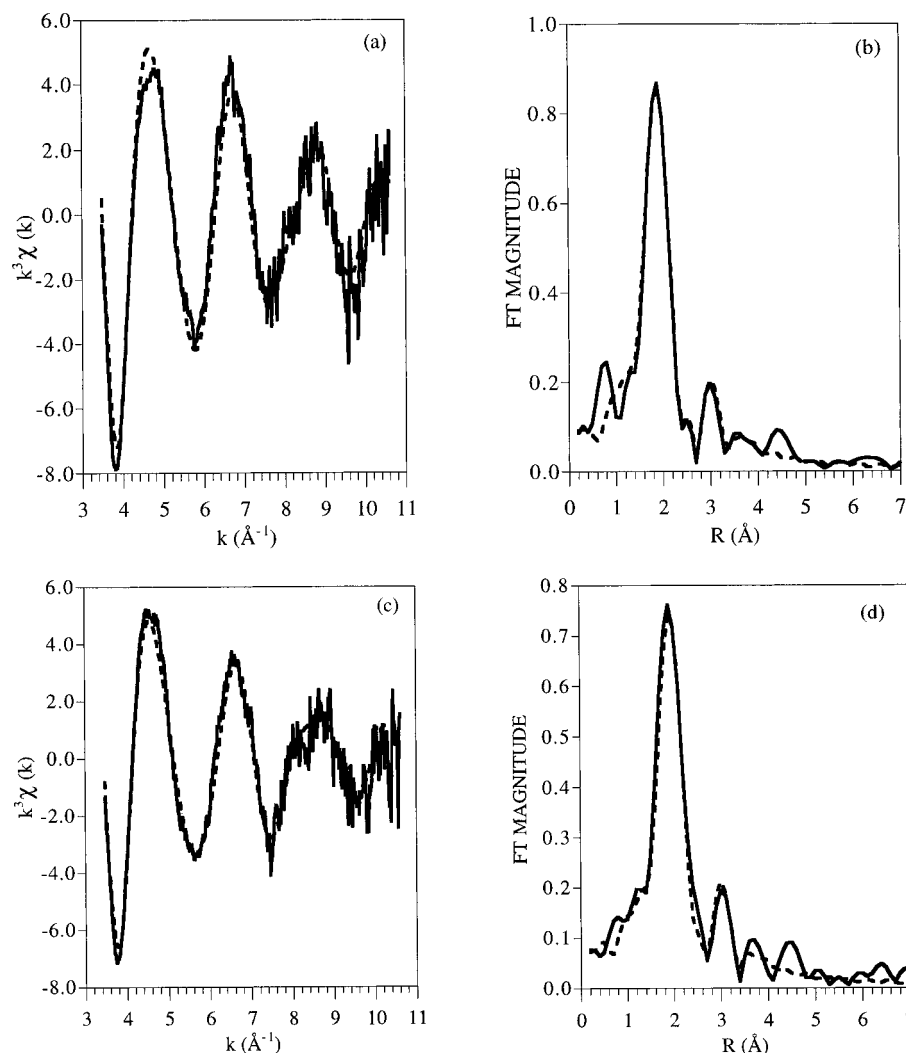


Figure 6. Co K-edge EXAFS and associated FT's for the reduced and subsequently acetonitrile-adsorbed CoAlPO-5: (a) EXAFS of reduced CoAlPO-5; (b) associated FT for the reduced CoAlPO-5; (c) EXAFS of acetonitrile adsorbed on the reduced CoAlPO-5; (d) associated FT for the acetonitrile adsorbed on reduced CoAlPO-5. The solid curve shows the experimental data, and the dashed curve represents the best fit obtained using multiple-scattering approach.

contrast with our results for CoAlPO-5 strongly suggest that extraframework cobalt species are not present in high concentrations in the CoAlPO-5 catalyst. Surprisingly, the white line intensity of the acetonitrile adsorbed on the reduced CoAPSO-44 catalyst is similar to cobalt-exchanged SAPO-18 (see Figure 2), although equivalent amounts of acetonitrile were adsorbed in all the cases. These differences in white line intensity are attributable to the nature of the interaction between cobalt K and the adsorbate, which is more apparent in the EXAFS data discussed below.

EXAFS Results. We consider first CoAlPO-18—a catalyst that overwhelmingly possesses framework-sited Brønsted acid centers—and describe in detail the data analysis procedure that resulted in the model corroborating our earlier IR results.

