



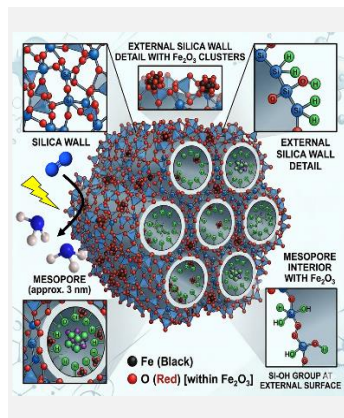
Iron- and Aluminum-Modified Mesoporous Silicates for Photocatalytic Nitrogen Reduction

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Over the past decades, the advancement of climate change, driven mainly by the burning of fossil fuels, has intensified alarmingly, demanding sustainable solutions from the chemical industry. In this context, the search for clean energy alternatives stands out, such as the production of ammonia and its conversion into hydrogen, whose feasibility has been studied through the photoreduction of nitrogen (N_2) in the presence of water using structured catalysts. Hence, this work evaluated the synthesis of mesoporous silica-based molecular sieves modified with iron and aluminum metal salts, aiming to improve their acid-base properties and photocatalytic performance. The results were limited to a maximum ammonia concentration of approximately 0.20–0.26 ppm, highlighting that the catalysts were subjected to ammonium fluoride etching and indicating pathways to more efficient and accessible catalysts for ammonia production.

Introduction

Zeolites are microporous aluminosilicates with highly ordered pore structures, widely used as heterogeneous catalysts in several chemical processes. However, their micropores limit the diffusion of bulky reactants and products, restricting their application in certain reactions of interest. Thus, techniques to synthesize materials with zeolite-like structures but with mesoporous systems have been developed in recent decades. In addition, it has been demonstrated that modifying the composition of these materials allows tuning of their surface properties, expanding their range of applications. Among these applications, photocatalytic ammonia (NH_3) production has attracted attention due to its importance, particularly in fertilizer production, which accounts for approximately 80% of global ammonia consumption [1]. Since the conventional Haber–Bosch process operates at high temperatures and pressures and accounts for about 1% of global greenhouse gas emissions [1], this work proposes an alternative photocatalytic route for ammonia synthesis. The approach employed aluminosilicate-based structures modified with iron to enhance surface properties and improve photocatalyst performance for ammonia production.

Material and Methods

The synthesis of Fe–Al–Si–MCM structures was based on the method described by Martins et al. [2] and Souza et al. [3]. Briefly, it consisted of a hydrothermal sol–gel synthesis, using fumed silica (Aerosil) as silica source and Cetyltrimethylammonium bromide (CTABr) as

structure-directing agent, with a molar composition of $1SiO_2:0.016Al_2O_3:0.27Na_2O:0.27CTMABr:100H_2O:xFe$, where x varied from 0 to 35. The resulting mixture was then transferred to a Teflon-lined autoclave and subjected to hydrothermal treatment at 140 °C for 48 h. Finally, the obtained structures were calcined at 550 °C for 6 h to remove the surfactant and generate the mesoporous structure. Some synthesized samples were etched with a 30 w/% aqueous ammonium fluoride (NH_4F) solution under stirring for 75 min at room temperature, followed by filtration, washing, and drying at 110 °C overnight. This treatment aimed to increase pore size and evaluate its effect on photocatalytic ammonia synthesis. Additionally, pure silica structures were impregnated with iron to achieve Fe/Si molar ratios of 5% and 10%. Finally, the materials were characterized by low-angle X-ray diffraction and by nitrogen physisorption.

