Process Intensification in Nano Scale: Zeolite-SiC Hybrid Materials for Efficient Microwave Heating

Alexandre F. Young[1], Julia T. de Souza[1], Daniela O. Campos[1], Pedro N. Romano[1], Donato A.G. Aranda[1] and João M.A.R. de Almeida[1*]

[1] *Laboratório de Intensificação de Processos e Catálise, Universidade Federal do Rio de Janeiro, Rio de Janeiro 21941-909 (Brazil);*

**Corresponding author: j.monnerat@iq.ufrj.br*

Highlights

- Process intensification through sustainable non-conventional heating.
- SiC-supported zeolites as promoters of microwave-assisted reactions.
- Electrifiable heating method applied to processes involving nonpolar reagents.

1. Introduction

Employing non-conventional heating through microwaves emerges as an environmentally sustainable option compared to traditional methods, standing out for its electrifiable nature and the ability to promote homogeneous and rapid heating of compounds. In contrast to conventional convection-based processes, microwave heating appears as a promising alternative due to its uniformity and energy efficiency, crucial aspects in the pursuit of greener and more effective methods in chemical processes [1].

Zeolites are widely studied microporous materials finding applications in many different catalytic processes in industry due to its combination of shape selectivity and acidity properties. The synthesis of these materials employing microwave irradiation has been extensively investigated in literature. Most of the effort has been concentrated in tuning synthesis parameters and morphological features through this alternative heating method. However, to the best of our knowledge, very little literature has been devoted to the design of new zeolitic materials that can be efficiently employed in microwave reactors [2]allowing process intensification. In fact, zeolites in acidic form possess very poor microwave adsorption properties [3].

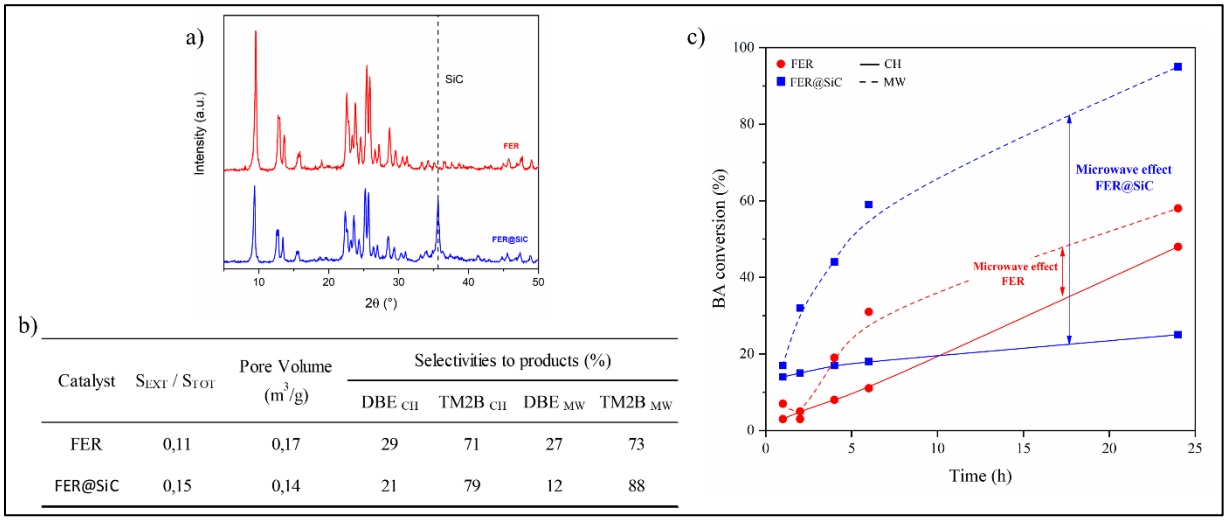
In this work, we present a new strategy for designing zeolitic materials that can be efficiently coupled with microwave heating using SiC, a ceramic known for its high dielectric constant, that has commonly been employed in conventional reactive systems to promote thermal uniformity and heat dissipation [4]. To gain a better understanding of the performance of these materials compared to the conventional ones we employed a Friedel-Crafts alkylation between mesitylene and benzyl alcohol as a model acid catalyzed reaction, using both conventional and microwave heating.