CoAlPO-18. Detailed information on the nature of the interaction of acetonitrile with cobalt centers associated with the Brønsted acid sites is seen directly in the analysis of the EXAFS data. A comparison of the EXAFS and the associated Fourier transforms (FT) for reduced CoAlPO-18 with that for the sample after subsequent acetonitrile adsorption is shown Figure 3. It is readily seen in the FT of the catalyst containing acetonitrile that there is a distinct enhancement in the magnitude of the peak around 3.1 Å. Initial analysis of the EXAFS data for the first coordination sphere revealed that the average

coordination number of the first shell is close to 4 with slightly larger static disorder (as indicated by the Debye–Waller factor) as compared to the results for the as-prepared catalysts. However, the results are similar to those for the reduced catalyst and the analysis of which indicates a 4-fold coordination around cobalt, with no evidence for an increase in coordination number. This implies a distorted site acetonitrile sorbed system that is most easily explained by the presence of a low Z scatterer either oxygen or nitrogen being present in the coordination sphere; it is not possible to distinguish these two possibilities, since both oxygen and nitrogen will have similar scattering powers. It is, however, likely to be a nitrogen neighbor associated with the acetonitrile molecule for two reasons. First, there is evidence for a Co–N–C interaction, as discussed below, and second, the nature of the X-ray absorption spectrum is reversible upon adsorption and desorption. On the basis of this chemical reasoning, analysis of the data indicates that there is a Co–N interaction around 2.0 Å and correspondingly a Co–C interaction around 3.1 Å consistent with linear coordination of the acetonitrile, thereby increasing the amplitude of the signal due to multiple scattering effects as a result of linear coordination of the type Co–N–C; other oxygen shells are present around 1.95 Å. Reliable numbers for the Co–C (higher shell) interaction could not be obtained, since the Co–P distances of

