Experimental Section

Reaction of *N*-methyldihydropyridine with carbene complexes (general procedure): A solution of *N*-methyldihydropyridine (3 equiv) in CH_2Cl_2 (0.5 mL per mmol of amine) was added dropwise to a solution of carbene complex (1 equiv) in CH_2Cl_2 (25 mL per mmol of carbene) at $-10\,°C$ under argon. After 15 min, the ice bath was removed and the mixture was stirred at room temperature for 24 h. The solution slowly turned dark red. The solvent was evaporated under vacuum, and the residue purified by chromatography on silica gel with petroleum ether (PE)/Et_2O as eluent.

The general procedure was followed with carbene complex **10a** (2.03 g, 5 mmol). Elution with PE/Et_2O (70/30) gave a 4:3 mixture of two isomers (0.953 g, 70%). **11a** (*trans*): ^1H NMR (200 MHz, $CDCl_3$): $\delta = 7.49 - 7.24$ (m, 5H; ArH), 4.74 (d, ^3J (H,H) = 8.4 Hz, 1H; H^{7a}), 4.06 (m, 1H; OCH_2), 3.60 (m, 1H; OCH_2), 2.81 (dd, ^3J(H,H) = 10.2, 8.4 Hz, 1H; H^7), 2.32 (m, 1H; H^4), 1.90 (m, 1H; H^4), 1.56 (m, 1H; H^5), 1.75 (m, 1H; H^6), 1.24 (t, ^3J (H,H) = 7 Hz, 3H; CH_3), 1.08 (d, ^3J (H,H) = 6.3 Hz, 1H; H^8), 0.84 (m, 1H; H^5); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 172.6$ (CO), 161.2 (C^3), 129.5, 128.8, 128.5, 128.3, 128.1 (Ar), 124.4 (C^{3a}), 87.8 (C^{7a}), 85.9 (C^7), 67.9 (OCH_2), 35.9 (C^6), 32.3 (C^4), 25.7 (C^5), 17.4 (C^8), 15.5 (CH_3). **11a** (*cis*): ^1H NMR (200 MHz, $CDCl_3$): $\delta = 7.49 - 7.24$ (m, 5H; ArH), 4.82 (d, ^3J(H,H) = 3.4 Hz, 1H; H^{7a}), 3.82 (br s, 1H; H^7), 3.72 (m, 1H; OCH_2), 3.57 (m, 1H; OCH_2), 3.01 (m, 1H; H^4), 2.30 (m, 1H; H^4), 1.80 (m, 1H; H^6), 1.58 (m, 2H; H^5), 1.08 (d, ^3J (H,H) = 6.3 Hz, 3H; H^8), 1.05 (t, 3H; ^3J(H,H) = 9 Hz, 3H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 173.3$ (CO), 161.0 (C^3), 130.5, 129.2, 128.9, 128.8, 128.6 (Ar), 125.7 (C^{3a}), 83.0 (C^{7a}), 80.9 (C^7), 69.8 (OCH_2), 34.5 (C^6), 26.7 (C^4), 26.1 (C^5), 17.8 (C^8), 15.9 (CH_3); HR-MS (positive EI) calcd. for $C_{17}H_{21}O_3$: 273.1491; found: 273.1495.

