Ionothermal Synthesis

DOI: 10.1002/anie.200804891

Ionothermal Synthesis of Zirconium Phosphates and Their Catalytic Behavior in the Selective Oxidation of Cyclohexane**

Lei Liu, Yang Li, Haibo Wei, Mei Dong, Jianguo Wang, Alexandra M. Z. Slawin, Jinping Li, Jinxiang Dong, and Russell E. Morris*

Since the discovery of the aluminophosphate family of molecular sieves,[1] many other elements have been incorporated into these structures to form microporous materials (for example, zincophosphates and zirconium phosphates) and the preparation of these types of solids continues to be the focus of a large body of work. Zirconium phosphates are especially interesting as they exhibit unique properties in the fields of photochemistry,[2] molecular and chiral recognition,[3] biotechnology,[4] and catalysis.[5] Zirconium phosphates with one-, two-, and three-dimensional connectivities are usually prepared using a solvothermal approach in water or organic solvents as the mother liquid. The nature of the interaction between the solvent and reacting species is undoubtedly critical, not only for control over the final crystal structure of the products, but also their crystal size and morphology,[6] both of which are important for synthetic chemists and materials scientists. Choosing the proper solvent is vital to the success or failure of the attempted syntheses.

Ionothermal synthesis, a new method for the preparation of aluminophosphate molecular-sieve analogues[7–14] and other materials,[15–18] was developed in 2004 and has interesting features and potential advantages over the traditional method of molecular-sieve synthesis. For example, the cation of the ionic liquid can act both as the solvent and the structure-directing agent, and synthesis can take place at ambient pressure, eliminating safety concerns associated with high solvent pressures. As there are at least a million binary ionic liquids and potentially more than 10^{18} ternary ionic liquids and eutectic mixtures,[7] compared to only about 600 molecular solvents used for solvent thermal synthesis, this preparative method offers many opportunities for the synthesis of new porous frameworks by selecting solvents with different organic groups. In contrast to the large and wide-ranging studies that have been undertaken on the hydrothermal synthesis of molecular sieves, ionothermal synthesis has only begun recently. Nevertheless, the work that has been done shows exciting possibilities for the preparation of hitherto unknown materials for improved preparation of previously synthesized materials and for mechanistic studies.

To the best of our knowledge, no description of the synthesis of zirconium phosphate compounds by the ionothermal method exists in the literature. In an attempt to synthesize this kind of solid material, a series of syntheses in deep eutectic solvents (DES) have been carried out using HF, zirconium(IV) oxychloride, and H_3PO_4 as initial reactants. The addition of fluoride in the form of HF is relatively well-known in the synthesis of open framework materials, and helps to solubilize all the starting materials in the reaction solvent.[7,19] As a result, three different frameworks have been successfully synthesized in the present study. Two of these compounds are new phases with chain and layer framework structures, and their structures were solved by single-crystal X-ray diffraction data. The third compound is identical to the known phase of $[Zr_{12}P_{16}O_{60}(OH)_4F_8]$ $(C_5H_6N)_4$ $(H_2O)_2$ (ZrPOF-pyr),[20] and is identified by the powder X-ray diffraction pattern.

Using the deep eutectic solvent consisting of urea and tetramethylammonium chloride, with different amounts of HF added to the initial mixture, two different zirconium phosphate frameworks were obtained. With a F/Zr ratio of 2.8, a novel compound, $(NH_4)_4[Zr(PO_4)_2F_2]$, designated as $ZrPO_4$-DES1, was formed with a chain framework structure. Figure 1 shows the polyhedral structure of $ZrPO_4$-DES1. For each phosphate tetrahedron, two of its coordinating oxygen atoms bridge to zirconium atoms, with P−O bond lengths of 1.558(6) Å and 1.547(7) Å. The other two oxygen atoms are found in the form of terminal P=O units. For the $\{ZrO_4F_2\}$ octahedra, the two bridging Zr−O bond lengths are 2.052(7) and 2.068(7) Å, and the two terminal Zr−F bonds are shorter, with equal bond lengths of 2.009(6) Å. Each $\{ZrO_4F_2\}$ octahedron links four different $\{PO_4\}$ tetrahedra with each pair at the corners of one diagonal to form infinite macro-anionic $[ZrP_2O_8F_2)]_n^{4n-}$ chains running along the [001] direction, and forming four-membered rings along [100], with triclinic topological symmetry. The NH_4^+ cations are located among the chains. As no extra NH_4^+ cations were added in these syntheses, they result from the partial decomposition of the urea, a component of eutectic mixture, which acts to template the structure and balance on the anion framework. The elemental analysis results are in good agreement with the calculated ratio H/N = 4:1 for the formula