2. Methods

Ferrierite zeolites (FER) were synthesized employing hydrothermal method assisted with microwave heating. Ethylenediamine (En) was used as OSDA and the initial gel with a molar composition of 19.7 En: 1.85 Na_2O: 15.2 SiO_2: 1.0 Al_2O_3: 590.0 H_2O was crystallized in a microwave reactor at 180 °C for 72 hours. In the case of SiC supported FER (FER@SiC), 33% (w./w.) of SiC combined with Poly(diallyldimethylammonium chloride) (PDDA) was added to the initial gels.The acidic forms of the catalysts were obtained through ion exchange with NH_4Cl and further calcination.

For the analysis of synthesized materials, X-ray diffraction (XRD)complemented by N_2 physisorption using the BET, t-plot, and NL-DFT methods were conducted. In the catalytic evaluation, the Friedel-Crafts alkylation reaction between mesitylene and benzyl alcohol (BA) was executed to further assess the textural properties of the catalysts. The experimental setup included 95 mmol of mesitylene, 1 mmol of benzyl alcohol, and 100 mg of zeolite mass, maintained at 120 °C either with conventional heating or in a microwave reactor. GC-FID analysis was performed to assess the conversion of benzyl alcohol and the selectivity for 1,3,5-trimethyl-2-benzylbenzene (TM2B) and dibenzyl ether (DBE).

3. Results and discussion



b)

Catalyst	S_{EXT} / S_{TOT}	Pore Volume (m^3/g)	Selectivities to products (%)			
			DBE_{CH}	$TM2B_{CH}$	DBE_{MW}	$TM2B_{MW}$
FER	0,11	0,17	29	71	27	73
FER@SiC	0,15	0,14	21	79	12	88

Figure 1. XRD profile of the prepared catalysts (a), textural properties and selectivities to products in the Friedel-Crafts alkylation of mesitylene and benzyl alcohol for each catalyst (b) and benzyl alcohol conversion for each catalyst using both conventional heating (solid lines) and microwave heating (dashed lines) (c).

The diffractograms (Figure 1 (a)) clearly depicts that the zeolitic phase of both materials consists of ferrierite crystals. Remarkably, the use of SiC in the gel resulted in a material with a significantly higher ratio of external surface area to total surface area when compared with the pure FER sample. This feature can be attributed to the reduction in the total pore volume (Figure 1 (b)).

The Friedel-Crafts reaction between mesitylene and benzyl alcohol (BA) is very useful to access both catalyst activity and selectivity. The inability of mesitylene molecules to access zeolite pores, unlike BA molecules, makes external surface area a determining factor the formation of alkylation product (TM2B) while self-etherification product (DBE) can be formed inside pores. As expected, the SiC modified ferrierite, due to its larger external surface area, demonstrated an enhanced selectivity for TM2B, under both conventional (CH) and microwave (MW) heating. When we compare catalyst activities by looking at the conversion over time, we can observe that under conventional heating the FER is more efficiently in converting BA than FER@SiC. This was already expected as one third of the FER@SiC is composed of SiC which does not present catalytic activity for the reaction. However, when we compare the same materials under microwave heating the trends invert and FER@SiC outperforms FER. This interesting result can be explained by nanoscale superheating of SiC nanoparticles that are near the zeolite acid sites under microwave heating.

4. Conclusions

In this work we present a new strategy for designing zeolitic materials that are suitable to be employed with microwave heating. These materials even possessing less catalytic sites than the conventional materials outperform them under microwave irradiation due to its higher microwave adsorption properties. This new material opens the way to explore process intensification and electrification of reactions involving reactants with poor microwave absorption properties catalyzed by this new zeolite-SiC hybrid materials.

References

[1] A. Deneyer; Q. Ke; J. Devos; M. Dusselier. Chemistry of Materials 32 (2020) 4884-4919
[2] F. Kishimoto; T. Yoshioka; R. Ishibashi; H. Yamada; K. Muraoka; H. Taniguchi; T. Wakihara; K. Takanabe. Science Advances 9 (2023) eadi1744
[3] B. I. Whittington; N. B. Milestone. Zeolites 12 (1992) 815-818
[4] A. A. Dabbawala; B. V. Vaithilingam; H. Mittal; Y. A. Wahedi; S. Khan; T. Joseph; G. Singaravel; S. Morin; M. Berthod; S. M. Alhassan. Applied Catalysis A: General 608 (2020)

Keywords
Microwave heating; SiC-supported zeolites; Friedel-Crafts alkylation; Process intensification.