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Coordination Environment and Redox Property of Co(II) in the Framework of CoAPO-36 Molecular Sieve

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The interaction of water, ammonia, methanol, and tetrahydrofuran molecules with Co(II) ions in CoAPO-36 was examined by means of diffuse reflectance UV-vis spectroscopy. The Co(II) ions in CoAPO-36 are in a tetrahedral environment. Upon adsorption of water or ammonia molecules, the coordination environment of a part of the Co(II) ions changes into octahedral, indicating the direct coordination of water or ammonia molecules to the Co(II) ions. The remainder of the Co(II) ions are slightly modified in their electronic state by the adsorption of these molecules in a close proximity. Adsorption of methanol and tetrahydrofuran molecules also causes a modification of the coordination environment, though they do not directly coordinate to the Co(II) ions.

The redox properties of Co(II) ions in CoAPO-36 were also studied. Heating CoAPO-36 in oxygen at 673 K brings about oxidation of a part of the Co(II) ions into Co(III) ions, which are reduced to Co(II) by a hydrogen-treatment at 573 K. In addition, a reduction of the Co(III) ions occurs upon adsorption of water or ammonia on the oxidized CoAPO-36, even at room temperature. The Co(III) ions react with toluene at room temperature and with methane at 673 K. The oxidation-reduction cycle of the Co ions in CoAPO-36 is also brought about by the adsorption-desorption cycle of NO.

Aluminum atoms in aluminophosphate molecular sieves ($AlPO_4$-*n*) are, in general, located in a tetrahedral environment. However, ^{27}Al NMR studies have revealed that the coordination environment of aluminum atoms changes from tetrahedral to octahedral upon adsorption of water in some $AlPO_4$-*n* materials, such as $AlPO_4$-17$^{1)}$ and $AlPO_4$-5.$^{2)}$ The octahedral coordination environment of aluminum atoms in $AlPO_4$-5 is also formed by the adsorption of ammonia.$^{3)}$ Coordination of water or ammonia to the framework aluminum atoms has never been observed in zeolites, and is thus unique to $AlPO_4$-*n* materials. In metal-containing aluminophosphates (MeAPO-*n*), metal ions such as Mg(II) and Co(II) are substituted for aluminum sites in the framework. It is, therefore, expected that the metal cations in MeAPO-*n* are directly coordinated by adsorbed water or ammonia.

MAPO-36 is a magnesium-containing aluminophosphate, which is known to have large pores of ca. 0.8 nm.$^{4,5)}$ The exact structure was recently determined.$^{6)}$ We have shown by ^{27}Al NMR studies that aluminum ions in the MAPO-36 framework also undergo a change in the coordination environment upon the adsorption of water, and that the number of such aluminum sites is about one third of the total tetrahedral aluminum in the framework.$^{7)}$ CoAPO-36 is isostructural with MAPO-36 and contains Co(II) ions instead of Mg(II). Thus, the structural Co(II) ions in the CoAPO-36 framework are expected to experience a reversible coordination of water molecules as structural Al(III) in MAPO-36. It is of interest to know if molecules other than water can interact with Co(II) in the CoAPO-36 framework.

The redox properties of Co(II) ions in cobalt-containing aluminophosphates have been studied in a few kinds of structures by mean of diffuse reflectance UV-vis spectroscopy.$^{8-11)}$ It was reported that a part of the Co(II) is oxidized to Co(III) by calcination under oxygen in the cases of CoAPO-5,$^{8-10)}$ CoAPO-11$^{10)}$ and CoAPO-34.$^{11)}$ However, the coordination environment of the Co(III) species has not been fully understood.

The purpose of this work is to clarify whether Co(II) ions in the CoAPO-36 framework undergo the coordination of water, ammonia, methanol, and tetrahydrofuran molecules, and to examine the redox properties of Co(II) in the framework by means of diffuse reflectance UV-vis spectroscopy. The species of ammonia adsorbed on CoAPO-36 were investigated by means of infrared spectroscopy. Moreover, the interaction of NO molecules with Co(II) in the CoAPO-36 framework was examined by means of diffuse reflectance UV-vis spectroscopy and infrared spectroscopy. For a comparison, the change in the coordination environment and the oxidation state of cobalt ions in CoAPO-5 will also be discussed.

Experimental

Synthesis of CoAPO-5 and CoAPO-36 Materials. CoAPO-5 and CoAPO-36 materials were synthesized based on the method described in a patent.$^{12)}$ The general procedure of gel preparation is as follows: Pseudo-boehmite alumina (26.4 g, Cataloid AP from Catalysts & Chemicals Ind., Co.) was added to a solution of 26.0 cm^3 of phosphoric acid (85 wt%, Merck) in 123 cm^3 of water. Then, a solution of 9.60 g of cobalt(II) acetate tetrahydrate in 40.0 cm^3 of water was added. Tripropylamine (72.8 cm^3) as an organic base was added to the mixture. The composition of the final mixture in molar ratio was Co/P=0.10, Al/P=0.90, base/P=1.0, and H_2O/P=25.

The mixture was transferred into a Teflon vessel placed in a stainless-steel autoclave with a capacity of ca. 300 cm^3. CoAPO-5 material was synthesized after heating the final mixture at 413 K for 44 h. On the other hand, CoAPO-36 material was obtained after the mixture, to which an as-synthesized sample of MAPO-36 (1.0 g, Mg/P=0.04)[7] was added as a seed, was heated at 398 K for 44 h. Each product was washed and dried at 493 K overnight. The color of both products was deep blue. The structure of the sample was identified by its X-ray diffraction pattern. The product was calcined at 823 K in dry air for 24 h, and stored in a vessel of saturated humidity. The compositions of the products were determined by X-ray fluorescence analysis for cobalt, aluminum, phosphorus, and magnesium. The X-ray fluorescence analysis was carried out on a Philips PW-1400 instrument using the glass-beads method.

The compositions of the calcined samples of CoAPO-5 and CoAPO-36 are summarized in Table 1.

