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Hot Paper

Unveiling the Potential of Heterogeneous Catalysts for Molecular Solar Thermal Systems

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Solar energy utilization has gained considerable attention due to its abundance and renewability. However, its intermittent nature presents a challenge in harnessing its full potential. The development of energy storing compounds capable of capturing and releasing solar energy on demand has emerged as a potential solution. These compounds undergo a photochemical transformation that results in a high-energy metastable photoisomer, which stores solar energy in the form of chemical bonds and can release it as heat when required. Such systems are referred to as Molecular Solar Thermal (MOST)-systems. Although the photoisomerization of MOST systems has been vastly studied, its back-conversion, particularly using heteroge-

neous catalysts, is still underexplored and the development of effective catalysts for releasing stored energy is crucial. Herein we compare the performance of 27 heterogeneous catalysts releasing the stored energy in an efficient Norbornadiene/Quadricyclane (NBD/QC) MOST system. We report the first benchmarking of heterogeneous catalysts for a MOST system using a robust comparison method of the catalysts' activity and monitoring the conversion using UV-Visible (UV-Vis) spectroscopy. Our findings provide insights into the development of effective catalysts for MOST systems. We anticipate that our assay will reveal the necessity of further investigation on heterogeneous catalysis.

Introduction

In recent years, the need for sustainable energy solutions has become increasingly urgent due to the high demands of our modern world.^[1] Energy-storing compounds based on solar-

induced photoisomerization reactions have emerged as a promising avenue for addressing this challenge. These compounds undergo a photochemical transformation, resulting in the generation of a high-energy metastable photoisomer that stores solar energy in the form of chemical bonds. This energy can be released as heat when needed, making these systems ideal for providing energy on demand. Known as MOlecular Solar Thermal (MOST) systems,^[2–5] they hold significant potential for revolutionizing the way we generate and store energy.^[22–25]

To be used as MOST systems, molecules must possess several key features (Figure 1a). First, they should absorb solar light efficiently, thanks to a good match between the solar spectrum and their absorption spectrum. Secondly, they should provide a high energy storage density, balancing storage energy and molecular weight. Finally, the back-conversion barrier from the high-energy photoisomer to the parent molecule should be large enough to store energy without reverting spontaneously, but easy to overcome when using a catalyst. In recent developments within the field, there have been endeavors to employ heterogeneous catalysts as triggers for the heat release in NBD/QC based MOST systems,^[6–15] particularly cobalt,^[7,16,22] and gold-based ones.^[3,18–20] Additional desirable features for its integration into a device include a closed-cycle system that does not involve hazardous chemical elements in its daily performance.

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Experimental Section

Protocol for Batch Catalytic Testing

All catalysts tested were provided by Johnson Matthey (JM) and we selected the one of the best performing NBD/QC molecule-pair^[17]