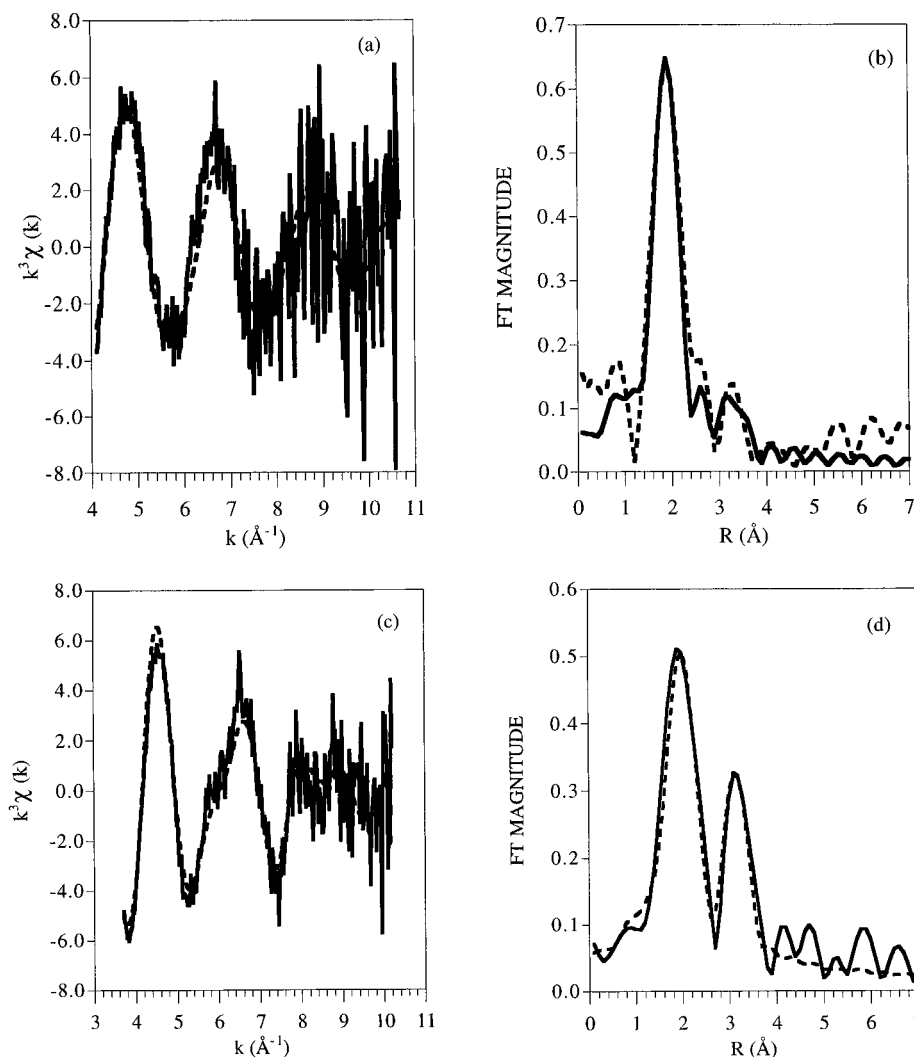


Figure 7. Co K-edge EXAFS and associated FTs for the dehydrated and subsequently acetonitrile adsorbed cobalt-exchanged SAPO-18: (a) EXAFS of dehydrated cobalt-exchanged SAPO-18; (b) associated FT for the dehydrated cobalt-exchanged SAPO-18; (c) EXAFS of acetonitrile adsorbed on the dehydrated cobalt-exchanged SAPO-18; (d) associated FT for the acetonitrile-adsorbed dehydrated cobalt-exchanged SAPO-18. The solid curve shows the experimental data, and the dashed curve represents the best fit obtained using multiple-scattering approach.

the framework structure occur at ca. 3.2 \AA , which is close to the Co–C distance.

To obtain more accurate structural information, the EXAFS data of the as-prepared CoAlPO-18 sample were analyzed initially with the inclusion of the second phosphorus shells. Although it is possible to analyze these data directly by considering four oxygens at 1.93 \AA , two phosphorus at 3.15 \AA and two at 3.38 \AA , more reliable information is obtained by carrying out multiple scattering calculations.³² The advantage with this approach is that it not only produces distances that are close to those found by single-crystal diffraction, for DAF-2,²⁶ which has the highest number of cobalt sites (in tetrahedral coordination) in any known phosphate-related microporous structure, but also directly provides Co–O–P bond angles. This analysis has also the advantage of allowing us to restrain the average P–O distance (a option in EXCURV92 program²⁴) to a value close to 1.51 \AA reported for many aluminophosphates including DAF-2.²⁶ The resulting best fit using this multiple scattering approach for the as-prepared CoAlPO-18 is shown in Figure 4. Extending this procedure to the reduced catalyst using a model comprising three short and one long Co–O distances, as reported in our earlier work,^{4,6} is shown in Figure 5. This procedure clearly establishes the Co–P distances, thus allowing us to determine accurately the presence of other coordinating atoms after adsorbing the acetonitrile molecule;

of particular importance here is the Co–C interaction and the Co–N–C bond angle.

To determine the nature of acetonitrile coordination, we kept the Co–O and Co–P distances fixed, as that obtained for the reduced catalyst, and introduced a Co–N (instead of the long Co–O distance) to maintain the coordination close to four for the reasons mentioned earlier and the associated Co–C distance at ca. 3.1 \AA . The multiple scattering analysis was performed with the Co–N–C bond angle as one of the variables while restraining the N–C distance close to 1.15 \AA , which is a typical distance for a triple bonded systems. The best fit (see Figure 5) resulted in a model containing three Co–O and one Co–N distances of 1.95 and 2.05 \AA , respectively, in addition to the carbon shell at 3.15 \AA with the Co–N–C bond angle close to 180° (see Table 1). The coordination number, in particular for the carbon shell, of close to 1 suggests strongly that only one acetonitrile molecule is interacting with the cobalt centers. This result suggests that the increase in white line intensity in the XANES data is due to an increase in the multiple scattering contribution rather than an increase in coordination number. This finding is consistent with the model proposed on the basis of the earlier IR work wherein the CD_3CN molecule coordinates directly to the Co^{2+} centers associated with the Bronsted acid sites.¹⁵ These sites can act as Lewis acid centers when the OH

