

Photoacoustic Spectroscopy Study of CoAPO-5 and CoZSM-5 Molecular Sieves

The synthesis and characterization of CoAPO-5 and CoZSM-5 molecular sieves have been reported (1-4). The state of cobalt ions of these molecular sieves can be affected by calcination to remove the organic templates.

In the present work a photoacoustic cell capable of high temperature and vacuum treatment was constructed and the photoacoustic spectroscopy (PAS) technique was applied to study the local environments of Co(II) ions incorporated in CoAPO-5 and CoZSM-5 as well as the effect of calcination on the state of Co(II) ions. PAS is well suited for the spectroscopic examination of samples which are opaque and have irregular surfaces such as coked catalysts (5). PAS technique also facilitates the acquisition of optical absorption spectra of weakly absorbing species in the presence of strongly absorbing species (6).

The photoacoustic spectrometer system is represented schematically in Fig. 1. The light source is a 1000-W high-pressure xenon lamp (Oriental Model 6269). The output of the monochromator (Oriental Model 77250) with a spectral resolution of about 8 nm is focused onto the sample in the cell and the light beam is modulated by a mechanical chopper with a typical modulation frequency of 39 Hz. The microphone signal from the cell is amplified by a preamplifier (SRS Model 550) and a lock-in amplifier (SRS Model 510). Data acquisition and analysis are performed by a computer (IBM-PC/AT). The photoacoustic cell was constructed by sealing a quartz window to the cell body with a thin

aluminum foil. This cell resembles the cell described by McGovern *et al.* (7) and the form of an extended Helmholtz resonator. The sample can be heated to 550°C by 250-W coil heater. Spectral measurements were made in the He-filled cell. Spectra at high temperature were obtained after treating samples at high temperature and filling the inner volume of the cell with He gas. The photoacoustic signal of a sample was normalized to that of carbon black taken at the same temperature. PA signal (at 585 nm) of both carbon black and molecular sieve samples showed the same temperature dependence.

CoZSM-5 was prepared by adding a cobalt-containing amorphous aluminosilicate material to ZSM-5 synthesis gel (2). First, a mixture having the composition of $4.5\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : 3.0\text{SiO}_2 : 185\text{H}_2\text{O} : 0.176\text{Co}$ was prepared from sodium silicate ($\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$, Fisher), $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (Fisher), sodium aluminate (65%, NaAlO_2 , Kanto), and sodium hydroxide (Fisher) and heated at 95°C for 1 h. By adding this to the second mixture composed of sodium hydroxide, colloidal silica (40%, Dupont) and tetrapropylammonium bromide (Fluka), the final mixture having the composition of $5\text{Na}_2\text{O} : 0.2\text{Al}_2\text{O}_3 : 90\text{SiO}_2 : 5.3\text{TPA} : 810\text{H}_2\text{O} : 0.2\text{Co}$ was prepared and crystallized at 190°C for 1-2 days.

CoAPO-5 synthesis gel having the composition of $\text{PR}_3\text{N} : \text{Al}_2\text{O}_3 : \text{P}_2\text{O}_5 : 0.14\text{Co} : 30\text{H}_2\text{O}$ was prepared from orthophosphoric acid (85%, Kanto), cobalt acetate ($\text{CoAc}_2 \cdot 4\text{H}_2\text{O}$, Fluka), pseudoboehmite (74.2 wt%

Al_2O_3 , Conoco), and tripropylamine (Aldrich), and was crystallized at 150°C for 2–5 days.

X-ray powder diffraction patterns were obtained with a Philips diffractometer employing $\text{CuK}\alpha_1$ radiation. The bulk chemical analysis of the samples was obtained by the wet technique and atomic absorption spectroscopy. The XPS measurements were performed by a VG Scientific XP-SLAB MK-2 Spectrometer with an X-ray source comprising an aluminum anode ($\text{AlK}\alpha = 1486.6 \text{ eV}$) operated at 15 KV and 20 mA.

X-ray powder diffraction patterns of as-synthesized CoAPO-5 and CoZSM-5 were in agreement with those of CoAPO-5 and ZSM-5 in the published literatures (1, 8).