The general procedure was followed with carbene complex **13a** (2 g, 4.69 mmol). Elution with PE/Et_2O (80/20) gave **14a** as a white solid (0.631g, 46%), m.p. $59\,°C$. ^1H NMR (200 MHz, $CDCl_3$): $\delta = 7.58 - 7.35$ (m, 10H; ArH), 4.75 (d, ^3J(H,H) = 8.8 Hz, 1H; H^{7a}), 4.38 (dd, ^3J(H,H) = 11.4 Hz, 1H; H^5), 4.15 (d, 1H; ^3J(H,H) = 8.8 Hz, 1H; H^7), 3.52 (td, 1H; ^3J(H,H) = 11.4, 3 Hz, 1H; H^5), 3.15 (dd, 1H; ^3J(H,H) = 2.5, 14 Hz, H^4), 2.91 (ddd, ^3J(H,H) = 14, 11.8, 6 Hz, 1H; H^4); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 171.9$ (CO), 159.4 (C^3), 138.0 (C^{3a}), 129.3, 128.9, 128.8, 128.6, 126.3, 124.8 (Ar), 85.0 (C^7), 81.1 (C^{7a}), 67.8 (C^5), 29.3 (C^4); elemental analysis calcd for $C_{19}H_{16}O_3$: C 78.08, H 5.49; found: C 77.93, H 5.49. HR-MS (positive EI) calcd for $C_{19}H_{17}O_3$: 293.1178; found: 293.1174.

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Spectroscopy of the Formation of Microporous Transition Metal Ion Containing Aluminophosphates under Hydrothermal Conditions**

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One of the greatest challenges of experimentalists working in the field of molecular sieve science is the understanding of the principles that determine how porous crystalline materials are formed starting from a precursor gel under hydrothermal conditions.[1] This is far from easy because hydrothermal crystallizations take place in a closed vessel, where many interactions, equilibria, and chemical processes continuously change with crystallization time.[2] The lack of knowledge about these phenomena means that a rational a priori design of novel molecular sieves is still impossible and, consequently to date, the synthesis of such materials requires a systematic and intelligent screening of the *n*-dimensional reaction. Recently, the concepts of combinatorial chemistry[3] and experimental design[4] have been successfully explored in order to speed up this screening process. Clearly, a more detailed understanding of the processess occurring during the synthesis of these materials is required, which can lead to a more rational approach towards zeolite syntheses.

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A very attractive but almost unexplored way of probing the hydrothermal crystallization process is to do in situ studies in real time and under realistic laboratory conditions; that is, at high temperatures and pressures. To the best of our knowledge, only IR,[5] NMR,[6] X-ray diffraction,[7] extended X-ray absorption fine structure (EXAFS), [8] and small-angle/wide-angle X-ray scattering (SAXS-WAXS)[9] have been used up to now for performing such in situ studies. Herein, we present a novel methodology based on diffuse reflectance spectroscopy (DRS) in the UV/Vis region and electron spin resonance (ESR) for probing the changes in coordination of transition metal ions during the hydrothermal crystallization of molecular sieves. The method is generally applicable to metal ions that are paramagnetic and possess d–d transitions. Its application not only requires the use of specially designed autoclaves, which allow one to perform such spectroscopic measurements, but also the development of procedures for performing hydrothermal synthesis of molecular sieves in these spectroscopic cells.

Figure 1 (see also the illustration in the table of contents) shows the specially developed in situ DRS cell, which consists of a small container with an internal volume of 12.66 cm^3
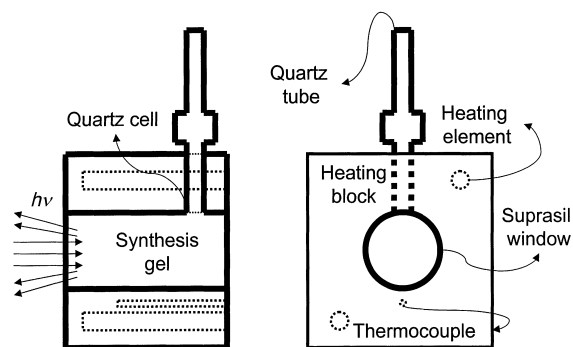

Figure 1. In situ DRS cell for monitoring the coordination environment of transition metal ions during the synthesis of molecular sieves at high temperatures and pressures. See text for details.

temperature did not significantly affect the synthesis process of the molecular sieves.