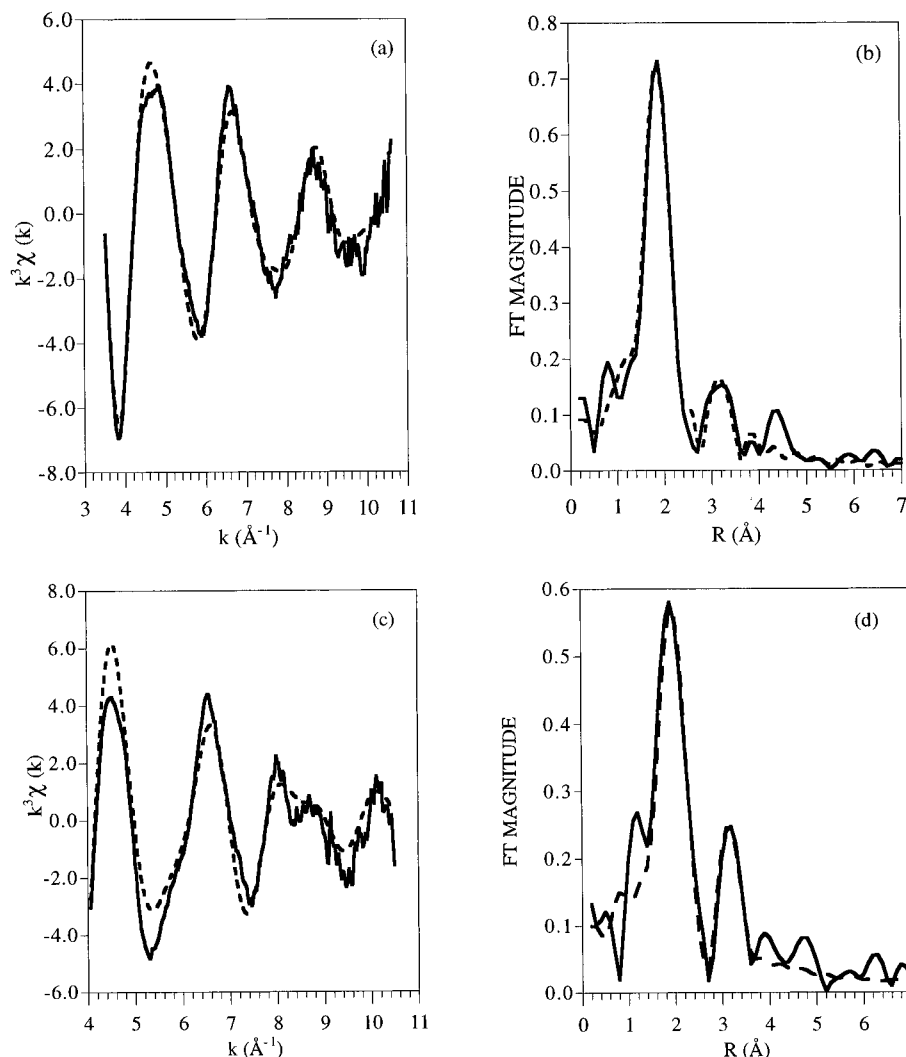
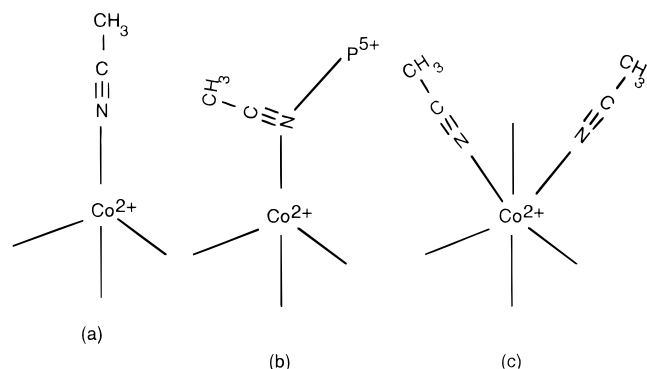


Figure 8. Co K-edge EXAFS and associated FT's for the reduced and subsequently acetonitrile-adsorbed CoAPSO-44: (a) EXAFS of reduced CoAPSO-44; (b) associated FT for the reduced CoAPSO-44; (c) EXAFS of acetonitrile adsorbed on the reduced CoAPSO-44; (d) associated FT for the acetonitrile adsorbed on reduced CoAPSO-44. The solid curve shows the experimental data, and the dashed curve represents the best fit obtained using the multiple-scattering approach.

CHART 2



groups become detached upon coordination of the CD_3CN molecule to the cobalt centers (also see Scheme 1 in ref 15).

This procedure, in which we first examine the as-prepared material and then the reduced catalysts before analyzing the final acetonitrile-containing catalysts, has been used consistently for the other systems.

CoAlPO-5. Comparisons of the Co K-edge EXAFS data and their associated FT's for the reduced CoAlPO-5 and for the sample after acetonitrile adsorption are shown in Figure 6 together with the best fit to these data. There is no distinct

enhancement in the magnitude of the FT around 3.1 \AA as seen for CoAlPO-18. A detailed analysis employing a strategy identical to that used for CoAlPO-18, however, reveals that there is an increase in the first shell coordination (from 3.9 to 4.2) and particularly in the static disorder, in a similar way to that observed for CoAlPO-18, which can be directly attributed to the presence of a nitrogen coordination in addition to the oxygen shells. We do not find any appreciable increase (to 5 or above) in coordination number for the first shell. We note here that we had earlier⁶ proposed that the reduced CoAlPO-5 catalyst possesses both coordinatively unsaturated (coordination number less than 4) and four coordinated sites, thereby yielding an average coordination number close to 3.5 for these centers, apart from the presence of small amounts of distorted four coordinated Brønsted acid sites. Thus, a coordination number close to 4 for the reduced catalyst reflects average effects of all these sites. Moreover, the correlation effects between the Debye–Waller factor and coordination number prevent any reliable estimation of these parameters. To avoid these complexities, and in particular to derive the nature of Co–N–C interaction with cobalt associated with Lewis acid centers in the acetonitrile-adsorbed catalyst, we have considered only the idealized cobalt environment. Thus, we have assumed an average Co–O coordination number of 3.5 and included a nitrogen shell to

achieve a total coordination number close to 4 for the analysis. The resulting best fit is shown in Figure 6, and the parameters are listed in Table 1.

