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# Preparation of calcium and magnesium fluorides with extended surface areas using β-cyclodextrin as a structure-forming agent

**Sergey Yu. Arkhipenko,[a] Anna A. Fedorova,*[a] Igor V. Morozov[a] and Aleksei S. Shaporev[b]**

[a] *Department of Chemistry, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation. Fax: +7 495 939 0998; e-mail: fedorova@inorg.chem.msu.ru*

[b] *N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation*

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**A new method for the synthesis of calcium and magnesium fluorides with high surface areas is proposed; the fluorides obtained by the decomposition of β-cyclodextrin–metal trifluoroacetate mixtures have surface areas of about 80 and 60 $m^2\ g^{-1}$ for $CaF_2$ and $MgF_2$, respectively.**

Metal fluorides are promising supports for oxide-based, metal-based and heteropoly acid-based catalysts.[1] They have good thermal stability and do not react with an active phase of the catalyst unlike other supports; for example, alumina can form aluminates, thus lowering the catalytic activity.[2] It was shown[3] that Cu–Mn oxide catalysts have higher activity in the reaction of NO reduction by propene if $MgF_2$ rather than $Al_2O_3$ is used as a support.

The synthesis of dispersed metal fluorides is difficult to perform. On one hand, sol-gel methods[4] lead to magnesium fluoride with a surface area of 150–350 $m^2\ g^{-1}$ for X-ray amorphous nanocrystalline $MgF_2$.[5] However, these methods require anhydrous hydrogen fluoride and special equipment. Simple methods for obtaining dispersed metal fluorides[6] produce fluorides with a surface area of only ~40 $m^2\ g^{-1}$, for example, the decomposition of calcium trifluoroacetate[7] leads to calcium fluoride with a surface area of 44 $m^2\ g^{-1}$.

Here, we propose a procedure for the preparation of calcium and magnesium fluorides having high surface areas (60–80 $m^2\ g^{-1}$) with the use of β-cyclodextrin as a structure-forming agent in mixtures with trifluoroacetate hydrates.[†] β-Cyclodextrin forms ordered structures with organic compounds,[8] and we expected the trifluoroacetate ion to participate in this process.

The thermogravimetric analysis of calcium and magnesium trifluoroacetate hydrates [$Ca(CF_3COO)_2 \cdot H_2O$ and $Mg(CF_3COO)_2 \times 4H_2O$, respectively] showed that decomposition proceeds in two steps, the loss of water (100–110 °C) and the conversion of a metal trifluoroacetate into the corresponding fluoride (220–280 and 290–320 °C for magnesium and calcium, respectively). According to the reference data the major part of anhydrous salt decomposes at 266–305 °C in case of calcium[9] or 270–310 °C in case of magnesium[10] [a gel obtained from $Mg(OEt)_2$, isopropanol and trifluoroacetic acid]. Calcium trifluoroacetate hydrate decomposes without melting, whereas magnesium trifluoroacetate hydrate undergoes melting followed by the loss of water.

The thermograms of β-cyclodextrin–trifluoroacetate mixtures differ significantly from the thermograms of pure compounds. Thus, the main stage of weight loss of a β-cyclodextrin–calcium trifluoroacetate mixture (1:1, by weight) occurs in a narrow temperature range and starts at a lower temperature (240 °C) than in case of pure β-cyclodextrin (280 °C) and calcium trifluoroacetate (290 °C).

The products of metal trifluoroacetate–β-cyclodextrin decomposition were corresponding fluorides, as found by comparing their X-ray patterns with data from ICDD PDF2.[11]

The black color of decomposition products indicates the presence of carbon-bearing impurities in the fluorides. The products were annealed in air for 8–13 h at 400 °C to eliminate these impurities. Note that the fluorides have a high surface area (~60–80 $m^2\ g^{-1}$) despite relatively long heating at 400 °C. For comparison, calcium fluoride[12] obtained by the interaction of soda lime with aqueous hydrogen fluoride and dried at 200 °C has a surface area of 50 $m^2\ g^{-1}$ but when heated at 400 °C for 3 h the surface area decreases to 20 $m^2\ g^{-1}$.