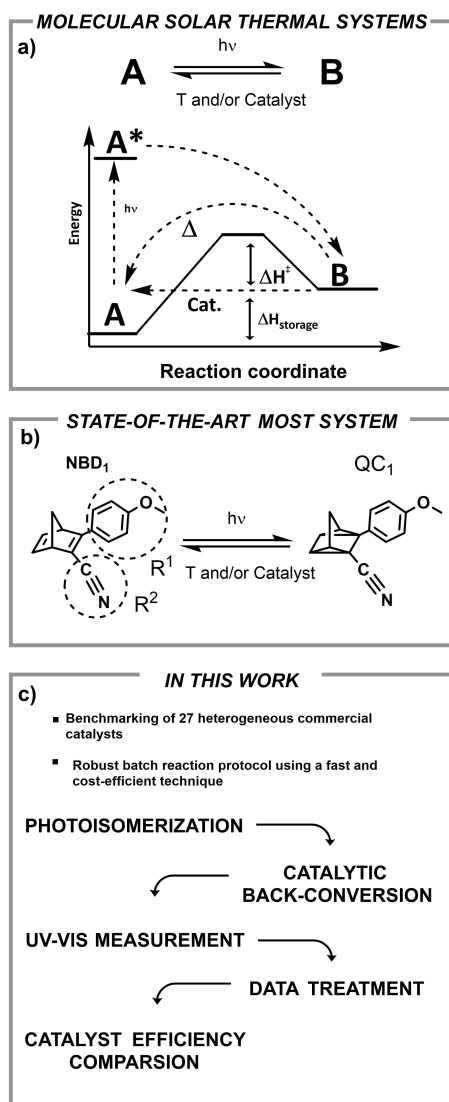


Figure 1. a) Schematic view of a MOST system. b) 2-Cyano-3-(4-methoxyphenyl)-norbornadiene (NBD1) isomerization into 2-Cyano-3-(4-methoxyphenyl)-quadricyclane (QC1). c) Output of this work.

to develop our protocol (see Figure 1(b) for the molecule studied and Table S1 and Table S2 from the Supporting Information for the detailed list of catalysts). Then, we developed a simple protocol to compare different heterogeneous catalysts robustly and rapidly using UV-Vis spectroscopy to characterize the conversion, thanks to the very small overlap between NBD and QC absorption.

To start the catalyst testing, NBD1 is first solubilized in toluene and then subjected to full irradiation towards QC1 using a Luzchem™ photoreactor that utilizes 14×8 W lamps with alternated UV-A and UV-B wavelength emission (see Figure 2). The duration of irradiation varies depending on the concentration and volume of the solution, but it typically ranges around 30 min for 10 mL of NBD1 at 10^{-4} M concentration. To confirm the conversion of NBD1 to QC1, UV-Vis spectroscopy measurements are utilized ($\lambda_{\text{NBD1}} = 326$ nm, $\lambda_{\text{QC1}} = 290$ nm). A threshold below 5% of the intensity of NBD1 absorption band determines when the NBD1 has been fully irradiated. A calibration curve was prepared to assess this value and the range of linearity of the curve spans from 1×10^{-5} M to 1×10^{-4} M (see Figure 2). The value of absorption intensity of the NBD1 at 340 nm is used to calculate the concentration, to minimize the overlap

between NBD1 and QC1 absorption bands, which is significant at the absorption maximum at 326 nm. After complete irradiation of the sample, catalysis was performed to investigate the activity of several catalysts in the back-conversion process.

To assess the catalyst efficiency, a weight ratio of 10% w/w catalyst with respect to NBD1 is used, which typically involves adding the NBD1 solution to a vial containing 1 mg of catalyst per 10 mg of NBD1 in 10 mL of toluene, resulting in an NBD1 concentration of 4.5×10^{-3} M. Due to the concentration exceeding the detection range of the UV-Vis spectrometer, dilution is required prior to measurement, typically at a ratio of 1:100, resulting in an NBD1 concentration of 4.5×10^{-5} M before irradiation. In addition, solution is filtrated through a 0.22 μm PTFE filter to avoid dispersion artifacts in the measurement (See Figure S35 in the Supporting Information). Photometric quantification using UV-Vis has the disadvantage that does not allow to identify trace amounts of byproducts. An NMR experiment was set up (see Figure S34) to thoroughly assess the full conversion of NBD1 into QC1 and the catalyzed back-reaction, while also discarding the presence of any byproduct.

After recording the UV-Vis spectrum, the concentration of NBD1 is calculated using a previously established calibration curve. This enables a straightforward comparison of catalyst efficiency.

To recover the NBD1 from the catalytic media, a crystallization process was followed. The process involved the following steps: i) removing the catalyst from the solution by filtration using a 0.22 μm PTFE filter; ii) thoroughly drying the solution to eliminate any traces of toluene; iii) diluting the oily residue in the minimum amount of ethyl acetate necessary to dissolve the 10 mg of NBD1; iv) subsequently adding three times more hexane. It is worth noting that smaller volumes yield better results due to the higher final concentration achieved; v) heating the solution using a heat gun until complete solubility is achieved; and vi) allowing it to crystallize overnight in a freezer. The quantity of solvent used may vary, but a reasonable approximation is around 1 mL of ethyl acetate and 3 mL of hexane per experiment (10 mL of toluene for every 10 mg of NBD1). Typically, the various experiments were recovered simultaneously to increase concentration and facilitate crystallization.

