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Spectroscopic investigation of redox and acidic properties of Co-substituted aluminophosphate CoAPO-11

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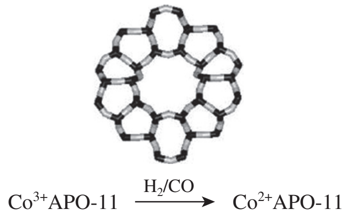
Acid sites in Co-substituted aluminophosphate CoAPO-11 and its redox properties have been investigated using UV-VIS and IR spectroscopy. The acquired data revealed the absence of the bridged OH groups as a common feature of M^{II}-containing aluminophosphates. The behavior of Co^{2+}/Co^{3+} couple in redox reactions was very different from that characteristic of supported cobalt ions.


$\mathrm{Co^{3+}APO\text{-}11} \xrightarrow{\mathrm{H_2/CO}} \mathrm{Co^{2+}APO\text{-}11}$

Crystalline aluminophosphates (APOs), silicoaluminophosphates, and isomorphously substituted aluminophosphates[1–3] represent a new type of molecular sieves, which are considered as potential catalysts, adsorbents, and a platform for the design of new hybrid nanomaterials.[4–7] It is commonly accepted that APOs containing bivalent metal cations (MAPOs) possess negatively charged framework fragments, where each ion can give rise to the formation of an acidic Brønsted site. However, the corresponding bridged hydroxyl groups have not been yet directly observed for different MAPOs. On the other hand, the introduction of transition metal ions establishes redox properties of MAPOs, which make them perspective catalysts for redox type reactions.

In the case of Co-substituted APOs, there is a system that may combine both redox and acidic properties.[2,3] Bivalent cobalt-substituted hexagonal mesoporous APO demonstrated an excellent activity in the oxidation of cycloalkanes, such as cyclohexane, cyclooctane, and cyclododecane, under mild reaction conditions.[8,9] In some cases, the microwave activation was shown to be very efficient in the synthesis of CoAPOs, for instance, Co-SSZ-51.[10] Recently,[11] CoAPO with a large-pore cloverite structure has been successfully synthesized in the ionic liquid 1-ethyl-3-methylimidazolium bromide with 1,6-hexanediamine as the structure-directing agent, which resulted in four-coordinated Co^{II} predominating in the framework. Additionally, some hierarchical CoAPOs were prepared.[12] The coordination and properties of cobalt in the molecular sieves CoAPO-5 and CoAPO-11 were studied in detail previously.[13] The acidic properties of CoAPO-11 have also been reported.[14] In particular, the substitution of cobalt in AlPO-11 was found causing a considerable increase in the strength of Brønsted acid sites as compared with SAPO-11 molecular sieve. The reduction of Co^{3+} to Co^{2+} in CoAPOs leads to the increased concentrations of Brønsted and Lewis acidic sites.[2] However, the real nature and properties of these sites in CoAPOs (and also in other MeAPOs) are still remaining unclear.

In the present work, the acid sites in CoAPO-11 and its redox properties have been investigated by diffuse reflectance UV-VIS and IR spectroscopy.[†]

Figure l shows the UV-VIS spectra of the CoAPO-11 sample containing the template, those after calcination in O$_2$ atmosphere at 823 K, and the spectra of the calcined sample, which was subsequently reduced by CO and H$_2$ at 770 K.

The appearance of the absorption bands at 520, 580 and 630 nm in the UV-VIS spectra of CoAPOs is responsible for the blue color of these catalysts, which is considered as a proof of the tetrahedral cobalt coordination[2,3] and isomorphous replacement of Al^{3+} by Co^{2+}. These three bands are characteristic of *d–d* electron transition of tetrahedrally coordinated Co-ions with *d* configuration and distortion caused by the Jahn–Teller effect.

