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Hydrogen Evolution and Photochemical Stability of Sepiolite/UiO-66-NH_2 Composites

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Abstract

Adding a metal–organic framework (MOF) to sepiolite may offer new ways to tune its photocatalytic properties, but a greater MOF content does not necessarily lead to more hydrogen. Here, sepiolite/UiO-66(Zr)-NH_2 composites with different nominal compositions were examined to establish how MOF distribution affects their structure, photoresponse and behaviour during irradiation. Structural and microscopic analyses revealed a gradual change from exposed sepiolite fibres to MOF-rich aggregates, accompanied by changes in pore accessibility. SUiO-32 showed the strongest photocurrent and retained its relative linker-associated infrared features more effectively than the other composites after irradiation. Yet its photoelectrochemical response was not matched by a corresponding advantage in hydrogen evolution from aqueous methanol. Photocatalyst-free irradiation of the same mixture also generated substantial hydrogen, complicating any assignment of the total yield to catalysis. In pure water, hydrogen formation increased with MOF enrichment, but changes in MOF-derived domains raised the possibility that framework-associated organics participated in the reaction. The results demonstrate why hydrogen evolution, photolysis and catalyst stability need to be considered together when evaluating MOF–clay photocatalysts.

1. Introduction

Metal–organic frameworks offer considerable freedom in the design of photoresponsive materials, yet their performance depends on more than their ability to absorb light. Charges must reach accessible reaction sites, and the framework must withstand the conditions under which it operates. UiO-66(Zr)-NH_2 is of interest because its amino-functionalised linker contributes to light absorption, while sepiolite offers a fibrous, hydroxyl-rich surface on which the MOF can be distributed. Such a combination may improve interfacial contact, but excessive MOF growth can also cover the clay surface and produce aggregates [1]. Sepiolite itself cannot simply be treated as an inactive carrier: its ability to support hydrogen formation under UV-C irradiation has been reported previously [2].

This makes MOF loading a question of balance rather than maximisation. Equally important is the origin of the hydrogen detected during irradiation. Methanol can undergo direct photochemical reactions, while the organic components of UiO-66-NH_2 may change under reactive conditions [5, 6]. We therefore compared a series of sepiolite/UiO-66-NH_2 composites with both parent materials, tested hydrogen evolution in methanol–water and pure water, and examined the solids before and after irradiation. This approach allows changes in photoresponse to be interpreted alongside material preservation and appropriate controls.

2. Materials and Methods

2.1. Materials and preparation

The composites (SUiO-14, SUiO-23, SUiO-32 and SUiO-41) were prepared using an adapted solvothermal procedure for growing UiO-66-NH_2 in the presence of sepiolite [3]. The sample names denote nominal compositions calculated from the synthesis precursors; they should not be taken as measured MOF mass fractions. Unmodified sepiolite and separately synthesised UiO-66-NH_2 served as references.

2.2. Characterisation

Powder X-ray diffraction (XRD) and attenuated-total-reflectance Fourier-transform infrared spectroscopy (ATR–FTIR) were used to follow crystalline phases and characteristic chemical groups. Scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM–EDS) provided information on aggregate morphology and local elemental composition. Nitrogen physisorption characterised the accessible pore structure, with apparent BET surface areas evaluated using established consistency criteria [4]. Optical absorption, photoluminescence, transient photocurrent and thermal behaviour were examined using complementary methods. XRD, FTIR and microscopy were repeated on recovered solids to assess changes associated with irradiation.

2.3. Hydrogen evolution and controls

Hydrogen evolution was measured in sealed, argon-purged batch suspensions under UV-C irradiation. Methanol–water mixtures were compared with pure water, where no external sacrificial electron donor had been added. Gas chromatography with thermal conductivity detection was used to quantify the evolved hydrogen. Fresh and pre-irradiated samples were tested alongside dark and photocatalyst-free controls. The photolysis controls were particularly important because they established how much of the observed response could arise without a solid catalyst.

