



DEVELOPMENT OF CATALYSTS FOR THE PHOTOCATALYTIC SYNTHESIS OF AMMONIA

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Objectives

Zeolites are microporous aluminosilicates with an organised pore structure, widely used as heterogeneous catalysts in several chemical processes. Techniques for synthesising structures with pore systems similar to those of zeolites have been developed in recent decades, making it possible to modify pore size and the composition of these structures, thereby conferring different surface potentials and broadening their application field. Among these applications is the photochemical production of ammonia (NH_3), an important substance in fertiliser production: 80% of its consumption is in this sector [1]. Thus, this work proposes to study an alternative photocatalytic route for the production of ammonia, using aluminosilicate-based structures modified by the addition of iron during synthesis, creating more favourable conditions for their use as photocatalysts in ammonia production.

Methods and Procedures

The synthesis of the Fe-Al-Si-MCM structures was based on the production method described by Martins et al. [2] and Souza et al. [3]. This is a hydrothermal synthesis from a “sol-gel” solution with molar composition $1\text{SiO}_2:0.016\text{Al}_2\text{O}_3:0.27\text{Na}_2\text{O} : 0.27\text{CTMABr} : 100\text{H}_2\text{O}:\text{xFe}$, involving the mixture of the following solutions:

silicon source (pyrogenic silica) for construction of the walls, surfactant solution (structure-directing agent for pore system formation – CTABr), and heteroatom solution (Al and Fe) for the creation of active sites on the structure surface. The mixture was then subjected to the hydrothermal synthesis proper in a stainless steel autoclave lined with Teflon at $140\text{ }^\circ\text{C}$ for 48 h. Finally, the solid structures obtained were calcined at $550\text{ }^\circ\text{C}$ for 6 h to unblock the pores and subjected to characterisation analyses using XRD and BET techniques.

The photocatalytic synthesis was carried out in an annular-type photochemical reactor, equipped with a concentric tubular UV-C lamp emitting monochromatically at 254 nm (4.88 eV). The reactor was fed by a peristaltic pump that circulated the reaction solution from a 500 ml glass flask containing the catalyst solution (1 g catalyst / L solution) under constant mechanical stirring at 390 rpm and nitrogen bubbling to ensure system saturation ($\sim 17\text{ mg/kg}$ at $30\text{ }^\circ\text{C}$). Aliquots of 5 ml were collected every 30 minutes of reaction to assess ammonia production by the mentioned process. Sample analysis was based on the Berthelot reaction [4].

Results

Table 1 – Experimental results

#	% Fe (mol)	Fe/Al (mol)	A _{BET} (m ² /g)	Dp (nm)	tipo estrutura	[NH ₃] (ppm)
1	1,16	2,0	422,73	9,088	MCM-41	0,023
2	2,30	2,0	676,99	10,39	MCM-41	0,080
3	1,16	2,0	866,76	3,861	MCM-41	0,03
4	10,0	18,2	420,01	12,28	Indef	0,029
5	5,02	8,8	486,47	12,81	Indef	0,023
6	2,30	4,0	574,63	13,03	Indef	0,080

Initially, it was found that the most organised structures (MCM-41) were those synthesised with the lowest iron content and lowest Fe/Al ratio.

When the concentration of iron heteroatom incorporated into the synthesis was increased, the structures no longer showed an organised pore system, an effect that requires further investigation.

Regarding ammonia production, an increase in the amount produced was observed with the initial increase of iron content in the catalytic structures. However, despite samples 4 and 5 having the highest iron concentrations, ammonia formation was lower than in those with intermediate contents of 2.3%. A possible explanation for this phenomenon is that, as catalysts 4 and 5 contained the highest iron contents, they had greater density, precipitated at the bottom of the flask, and were not fully transferred to the reactor, thereby reducing ammonia production efficiency.

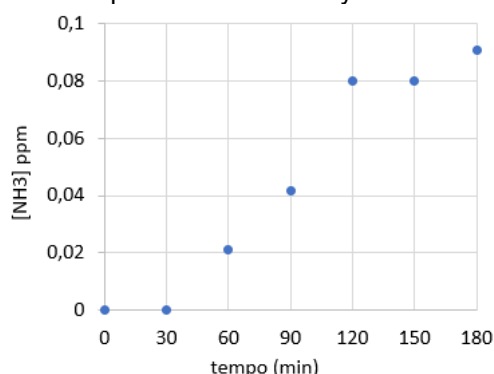


Figure 1: Ammonia concentration profile over time during synthesis with catalyst "sample 2".

A rising profile of ammonia concentration in solution is observed over time, apparently reaching a plateau at longer reaction times.

New studies will be carried out to confirm this behaviour and understand the reasons for the plateau, since nitrogen (the reactant) continues being fed into the system.

Conclusions

It was possible to obtain and analyse mesoporous structures incorporated with different iron concentrations and to evaluate their effects on photocatalytic ammonia production, with the best results obtained with 2.3% Fe. For improved results with the 5% and 10% samples, a new reactor will be used in future tests.

The authors declare no conflict of interest. Author BR and RC conceived and planned the study. Author GVP carried out data collection and analysis. Authors GVP and RC participated in the writing and final review of the manuscript. All authors approved the final version of the abstract.

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