The surface areas of calcium and magnesium fluorides strongly depend on the mass fraction of β-cyclodextrin in the mixtures

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[†] The following compounds were used for the synthesis: $MgCO_3 \times Mg(OH)_2 \cdot 3H_2O$; $CaCO_3$; β-cyclodextrin hydrate $(C_6H_{10}O_5)_7 \cdot 8.5H_2O$ and $CF_3COOH$ (99%).

Trifluoroacetic acid in a 20% excess was added to calcium carbonate, affording calcium trifluoroacetate hydrate after evaporating the solution and drying the white solid product in air. A similar procedure was carried out with magnesium base carbonate, giving magnesium trifluoroacetate hydrate.

The following procedure was used to decompose the mixtures of β-cyclodextrin with calcium trifluoroacetate to obtain calcium fluoride: β-cyclodextrin was mixed with calcium trifluoroacetate hydrate in mass ratios of 1:5, 1:2, 1:1, 2:1 and 5:1. Water was added to the mixtures; the solutions were heated to 150–170 °C, and solid gelatinous products were formed after heating for 1 h. These gels were heated to 400 °C and kept at this temperature for 8–13 h to anneal carbon. Magnesium fluoride was obtained by the similar procedure.

For comparison, calcium and magnesium fluorides were also synthesised by heating corresponding pure metal trifluoroacetates at 400 °C for 1 h.

The metal fluorides were annealed at 1000 °C for 2 h to investigate their stability to pyrohydrolysis.

The XRD patterns of fluorides and products of their pyrohydrolysis were collected on Enraf-Nonius FR-552 and Rigaku D/MAX 2500 X-ray diffractometers with CuKα radiation. The data were processed using the STOE software. The ICDD PDF2 data base[11] was used to identify phases in the solid materials.

The thermal analysis of calcium and magnesium trifluoroacetate hydrates and their mixtures with β-cyclodextrin was performed on a NETZSCH STA 409 PC/PG instrument in the temperature range of 20–600 °C at a heating rate of 10 K $min^{-1}$ in an air flow.

SEM was performed on a LEO SUPRA 50 VP instrument in a low vacuum mode.

The BET surface areas and pore size distributions were measured by $N_2$ adsorption and desorption isotherms at 77 K on an ATX-06 analyzer.

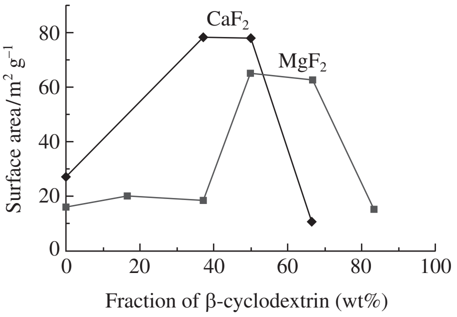

**Figure 1** Dependence of the surface areas of MgF$_2$ and CaF$_2$ on the mass fraction of β-cyclodextrin (wt%) in the reaction mixture.

with corresponding trifluoroacetate hydrates (Figure 1). Thus, an increase in the mass fraction of β-cyclodextrin in a mixture with magnesium trifluoroacetate from 0 to 50 wt% leads to a triple increase in the surface area of MgF$_2$. The maximum value for MgF$_2$ is 63 m$^2$ g$^{-1}$ at 66 wt% β-cyclodextrin, and with further increase in the mass fraction of β-cyclodextrin the surface area decreases. The best surface area for CaF$_2$ is 78 m$^2$ g$^{-1}$ at 33 wt% β-cyclodextrin.