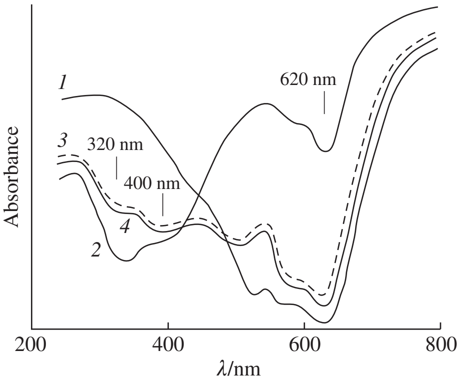


Figure 1 UV-VIS spectra of the CoAPO-11 sample measured (*1*) before and (*2*) after calcination in O$_2$ atmosphere at 823 K, and calcined sample reduced by (*3*) CO and (*4*) by H$_2$ at 770 K.

[†] CoAPO-11 with the composition of Co$_{0.011}$Al$_{0.508}$P$_{0.480}$O$_2$ was prepared in Eindhoven Technological University according to the known procedure[15] using diisopropylamine as a template. The samples were dried at 393 K for 1 h and calcined in flowing oxygen at 823 K for 5 h to remove the template before the spectroscopic measurements. The temperature was increased at the rate of 5 K min^{-1}. Calcined samples were subsequently heated at 770 K for 5 h *in vacuo*. Reduction (by H$_2$ or CO) and oxidation (by O$_2$ or N$_2$O) were performed at 570–770 K and an oxidant pressure of 50 Torr with further evacuation.

UV-VIS and IR diffuse-reflectance spectra were recorded on Hitachi-340 and Perkin Elmer 580 B spectrometers equipped with diffuse-reflectance units.[16] To identify Brønsted and Lewis acid sites, adsorbed pyridine, CD$_3$CN, and CO were used as IR molecular probes.

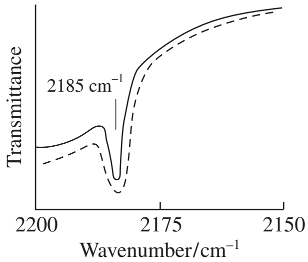


Figure 2 IR spectra of CO adsorbed at 300 K on the CoAPO-11 samples (*1*) calcined in O_2 atmosphere and (*2*) reduced by H_2 at 770 K.

Upon calcination in O_2 atmosphere, CoAPO-11 demonstrated a clear color change from blue to yellow-green. The intensity of the absorption bands at 500–650 nm was strongly decreased and the new absorption bands at 320 and 400 nm appeared. The latter were assigned to the ligand–metal charge transfer transition in Co^{3+} ions[3] formed by oxidaion of Co^{2+}.

However, it should be mentioned that even after prolonged treatment of CoAPO-11 with O_2 or N_2O at 720–820 K, the remaining absorption bands at 500–650 nm were still present in the UV-VIS spectra. This implies a part of Co^{2+} ions in CoAPO-11, which cannot be oxidized. It is known for such conditions that non-framework Co^{2+} ions introduced by ion-exchange into zeolites or supported on other catalysts are hardly oxidized into the Co^{3+} state.[17] This allows one to make the assumption that CoAPO-11 also contains non-stoichiometric species such as CoO or spinel, in addition to isomorphously substituted cobalt. At the same time, the existence of exchangeable cations resistant towards oxidation could not be fully excluded.

Figure 2 demonstrates the IR spectra of CO adsorbed at 300 K on the CoAPO-11 samples calcined in O_2 atmosphere and those reduced by H_2. The band at 2185 cm^{-1} could be assigned to the CO complexes with coordinatively unsaturated Co^{2+} ions. Its intensity does not practically change after the reduction of the sample. Therefore, this band may be attributed to those Co^{2+} species, which cannot be oxidized. Reduction of Co^{3+}APO-11 by CO or H_2 at the temperature higher than 570 K led to step-by-step transformation of Co^{3+} into Co^{2+}, a corresponding decrease in the intensities of the bands at 320–400 nm, and a growth of the bands at 500–650 nm. Thus, the transformation of Co^{3+} into Co^{2+} is reversible.