Table 1. Compositions of CoAPO-5 and CoAPO-36

Sample	Composition / molar ratio		
	Co/P	Al/P	Mg/P
CoAPO-5	0.10	0.93	—
CoAPO-36	0.10	0.92	0.01

Diffuse Reflectance UV-vis Spectroscopy. Diffuse reflectance UV-vis spectra of the disks (3.2 mg cm^{-2}) formed by pressing the samples were recorded on a Shimadzu MPS-2000 with a unit for reflectance measurement at room temperature. The cell used was made of quartz and the area of the front space was 10×30 mm, and could be connected to a conventional vacuum and gas-adsorption system. The relative reflectance to $BaSO_4$ was measured, and converted into the plots on Kubelka-Munk function vs. wavelength.

Infrared Spectroscopy. Infrared spectra of the samples (6.4 mg cm^{-2}) of selfsupported wafers were recorded on a Shimadzu IR-460 spectrometer at room temperature.

Results and Discussion

Effect of Water Adsorption on Coordination Environment of Co Ions in CoAPO-36. The UV-vis spectrum of a deep-blue sample of as-synthesized CoAPO-36 shows three peaks at 535, 580, and 620 nm (Fig. 1a). A triplet band in a region of 570—800 nm is assigned to the transition of $^4A_2$ to $^4T_1$ (P) of Co(II) ions in a tetrahedral coordination,[13] indicating that cobalt ions in the framework of as-synthesized CoAPO-36 are, as expected, divalent and tetrahedrally coordinated by four oxygen anions linked to phosphorus cations. The splitting of the triplet peaks of as-synthesized CoAPO-36 are larger than those found in typical tetrahedral complexes of Co(II) ions, i.e., $[Co^{II}Cl_4]^{2-}$, indicating that the symmetry of tetrahedral $Co^{II}O_4$ in as-synthesized CoAPO-36 is more distorted than that of typical tetrahedral Co(II) complexes.[14]

The as-synthesized sample was heated in oxygen (66 kPa) at 823 K for 3 h in an UV-vis cell. The color of the sample, thus calcined, was yellow-green. The spectrum of the calcined sample shows two new absorption bands at around 320 and 380 nm in addition to the triplet band (Fig. 1b). The new absorption bands are plausibly due to Co(III) ions, as observed in CoAPO-5 materials.[8—10] At the same time, the intensity of the triplet band due to tetrahedral Co(II) ions decreased. This may be caused by the adsorption of water molecules which are formed during calcination. This point is described in detail later.

The as-synthesized sample of CoAPO-36 was calcined in dry air at 823 K, and then fully hydrated. The color of the hydrated sample was pale blue. The spectrum of the hydrated sample is shown in Fig. 1c. The spectrum does not show any bands around 320 and 380 nm, in contrast to that of the calcined sample (Fig. 1b), indicating that Co(III) ions do not exist in a hydrated sample. In other words, Co(III) ions are probably converted into Co(II) ions upon the adsorption of water. This point will be discussed later.

In the spectrum of a hydrated sample, a triplet band due to tetrahedral Co(II) species was observed at 535, 580, and 620 nm. The intensity of the triplet band of the hydrated sample was far smaller than that of the as-synthesized material. This indicates that a part of the tetrahedral Co(II) ions in the framework is converted into a different coordination environment upon hydration. We have reported that water molecules coordinate a part of the aluminum ions in the MAPO-36 framework to give octahedral aluminum.[7] Therefore, it is plausible that the coordination environment of Co(II) ions in the framework changes from tetrahedral to octahedral by the coordination of water molecules. However, no new absorption bands appeared upon water adsorption. Though octahedral Co(II) complexes such as $[Co(H_2O)_6]^{2+}$ show a band around 515 nm, their extinction coefficients are about 60 times smaller than those of tetrahedral Co(II) complexes.[13] Therefore, it is very plausible that the bands due to octahedral Co(II) species might be smeared out by strong bands due to the remaining tetrahedral Co(II) ions.

The splitting of the triplet band due to tetrahedral Co(II) ions remaining after hydration are larger than those due to typical tetrahedral Co(II) complexes, indicating a larger distortion of the Co(II) tetrahedra in the CoAPO-36 framework.

The hydrated CoAPO-36 sample was then dehydrated by heating under a vacuum at 773 K for 1.5 h. The sample turned to deep blue. The spectrum of the sample, thus dehydrated, showed triplet peaks at 515, 600, and 650 nm (Fig. 1d). The intensity of the triplet band was higher than that in the hydrated sample, indicating an increase in tetrahedral Co(II) ions upon dehydration. Thus, desorption of water molecules turned the coordination state of a part of the Co(II) ions from octahedral to tetrahedral. From the intensity difference between hydrated and dehydrated samples, it is estimated that about 30% of the Co(II) ions are subject to a direct coordination of the water molecules upon hydration. We reported earlier that one third of the aluminum ions in the MAPO-36 framework undergo a direct coordination of water upon hydration.[7] The

