

# SYNTHESIS AND CHARACTERIZATION OF SILICALITE-1

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## INTRODUCTION

The influence of trace amounts of  $\text{Cr}^{3+}$  ions in Silicalite-1, synthesis mixtures is discussed. Chromium containing materials are interesting catalysts for the dehydrogenation of the alcohol, alkanes and the oligo- and polymerization of olefins. Chemical composition was NaOH, TPABr,  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{SiO}_2$  and distilled water. The hydrothermal synthesis of Cr-silicalite-1 was carried out by two different methods.

Crystallization took place lined  $30\text{cm}^3$  autoclaves at 553K for 65 and 85 hours under static conditions. The products were filtered washed with ample amounts of distilled water and dried at 493K for 15 minutes.

## I-MATERIALS AND METHODS

Chemicals used are NaOH, TPABr,  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{SiO}_2$  and distilled water. Identification of the different chromium species forming the catalyst sites is still a matter of much debate. In the case of the AIPO molecular sieves it is assumed that chromium is found in the framework as octahedral Cr(III) and partially as a tetrahedral Cr(VI) species, before and after calcination, respectively [1]. In the case of Cr-silicalite-1 no conclusive evidence was presented of dispersed chromium species with redox properties or of the isomorphous substitution of Cr(III) resulting in acidic performance. The ability, however, of cationic hydrated species of Cr(III) to occupy a zeolite framework site, probably as partially bonded

species, has been pointed out in the case of dealumination of zeolite Y with chromium(III) salts at 373K [1,2].

In method **A** all nutrients were mixed simultaneously, followed by shaking at room temperature for 3 hours. Molar oxide ratios were  $1 \text{ SiO}_2 : 0.5 \text{ Na}_2\text{O} : 0.5 \text{ TPA}_2\text{O} : 3.5 \cdot 10^{-4} - 2.9 \cdot 10^{-3} \text{ Cr}_2\text{O}_3 : 100 \text{ H}_2\text{O}$ . Crystallization took place in teflon lined  $35 \text{ cm}^3$  autoclaves at 453K for 65 and 86 hours under static conditions. As a reference, silicalite-1 was grown from the same gel mixture without chromium applying the same time and temperature. In method **B** the synthesis mixture without  $\text{SiO}_2$  ( $0.5 \text{ Na}_2\text{O} : 0.5 \text{ TPA}_2\text{O} : 8.6 \cdot 10^{-2} \text{ Cr}_2\text{O}_3 : 100 \text{ H}_2\text{O}$ ) was pre-aged under static conditions at 453K for 4-6 hours, followed by filtration of the  $\text{Cr}(\text{OH})_3$  precipitate through a  $0.22 \mu\text{m}$  millipore filter. The yellow supernatant was aged with  $\text{SiO}_2$  at room temperature for 8 hours. Molar oxide ratios were  $1 \text{ SiO}_2 : 0.5 \text{ Na}_2\text{O} : 0.5 \text{ TPA}_2\text{O} : 2.5 \cdot 10^{-4} - 3.9 \cdot 10^{-4} \text{ Cr}_2\text{O}_3 : 100 \text{ H}_2\text{O}$ . Crystallization took place at 453K for 3 days under static conditions. The crystal growth was monitored at 438K for 1-7.5 hours in both static and rotating autoclaves. The products were filtered, washed with ample amounts of distilled water and dried at 393K for 15 minutes. Calcination took place at 773K for 5 hours. For products from procedure **A** a colour change from green to yellow was observed, indicating a transition from Cr(III) to Cr(VI). Ion exchange was carried out by shaking in 0.1 M HCl solution for 30 hours with a solution/solid mass ratio of approximately 200. A Cr(VI) on  $\text{SiO}_2$  catalyst was prepared by reaction of  $1 \text{ cm}^3 \text{ CrO}_2\text{Cl}_2$  with 0.5 g  $\text{SiO}_2$  at 473K for 2 hours.

## CHARACTERIZATION

For characterization of the crystals is used a SEM analysis and XRD. Changes in unit cell dimensions were determined by measuring the shift of one particular line from the spectrum compared to the (112) line of quartz, using silicalite - 1 as a reference.

## CRYSTAL GROWTH EFFECTS

**Table 1** shows the influence of the amount of Cr(III) on the crystal size after 65 and 86 hours obtained from procedure **A**. The **c/a** aspect ratio of all elongated prismatic products remains equal to 2.5 - 3. As the amount of chromium in the gel increases, the gel density and the local concentration of nutrients increase, resulting in more nuclei and thus smaller crystals. An increasing amount of non crystalline material on the external surface of the crystals was observed with decreasing Si/Cr ratio.

**Table 1.**

Average crystal size ( $\mu\text{m}$ ) in the c-direction as function of the Si/Cr ratio in the gel for method **A**

time(h)	Si/Cr ratio				
	$\infty$	1400	700	350	157
65h	—	20	10	—	5
86h	150	125	60	40	25

The synthesis mixtures without  $\text{SiO}_2$  used in procedure **B** were analyzed by UV/VIS. The spectra of these solutions before aging at high temperature show peaks at 432nm and 588nm with an intensity ratio of 1.35, indicating monomers and small oligomers containing up to six Cr(III) atoms [3]. The oligomers consist of octahedrally coordinated chromium atoms with bridging OH groups or O atoms. After aging at 453K and filtration these peaks disappeared and large peaks at 377 and 276 nm appear, indicating larger oligomers of chromium and essentially no monomeric Cr(III) species.

**Table 2.**

Typical molar ratios of samples from method **A** and **B**

	synthesis		product		after ion exchange	
	Si/Cr	Si/Na	Si/Cr	Si/Na	Si/Cr	Si/Na
Method <b>A</b>	175	1.0	51	400	163	3614
Method <b>B</b>	1625*	1.0	2600	863	3051	18900

\* after filtration

From the results in **Table 2** it is concluded that after ion exchange with 0.1 M HCl the Si/Cr ratio becomes much smaller in the case of products from method **A** indicating that a large amount of chromium, probably Cr(VI), is unstable. The Si/Cr ratio for products from method **B** does not change significantly.

## CONCLUSIONS

No evidence is found for the isomorphous substitution of Cr(III) in the MFI lattice. This is due to fast oligomerization of Cr(III) and formation of chromium silicate species under

synthesis conditions, which are not suitable as building units in the crystal formation, but still can influence crystal growth. The chromium is presumed to be present in the silicate phase on the external surface of the crystals. After calcination chromium is mainly oxidized to Cr(VI) and probably Cr(V). All other possible chromium species mentioned in literature- Cr(III) as a cation or at a framework site, Cr(V) at a framework site and chromium oxide in the framework channels - are excluded.

#### REFERENCES:

[1] M.R. Klotz, US Pat.4,299,808 (**1981**); US Pat.4,363,718 (**1982**); US Pat.4,405,502 (**1983**); US Pat.4,431,748 (**1984**).

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