Figure 2 shows the photoacoustic spectra of CoZSM-5 and CoAPO-5. There are triplet bands around 600 nm in as-synthesized CoZSM-5 and CoAPO-5. These are due to the ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_2(\text{P})$ transition of Co(II) ions surrounded tetrahedrally by oxygen ions (9). However, the presence of Co(II) ions in octahedral environment cannot be ruled out since the intensity of the corresponding bands will be an order of magnitude lower and hence will be masked by the intense bands of the tetrahedral Co(II) ions. The local symmetries of cobalt ions in ion-exchanged zeolites and in other host structures have been studied by several authors using diffuse reflectance technique (10–12). The spectrum of as-synthesized CoZSM-5 is not symmetric and shows larger splitting on the high-energy side than the low-energy side, and the spectrum is similar to that of the Co(II) ion in sodium silicate glass (11). Klier *et al.* (12) studied the electronic spectra of the Co(II) ion in anhydrous Co(II) cation-exchanged Zeolite A in the presence of adsorbed unsaturated hydrocarbons and they attributed the observation of enhanced splitting on the high-energy side to a low symmetry perturbation to a tetrahedral Co(II) ion by adsorbed hydrocarbons. The splitting on the high-energy side larger than that of the low-energy side observed in the spectrum

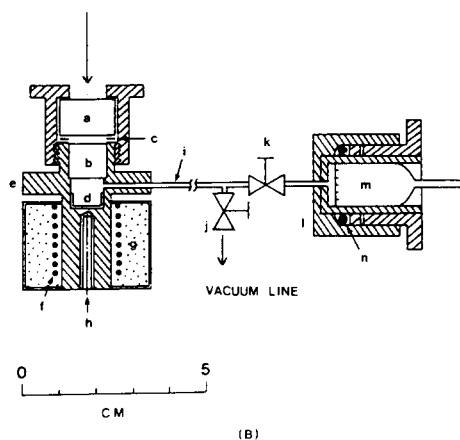
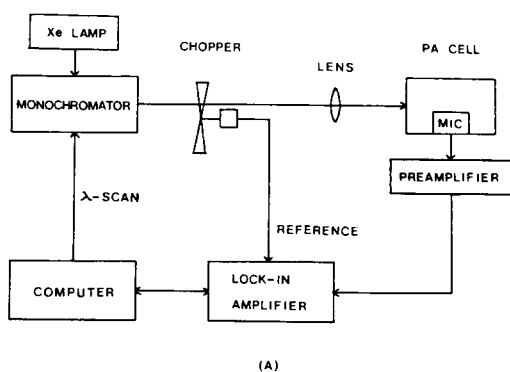


FIG. 1. The schematic diagram of the photoacoustic spectrometer (A) and photoacoustic cell for high temperature and vacuum treatment (B): (a) quartz window; (b) quartz rod; (c) aluminum foil; (d) sample holder; (e) cell body; (f) heating coil; (g) insulator; (h) thermocouple; (i) gas channel; (j) bellows metering valve; (k) bellows valve; (l) microphone holder; (m) microphone; (n) O-ring.

of CoZSM-5 may be attributed to the surface Co(II) ions similar to the Co(II) cation on Zeolite A.

During the calcination of CoZSM-5 and CoAPO-5 molecular sieves to remove the organic templates carbogeneous residue showed strong absorption. After calcination of CoZSM-5 in the PA cell by flowing O_2 at 550°C the intensity of the triplet band was increased. The frequencies of the triplet peaks were almost the same as those of as-synthesized CoZSM-5 though the resolution

