Crystal structure analysis of CA14[7] as reported for CA10. Monoclinic, space group $C2$, $a = 36.750(9)$, $b = 10.138(2)$, $c = 21.236(4)$ Å, $\beta = 116.18(2)^\circ$, $V = 7093.5$ Å^3 with half a molecule in the asymmetric unit, composition $(C_6H_{11}O_5)_{14} \cdot 27.3\,H_2O$, $\rho_{calcd} = 1.301$ g cm^{-3}, 4633 unique X-ray reflections. Crystallographic R factor 9.71 % for 3478 data with $F \geq 3\sigma_F$. O6 hydroxyl groups of glucose residues 1, 4, and 6 doubly disordered; 24 water positions, some partially (0.3 – 1.0) occupied. A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, M. Camalli, *J. Appl. Cryst.* **1994**, *27*, 435; G. M. Sheldrick, SHELXL76 *Program for Crystal Structure Determination*, University of Cambridge, UK, **1976**.

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[8] Atom numbering: O2(4) means oxygen atom O2 in glucose residue 4; units with primed labels belong to the second half of the molecule. Disordered O6(n)A is in the preferred $-$*gauche* and O6(n)B in the less common $+$*gauche* orientation.

[9] Definition of ϕ and ψ torsion angles: O5(n)-C1(n)-O4($n-1$)-C4($n-1$) and C1(n)-O4($n-1$)-C4($n-1$)-C3($n-1$); see IUPAC rules: *Eur. J. Biochem.* **1983**, *131*, 5 – 7.

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Combinatorial Approach to the Hydrothermal Synthesis of Zeolites

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Recent automated combinatorial chemical methods have been developed for systematic production and evaluation of materials in the fields of organic[1] and inorganic[2] chemistry. Until now, however, there have not been any reports of methods capable of dealing with the special conditions used in the synthesis of zeolites, such as temperatures above the normal boiling point of the reaction mixture and under elevated pressures. To address this problem we have developed an autoclave[3] capable of carrying out at least 100 crystallizations under hydrothermal conditions at temperatures up to 200 °C (Figure 1). The simplest most inexpensive design consists of a Teflon block in which 100 reaction chambers are formed by cylindrical holes, having properly designed profiles to accommodate Teflon-coated septa, which seal the chambers when they are "sandwiched" in between two steel plates.

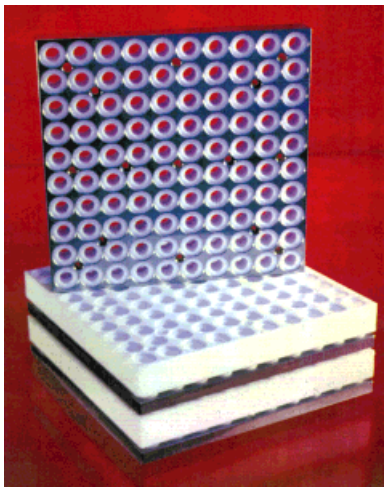

Figure 1. View of the multiautoclave showing the mode of stacking of the Teflon blocks and one of the alternative designs using Teflon inserts.

An important advantage of the system design, which highlights its versatility, is the capability of stacking identical synthesis blocks, allowing an expansion in the third dimension and the parallel synthesis of the order of 1000 combinations in one experiment. The autoclave fits into the compartment of commercial pipette robots for convenient formulation of the synthesis gels. After crystallization, the contents of the autoclave can be washed in situ before further processing. Procedures for a fully automated powder X-ray diffraction analysis of the arrays of materials that are obtained are in progress. To

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illustrate the functioning and potential of the autoclave, two different types of experiments were carried out.

The first experiment involved the detailed evaluation of the ternary phase system Na_2O-Al_2O_3-SiO_2-H_2O, perhaps the most intensively studied of all zeolite syntheses and known to produce several different zeolite structures when the compositional and environmental factors (temperature, time, water content, oxide sources, etc.) are varied. The phase diagram displayed in Figure 2a is reproduced from the very early work