---

[*] L. Liu, H. Wei, Prof. J. Li, J. Dong
Research Institute of Special Chemicals
Taiyuan University of Technology
Taiyuan 030024, ShanXi (P.R.China)
Fax: (+86) 351-611178
E-mail: dongjinxiangwork@hotmail.com
Y. Li, Prof. A. M. Z. Slawin, Prof. R. E. Morris
School of Chemistry, University of St Andrews
KY16 9ST (UK)
M. Dong, Prof. J. Wang
State Key Laboratory of Coal Conversion, Institute of Coal
Chemistry, Chinese Academy of Sciences (P.R.China)

[**] The Chinese group was financially supported by the NSFC, China (Grant No.20573077, 50672063, 20825623) and Shanxi Natural Science Foundation for Young Scientists (Grant No.2008021014).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200804891.

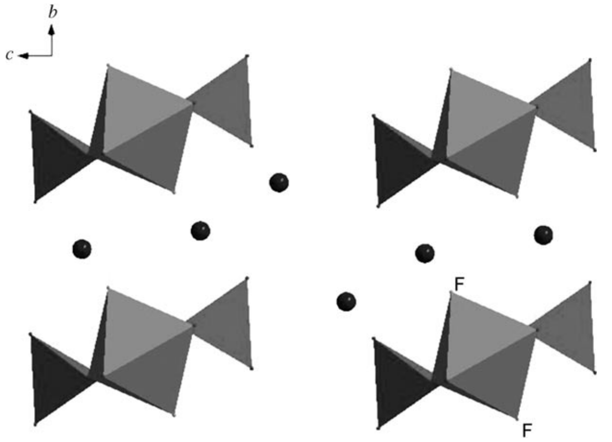

Figure 1. Polyhedral representation of $ZrPO_4$-DES1 (ZrO_4F_2 octahedra, PO_4 tetrahedra; F indicated in one octahedron, other apexes O; speheres NH_4^+).

$(NH_4)_4[Zr(PO_4)_2F_2]$. The structure of ZrPO4-DES1 is very similar to the one-dimensional chain zirconium phosphate,[21] $(NH_4)_3[Zr(OH)_2(PO_4)(HPO_4)]$, which is also based on layers of macroanionic chains separated by alternating layers of NH_4^+ cations.

At a F/Zr ratio of 0.61, a different zirconium phosphate compound with a two-dimensional layered structure, $(NH_4)_3[Zr(PO_4)_2F]$, was readily synthesized in the manner described above, and is designated as $ZrPO_4$-DES2. Figure 2 shows the structure of $ZrPO_4$-DES2.

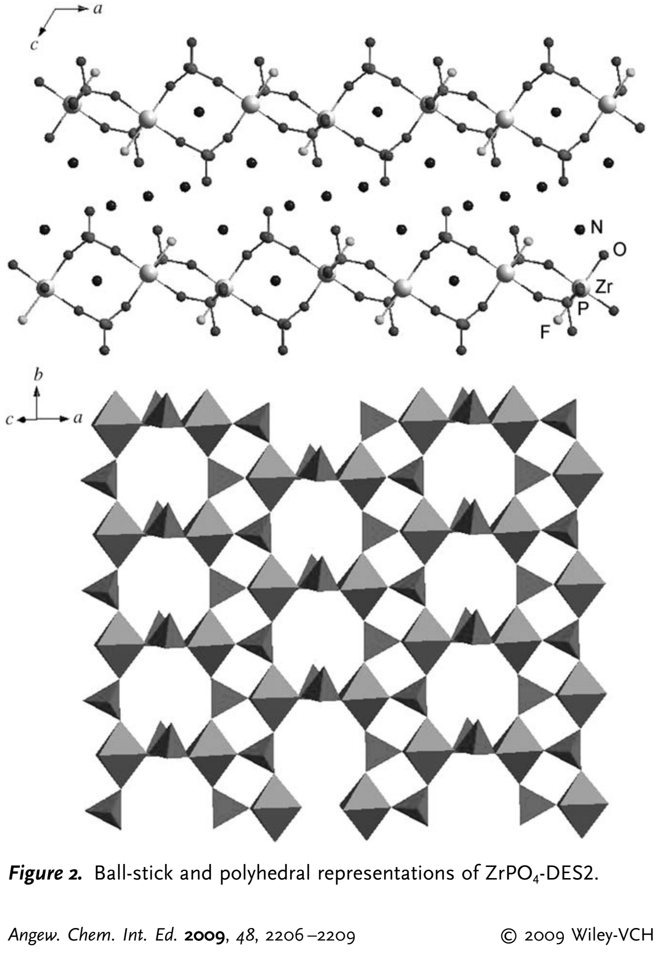

Figure 2. Ball-stick and polyhedral representations of $ZrPO_4$-DES2.