Photocatalytic experiments were carried out in a reactor equipped with a UV-C lamp (254 nm, 4.88 eV) placed inside a glass tube, surrounded by another tube containing the catalyst suspension (0.2 g/L) in distilled water. The system was maintained under magnetic stirring, and an ultrasonic bath was applied prior to the reaction to improve catalyst dispersion. Agitation and continuous nitrogen bubbling were used throughout the experiment to ensure saturation (~17 mg/kg at 30 °C). Ammonia concentration was determined by monitoring the profile for up to 180 min after the UV lamp was turned on, with aliquots collected every 30 min. Ammonia quantification was performed using the



Berthelot method [4]. Briefly, 0.4 mL of a phenol–nitroprusside–isopropanol solution was added to 5 mL of filtered sample (0.22 μm membrane), followed by 0.4 mL of a sodium hydroxide–sodium hypochlorite solution. The absorbance was measured at 670 nm using a UV–Vis spectrophotometer.

Results and Discussion

Overall, samples with Si/Al = 16 (samples 6, 7, 8, and 10) showed superior photocatalytic performance compared to those with Si/Al = 32, due to the higher aluminum content, which enhances the formation of active sites and improves iron anchoring. The increase in surfactant concentration (CTABr/Si = 0.54) also led to higher efficiencies for these structures compared to

non-etched ones, despite similar surface areas and pore diameters, indicating a positive effect on catalytic performance. Etched structures increased NH_3 production, indicating a more efficient diffusion of chemical species into the mesopores of the catalysts. Finally, the impregnation of etched structures enhanced Fe anchoring and active site strength, resulting in better catalytic performance, improved activity, even at lower Fe concentration (sample 1 compared to etched ones). Those structures allowed NH_3 production to reach approximately 0.20 ppm. Therefore, photocatalytic performance was found to depend primarily on the chemical-physical nature of the active sites and on the interaction of Fe species at the surface.



Figure 1. Batch reactor

Table 1. Characteristics of the Catalysts Employed and Ammonia Concentration

Sample	[Fe] (m%)	Si/CTABr ratio	Si/Al ratio	S_{BET} (m^2/g)	V_p (cm^3/g)	d_p (nm)	[NH ₃] (ppm)
2	5.7	0.27	32	977.7	0.932	3.86	0.089
3	10.5	0.27	32	658	1.58	13.0	0.099
4	20.9	0.27	32	504	1.56	12.8	0.077
5	35.5	0.27	32	436	1.316	12.3	0.122
6	10.5	0.27	16	886.5	1.53	8.65	0.066
7	10.5	0.54	16	990	1.64	7.83	0.124
8	20.9	0.54	16	677.5	1.2	6.73	0.19
9	10.5	0.54	32	798.9	1.8	12.5	0.199
10	20.9	0.27	16	763	1.28	7.59	0.176
4 etched	20.9	0.27	32	473	1.245	10.5	0.19
6 etched	10.5	0.27	16	566	1.18	10.7	0.284
9 etched	20.9	0.27	16	451	1.04	10.7	0.195
1 impregn.	5.1	0.27	32	471	1.425	17.2	0.197
1 impregn.	10	0.27	32	417	0.59	7.53	0.147

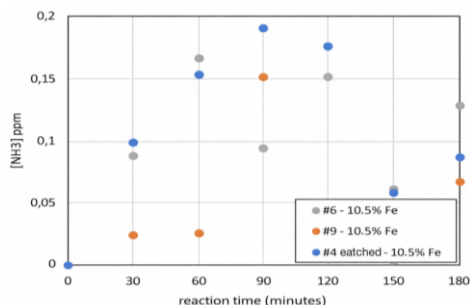


Figure 2. Ammonia concentration profile along the reaction.

Conclusions

It was possible to obtain and analyze mesoporous structures with different iron concentrations and to evaluate their effects on photocatalytic ammonia production. with the best performance at Si/Al = 16. thereby highlighting the role of aluminum in nitrogen activation. Furthermore, photocatalytic activity was found to depend more on chemical factors, such as

active Fe sites, Si/Al ratio, and structural defects, rather than on surface area or structural order. Finally. fluoride treatment and Fe impregnation effectively generated defects and strengthened active sites, thereby improving ammonia yield.

References

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