It is generally accepted that the replacement of Al^{3+} ions with other M^{3+} ions in APOs does not change electroneutrality of the structure and, therefore, it should not result in any Brønsted acidity. On the contrary, the introduction of M^{2+} ions into APO frameworks is considered as causing the formation of Brønsted acidic sites and thereby increasing the catalytic activity.[1] According to this point, the reduction of CoAPO-11 by H_2, which converts Co^{3+} to Co^{2+}, might be followed by generation of either bridged $\equiv$Co(OH)–P$\equiv$ groups or terminal POH groups in case of the weak interaction between bridged OH group and Co^{2+}. On the other hand, the treatment of CoAPO-11 with CO should result in anionic vacancies (Lewis acid sites) appearing due to oxygen removal from the framework.

Figure 3 shows the IR spectra of calcined CoAPO-11. The bands at 3800, 3680 cm^{-1}, and a low-intensity band at 3740 cm^{-1} correspond to the terminal AlOH and POH groups located at the outer surface of AlPOs.[18] A broad band near 3400 cm^{-1} could be assigned to H-bonded OH groups. It should be noted that the IR spectra of both oxidized and reduced samples are very similar to each other, which allows one to conclude that reduction of CoAPO-11 by CO or H_2 did not lead to the formation of either bridged OH groups or additional POH groups.

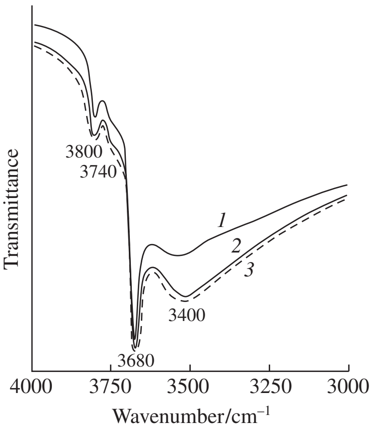


Figure 3 IR spectra of calcined CoAPO-11 (*1*) before and (*2*),(*3*) after reduction by (*2*) H_2 and (*3*) CO at 770 K.

It may be proposed that during the reduction of CoAPO-11 by H_2 (and also by CO), the oxygen atoms are removed from the framework with the formation of H_2O instead of the structural OH groups. Water may be easily desorbed from CoAPO-11 at the reduction temperatures higher than 570 K. It was mentioned above that the reduction of Co^{3+} in CoAPO-11 by H_2 or CO may be observed at the temperatures higher than 570 K. On the other hand, this reaction occurs at room temperature in the presence of methanol.[2] Water was found acting similar to methanol, *i.e.* it reduced cobalt ions in the framework.

Figure 4 depicts the UV-VIS spectra of CoAPO-11 measured before and after H_2O adsorption. The water adsorption led to a fast color change from yellow-green to blue. Simultaneously, the intensities of the bands at 500–650 nm increased and those at 320–400 nm decreased. Thus, the interaction with water at 300 K led to the partial reduction of Co^{3+} into Co^{2+}. Heating CoAPO-11 in water vapors at 370–720 K resulted in further reduction of Co^{3+}. According to the other work,[3] the reduction of CoAPO-11 by methanol occurred with formation of CH_2O. When water was used as a reducing agent, one could expect the formation of O_2 or H_2O_2. However, our attempts to identify these products using mass spectrometry failed.

In summary, the acquired data have revealed that CoAPO-11 exhibits the quite unusual acidic and redox properties. The absence of the bridged hydroxyl groups seems to be a common feature of M^{II}-containing MAPOs since our previous work[18] also showed the absence of bridged OH groups in various MAPOs (M was Mg, Be, and Zn). The behavior of the Co^{2+}/Co^{3+} couple in redox reactions was very different from that characteristic of supported cobalt ions. It may be explained in terms of stabilizing effects of the ionic lattice in aluminophosphates, which are more favorable for Co^{3+} species.

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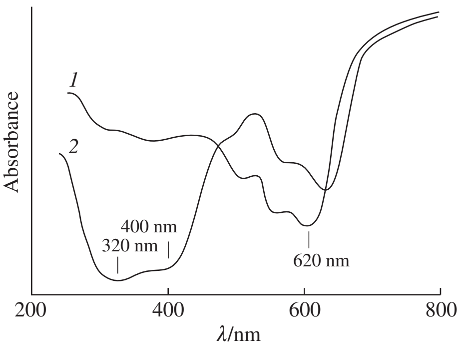

Figure 4 UV spectra of calcined CoAPO-11 measured (*1*) before and (*2*) after water adsorption at 300 K.