The structure of $(NH_4)_3[Zr(PO_4)_2F]$ is based on a sheet of zirconium-centered octahedra and phosphorus-centered tetrahedra. The zirconium atom is octahedrally coordinated to five oxygen atoms from the different phosphate groups and one fluorine atom. There are two crystallographically different $\{PO_4\}$ tetrahedra. For one of the phosphorous-centered tetrahedrons, two of its coordinating oxygen atoms bridge to zirconium atoms with P−O bond lengths of 1.531(1) Å and 1.527(9) Å. The other two oxygen atoms exist in the form of a terminal P=O double bond, with average bond length of 1.496(5) Å. For the other phosphorous-centered tetrahedrons, three of its coordinating oxygen atoms bridge to zirconium atoms with bond lengths in the range 1.525(7)–1.552(2) Å, and its terminal P=O bond length is 1.506(7) Å.

For the $\{ZrO_5F\}$ octahedra, the bridging Zr−O bond lengths are not identical and are in the range 2.044(7)–2.064(8) Å. The terminal Zr−F bond length (2.016(5) Å) is comparable to that of $ZrPO_4$-DES1. The $ZrPO_4$-DES2 has eight- and four-membered rings consisting of alternating $\{ZrO_5F\}$ octahedra and $\{PO_4\}$ tetrahedra, respectively, in the inorganic sheet. The elemental analysis shows that the content of nitrogen and hydrogen are equal to 12.2% and 3.5% by weight, respectively. These values are in good agreement with the calculated values: 12.0% for N and 3.4% for H.

As described above, the urea-derived ammonium cations incorporated into the zirconium phosphate frameworks provide a better template compared to the tetramethylammonium chloride component of the DES. To avoid the competition between the two ammonium cations, oxalic acid was used instead of urea to form the deep eutectic solvent with the quaternary ammonium salt, which is not likely to act as a template. Herein, a DES based on oxalic acid and tetramethylammonium chloride has been used in an ionothermal reaction, and as a result, another zirconium phosphate compound, different from the two phases mentioned above, has been synthesized. This zirconium phosphate compound has been designated as $ZrPO_4$-DES3, the X-ray diffraction pattern of which is in agreement with the powder diffraction pattern of the reported $[Zr_{12}P_{16}O_{60}(OH)_4F_8]$-$(C_5H_6N)_4(H_2O)_2$ (ZrPOF-pyr)[20] with an open framework (Supporting Information), however, having a different composition. The reported ZrPOF-pyr was hydrothermally synthesized using pyridine as a template, and has a three-dimensional framework structure with 10-ring and 8-ring channels. The elemental analysis for ZrPO4-DES3 are in good agreement with the calculated value (C/N = 4) for the tetramethylammonium cation, confirming that the organic cations are incorporated into the structure. Herein, it appears to be the tetramethylammonium cations that play the role of a template for the construction of the zirconium phosphate framework, and the acid–base properties of the solvent do not need to be adjusted by addition of an organic base. In contrast, for ionothermal synthesis of aluminophosphates using these kinds of DESs,[12] it is necessary to add bases, such as cyclam or pyridine, to the acidic DESs to control the acid-base properties of the solvent; otherwise only dense phases such as berlinite are formed. However, the by-products were easily formed when organic bases were added to the DESs.

Therefore, to synthesize the zirconium phosphate framework using quaternary ammonium cations as template, avoiding the strong template action of urea-derived ammonium cations is very important. Certainly, using the carboxylic acid-quaternary ammonium salt DESs in the ionothermal reaction is a good choice to accomplish this goal, probably leading to other novel materials.

The selective oxidation of cyclohexane to yield cyclohexanol and cyclohexanone has an important industrial significance, namely the production of nylon-6 polymers. In previous studies, transition-metal-ion-substituted aluminophosphates (transition metal (TM) = Co^{3+}, Fe^{3+}) have been shown to exhibit good catalytic performance and selectivity for cyclohexanol and cyclohexanone in this reaction,[22,23] owing to the highly dispersed redox active centers and unique shape selectivity in the TM-ion-substituted aluminophosphate molecular sieves. To the best of our knowledge, other than aluminophosphate-based materials, there has been no report describing the use of open-framework zirconium phosphates as catalysts in the oxidation of cyclohexane.