Herein, we present as an example the hydrothermal crystallization of CoAPO-5 molecular sieves in the DRS and ESR cells at 175 °C under autogeneous pressure and static conditions. Crystallizations of other molecular sieves, such as VAPO-5, CrAPO-5, and NiAPO-5, were equally successful. All these materials are known to be promising catalysts for various oxidation reactions and therefore the isomorphous substitution of transition metal ions in microporous aluminophosphates is an important topic in the literature.[10]

The in situ DRS spectra of the CoAPO-5 gel as a function of the synthesis time are given in Figure 2. The DRS spectrum of the initial pink CoAPO-5 gel is characterized by absorption
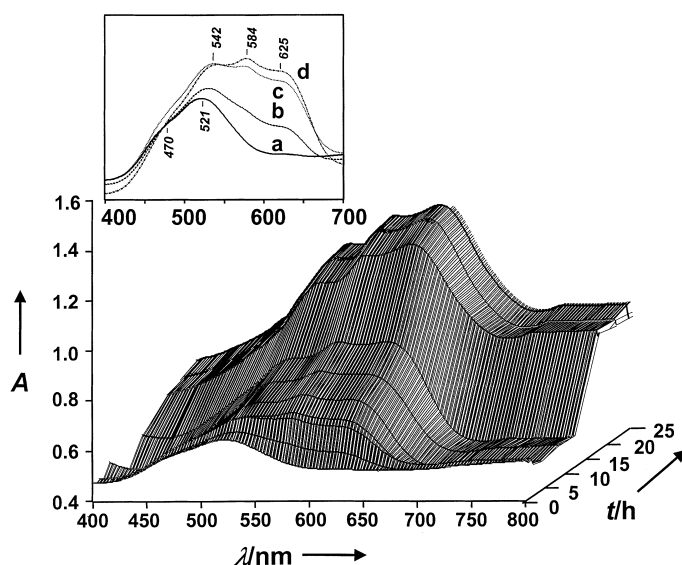

Figure 2. In situ DRS spectra of the CoAPO-5 gel as a function of the synthesis time. The insert shows some DRS spectra as a function of the heating temperature in the initial stages of the hydrothermal synthesis; a) room temperature, b) 60 °C, c) 100 °C, and d) 175 °C.

consisting of walls of high-purity quartz (thickness: 0.5 cm). The synthesis cell could be filled with the precursor gel through a 10 cm long quartz tube, which was equipped with an expansion volume for safety reasons. The quartz tube was sealed after filling the cell, and the cell was placed in a heating mantle, which was controlled with a Eurotherm thermoregulator. The flat front window of the synthesis cell allowed in situ spectra to be recorded with the diffuse reflectance attachment of the diffuse reflectance spectrometer. Important operational conditions for obtaining high-quality microporous materials in this in situ cell are the initial heating rate and the filling factor. High-purity quartz tubes with an internal volume of 0.47 cm^3 were used for performing ESR measurements on the synthesis gels. These quartz tubes were filled with the precursor gel and after sealing were placed either directly in the ESR cavity or in a separate furnace. The synthesis process was quenched by bringing the ESR tube immediately to liquid nitrogen or helium temperatures. This allowed reliable ESR measurements to be conducted. Slowly reheating the sample in the ESR tube to the actual synthesis

bands at 521 and 470 nm. The gel was heated up to 175 °C and an isosbestic point became clearly visible in the DRS spectra (see spectra a–d in Figure 2), indicating the presence of two distinct Co^{2+} species. The absorption band at 521 nm is due to the $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transition (ν_3 band) of high-spin [Co(H$_2$O)$_6$]$^{2+}$[11] present in the synthesis gel, while the shoulder at 470 nm can be assigned to the $^4T_{1g}(F) \rightarrow {}^4A_{2g}(P)$ transition (ν_3 band) of a tetragonally coordinated high-spin Co^{2+} species, most probably of the type [CoO$_4$(H$_2$O)$_2$] (with O, an oxygen atom-bound to phosphorus).[12] Heating the synthesis gel to 175 °C also results in a gradual change of the color from pink to light blue, and a triplet with absorption bands at 542, 584, and 625 nm is observed in the DRS spectrum. This triplet, which is assigned to the $^4A_2(F) \rightarrow {}^4T_1(P)$ transition (ν_3 band) of high-spin pseudo-tetrahedral Co^{2+},[11, 13] strongly increases in intensity with increasing synthesis time and becomes the most intense after 26 h. The sample was intense blue and about 1.5 g of highly crystalline single-phase CoAPO-5 material could be recovered from the cell. Importantly, no crystalline phase was formed during the first