The comparative method developed in this study employs minimal amounts of catalyst and generates a low waste of NBD1 and solvents, particularly when considering the recrystallization process. Compared to traditional NMR experiments, the use of UV-Vis spectroscopy provides a cost- and time-effective alternative, which is easily replicable and yields robust results across a variety of catalysts, including homogeneous ones.

Results and Discussion

A closer look at the 10 best-performing catalysts at shorter times showed that only 5 Pt-based catalysts convert more than 50% of QC to NBD and that two Pt catalysts over carbon support outperform the rest of the pool reaching at least 90% conversion around the 4 h of catalysis (Figure 3). Also, platinum-based catalysts represent 9 of the 10 best-performing catalysts, indicating the privileged role of this metal in the back-conversion reaction. We then analyzed the back-conversion at longer times (3 days) to explore the different factors that may affect the catalyst activity (Figure 4). We began by analyzing similar catalysts with different particle sizes, which can be extremely important when moving MOST systems to flow regimes.

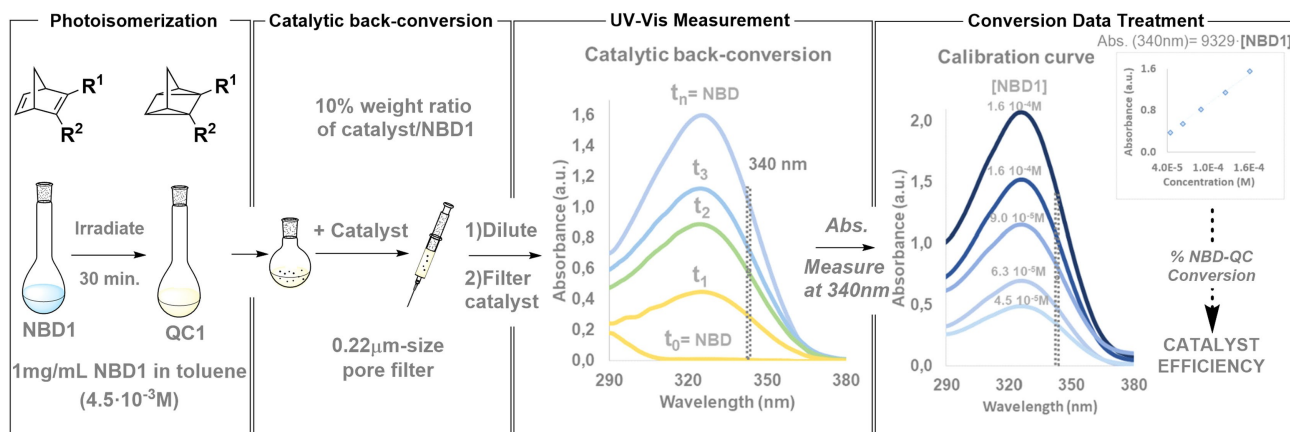


Figure 2. Schematic view of the catalyst comparison protocol. First, NBD1 is irradiated under UV-A/B light for 30 min.; then the catalyst is added at a 10% w/w to the sample. For every data point over time, an aliquot is diluted and filtered before the measurement. UV-Vis spectra of QC1 catalysis into NBD1 at different irradiation times are recorded. Measurements at 340 nm are interpolated into the NBD1 calibration curve and the percentage of back-conversion is calculated. Inset graph corresponds to NBD1 calibration curve.