Of the three zirconium phosphate compounds synthesized herein using DESs, $ZrPO_4$-DES3, with the 3D framework has high thermal stability up to 450 °C, but transforms to another phase at higher temperature. The two other compounds with 1D and 2D structures are very unstable, as expected, when calcined to high temperature for the removal of the templates. Herein, for comparison, we have investigated the catalytic behavior in cyclohexane selective oxidation of the three topologically distinct zirconium phosphates. Before the catalytic test, $ZrPO_4$-DES3 was calcined at 450 °C for 4 h, and the two other zirconium phosphates were used without thermal treatment. Gas adsorption experiments (CO_2, 273 K) on the $ZrPO_4$-DES3 indicate a small amount of internal accessible surface area (75 $m^2 g^{-1}$), and powder X-ray diffraction indicates crystallinity of the material following the thermal treatment (Supporting Information).

Catalytic properties of $ZrPO_4$-DES1, $ZrPO_4$-DES2, and $ZrPO_4$-DES3 were tested, and the results are presented in Table 1. $ZrPO_4$-DES3 exhibits high catalytic performance, with a cyclohexane conversion ratio of 32 % and the selectivity for cyclohexanone can reach up to 83 %. In contrast, the other two compounds having the chain and layered structures are relatively poor catalysts with low selectivity. The difference in catalytic properties and selectivity between the three catalysts probably results from their different framework structures. For the 3D $ZrPO_4$-DES3 catalyst that has high thermal stability, the guest molecules, such as water and template molecules that obstruct the pores, can be removed at least partially after calcination at 450 °C, giving rise to some internal surface area in the 10-ring or 8-ring pore channel. However, for the 1D or 2D zirconium phosphates used in this reaction, for which no thermal treatment was applied only the external surface is effective in the catalytic reaction. As a result, the activating treatment affords the $ZrPO_4$-DES3 catalyst many active sites, leading to high catalytic performance. X-ray diffraction was completed on the sample before and after the catalytic reaction and they showed that there had been no change in the crystalline framework (Supporting Information). In addition, the used catalysts were separated from the reaction mixture; inductively coupled plasma spectrometry (ICP) measurements indicated that there is no significant leaching of zirconium or phosphorous atoms from the materials into solution during the course of the reaction. As can be seen, the experimental catalytic results are very interesting. The mechanism of the reaction is still under investigation and we cannot make any definitive comments at the present time. However, it is most likely that the reaction proceeds using radical mechanisms, as has been known for other similar liquid phase oxidations.[22,24]

Table 1: Conversion and selectivity of cyclohexane oxidation over different catalysts.

Catalyst	Total conv. [%]	Selectivity [%]			-one/-ol[a]
		-one	-ol	Others[b]	
$ZrPO_4$-DES1	9	59	23	18	2.6
$ZrPO_4$-DES2	12	58	26	16	2.3
$ZrPO_4$-DES3	32	83	7	10	11.9

[a] Cyclohexanone = -one, cyclohexanol = -ol. [b] Others included mainly adipic acid and valeric acid.

Herein, three different zirconium compounds with one-, two-, and three-dimensional structures were successfully synthesized by the ionothermal approach. Comparison between the DESs based on urea and oxalic acid indicates that the urea-derived ammonium cations exhibit a stronger templating role in the formation of the zirconium phosphate framework than the quaternary ammonium cations in the DESs. For the DESs based on oxalic acid, the quaternary ammonium cations can exert its templating role to form zirconium phosphate framework. Thus, there is no need to control the acid-base properties of the solvent by adding organic amine to starting reactions, as is required for the synthesis of aluminophosphate frameworks. Our results show the potential for synthesizing zirconium phosphates by the ionothermal approach. Surprisingly, the $ZrPO_4$-DES3 compound exhibits good catalytic performance for the selective oxidation of cyclohexane.