hours of the synthesis process, whereas synthesis times higher than 26 h led to the formation of less crystalline and even other crystalline phases (e.g., CoAPO-C).

The ESR spectrum of the initial CoAPO-5 gel quenched in liquid nitrogen and cooled down to $-263\,^{\circ}C$ indicated the presence of one broad axial signal with $g_{xx} = g_{yy} = 2.643$, $g_{zz} = 2.020$, and $D = 25\,cm^{-1}$, which is typical for the presence of pseudo-octahedral Co^{2+}.[14] The ESR spectra gradually changed with synthesis time and after 24 h one single axial Co^{2+} signal with $g_{xx} = g_{yy} = 2.643$, $g_{zz} = 2.020$ and $D = 3.5\,cm^{-1}$ was observed. These ESR parameters, obtained by spectrum simulation, are typical for the presence of pseudo-tetrahedral Co^{2+};[14] about 0.05 g of highly crystalline single-phase CoAPO-5 could be recovered from the ESR cell.

Thus, both DRS and ESR spectroscopies, together with X-ray diffraction, indicate that the formation of CoAPO-5 molecular sieves is accompanied by the presence of a pseudo-octahedral $[CoO_4(H_2O)_2]$ intermediate in the initial synthesis stages and a gradual transformation of this intermediate species into a pseudo-tetrahedral framework Co^{2+} species. A possible reaction mechanism for the formation of CoAPO-5 molecular sieves can be proposed on the basis of these spectroscopic data, and this is illustrated in Scheme 1. $[Co(H_2O)_6]^{2+}$, which is present in the initial gel at pH 2, is a kinetic labile species ($k_1(Co(O_h)) = 10^6\,s^{-1}$ for the exchange of water ligands) and will readily undergo nucleophilic attack by $H_2PO_4^-$.[15] The reaction between $[Co(H_2O)_6]^{2+}$ and $H_2PO_4^-$ results in the formation of the $[CoO_4(H_2O)_2]$ intermediate.

This species can be envisaged as Co^{2+} linked to four phosphorus atoms through oxygen bridges, after a nucleophilic attack of four $H_2PO_4^-$ species onto one $[Co(H_2O)_6]^{2+}$ complex.[16] The entities formed after these initial reactions can be further condensed to an aluminophosphate gel, in which both Co^{2+} and Al^{3+} are present as octahedral species with two extra-lattice water ligands. Heating of the gel results in the expulsion of these water ligands from the first coordination sphere of Al^{3+} and Co^{2+}. Co^{2+} is thus gradually transformed from a species with pseudo-octahedral coordination into a tetrahedral framework species. Because of the small differences in crystal field stabilization energy (CFSE) between the octahedral ($71.5\,kJ\,mol^{-1}$) and tetrahedral coordination ($62.5\,kJ\,mol^{-1}$) of Co^{2+} (d^7),[17] this transformation process must be favorable and is indeed experimentally observed. The positively charged $(CH_3CH_2)_3NH^+$ template molecules will then compensate the negative charge, which results from the isomorphous substitution of Al^{3+} for Co^{2+} in the CoAPO-5 molecular sieves.