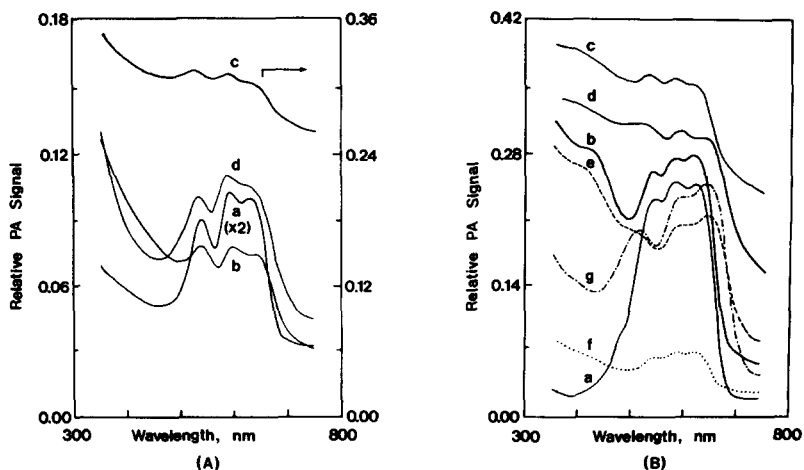


FIG. 2. PA spectra of CoZSM-5 (A) and CoAPO-5 (B). (A): (a) As-synthesized; (b) activated at 200°C (recorded at 200°C); (c) activated at 450°C (recorded at 350°C); (d) calcined. (B): (a) As-synthesized; (b) activated at 200°C (recorded at 200°C); (c) activated at 500°C for 3 h (recorded at 350°C); (d) activated at 500°C for 6 h (recorded at 350°C); (e) activated at 500°C for 12 h; (f) hydrated; (g) evacuated at 350°C (recorded at 350°C).

was slightly lower. The increased intensity of the triplet band in the calcined CoZSM-5 can be interpreted in terms of the formation of tetrahedral Co(II) on the surface (13). The surface to bulk cobalt ratio, expressed as the ratio of cobalt concentration obtained by XPS over chemical analysis, is considerably high in the case of CoZSM-5 (Table 1). These results indicate that the Co(II) ions are mainly located on the surface of the crystallite in as-synthesized as well as calcined CoZSM-5

The spectrum of as-synthesized CoAPO-5 shows the three almost symmetrically spaced peaks. The spectrum of as-synthesized CoAPO-5 can be assigned to Co(II) ions which are isomorphously substituted to the framework of $\text{AlPO}_4\text{-5}$ structure. For CoAPO-5 at.% of Al + Co nearly equals that of P as seen in Table 1. The ability of $\text{AlPO}_4\text{-5}$ system to substitute cobalt ions into its structure appears to be greater than that of ZSM-5.

Treating as-synthesized CoAPO-5 with

TABLE I
XPS and Chemical Analysis for CoAPO-5 and CoZSM-5

Samples	Composition (at.%)								(XPS/CA) ^a	
	XPS				CA					
	Co	Al	P	Si	Co	Al	P	Si		
CoAPO-5	As-synthesized	5.3	43	51	—	3.5	46	50	—	1.51
	Calcined	5.3	42	52	—	3.5	46	50	—	1.51
CoZSM-5	As-synthesized	4.9	—	—	95	0.17	<0.1	—	99.8	29.4
	Calcined	5.0	—	—	95	0.17	<0.1	—	99.8	29.4

^a Ratio of cobalt concentration by XPS over chemical analysis.

O₂ at 200°C resulted in an appearance of a new band around 400 nm, activation under vacuum at 200°C, but did not produce this new band. The band around 400 nm can be attributed to Co(III) ions. Activation in O₂ at 300 and 400°C resulted in a large increase in the background sample becoming almost black, but there was no change in the shape of the triplet band. By heating at 500°C there was a decrease in the background as well as a change in the shape of the triplet band. After activation for 12 h a triplet band appeared having large splitting on the higher-energy side. Calcination in N₂ or He followed by O₂ showed similar result. This indicates that the local environments of Co(II) ions are affected by the removal of organic templates. Hydration of calcined sample at room temperature resulted in a disappearance of the band around 400 nm and a sharp decrease in the intensity of the triplet band possibly due to the formation of octahedral Co(II) ions. It may be that the large portion of Co(II) ions is removed from the framework position by calcination and the triplet band observed in calcined CoAPO-5 can be attributed to Co(II) ions located on the surface. The fact that after hydration of CoAPO-5 the band having almost symmetrically spaced peaks, similar to that of as-synthesized sample, was observed, suggests that some of the Co(II) ions remained in the framework position after the calcination. Evacuation of hydrated CoAPO-5 at 250°C produced a spectrum similar to that of calcined sample. After evacuation of CoAPO-5 at 350°C, however, the band around 400 nm disappeared and the intensity of the triplet band was increased; this may be due to the reduction of Co(III) oxidized by calcination to Co(II).

From the above results it appears that Co(II) ions in as-synthesized as well as calcined CoZSM-5 are mainly located on the surface of the crystallite, and Co(II) ions in

as-synthesized CoAPO-5 are located mainly in the framework. There seems to be an interaction between framework Co(II) ion in as-synthesized CoAPO-5 and organic template, and the removal of organic template by the calcination caused the removal of large portion of Co(II) ions in as-synthesized CoAPO-5 from the framework position.

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