Experimental Section

General synthetic procedure: a teflon-lined autoclave (total volume 23 mL) was charged with appropriate quantities (see below) of deep eutectic solvent (DES),[25,26] zirconium(IV) oxychloride octahydrate (98 %, Aldrich), H_3PO_4 (85 wt % in water, Aldrich), and HF (48 wt % in water, Aldrich). The autoclave was then heated in an oven to the required temperature (180 °C for 3 days for all phases). The reaction conditions were optimized by changing the reaction compositions slightly and characterizing the resulting products by measuring their powder X-ray diffraction patterns (XRD), which were collected on a Rigaku D/max-2500 diffractometer with $Cu_{K\alpha_1}$ radiation (λ = 1.5406 Å). Quantities used:

$ZrPO_4$-DES1: urea (2.8 g, 46.6 mmol), tetramethylammonium chloride (2.4 g, 21.9 mmol), $ZrOCl_2{\cdot}8H_2O$ (250 mg, 0.76 mmol), HF (0.094 mL, 2.15 mmol), and H_3PO_4 (178 mg, 1.54 mmol).

$ZrPO_4$-DES2: urea (2.8 g, 46.6 mmol), tetramethylammonium chloride (2.4 g, 21.9 mmol), $ZrOCl_2{\cdot}8H_2O$ (250 mg, 0.76 mmol), HF (0.020 mL, 0.46 mmol), and H_3PO_4 (178 mg, 1.54 mmol).

$ZrPO_4$-DES3: oxalic acid dihydrate (2 g, 15.78 mmol), tetramethylammonium chloride (2.4 g, 21.9 mmol), $ZrOCl_2{\cdot}8H_2O$ (250 mg, 0.76 mmol), HF (0.094 mL, 2.15 mmol), and H_3PO_4 (178 mg, 1.54 mmol).

Caution! HF (48 wt % in water) is very toxic by inhalation, in contact with skin, and if swallowed. Suitable protective clothing, gloves, and eye/face protection should be used.

The X-ray data for $ZrPO_4$-DES1 and $ZrPO_4$-DES2 single crystals were collected with a Rigaku MM007/RA and Mercury CCD with silicon monochromated graphite monochromated $Mo_{K\alpha}$ radiation and a rotating anode generator at temperature of 93 K. All the datasets were corrected for absorption using multiscan methods. The structures were solved by direct methods and refined by full-matrix least-squares techniques, using the SHELXS, SHELXL, and WinGX packages. The non-hydrogen atoms were refined anisotropically. $ZrPO_4$-DES1: $(NH_4)_4[Zr(PO_4)_2F_2]$, triclinic, space group $P\bar{1}$, $\rho_{calcd}=2.062\ g\,cm^{-3}$, $a=5.294(3)$, $b=6.710(6)$, $c=9.849(11)$ Å, $\alpha=84.28(9)$, $\beta=76.26(8)$, $\gamma=68.07(7)°$, $V=315.24(1)$ Å^3, $R=0.084$. $ZrPO_4$-DES2: $(NH_4)_3[Zr(PO_4)_2F]$, monoclinic, space group C2, $\rho_{calcd}=2.251\ g\,cm^{-3}$, $a=18.273(8)$, $b=6.535(2)$, $c=10.112(4)$ Å, $\beta=121.120(3)°$, $V=1033.7(7)$ Å^3, $R=0.052$.

Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD-419944 ($ZrPO_4$-DES1) and CSD-419945 ($ZrPO_4$-DES2).

Catalytic tests and analytical procedures: The oxidation of cyclohexane over zirconium phosphate samples was carried out in a teflon-lined stainless steel batch reactor (12 mL total volume), using acetic ester as the reaction medium. Cyclohexane (0.5 g), catalyst (0.05 g), acetic ester (2.2 g), and *tert*-butyl hydroperoxide (0.001 g) as initiator were introduced into the reactor. The reactor was charged with O_2 (1.5 MPa), heated to 120 °C within 30 min with stirring, and the reactor was held at this temperature for 15 h. The products were analyzed on an FID gas chromatograph (Shimadzu GC-8A) equipped with a 3 m × 3.2 mm packed column of Carbowax 20M on Chromosorb WAW 80/100 with argon as carrier gas. Cyclooctane was used as the internal standard. Cyclohexane, cyclohexanone, and cyclohexanol were quantified directly, the acids formed were determined by detecting the methyl esters after esterification with BF_3 and CH_3OH.[27]

Received: October 7, 2008

Keywords: cyclohexane · eutectic solvents · oxidation · phosphates · zirconium

---

[1] S. T. Wilson, B. M. Bok, C. A. Messina, T. R. Cannon, E. M. Flanigen, *J. Am. Chem. Soc.* **1982**, *104*, 1146–1147.

[2] C. V. Kumar, A. Chaudhari, G. L. Rosenthal, *J. Am. Chem. Soc.* **1994**, *116*, 403–404.

