Ti-MCM-22 catalysts for selective oxidation of organic sulphides by H_2O_2

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Significance and Relevance

In recent years, environmental regulations on sulphur reduction in petroleum processing have become stricter. The widely used hydrodesulphurization (HDS) process demands high temperatures, pressure, and catalysts, increasing energy consumption and costs.[1] Additionally, handling sulphur-containing waste remains a challenge. Oxidative desulphurization (ODS) is emerging as a promising alternative, aiding in zero-sulphur fuel production and waste removal. This process also plays a crucial role in pharmaceuticals, as the oxidation of aromatic compounds like diphenyl sulphide (Ph_2S) produces key reagents for drug synthesis. While strong oxidants such as $KMnO_4$ are effective, they generate hazardous waste.[2] Hydrogen peroxide (H_2O_2) offers a greener alternative but requires catalytic conditions for efficiency. Ti-based catalysts have shown potential, though debate continues over the precise active sites in selective oxidation.

Preferred and 2nd choice for the topic: Green chemistry and biomass transformation, renewable resources conversion or Sustainable and clean energy production and transport.
Preferred presentation: Poster

Introduction and Motivations

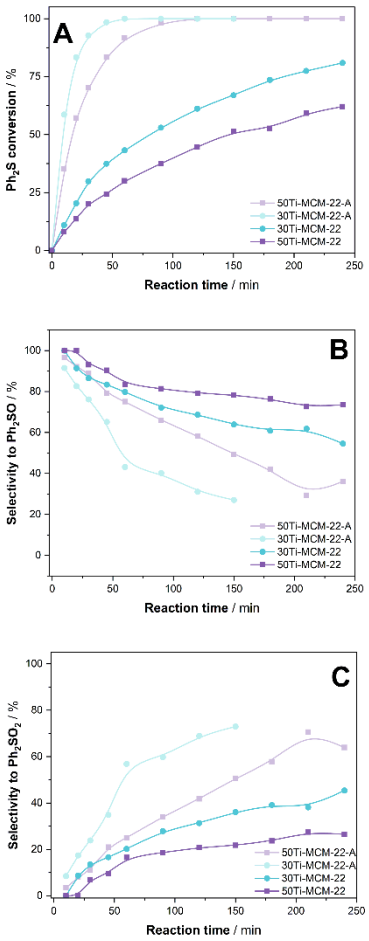
The MWW-structured zeolite, with MCM-22 as its key representative, is a notable example of a layered zeolite, obtained by calcining its precursor, MCM-22(P).[3] MCM-22 is widely utilized in hydrocarbon conversion and holds potential for various catalytic applications. Conventional zeolites like MCM-22 are crystalline aluminosilicates, but incorporating other metal cations into MWW structures enhances their catalytic properties. Specifically, introducing heteroatoms such as titanium into the zeolite framework expands possibilities for tailored applications in zeolite synthesis. Titanium-containing porous silica systems were found to be promising catalysts for the application in selective oxidation of organic sulphides by hydrogen peroxide.[2] Hence, the main goal of the presented studies was to determine the efficiency of the selective catalytic oxidation of Ph_2S by H_2O_2 in the presence of Ti-MCM-22 zeolite.

Materials and Methods

In this study, a modern heteroatom layered Ti-MCM-22(P) zeolite was synthesized by a one-pot method with two different Si/Ti molar ratios (30 and 50). The resulting layered precursors were then treated with nitric acid (HNO_3) to remove extra-lattice titanium species, ensuring that only framework titanium cations remained in the final material. This approach differed from the untreated precursor, which underwent calcination without prior acid treatment. The primary objective was to investigate how titanium aggregation affects the efficiency of selective catalytic oxidation of organic sulphides using H_2O_2. The synthesized zeolites were analyzed for their chemical composition (ICP-OES), structure (XRD, UV-vis DRS), textural properties (low-temperature N_2 sorption), and surface acidity (NH_3-TPD).

Results and Discussion

The study concluded that the synthesized Ti-MWW derivatives exhibited a high conversion rate and excellent selectivity toward sulfone (Figure 1). The variations in catalytic activity between the untreated zeolites (30Ti-MCM-22 and 50Ti-MCM-22) and those subjected to acid treatment during synthesis (30Ti-MCM-22-A and 50Ti-MCM-22-A) were attributed to differences in the form and aggregation of titanium within the materials.



After 240 minutes of reaction, Ph_2S conversion was achieved at the level of 62 and 81%, respectively, for samples with increasing titanium content in the material – 50Ti-MCM-22 and 30Ti-MCM-22 (Figure 1 A). The main reaction product for both samples is Ph_2SO (Figure 1 B), with selectivity at the level of 73% and 56% for 50Ti-MCM-22 and 30Ti-MCM-22, respectively. It can be observed that in the case when the complete conversion of the Ph2S substrate was not achieved, the oxidation of Ph_2SO to Ph_2SO_2 is less efficient (Figure 1 C). Samples refluxed with acid, despite having lower titanium content due to Ti extraction, exhibit better catalytic properties. Therefore, it can be stated that the key role in this case is played by monomeric, tetrahedrally coordinated titanium cations. In the case of acid-treated zeolites, their presence was confirmed by the analysis of UV-vis DRS (Figure 2). Under conditions of the HNO_3 modification at the synthesis stage, extra-lattice forms of titanium were extracted from the framework and a structure was obtained in which titanium was introduced mainly in the form of monomeric, tetrahedrally coordinated cations. For these materials, the absorption maximum occurs at about 230 nm, indicating the presence of mainly monomeric, tetrahedrally coordinated titanium cations.[4] In the spectra recorded for materials that were not subjected to such modification, the presence of more polymerized forms of titanium was identified. In those cases, absorption maxima occur at about 275 nm. They are related to the presence of extra-lattice, octahedrally coordinated titanium cations. The shoulder above 320 nm can be attributed to the presence of small amounts of TiO_2.[4]

Figure 1 Catalytic test results for Ti-MWW derivatives; **A**: Ph_2S conversion, **B**: selectivity to Ph_2SO, **C**: selectivity to Ph_2SO_2.

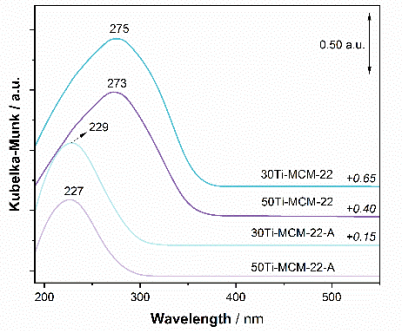


Figure 2 UV-vis DR spectra recorded for the Ti-MWW derivatives.

References

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