In summary, we have developed and explored the possibilities of combined DRS–ESR spectroscopies for monitoring the changes in the coordination environment of transition metal ions during the hydrothermal crystallization of molecular sieves at high temperatures and pressures. The spectroscopic data obtained allow a better understanding of the hydrothermal crystallization process of CoAPO-5 molecular sieves in terms of the coordination chemistry of Co^{2+} in the synthesis gel.
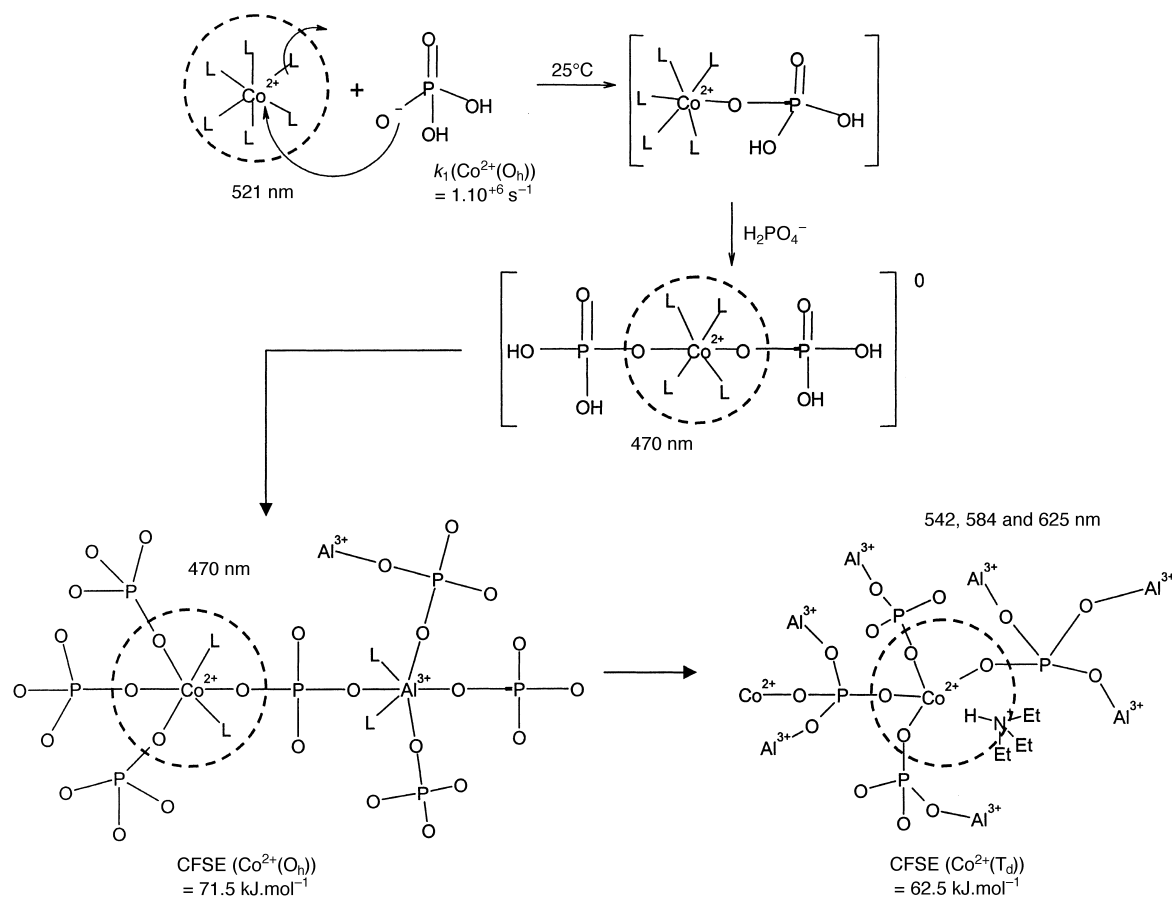
Scheme 1. Proposed mechanism for the processes taking place in the synthesis gel during the hydrothermal synthesis of CoAPO-5 molecular sieves.