[3] G. Cao, M. E. Garcia, M. Alcalà, L. F. Burges, T. E. Mallouk, *J. Am. Chem. Soc.* **1992**, *114*, 7574–7575.

[4] B. Bujoli, S. M. Lane, G. Nonglanton, M. Pipelier, J. Le'ger, D. R. Talham, C. Tellier, *Chem. Eur. J.* **2005**, *11*, 1980–1988.

[5] C. V. Kumar, A. Chaudari, *J. Am. Chem. Soc.* **2000**, *122*, 830–837.

[6] R. E. Morris, S. J. Weigel, *Chem. Soc. Rev.* **1997**, *26*, 309–317.

[7] E. R. Cooper, C. D. Andrews, P. S. Wheatley, P. B. Webb, P. Wormald, R. E. Morris, *Nature* **2004**, *430*, 1012–1016.

[8] E. R. Parnham , R. E. Morris, *Acc. Chem. Res.* **2007**, *40*, 1005–1013.

[9] E. R. Parnham, E. A. Drylie, P. S. Wheatley, A. M. Z. Slawin, R. E. Morris, *Angew. Chem.* **2006**, *118*, 5084–5088; *Angew. Chem. Int. Ed.* **2006**, *45*, 4962–4966.

[10] E. R. Parnham, P. S. Wheatley, R. E. Morris, *Chem. Commun.* **2006**, 380–382.

[11] E. R. Parnham, R. E. Morris, *Chem. Mater.* **2006**, *18*, 4882–4887.

[12] E. A. Drylie, D. S. Wragg, E. R. Parnham, P. S. Wheatley, A. M. Z. Slawin, J. E. Warren, R. E. Morris, *Angew. Chem.* **2007**, *119*, 7985–7989; *Angew. Chem. Int. Ed.* **2007**, *46*, 7839–7843.

[13] Y. P. Xu, Z. J. Tian, S. J. Wang, Y. Hu, L. Wang, B. C. Wang, Y. C. Ma, L. Hou, J. Y. Yu, L. W. Lin, *Angew. Chem.* **2006**, *118*, 4069–4074; *Angew. Chem. Int. Ed.* **2006**, *45*, 3965–3970.

[14] E. R. Parnham, R. E. Morris, *J. Am. Chem. Soc.* **2006**, *128*, 2204–2205.

[15] Z. Lin, D. S. Wragg, J. E. Warren, R. E. Morris, *J. Am. Chem. Soc.* **2007**, *129*, 10334–10335.

[16] Z. Lin, A. M. Z. Slawin, R. E. Morris, *J. Am. Chem. Soc.* **2007**, *129*, 4880–4881.

[17] C. P. Tsao, C. Y. Sheu, N. Nguyen, K. H. Lii, *Inorg. Chem.* **2006**, *45*, 6361–6364.

[18] M. F. Tang, Y. H. Liu, P. C. Chang, Y. C. Liao, H. M. Kao, K. H. Lii, *Dalton Trans.* **2007**, 4523–4528.

[19] R. E. Morris, A. Burton, L. M. Bull, S. I. Zones, *Chem. Mater.* **2004**, *16*, 2844–2851.

[20] J. X. Dong, L. Liu, J. Li, Y. Li, C. Baerlocher, L. B. McCusker, *Microporous Mesoporous Mater.* **2007**, *104*, 185–191.

[21] D. Wang, R. Yu, X. Xing, Y. Chen, Zh. Guo, N. Kumada, N. Kinomura, M. Takano, *Solid State Ionics* **2004**, *175*, 751–754.

[22] R. Raja, G. Sankar, J. M. Thomas, *J. Am. Chem. Soc.* **1999**, *121*, 11926–11927.

[23] R. Zhang, Z. Qin, M. Dong, G. Wang, J. Wang, *Catal. Today* **2005**, *110*, 351–356.

[24] D. A. Van Oppen, P. A. Jacobs, *Catal. Today* **1999**, *49*, 177–183.

[25] A. P. Abbott, D. Boothby, G. Capper, D. L. Davies, R. K. Rasheed, *J. Am. Chem. Soc.* **2004**, *126*, 9142–9147.

[26] A. P. Abbott, G. Capper, D. L. Davies, R. K. Rasheed, V. Tambyrajah, *Chem. Commun.* **2003**, 70–71.

[27] R. Raja, P. Ratnasamy, *Catal. Lett.* **1997**, *48*, 1–10.