References

1 E. M. Flanigen, B. M. Lok, R. L. Patton and S. T. Wilson, in *New Developments in Zeolite Science and Technology*, eds. Y. Murakami, A. Ijima and J. W. Ward, Kodansha Ltd., Tokyo, 1986, pp. 103–112.

2 B. Kraushaar-Czarnetzki, W. G. M. Hoogervorst, R. R. Andréa, C. A. Emies and W. H. J. Stork, *J. Chem. Soc., Faraday Trans*., 1991, **87**, 891.

3 L. E. Iton, I. Choi, J. A. Desjardins and V. A. Maroni, *Zeolites*, 1989, **9**, 535.

4 V. P. Ananikov, *ACS Catal*., 2015, **5**, 1964.

5 V. P. Ananikov, K. I. Galkin, M. P. Egorov, A. M. Sakharov, S. G. Zlotin, E. A. Redina, V. I. Isaeva, L. M. Kustov, M. L. Gening and N. E. Nifantiev, *Mendeleev Commun*., 2016, **26**, 365.

6 V. I. Bukhtiyarov, V. I. Zaikovskii, A. S. Kashin and V. P. Ananikov, *Russ. Chem. Rev*., 2016, **85**, 1198.

7 V. P. Ananikov, D. B. Eremin, S. A. Yakukhnov, A. D. Dilman, V. V. Levin, M. P. Egorov, S. S. Karlov, L. M. Kustov, A. L. Tarasov, A. A. Greish, A. A. Shesterkina, A. M. Sakharov, Z. N. Nysenko, A. B. Sheremetev, A. Yu. Stakheev, I. S. Mashkovsky, A. Yu. Sukhorukov, S. L. Ioffe, A. O. Terent'ev, V. A. Vil', Yu. V. Tomilov, R. A. Novikov, S. G. Zlotin, A. S. Kucherenko, N. E. Ustyuzhanina, V. B. Krylov, Yu. E. Tsvetkov, M. L. Gening and N. E. Nifantiev, *Mendeleev Commun*., 2017, **27**, 425.

8 P. Selvam and S. K. Mohapatra, *J. Catal*., 2005, **233**, 276.

9 P. Tian, Z. M. Liu, Z. B. Wu, L. Xu and Y. L. He, *Catal. Today*, 2004, **93–95**, 735.

10 S. Pai, B. L. Newalkar and N. V. Choudary, *Microporous Mesoporous Mater*., 2006, **96**, 135.

11 D. Li, Y. Xu, Y. Wang, H. Liu, B. Wang, H. Ma, R. Xu and Z. Tian, *Microporous Mesoporous Mater*., 2014, **198**, 153.

12 L. Zhou, T. Lu, J. Xu, M. Chen, C. Zhang, C. Chen, X. Yang and J. Xu, *Microporous Mesoporous Mater*., 2012, **161**, 76.

13 J. Šponer, J. Čejka, J. Dědeček and B. Wichterlová, *Microporous Mesoporous Mater*., 2000, **37**, 117.

14 M. Höchtl, A. Jentys and H. Vinek, *Microporous Mesoporous Mater*., 1999, **31**, 271.

15 M. P. J. Peeters, L. J. M. van de Ven, J. W. de Haan and J. H .C. van Hooff, *Colloids Surf. A*, 1993, **72**, 87.

16 V. B. Kazansky, V. Yu. Borovkov and L. M. Kustov, *Proceedings of the 8^th^ International Congress on Catalysis*, Verlag Chemie, Berlin, 1984, vol. 3, pp. 3–14.

17 J. C. Kim and S. I. Woo, *Appl. Catal*., 1988, **39**, 107.

18 S. G. Hegde, P. Ratnasamy, L. M. Kustov and V. B. Kazansky, *Zeolites*, 1988, **8**, 137.

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