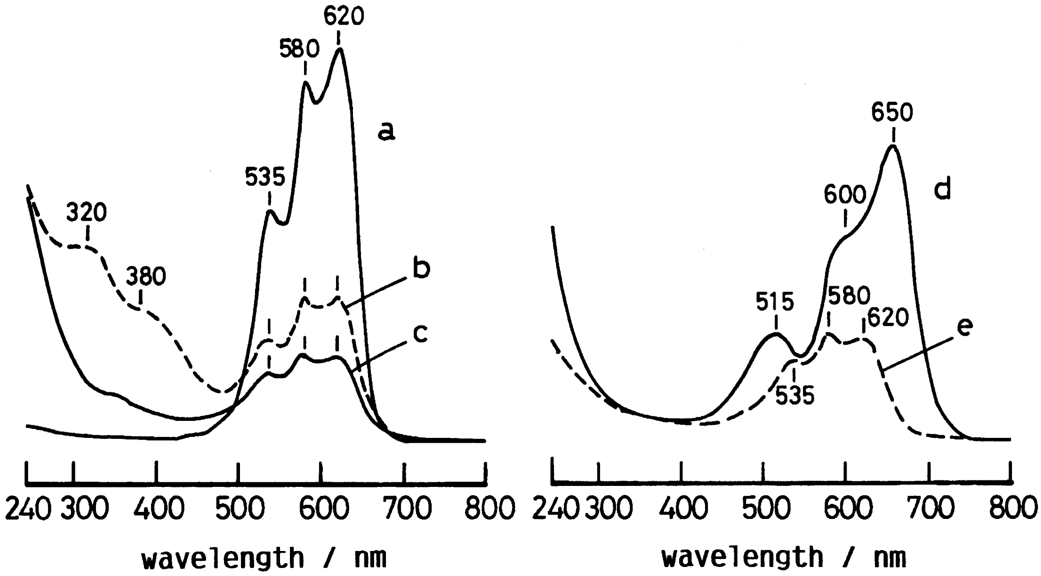


Fig. 1. Diffuse reflectance UV-vis spectra of CoAPO-36. As-synthesized (a), the sample after heating the as-synthesized sample in O_2 (66 kPa) at 823 K for 3 h in UV-vis cell (b), the sample hydrated by keeping the calcined sample under saturated humidity (c), the sample dehydrated by evacuating the hydrated sample at 773 K for 1.5 h (d), and the sample rehydrated by keeping the dehydrated sample under saturated humidity for 3 h (e).

agreement of the two values shows that Co(II) ions are randomly distributed in the CoAPO-36 framework at the sites of the Al(III) ions.

The splitting of the triplet band due to tetrahedral $Co^{II}O_4$ increased upon dehydration, indicating that the tetrahedral symmetry is more distorted in a dehydrated sample. This suggests that adsorbed water molecules interact with oxygen anions surrounding tetrahedral Co(II) ions to modify the coordination environment.

The dehydrated sample was then rehydrated by keeping it under water vapor at saturated pressure at room temperature for 3 h. The color of the rehydrated sample was pale blue, as was that of the hydrated sample. A triplet band was observed at 535, 580, and 620 nm, and the intensity decreased compared with that before rehydration, as shown in Fig. 1e. The intensity decrease upon rehydration indicates that a part of the CoO_4 tetrahedra is again coordinated by water molecules. Thus, the coordination of water molecules to framework Co(II) ions is reversible, as is the coordination of water to aluminum ions in MAPO-36.$^{7)}$

The position of the band due to CoO_4 tetrahedra, which do not undergo direct coordination of water molecules, was the same as that before dehydration, indicating that the interaction of adsorbed water with lattice oxygen of CoO_4 tetrahedra is also reversible.

Effect of Water Adsorption on the Coordination Environment of Co Ions in CoAPO-5. The effect of hydration on the coordination environment of Co(II) ions in CoAPO-5 was examined. The results are shown in Fig. 2.

A hydrated sample of CoAPO-5 was prepared by keeping the calcined material in a vessel of saturated humidity. The color of the sample was pale blue. The spectrum of the hydrated sample shows a triplet band at 535, 580, and 620 nm due to tetrahedral $Co^{II}O_4$ (Fig. 2a). The spectrum is essentially the same as that of hydrated CoAPO-36 (Fig. 1c).

The sample was then dehydrated by heating it under vacuum at 673 K for 1.5 h. The color turned to deep blue. The spectrum of the dehydrated sample shows peaks at 515, 600, and 650 nm (Fig. 2b). The intensity of the band due to tetrahedral $Co^{II}O_4$ increased compared with that of the hydrated sample.

The broadening of the band due to tetrahedral Co(II) upon dehydration is attributed to a further distortion of the tetrahedra into lower symmetry.

Spectrum (c) in Fig. 2 was obtained when the dehydrated sample was rehydrated by exposing it to water vapor of saturated pressure at room temperature for 3 h. The intensity and band position turned back to those in the sample before dehydration. This indicates a reversible adsorption of water molecules to the coordination sphere of Co(II) ions in CoAPO-5.

The results described above are essentially the same as those observed for CoAPO-36, and can be summarized as follows: (1) Co(II) ions in CoAPO-5 are in a tetrahedral environment. (2) Part (ca. 10%) of the tetrahedral Co(II) ions undergo a direct coordination of water molecules. (3) The remainder of the CoO_4 tetrahedra undergo a modification of their coordination environment upon hydration due to the adsorption of water molecules in the close proximity of the tetrahedra. (4) The effects of water adsorption on the coordination environment are reversible.

Adsorption of Ammonia on CoAPO-36. Spec-

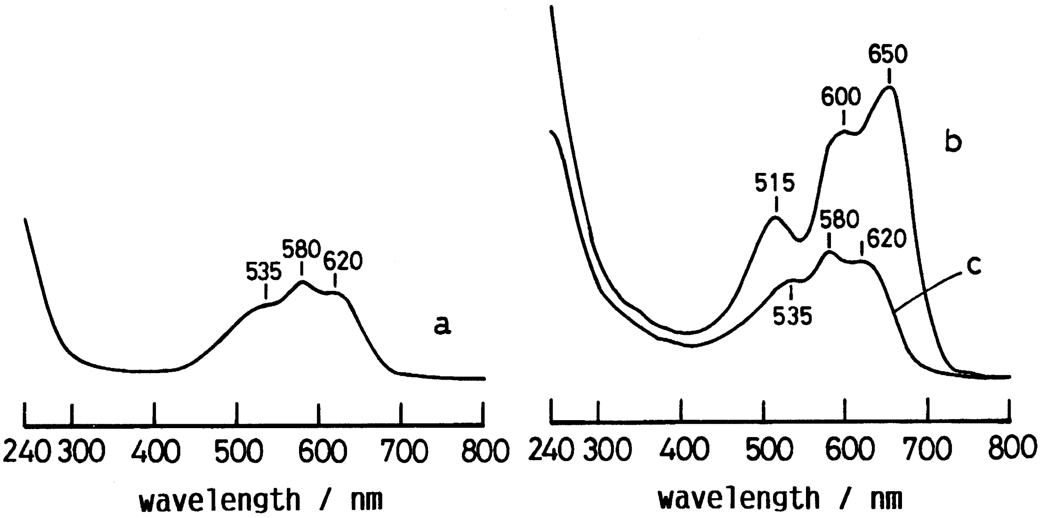


Fig. 2. Diffuse reflectance UV-vis spectra of hydrated, dehydrated and rehydrated samples of CoAPO-5. The hydrated sample prepared by keeping the calcined sample in a vessel of saturated humidity (a), the sample dehydrated by evacuation at 673 K for 1.5 h (b), and the sample rehydrated by keeping the dehydrated sample under saturated humidity for 3 h (c).