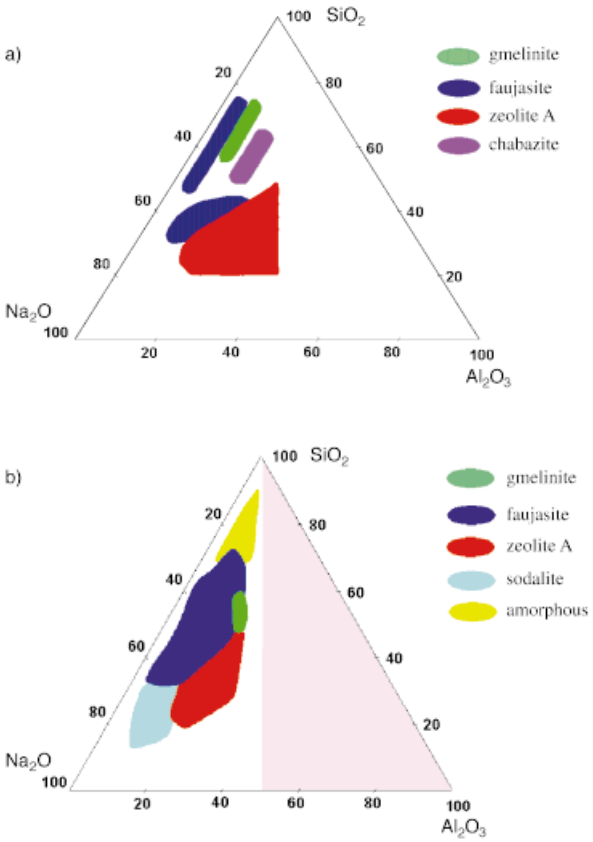

Figure 2. Ternary phase diagram of the Na_2O-Al_2O_3-SiO_2-H_2O system. a) As compiled by Breck from a range of individual syntheses and b) by using the multiautoclave. The light red region is inaccessible due to solubility constraints.

of Breck[4] conducted at temperatures around 100 °C by using colloidal silica and water contents in the range of 90–98 mol %. We have reinvestigated the whole phase diagram in a single experiment under truly identical conditions using the multiautoclave to cover all relevant compositional space. The array of synthesis mixtures were obtained by combining appropriate amounts of three solutions containing the sources of alumina, silica, and soda, respectively. Coordinates in the ternary phase diagram were regularly distributed, giving a total volume of each sample gel of no more than 0.5 mL.

The new results are presented in Figure 2b. As expected the crystalline phases zeolite A, faujasite, and gmelinite were obtained in discrete regions, with some batches containing more than one phase in the boundary regions. The results obtained are only partly in agreement with those of Breck, probably because only the bulk chemical composition of the reaction mixtures were reproduced. Nevertheless, the region for crystallization of zeolite A coincides almost perfectly, and we obtained faujasites in the regions where Breck reported zeolites X and Y. Interestingly, we also obtained faujasite in the regions where Breck reported chabazite and gmelinite, and finally, sodalite was obtained in a rather extended region in the sodium-rich end, which is partly blank in Breck's diagram. While the water content varied to some extent among the syntheses reported by Breck, in the present experiment the water content has been fixed rigorously with respect to the total system. Subsequently, the phase diagram can be extended in the third dimension by varying the water content to produce stability fields that would appear as solid volumes within a quaternary phase diagram.

As a next step in increasing the complexity, the Na_2O-Al_2O_3-SiO_2 system was modified by introducing additional cations. Thus, the goal of the second experiment was to make use of the multiautoclave to screen the effect of binary, ternary, and quaternary cation combinations by using tetramethylammonium hydroxide (TMAOH),[5] Li ions, and Cs ions,[6] in addition to Na ions.

We chose a strategy in which three-quarters of the synthesis capacity was dedicated to the screening of the two ternary combinations Li_2O-TMA_2O-Na_2O-Al_2O_3-SiO_2 and Cs_2O-TMA_2O-Na_2O-Al_2O_3-SiO_2, the remaining quarter covering an experimental mixture-design involving all four cations. In effect, these experiments span a quaternary phase diagram in the range of molar ratios between 0 and 1.0 for Na_2O and 0 and 0.9 for Li_2O, Cs_2O, and TMA_2O.

Under these conditions, the major phase is analcime (ANA) whenever Cs is present in the gels (Figure 3). In the

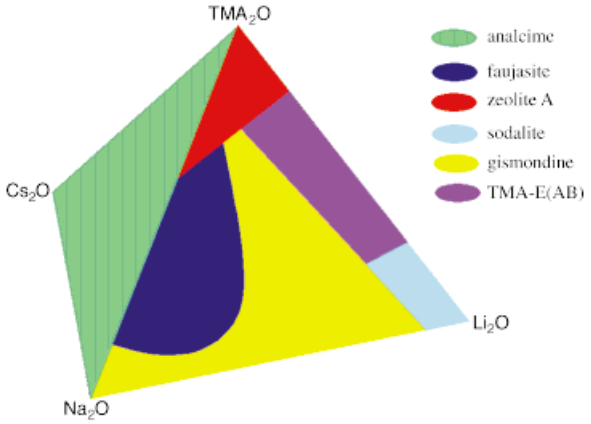

Figure 3. Quaternary phase diagram of the four oxides TMA_2O, Cs_2O, Li_2O (molar ratios 0–0.9), and Na_2O (molar ratios 0–1.0) in the system R_2O-Na_2O-Al_2O_3-SiO_2-H_2O, in which R_2O is the sum of the oxides of the four univalent cations.

absence of Cs, five different zeolites were formed, all of which have been obtained previously by using various combinations of the cations. The screening of the TMA_2O-Li_2O-Cs_2O-Na_2O-Al_2O_3-SiO_2 system maps the zeolite phases and approximate stability regions that may be expected under the synthesis conditions specified below and would serve as a starting point for more detailed studies in a manner similar to that of the first example. These results demonstrate a potential improvement in efficiency of two orders of magnitude achievable by applying combinatorial strategies. In our

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opinion, these strategies will play a significant role in the development of catalysts and absorbents through the use of highly specialized and dedicated multifunctional units for sample preparation and identification/characterization, and through operation with a minimum of manual intervention.

