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Isomorphous substitution in zeolites

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Abstract

This chapter deals with the isomorphous substitution in the zeolitic framework. Some specific cases among the research works of the authors have been selected. B-MFI, Fe-MFI, Fe-BEA and Fe-MOR zeolites have been examined optimizing the synthesis parameters. B-MFI zeolite has been synthesized in fluoride media, while the other zeolites have been prepared in alkaline media. In all cases isomorphous substitution in the zeolitic structure, even if not complete, is obtained. It should be pointed out that in fluoride media and in presence of K⁺ and Cs⁺ ions more than four boron atoms per unit cell can be incorporated in the MFI structure. **To cite this article:** R. Aiello et al., C. R. Chimie 8 (2005).

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Résumé

Cet article traite de la substitution isomorphe dans la charpente zéolitique. Des cas spécifiques ont été choisis parmi les travaux de recherche des auteurs. Ainsi, les B-MFI, Fe-MFI, Fe-BEA, et Fe-MOR sont examinés du point de vue de leurs paramètres de synthèse. B-MFI a été synthétisé en utilisant la voie fluorure, tandis que les trois autres zéolithes ont été synthétisées en milieu alcalin. Dans tous les cas, la substitution isomorphe a eu lieu, même si elle n'est pas complète, dans la structure zéolitique. Il faut souligner qu'en milieu fluorure et en présence d'ions K⁺ ou Cs⁺, plus de 4 atomes de bore peuvent être introduits par maille dans la structure de MFI. **Pour citer cet article :** R. Aiello et al., C. R. Chimie 8 (2005).

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1. Introduction

The isomorphous substitution of Si by other tetrahedrally coordinated heteroatoms such as B^{III} [1,2] Al^{III} (ZSM-5) [3] Ti^{IV} (TS-1) [4–9], Ga^{III} [10–14] and Fe^{III} [15–18] in small amounts (up to 2–3 wt.%) provides new materials showing specific catalytic properties in oxidation and hydroxylation reactions related to the coordination state of the heteroatom [19]. Moreover, MFI-type materials with trivalent metal present in tetrahedral (T) sites have had a tremendous impact as new shape-selective industrial catalysts having tunable acidic strength. In fact, the acidic strength of the protons in the bridged Si(OH)M^{III} (M = B, Al, Fe, Ga) groups depends on the nature of the trivalent heteroatom. Indeed, the choice of M^{III} critically affects this acidic property according to the sequence Al > Fe = Ga >> B [20–23]. In this paper, we shall emphasize the preparation of B-MFI, Fe-MFI, Fe-BEA and Fe-MOR. All the reported results stem from our research work.

The B-MFI is synthesized in fluoride medium, because, as we shall see, even in presence of tetrapropylammonium bromide (TPABr) more than four B can be introduced per unit cell into the MFI framework. In alkaline media, this can only be achieved if ethylenediamine is used instead of TPABr [24]. On the other hand, we also show, that the alkaline media is also convenient for the isomorphous substitution, provided that appropriate complexing agents are chosen to stabilize the metal ions to be introduced into the zeolitic structure.

2. Results and discussion

2.1. Synthesis of B-MFI using the fluoride route [25]

Borosilicalites of MFI structure were obtained with all the different cations used and over the whole range of concentrations. Table 1 shows the physicochemical characterization data and Table 2 the ¹¹B-NMR data for the different borosilicalite samples obtained with different amounts of H₃BO₃ and different alkali cations. Fig. 1 shows typical ¹¹B-NMR spectra of a precursor and the corresponding calcined samples. The framework tetrahedral boron (T) is characterized by a chemical shift of ca. –3.9 ppm with respect to BF₃–

Table 1

Physicochemical characterization of precursor samples of borosilicalites synthesized from 9 MF–*x* H₃BO₃–10 SiO₂–1.25 TPABr–330 H₂O at 170 °C

<i>x</i>	M	B/u.c. ^a	M/u.c. ^b	TPA/u.c. ^c
0.1	NH ₄	0.8	–	3.8
	Na	1.2	0.5	3.7
	K	1.0	0.7	3.4
	Cs	1.2	0.1	3.8
10	NH ₄	4.4	–	3.5
	Na	6.3	2.0	3.7
	K	8.4	3.2	2.8
	Cs	9.4	3.7	2.4

^a NMR values.

^b Atomic absorption values.

^c Thermal analysis values.

OEt₂ [26]. In the presence of Cs and 10 mols of H₃BO₃ in the initial gel, up to 9.4 tetrahedral B/u.c. can be incorporated in the structure.

However, during the calcination a large amount of boron is eliminated from the structure (Table 2) and the relative amount of boron in the tetrahedral configuration decreases. The extra-framework boron is in a tetrahedral configuration in most of the cases, characterized by chemical shift of –2.0 ppm. Sometimes, some of the extra-framework boron can also take a trigonal configuration, as in the various borates. In this case, the broad NMR line is situated between 5.5 and 27 ppm. The quantitative determination of the trigonal boron was made by considering an average value of the quadrupole coupling constant of ca. 2.5 MHz [27] and using the corrections for the line intensities depending on the value of $\nu_Q^2/\nu_L \cdot \nu_{rot}$ with $\nu_Q = 1.25$ MHz, $\nu_L = 128.3$ MHz and $\nu_{rot} = 9$ kHz [28,29]. The measured intensities were corrected by a factor of $1/0.33 = 3$. No correction was made for the intensities of the lines of the tetrahedral boron ($Q_{cc} = 0.2$ MHz [27]). The total amount of TPA/u.c. is equal to 3.4–3.8 for samples synthesized with 0.1 mols of H₃BO₃. For the K- and Cs-borosilicalite samples, the amount of TPA/u.c. decreases to 3.2 and 2.7 for samples synthesized with 4 mols of H₃BO₃ and to 2.8 and 2.4 for samples obtained with 10 mols of H₃BO₃. The decrease in TPA/u.c. is also indicative of boron incorporation into the MFI structure. Indeed, it was previously observed that the increase in Al in the zeolitic framework was accompanied by a decrease in TPA/u.c. [30]. The M/u.c. remains quite low for low B-containing samples (Table 1). It varies from 0.1 to 0.7. As more

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