The lack of a significant contribution from a carbon shell around 3.1 Å can be explained on the basis that this Co–N–C interaction is not linear as observed for CoAlPO-18. However, a reliable model with a carbon shell at ca. 2.9 Å and a bond angle of ca. 130° (see Table 1) can be obtained from the analysis. It is possible to explain, in this case, that acetonitrile coordinates to both the cobalt and phosphorus at the site where we proposed previously that there is an oxygen ion vacancy.⁶ A cobalt local structure of this kind will clearly result in a nitrogen at an acceptable distance of close to 2 Å with a Co–N–C bond angle much lower than 180°. This Co–N–C bond angle of 130°, which is significantly lower than 180°, will clearly decrease the multiple scattering contribution, which is reflected both in the EXAFS and in the XANES (where there is no significant increase in the white line intensity).

To substantiate further that the acetonitrile interaction is different for extraframework cobalt species, compared with that found for CoAlPO-5, a detailed data analysis for the acetonitrile-adsorbed cobalt-exchanged SAPO-18 sample was carried out. For this material, the FT shows considerable enhancement in the magnitude of the second shell (see Figure 7d) following acetonitrile adsorption compared to CoAlPO-5. The EXAFS data analysis employing multiple scattering (see Figure 7) revealed that there is more than one acetonitrile molecule coordinating to the cobalt. The structural parameters derived from the EXAFS analysis, summarized in Table 1, clearly show that there are close to two Co–N–C interactions with a bond angle of 180° distinctly different from the situation observed in adsorbed CoAlPO-5. These findings are fully consistent with the higher white line intensity seen in the XANES data (reported earlier in this paper) for this cobalt-exchanged sample and thus suggest that a different type of cobalt species is present in CoAlPO-5.

CoAPSO-44. The FT of the acetonitrile adsorbed CoAPSO-44 catalyst shows a distinct increase in the magnitude at ca. 3.1 Å (Figure 8d) similar to that observed for Co-exchanged SAPO-18 but higher than that for CoAlPO-18. The EXAFS analysis performed in the manner described above, however, reveals that there is more than one acetonitrile molecule coordinate to the cobalt but less than that observed for cobalt-exchanged SAPO-18. The structural parameters obtained from the analysis are again reported in Table 1.

Both XANES and EXAFS results show a clear trend in the nature of the interaction of acetonitrile with these cobalt-containing aluminophosphates. Our earlier EXAFS study of CoAPSO-44, CoAlPO-18, and CoAlPO-5 in combination with IR revealed that CoAlPO-18 has the maximum Brønsted acidity.⁶ CoAPSO-44 was considered,⁶ in terms of the type of acid centers, to be similar to CoAlPO-18 with CoAlPO-5 having the least amount of Brønsted acidity, consistent with other catalytic and adsorption studies.^{7,29–31} Although it is difficult to infer the extent of Brønsted acidity generated due to the presence of cobalt in CoAPSO-44 from adsorption and catalytic studies,²³ since both silicon and cobalt influence its formation, our EXAFS results⁶ proposed about 80% of Brønsted acid centers in this catalyst. The present investigation suggests that there are also some extraframework cobalt ions that interact strongly with acetonitrile, in a similar fashion to cobalt-exchanged SAPO-18, thereby yielding both white line intensity that is closely comparable and higher coordination numbers for Co–N and Co–C interaction. On the basis of these results, we propose the following scenario (see Chart 2) for the

interaction of acetonitrile with the cobalt centers in the three types of cobalt environments with (a) representing the acetonitrile interaction with the Brønsted acid center as in CoAlPO-18, (b) a bridging type of interaction yielding a nonlinear bond, and (c) several acetonitrile molecules interacting with extraframework Co²⁺ centers.

In CoAlPO-18 (a) dominates; whereas (b) is the major center in acetonitrile adsorbed CoAlPO-5 with small amounts of (a) type sites; (c) is present in Co²⁺-exchanged SAPO-18. In the case of CoAPSO-44, our results suggest both (a) and (c) type of sites coexist.

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