Experimental Section

Routine X-ray diffraction analysis was carried out on small sample quantities (1–10 mg) with steps of 0.05° (2θ) and counting times of 0.5 s. For selected diffractograms, the quality was enhanced greatly by using maximum likelihood noise filtration strategies.

Mixing procedures: For the Na_2O-Al_2O_3-SiO_2 system, the composition of the reaction mixtures was defined according to relation (1) (molar ratios) in which $a/(a+x+y+z)=0.95$.

$$x\,Na_2O{:}y\,Al_2O_3{:}z\,SiO_2{:}a\,[H_2O] \quad (1)$$

For the TMA_2O-Cs_2O-Li_2O-Na_2O-Al_2O_3-SiO_2-H_2O system, the composition of the reaction mixtures were defined according to relation (2) in which $0 \le r, s, t \le 12.15$; $1.45 \le x \le 13.6$; $r+s+t+x=13.6$; $a/(a+r+s+t+x+y+z)=0.93$; $z/y=17.3$; $0 \le r/x \le 8.8$.

$$r\,TMA_2O{:}s\,Cs_2O{:}t\,Li_2O{:}x\,Na_2O{:}y\,Al_2O_3{:}z\,SiO_2{:}a\,[H_2O] \quad (2)$$

The mixtures were prepared by using the following sequence of aqueous solutions 1) NaOH; 2) LiOH; 3) CsOH; 4) TMAOH; 5) Ludox LS 30 % silica sol; 6) $NaAlO_2$ + NaOH. The water contents were corrected for by adding distilled water, giving a total volume of 0.5 mL. The sequence of mixing was elaborated in separate experiments before it was applied to all 100 syntheses. Homogenization of the mixtures was performed in a number of ways; for the prototype presented here, we chose to stir the autoclave contents consecutively, after the addition of all reagents, by using a simple stirring device. The gel mixtures were aged for 24 h at room temperature and the autoclave subsequently placed in an oven for one and six days at 100 °C, for the above-mentioned mixtures, respectively. Washing and isolation of the products was done in situ in the autoclave block by removing both top and bottom seals (Figure 1), and the products were flushed onto a single plate/sheet of adsorbent material with water. Once the products were thoroughly washed, they were transferred to sample holders ready for X-ray analysis and dried at room temperature.

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$[Mo_{12}S_{12}O_{12}(OH)_{12}(H_2O)_6]$: A Cyclic Molecular Cluster Based on the $[Mo_2S_2O_2]^{2+}$ Building Block

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Dedicated to Professor Achim Müller on the occasion of his 60th birthday

Polyoxoanions of tungsten, molybdenum, and vanadium have been the subject of interest since their wide variety of compositions, structures, and properties gave rise to numerous important applications.[1] Polyoxometalates are regarded as models for MO_3 oxide surfaces, and they are very strong acids and active oxidation catalysts. For example, the superacid $H_3[PW_{12}O_{40}]$ promotes esterification reactions and activates C_6 alkanes,[2] while salts of $[PMo_{12}O_{40}]^{3-}$ catalyze the mild oxidation of isobutyric acid to methacrylic acid.[3]

Conversely, alumina-supported molybdenum and tungsten sulfides are hydrogenation catalysts with applications in the hydrodesulfuration of crude oil and the activation of dihydrogen.[4] If these compounds are regarded as functional analogues of the active surface of MoS_2, then binary compounds with discrete M–S units could serve as models for studying the reactivity of the corresponding solids.[5] However, thiometalates are far less common than oxometalates.[6] In addition to their remarkable structural diversity, polyoxometalates can contain a large number of metal centers. In contrast, only low-nuclearity thiometalates have been obtained so far by sulfurization of oxo precursors.[7] Therefore, the synthesis of high-nuclearity sulfur-containing species by combining polyoxometalate and thiometalate chemistry represents a stimulating challenge.

The first method for introducing sulfur into a Keggin-type polyoxoanion was illustrated by the synthesis of α-$[PW_{11}NbSO_{39}]^{4-}$, by selective substitution of the terminal oxygen atom of an Nb=O group by a sulfur atom, and its subsequent characterization.[8] The second technique was the stereospecific addition of an $[Mo_2S_2O_2]^{2+}$ fragment to the cavity-containing polyanion γ-$[SiW_{10}O_{36}]^{8-}$.[9] These strategies are convenient for preparing thio complexes that are derived from well-defined structural types, but are unsuitable for the synthesis of new structures or frameworks with higher sulfur contents.

Here we present a new method for increasing the sulfur content; it is based on the one-step self-condensation of sulfur-containing building blocks. The $[Mo_2S_2O_2]^{2+}$ unit was first prepared by selective oxidation of the terminal S_2 ligands of $[(S_2)MoO(\mu_2\text{-}S)_2MoO(S_2)]^{2-}$ with iodine.[10, 11] The self-condensation reaction was performed by controlled addition of potassium hydroxide to an aqueous solution of the building

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