trum (b) in Fig. 3 was recorded after a dehydrated sample of CoAPO-36 was exposed to ammonia of 80 kPa at room temperature for 1 h. Compared to the spectrum of dehydrated CoAPO-36 (Fig. 3a), the intensity of the triplet band decreased, indicating that ammonia directly coordinates to tetrahedral $Co^{II}O_4$ to form octahedral species, as in the case of water adsorption. From the change in the intensity of the triplet band, it is estimated that about 14% of the tetrahedral Co ions undergo a direct coordination of ammonia.

The electronic state of the remainder of Co ions is also modified by the adsorption of ammonia, as evidenced by the decrease in the splitting of the triplet band. This indicates that the distortion of the tetrahedral coordination is reduced by the adsorption of ammonia in the close proximity of the tetrahedra.

The infrared spectrum of adsorbed ammonia was examined. A dehydrated sample of CoAPO-36 was exposed to ammonia of 80 kPa at room temperature; the system was then evacuated at room temperature for 5 min. Two bands were observed at 1620 and 1460 cm^{-1}. The band at 1460 cm^{-1} is attributed to ammonium ions,[15] indicating the presence of Brønsted acid sites. The existence of Brønsted acid sites is expected from the isomorphous substitution of Co(II) for Al(III) in the structure. The band at 1620 cm^{-1} may be due to ammonia coordinating to Lewis acid sites.[15] Thus, this band may be related to ammonia molecules coordinating to framework Co(II) ions.

Adsorption of Methanol and Tetrahydrofuran on CoAPO-36. A dehydrated sample of CoAPO-36 was exposed to methanol (9.3 kPa) or tetrahydrofuran (9.3 kPa) at room temperature for 1 h. In contrast to the adsorption of water or ammonia, the intensity of the triplet band was not affected by the adsorption of methanol and tetrahydrofuran molecules, indicating that these molecules do not directly coordinate to Co(II) ions in the framework, as shown in Figs. 3c and 3d, respectively. The access of these molecules to the Co(II) ions may be sterically hindered by lattice oxygen anions because of the larger size of the adsorbed molecules.

Though the intensity of the triplet band was not affected, the splitting of the band decreased by adsorption of methanol or tetrahydrofuran. This again indicates that adsorption of these molecules in the close proximity of the tetrahedra reduces the distortion of CoO_4 tetrahedra.

Redox Property of Co Ions in the CoAPO-36 Framework. Spectrum (b) in Fig. 4 was obtained after a dehydrated sample of CoAPO-36 was exposed to oxygen of 33 kPa at 673 K for 1.5 h; the system was then evacuated at the same temperature for 15 min. The color of the sample turned into yellow-green from deep blue. Two absorption bands at 310 and 390 nm appeared, which did not exist in the dehydrated sample (Fig. 4a). On the other hand, the intensity of the triplet band at around 600 nm did not change appreciably.

The new bands are ascribed to the Co(III) species. Two absorption maxima were observed at 315 and 400 nm in the spectrum of calcined CoAPO-11.[9] Similar bands also appear in the spectrum of CoAPO-5, as will be described below. As discussed by Iton et al.,[10] the existence of oxides with Co(III) in a high spin tetrahedral environment is rare, but precedented. For example, 12 -tungstocobaltate(III), $[Co^{III}W_{12}O_{40}]^{5-}$, shows a band due to the ^5E-$^5T_2$ transition at 389 nm.[16] The appearance of the two bands in the case of oxidized CoAPO-36 may be caused by distortion from the tetrahedral symmetry. The formation of Co(III) in CoAPO-36 may be expressed as the following charge-transfer

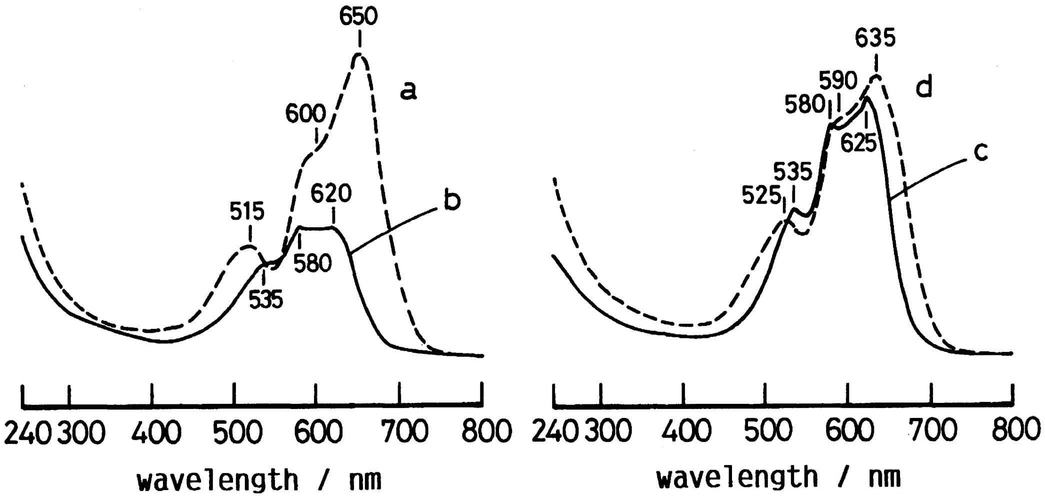


Fig. 3. Diffuse reflectance UV-vis spectra of CoAPO-36 with the adsorption of ammonia, methanol and tetrahydrofuran. The dehydrated sample (a), the samples after adsorption of ammonia (80 kPa) for 1 h (b), methanol (9.3 kPa) for 1 h (c), and tetrahydrofuran (9.3 kPa) for 1 h (d).