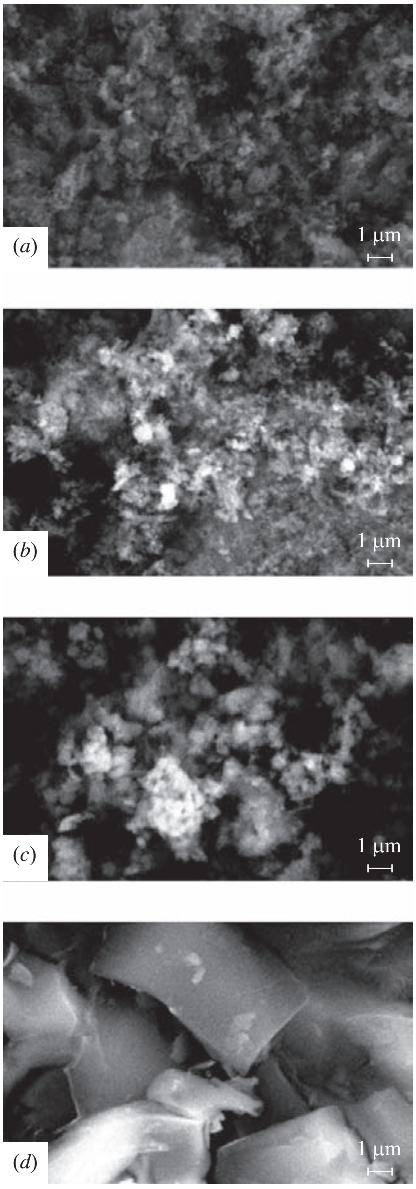

**Figure 2** Results of scanning electron microscopy of magnesium fluoride obtained by decomposition of β-cyclodextrin–magnesium trifluoroacetate hydrate mixtures with different mass ratios: (*a*) without cyclodextrin and with mass ratios of (*b*) 1:5, (*c*) 1:1 and (*d*) 5:1.

Figure 2 shows the results of scanning electron microscopy (SEM) of MgF$_2$. The mass ratio of β-cyclodextrin to magnesium trifluoroacetate hydrate in the reaction mixture influences the texture and morphology of the resulting fluoride. The particle size increases with the mass fraction of β-cyclodextrin. However, this does not lead to a decrease in the surface area of fluorides. These results suggest that β-cyclodextrin in the reaction mixture affects the process of trifluoroacetate decomposition.

To analyze the stability of calcium and magnesium fluorides obtained by this method to pyrohydrolysis, they were annealed in air at 1000 °C for 2 h. A comparison of X-ray patterns of obtained products with the ICDD PDF2 database[11] showed that the behaviors of calcium and magnesium fluorides were different. Magnesium fluoride is completely converted into oxide, which is in agreement with reported data.[6,13] However, calcium fluoride showed no conversion into oxide at all, which underlines its remarkable chemical stability.

Thus, the decomposition of the mixtures of β-cyclodextrin with calcium and magnesium trifluoroacetate hydrates affords corresponding fluorides with high surface areas (up to 80 m$^2$ g$^{-1}$), which are potentially suitable as supports for catalysts.

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## References

1 M. Wojciechowska, M. Zielicski and M. Pietrowski, *J. Fluorine Chem.*, 2003, **120**, 1.
2 O. V. Krylov, *Geterogennyi kataliz* (*Heterogeneous Catalysis*), Akademkniga, Moscow, 2004 (in Russian).
3 M. Wojciechowska, M. Zielicski, A. Malczewska, W. Przystajko and M. Pietrowski, *Appl. Catal., A*, 2006, **298**, 225.
4 J. K. Murthy, U. Groß, S. Rüdiger, E. Ünveren and E. Kemnitz, *J. Fluorine Chem.*, 2004, **125**, 937.
5 J. K. Murthy, U. Groß, S. Rüdiger, E. Kemnitz and J. M. Winfield, *J. Solid State Chem.*, 2006, **179**, 739.
6 S. V. Kuznetsov, V. V. Osiko, E. A. Tkachenko and P. P. Fedorov, *Usp. Khim.*, 2006, **75**, 1193 (*Russ. Chem. Rev.*, 2006, **75**, 1065).
7 T. Yu. Glazunova, A. I. Boltalin and P. P. Fedorov, *Zh. Neorg. Khim.*, 2006, **51**, 1061 (*Russ. J. Inorg. Chem.*, 2006, **51**, 983).
8 H. Dodziuk, *Cyclodextrins and Their Complexes*, Wiley-VCH, Weinheim, 2006.
9 M. Khristov, P. Peshev, O. Angelova, R. Petrova and J. Macicek, *Monatsh. Chem.*, 1998, **129**, 1093.
10 S. Fujihara, M. Tada and T. Kimura, *Thin Solid Films*, 1997, **304**, 252.
11 *PCPDFWIN, Version 2.2*, June 2001, JCPDS-ICDD.
12 H. D. Quan, M. Tamura, R. X. Gao and A. Sekiya, *J. Fluorine Chem.*, 2002, **116**, 65.
13 B. P. Sobolev, *The Rare Earth Trifluorides*, Barcelona, 2001, part 2.

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