COMMUNICATIONS

Experimental Section

CoAPO-5 was prepared according to a standard recipe procedure[13] starting from the following gel composition: $0.75 R[Co_{0.02}Al_{0.98}P_1]O_4 \cdot 20 H_2O$ with R, the template molecule triethylamine (Janssen Chimica, 99%), and with $Co(CH_3CO_2)_2 \cdot 4 H_2O$ (Acros, p.a.). Pseudo-boehmite from Vista (Capatal Alumina 70% Al_2O_3) was used as the Al source, and H_3PO_4 (Janssen Chimica, 85% in H_2O) as the P source. Diffuse reflectance spectra in the UV/Vis–NIR region were measured by using a Varian Cary 5 spectrometer equipped with a diffuse reflectance attachment with integration sphere. The spectra were recorded against a halon white reflectance standard in the range 2500–200 nm. ESR measurements were recorded on a Bruker ESP300E spectrometer with an Oxford Instruments liquid helium cryostat at $-263\,°C$. Simulations of the ESR spectra were performed by simulation programs developed by Mabbs and Collison.[18] Powder X-ray diffraction patterns of the obtained solids were recorded on a Siemens D5000 diffractometer by using $Cu_{K\alpha}$ radiation.

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two transitions, $^4T_{1g}(F) \rightarrow {}^4A_{2g}(P)$ and $^4T_{1g}(F) \rightarrow {}^4E_g(P)$, which are located at 450 and 538 nm, respectively, for, for example, $[Co(H_2O)_4Cl_2]$ (see ref. [11]). We are only able to observe the $^4T_{1g}(F) \rightarrow {}^4A_{2g}(P)$ transition of the $[CoO_4(H_2O)_2]$ species as a shoulder at 470 nm and the $^4T_{1g}(F) \rightarrow {}^4E_g(P)$ transition must be overshadowed by the $^4T_{1g}(F) \rightarrow {}^4E_g(P)$ transition at 521 nm of the more abundant $[Co(H_2O)_6]^{2+}$ species in the synthesis gel. Although $[CoO_x(H_2O)_{6-x}]^{2+}$ (with $x = 1-3$) intermediates can also be formed, only the most stable tetragonally coordinated Co^{2+} species is experimentally observed.

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[17] The pH of the initial gel at 25 °C, as measured with a Consort P514 pH meter, was equal to 2 and this value increased to around 3.5 after heating the synthesis gel to 175 °C. After synthesis the pH was around 7. In this pH range, the dominant species in aqueous solutions are $[Co(H_2O)_6]^{2+}$ and $H_2PO_4^-$ (N. N. Greenwood, A. Earnshaw, *Chemistry of the Elements*, Pergamon, Oxford, **1984**). Importantly, in view of the work of Gerardin et al. (C. Gerardin, M. In, L. Allouche, M. Haouas, F. Taulelle, *Chem. Mater.* **1999**, *11*, 1285) the reported pH values have to be taken with caution.

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First Catalytic Aldol-Transfer Reaction via Aluminum Enolates: A New Way To Generate Aldol Adducts of Aldehydes from Aldol Adducts of Ketones**

Ilkka Simpura and Vesa Nevalainen*

The addition of nucleophiles to carbonyl compounds has been under investigation for decades.[1] Examples include the addition of enolates to aldehydes and the Meerwein–Ponndorf–Verley (MPV) reduction of ketones[2] (hydride as the nucleophile, Figure 1, (a)). Amongst recent achievements in this area are: alkynyl transfer reactions reported by Maruoka and co-workers[3] (Figure 1 (b)), allyl-transfer reactions reported by Nokami et al.[4] (Figure 1, (c)), which as the reaction is proposed to occur by a stepwise ionic mechanism[4] is only formally analogous to the MPV reaction, and cyanide-transfer reactions reported by Inoue and co-workers[5] (Figure 1, (d)). The major advantage of these nucleophile-transfer reactions

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