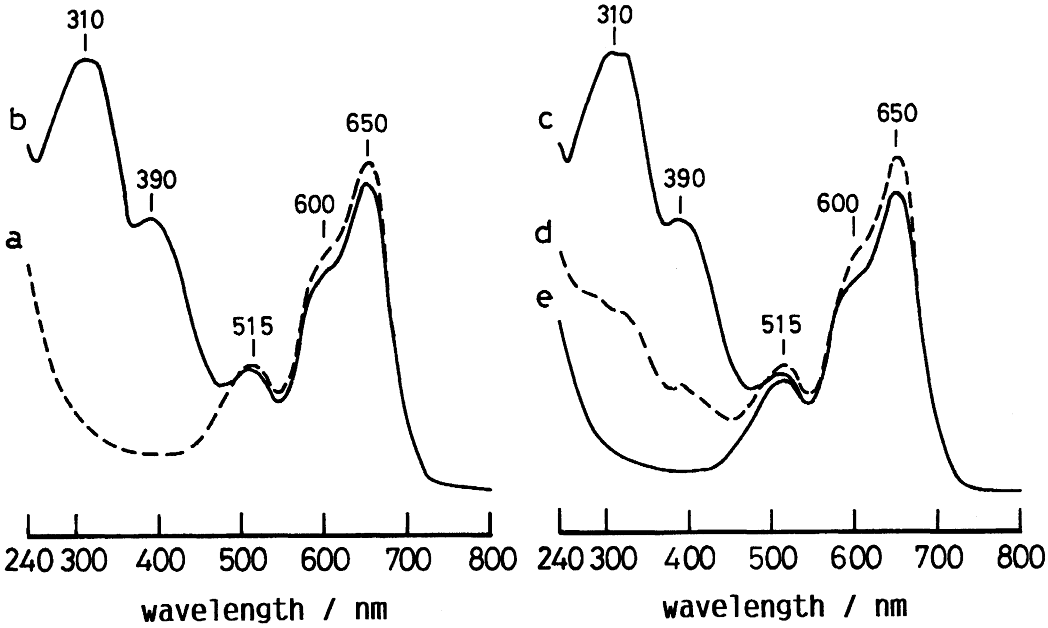


Fig. 4. Change in the diffuse reflectance UV-vis spectra of CoAPO-36 by oxidation and reduction. The dehydrated sample (a), the sample oxidized by heating the dehydrated sample in O_2 (33 kPa) at 673 K for 1.5 h followed by evacuation at 673 K for 15 min (b), the samples after heating the oxidized sample in H_2 (33 kPa) at room temperature (c), 473 K (d), and 573 K (e) for 1.5 h.

reaction:

$$\mathrm{Co^{II}O_4} + \mathrm{O_2} \longrightarrow \mathrm{Co^{III}O_4} + \mathrm{O_2^-} \quad (1)$$

The attempt to detect O_2^- ions by esr, however, failed. It is plausible that the O_2^- signals were broadened by a dipole-dipole interaction between the unpaired electrons of O_2^-, the paramagnetic counter cations, Co(III), or the remaining Co(II) ions in the lattice. It is also plausible that the spins in O_2^- ion are delocalized by its interaction with lattice oxygen, since the formation of O_2^- ions occurs as the result of an outer-sphere charge-transfer between Co(II) ions in the lattice and adsorbed oxygen.

As mentioned above, the intensity of the Co(II) band did not change upon oxidation, in spite of the formation of Co(III) ions, indicating that the extent of the conversion of Co(II) into Co(III) is small. It should be noted that the extinction coefficient of the Co(III) band is probably much larger than that of the Co(II) band. In fact, the extinction coefficient of the 389 nm band of 12-tungstocobaltate(III) is ca. 6 times as large as that of the 625 nm band of 12-tungstocobaltate(II).[16)]

The samples of CoAPO-36 oxidized at 673 K were kept in hydrogen of 33 kPa at room temperature, 473 K

