PhD proposal

Title : Hydrothermal synthesis : process improvements by emissions measurements

Titre : Les synthèses hydrothermales : amélioration du procédé par l'analyse des émissions

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Research topic :

Zeolite molecular sieves, as a class of crystalline microporous oxides with well-defined pores and cavities of molecular dimensions, are successfully used since more than 60 years in industrial applications. They are mainly used for adsorption and separation processes (CO_2/CH_4, CO_2/N_2 or olefins−paraffins), and catalysis (methanol-to-olefins, selective catalytic reduction of NO_x or cluster encapsulation)[1,2]. Notably, most **zeolites are usually prepared under hydrothermal conditions at temperatures ranging from 80 to 200 °C under autogenous pressure**[3-5]. In the past decades, great discoveries and progress have been made in the field of zeolite synthesis, especially in hydrothermal crystallization synthesis from the 1940s up to the present. **However, the environmental impacts arising from the traditional hydrothermal process have not been looked into until recently, and even less solved**[6-8]**.** Indeed, **the hydrothermal synthesis of zeolite is not a green process**. In general, the traditional and industrial hydrothermal process require the presence of **toxic organic molecules**[6]. **These not-environmental-friendly organic compounds, and unhealthy for workers,** are supposed to react or interact with the different heteroatom sources to form the zeolite crystalline framework during the hydrothermal synthesis. However, it is possible to imagine that they **could also be released, or their derivatives, at elevated temperature and pressure after hydrothermal process. To overcome the above environmental disadvantages** of conventional hydrothermal processes of zeolites, **alternative green routes have recently been sought**[6-8], such as: the reduction or elimination of organic templates, the use of nontoxic templates and template recycling steps, the use of green solvents such as ionic liquids or complete elimination of solvent, and the efficient heating of the starting gels. **However, these promising green alternatives are still fundamental approaches,** stirring up many questions, and **its potential for large-scale applications is still a real challenge.** Thus, replacing the conventional hydrothermal routes of zeolite preparation is still far away.

The PhD project aims at evaluating the potential health hazards caused by hydrothermal synthesis by measuring the real gases emissions and identifying new greener methods for the synthesis. This project requires the development of **new analytical methods** in order to identify the emitted gases, to minimize or even eliminate them, and to correlate their formation to the phenomena taking place in the liquid phase. A better understanding of the complex chemistry taking place in the synthesis reactor is key to decrease its potential adverse effects.

In a preliminary work, a dedicated autoclave was built so as to allow both the hydrothermal synthesis of zeolites and the *in-situ* and real-time analysis of the gases emitted inside the reactor. However, the **development of the *in-situ* analysis techniques** remains to be optimized. On one hand, ***Membrane Inlet Mass Spectrometry* (MIMS)**[9] technique will be employed to identify and then quantify the species emitted during the synthesis. On a second hand, to better understand the **mechanisms of by-products emitted formation**, a deep knowledge of the complex zeolite chemistry is required, leading the possibility to correlate the gas phase and liquid phase and to determine the influential parameters. Thus, **an *operando* analysis by infrared spectroscopy (IR)**. *In-situ* analysis is crucial to understand the formation of intermediate species during hydrothermal synthesis[9-11], but has to overcome the high temperature and high pressure conditions necessary to zeolite formation.

The PhD student will initially validate the autoclave, then develop the *in-situ* and real-time analyses, as well as their adaptation for a combined analysis (IR and MS coupling), and finally make a correlation between the obtained results and literature (results compared with the Occupational Exposure Limits). Concomitant study of the liquid phase and the gaseous phase will be carried out in order to establish a reaction mechanism and to subsequently propose improvements with less environmental and health impact.

The objective of the thesis is then to develop a complete new analysis methodology (MS and IR) with coupled analytical methods allowing real-time and *in-situ* analysis of the liquid phase, of the solid formed and of the gases emitted. These analyzes will allow a fine understanding of the phenomena taking place during the synthesis to improve its health and environmental impact. Several syntheses of interests will be studied to validate the methodology.

PhD candidate should prove to be motivated for a new and unexplored subject leading to new understanding and high perspectives on environmental and health issues. The candidate should have a master's degree in a related field such as environmental chemistry, physical chemistry, analytical chemistry or catalysis. The candidate is expected to build experiments based on mass spectrometry and optical absorption spectroscopy. She/He should be experienced or have good knowledge in material chemistry and catalysis, skills in spectroscopy (MS and IR) will be appreciated.

Références :

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