3. Results and Discussion

3.1. Structural, textural and irradiation response

The diffraction patterns showed that the sepiolite framework and crystalline UiO-66-NH_2 coexist across the composite series. As the nominal MOF content increased, its characteristic reflections became more apparent, while sepiolite remained identifiable. This progression was also evident in the micrographs. Clay-rich samples retained visibly exposed fibres; at higher loadings, granular MOF-rich deposits increasingly obscured them and eventually formed substantial aggregates. The local elemental composition followed the same general trend. Porosity, however, did not increase steadily with MOF content. The first additions reduced accessible surface area and microporosity, consistent with partial blockage of the clay pore network. With further MOF enrichment, the contribution of the porous framework became more prominent and pore accessibility increased.

Irradiation left the principal diffraction features largely intact, although this should not be mistaken for proof that the framework was chemically unchanged. The infrared spectra revealed shifts in the relative contributions of linker-associated and silicate bands, especially after exposure in pure water. Of the

composites, SUiO-32 retained the most similar relative linker-to-silicate spectral signature. Local SEM–EDS measurements also suggested changes in the distribution of zirconium-rich regions, most noticeably in the MOF-rich material. Together, these observations point to composition- and medium-dependent alterations. They do not, on their own, distinguish linker degradation from loss or redistribution of MOF-containing particles.

3.2. Optical, photoelectrochemical and thermal response

The optical measurements reflected both the changing phase composition and the complex way in which these powders scatter light. With increasing MOF content, the absorption onset moved slightly toward longer wavelengths, but this trend should not be interpreted as a definitive change in an intrinsic band gap. Photoluminescence likewise varied across the series without simply tracking MOF loading. A clearer contrast emerged in the chopped-light photocurrent measurements: SUiO-32 produced the strongest electrode response, whereas the most heavily agglomerated composite responded only weakly. This suggests that the accessibility and connectivity of photoresponsive domains matter as much as their abundance. SUiO-32 also displayed the highest-temperature principal thermal decomposition event within the series. Although consistent with a distinct thermal response, that observation does not by itself establish photochemical durability.

3.3. Hydrogen evolution and interpretation

The hydrogen-evolution experiments told a different story from the electrode measurements. In aqueous methanol, adding more UiO-66-NH_2 did not consistently improve hydrogen production. Sepiolite and the clay-rich composites remained competitive, reinforcing the view that the mineral contributes to the overall system rather than merely supporting the MOF. More importantly, irradiation of the methanol–water mixture without any photocatalyst produced a substantial hydrogen signal. The total gas yield therefore includes a photolytic background and cannot be attributed wholly to a catalytic pathway. Pre-irradiation generally increased the hydrogen yields of the MOF-containing samples, but these changes did not follow the order of their photocurrents. Charge collection at a coated electrode and hydrogen formation in a stirred suspension probe different processes and should not be expected to correlate directly.

A different tendency appeared in pure water: hydrogen evolution generally became more pronounced as the materials grew richer in MOF, particularly after pre-irradiation. At the same time, FTIR and SEM–EDS indicated changes in linker-associated environments and MOF-rich regions. One plausible explanation is that framework-derived or residual organic species are oxidised and thereby provide electrons for hydrogen formation [5, 6]. The evidence remains indirect, however. Changes in the accessibility of reactive sites, particle distribution and interfacial charge transfer may also influence the measured response. Without identifying oxidation products and measuring the accompanying oxygen evolution, hydrogen detected in pure water must not be equated with demonstrated overall water splitting [7].

4. Conclusions

The effect of UiO-66-NH_2 loading on sepiolite-based composites proved to be more complex than a simple increase in photoactivity. Additional MOF changed the morphology, porosity and light response, but did not provide a consistent benefit for hydrogen evolution in aqueous methanol. SUiO-32 offered a particularly promising combination of photoelectrochemical behaviour and retention of linker-related spectral features after irradiation; it should nevertheless be viewed as a candidate for further study, not an established optimum for hydrogen production. The substantial photolytic contribution in methanol and the possibility of framework-associated oxidation in water remain central limitations. Future work should identify the relevant oxidation pathways, assess framework integrity directly and seek better interfacial charge utilisation without relying on higher MOF loading alone.

Declarations

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