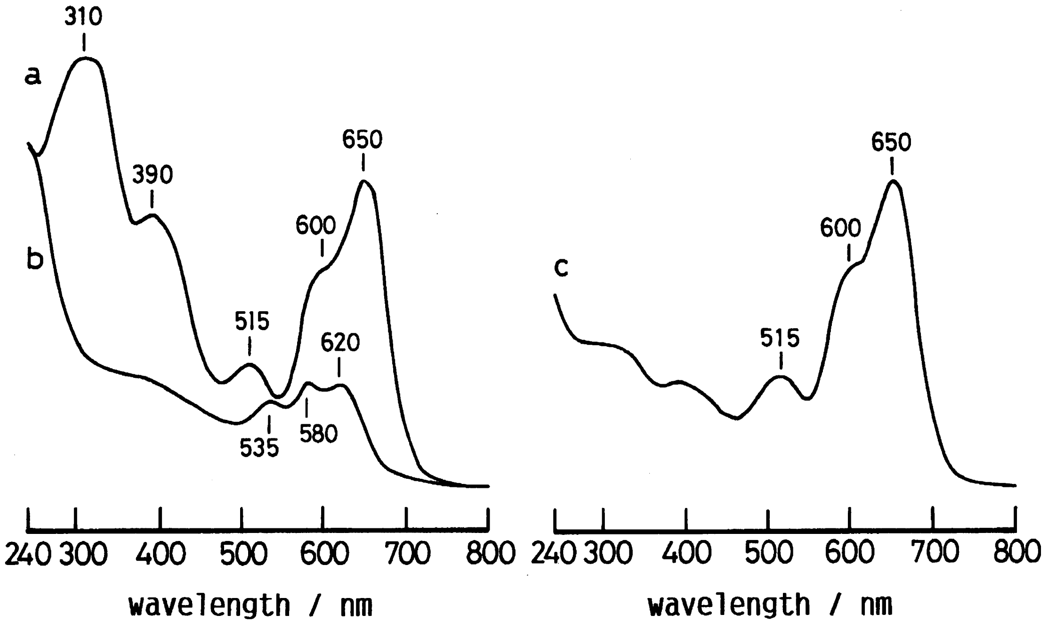


Fig. 5. Effect of hydration on the diffuse reflectance UV-vis spectra of oxidized CoAPO-36. The sample oxidized by heating a dehydrated sample in O_2 (33 kPa) at 673 K for 1 h followed by evacuation at 673 K for 15 min (a), the sample hydrated by keeping the oxidized sample in saturated humidity at room temperature for 3 h (b), and the sample after evacuation at 673 K for 1.5 h (c).

and 573 K for 1.5 h. The spectra of the samples after hydrogen treatment at the three temperatures are shown in Figs. 4c, 4d, and 4e. The intensities of the Co(III) bands did not change upon hydrogen treatment at room temperature, while they considerably decreased upon treatment at 473 K. The bands completely disappeared upon hydrogen treatment at 573 K, indicating that all of the Co(III) ions in CoAPO-36 were reduced to Co(II) ions at this temperature.

Effect of Hydration on Co(III) Ions in CoAPO-36 and CoAPO-5. The effect of adsorption of water on the Co(III) ions in CoAPO-36 and CoAPO-5 was examined. The results are shown in Figs. 5 and 6, respectively.

Spectrum (a) in Fig. 5 shows the spectrum of CoAPO-36 oxidized at 673 K. Spectrum (b) in Fig. 5 was obtained after the oxidized sample of CoAPO-36 was hydrated by exposing it to water vapor saturated at room temperature for 3 h. The bands due to the Co(III) ions disappeared upon hydration, and the intensity of a triplet band due to tetrahedral $Co^{II}O_4$ decreased. This indicates that the Co(III) species are converted into Co(II) ions upon hydration, while the decrease in the intensity of the triplet band due to tetrahedral $Co^{II}O_4$ is ascribed to the conversion of a part of the Co(II) ions into octahedral species by water-coordination, as described above. Spectrum (c) in Fig. 5 was obtained after the hydrated sample was dehydrated by heating it under vacuum at 673 K for 1.5 h. The spectrum was essentially the same as that of the dehydrated sample of CoAPO-36, which did not undergo oxidation-treatment (Fig. 1d).

It is of interest that the reduction of Co(III) ions easily proceeds by the adsorption of water, even at room temperature, but does not occur upon a hydrogen-treatment at the same temperature. The reduction of Co(III) by the adsorption of methanol has been reported for various CoAPO-*n* materials.[9,10] However, the results described above clearly show that the reduction of Co(III) occurs even by the adsorption of water. However, the oxidation of water by Co(III) may be difficult to occur. The reduction of Co(III) upon water-adsorption may be expressed as the following reverse charge-transfer reaction:

$$\mathrm{Co(III)} \cdots \mathrm{O_2^-} + \mathrm{H_2O} \longrightarrow \mathrm{Co(II)}\text{-}\ \mathrm{H_2O} + \mathrm{O_2} \qquad (2)$$

Thus, the adsorbed oxygen species are expelled by a stronger coordination of a water molecule to Co(II) ions. Reaction (2) also explains why water is a better "reductant" than hydrogen.

The effect of hydration on the Co(III) species produced by oxidation of structural Co(II) ions in CoAPO-5 was also examined. Spectrum (a) in Fig. 6 was obtained after a dehydrated sample of CoAPO-5 was heated in oxygen (27 kPa) at 673 K for 1 h. The spectrum shows that an oxygen-treatment of the CoAPO-5 sample at 673 K generates new absorption bands at ca. 320 and 400 nm, indicating the formation of Co(III) species.

Spectrum (b) in Fig. 6 was recorded after the oxidized sample was hydrated by keeping it in water vapor saturated at room temperature for 1 h. The spectrum shows that hydration brings about the reduction of the Co(III) species into Co(II) ions, and produces octahe-

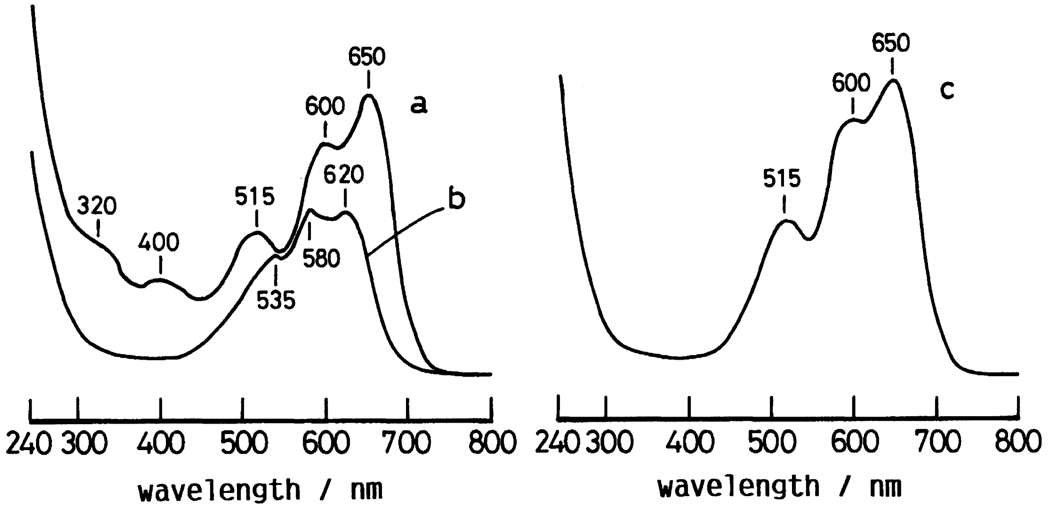


Fig. 6. Effect of hydration on the diffuse reflectance UV-vis spectra of oxidized CoAPO-5. The oxidized sample prepared by heating the dehydrated sample in O_2 (27 kPa) at 673 K for 1 h (a), the sample hydrated by keeping the oxidized sample in saturated humidity at room temperature for 1 h (b), and the sample after evacuation at 673 K for 1.5 h (c).

dral Co(II) ions by water-coordination.

Spectrum (c) in Fig. 6 was recorded after the hydrated sample was dehydrated by evacuating the system at 673 K for 1.5 h. The spectrum is essentially the same as that obtained after dehydration of CoAPO-5, which was not subject to an oxidation-treatment (Fig. 2b).

Effect of Ammonia Adsorption on Co(III) Ions in CoAPO-36. In the previous section, we proposed a reverse charge-transfer between Co(III) ions and O_2^- upon the adsorption of water (Eq. 2). Since ammonia can directly coordinate to Co(II) ions, a similar phenomenon is expected upon its adsorption.

The spectrum shown in Fig. 7a was obtained after CoAPO-36 oxidized at 673 K was exposed to ammonia of 9.3 kPa at room temperature for 1 h. Upon adsorption of ammonia, the bands due to Co(III) ions disappeared, and the intensity of a triplet band due to tetrahedral Co(II) ions decreased. When the sample was then evacuated at 673 K for 1.5 h, the intensity of the triplet band increased to that of the dehydrated sample, as shown in Fig. 7b. These phenomena upon adsorption and desorption of ammonia are essentially the same as those observed upon the adsorption-desorption of water. Thus, upon ammonia adsorption, Co(III) ions are reduced to Co(II) ions by the reverse charge-transfer to O_2^- along with a concomitant coordination of ammonia to a part of the Co(II) ions. Ammonia desorption upon heating at 673 K restores tetrahedral Co(II) ions.

Reactivity of Co(III) Ions in CoAPO-36 towards Toluene and Methane. The reactions of Co(III) ions in CoAPO-36 with toluene and methane were examined.

The spectrum shown in Fig. 8a was obtained when an oxidized sample of CoAPO-36 was exposed to toluene of 2.7 kPa at room temperature for 1 h. The bands at 310 and 390 nm due to Co(III) ions completely disappeared and a new band appeared at 455 nm, besides a band in the region of 240—280 nm due to the aromatic ring of toluene. The band at 455 nm may be assigned to an oxidized product of toluene. It may not be possible that large molecules like toluene directly interact with Co(III) ions. The reaction of toluene and Co(III) may occur via an outer-sphere charge-transfer to form toluene cation radicals, which lose a proton to yield benzyl radicals. The benzyl radicals may then be oxidized by Co(III) to the corresponding carbenium ions.

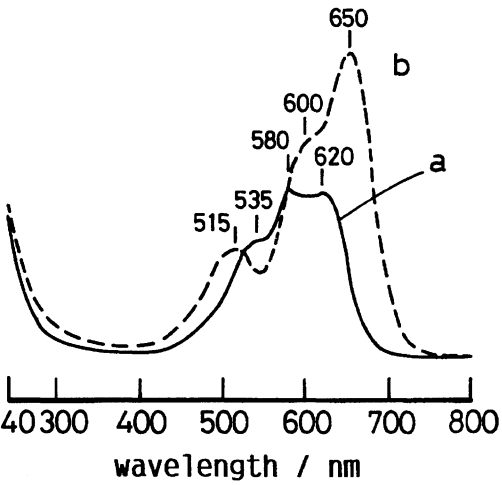
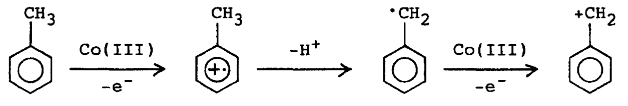


Fig. 7. Effect of ammonia adsorption on the diffuse reflectance UV-vis spectra of oxidized CoAPO-36. The sample after adsorption of ammonia (9.3 kPa) on the oxidized sample at room temperature for 1 h (a), and the sample after evacuation at 673 K for 1.5 h (b).



(3)

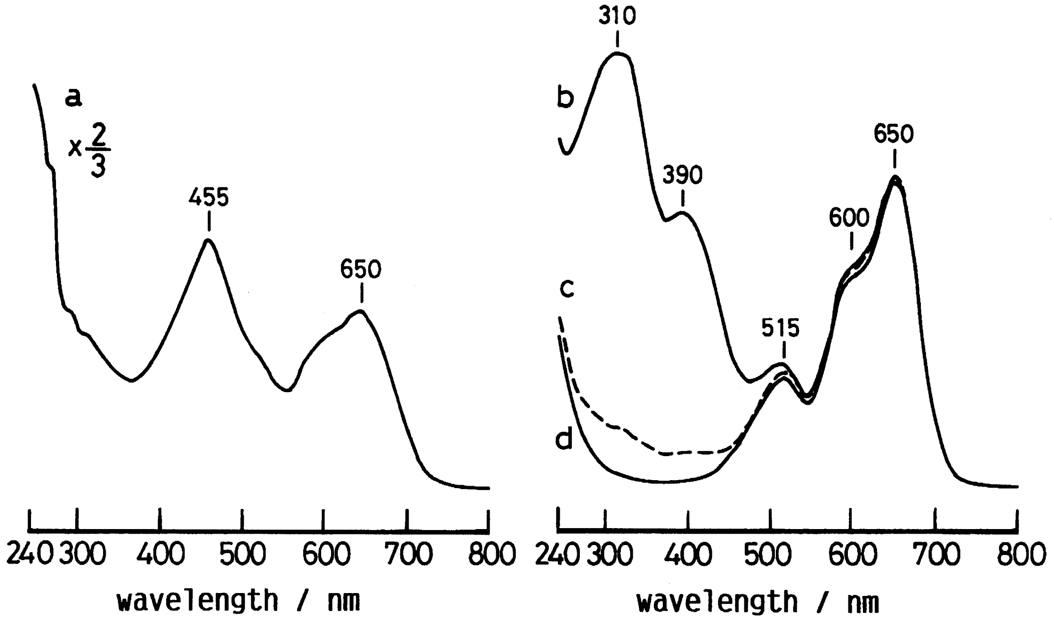


Fig. 8. Change in the diffuse reflectance UV-vis spectra of oxidized CoAPO-36 upon adsorption of toluene and methane. The sample after toluene (2.7 kPa) was adsorbed on the oxidized sample at room temperature for 1 h (a), the samples after methane (33 kPa) was adsorbed on the oxidized sample at 473 K (b), 573 K (c), and 673 K (d) for 0.5 h.

This type of mechanism of toluene oxidation with Co(III) has been proposed in the oxidation with Co(III) acetate and 12-tungstocobaltate(III).[18—20] In fact, Heiba et al. found a band at 460 nm due to an intermediate of toluene oxidation by Co(III) acetate.[18] The oxidation of toluene with dodecatungstocobaltate(III) yields methyl-*p*-toluilmethane as a major product, which might be formed by the attack of benzyl radicals or carbenium ions on the aromatic ring.[19,20] The band at 455 nm may be assigned to diaryl carbenium ions.[21]

Spectra (b), (c), and (d) in Fig. 8 were recorded after an oxidized sample of CoAPO-36 was exposed to methane of 33 kPa for 0.5 h at 473, 573, and 673 K, respectively. Upon contact with methane, the intensities of the bands due to Co(III) ions decreased, and the extent of the intensity decrease was larger at higher temperature. The bands completely disappeared by a reaction at 673 K. Co(III) ions in the CoAPO-36 framework probably subtract hydrogen atoms from methane molecules to form methyl radicals. Iton et al. have already mentioned that calcined CoAPO-*n* have a capacity to oxidatively homologate methane to higher hydrocarbons at a temperature of 673 K.[10]

Adsorption of NO on CoAPO-36. Spectrum (a) in Fig. 9 was obtained when a dehydrated sample of CoAPO-36 was exposed to NO of 15 kPa at room temperature for 1 h; the system was evacuated at the same temperature for 1 h. Adsorption of NO generates new absorption bands at 325 and ca. 380 nm, indicative of the formation of Co(III) ions, as in the case of oxygen treatment at higher temperature of 673 K. Spectrum (b) in Fig. 9 was recorded after the sample was heated under a vacuum at 673 K for 1.5 h. Desorption of adsorbed NO leads to the disappearance of the bands due to Co(III) ions, indicating that the formation of the Co(III) ions by NO adsorption is reversible.

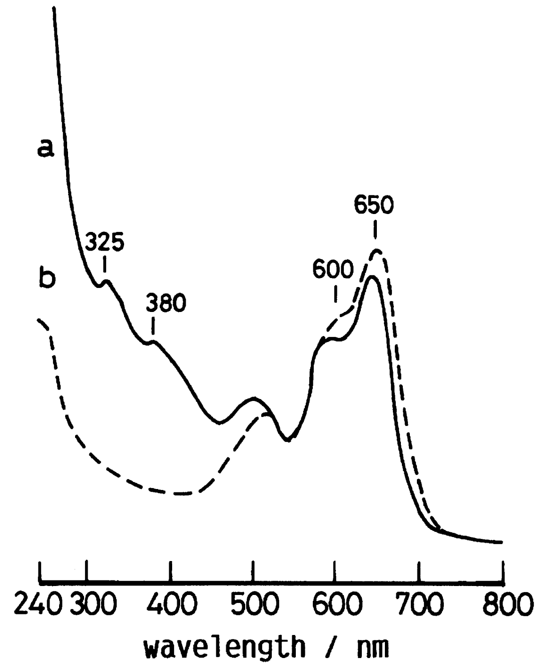


Fig. 9. Diffuse reflectance UV-vis spectra of CoAPO-36 with adsorption of NO. The sample after adsorption of NO (15 kPa) at room temperature for 1 h followed by evacuation at the same temperature for 1 h (a), and the sample after evacuation at 673 K for 1.5 h (b).

The adsorption of NO was studied by means of infrared spectroscopy. The adsorption of NO at room temperature, followed by evacuation for 1 h, brought about a band at 1811 cm^{-1} and a smaller band at 1894 cm^{-1} in a region of NO stretching. The band at 1811 cm^{-1} is assigned to a slightly negative species of NO molecule; a smaller band at 1894 cm^{-1} is assigned to a slightly positive NO molecule.[22] The formation of the negative species may be related to the formation of Co(III) ions upon the adsorption of NO. When the system was evacuated at 673 K for 0.5 h, both bands at 1811 and 1894 cm^{-1} disappeared. This indicates that the formation of adsorbed NO species is reversible in conformity with the reversible formation of Co(III) ions, as shown by UV-vis studies.

Conclusion

Cobalt ions (II) in dehydrated CoAPO-36 and CoAPO-5 are located in a tetrahedral environment. A part of Co(II) ions undergo reversible coordination of water and ammonia molecules to alter the coordination environment to octahedral upon the adsorption of these molecules. Methanol or tetrahydrofuran molecules do not directly coordinate to the Co(II) ions in the CoAPO-36 framework, though the adsorption of these molecules slightly modifies the electronic state of the tetrahedral Co(II) ions.

A part of the Co(II) ions in the CoAPO-36 and CoAPO-5 frameworks is oxidized to Co(III) ions by oxygen-treatment at 673 K. However, the Co(II) ions are restored simply by the adsorption of water or ammonia at room temperature.

The Co(III) species reacts with toluene at room temperature and with methane at 673 K.

The reversible redox cycle of Co(II) and Co(III) ions can also be achieved by the adsorption-desorption of NO molecules on CoAPO-36.

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