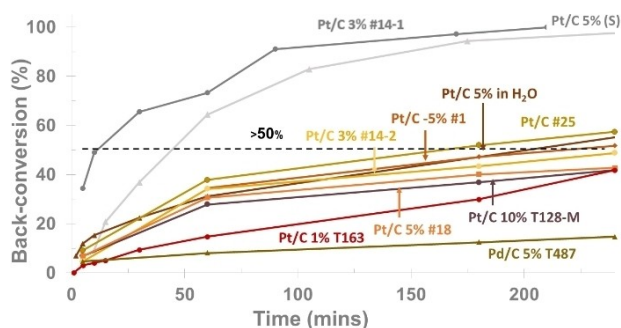


Figure 3. Back-conversion activity of the 10 best-performing catalysts in the first 4 h of catalysis.

Most of the catalysts were in a powder form, although a series of them was acquired in relatively large particle size (Pt and Pd 200 μm -particles, Pd-2 mm chunks, and Pt-spheres under 1 mm). All these catalysts are dispersed over carbon-based support. Although conversion was partial, due to the limited surface area of the catalyst, palladium achieved higher conversion than platinum throughout the tests. These results suggest that smaller particle size provides a higher back-conversion when the metal-core is matched, which can be correlated to the higher surface area in contact with the solution at the same time.

This leads to the next categorization of the catalysts: the metal loading. Two catalysts were acquired with the same support and same particle size (powder around 50 μm) with

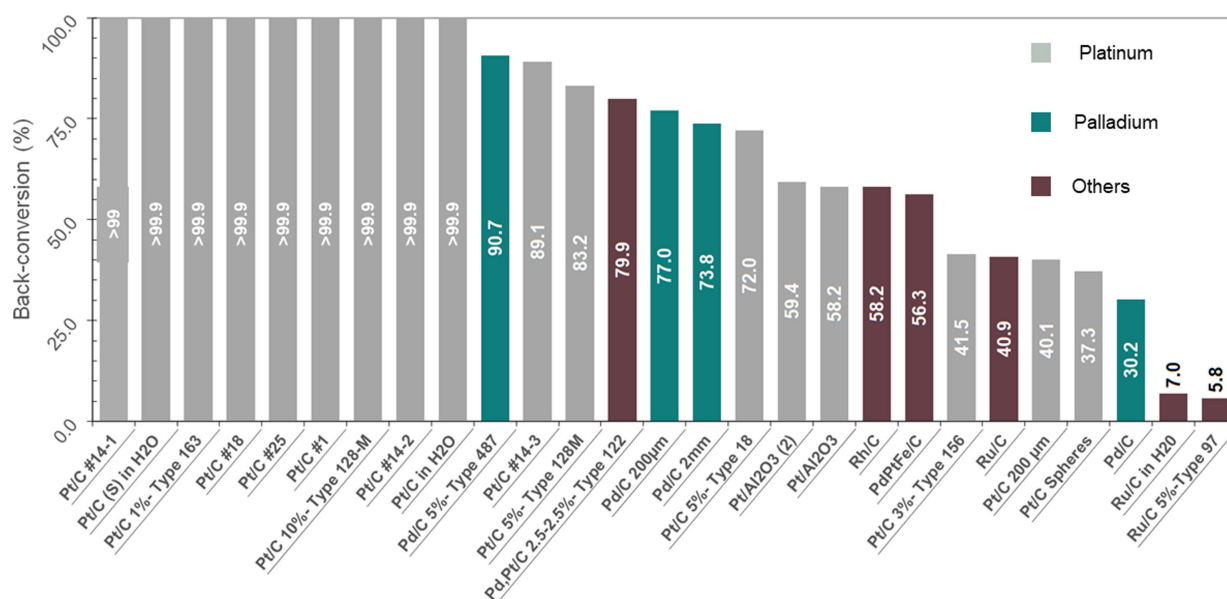


Figure 4. Back-conversion achieved by every catalyst evaluated after a 3-day protocol. Platinum-based catalysts outperform the rest of the pool, representing 9 of the top 10 catalysts. Further details on the catalysts in Table S1 and Table S2 in the Supporting Information. Color code: Pt (grey), Pd (blue), Ru (brown).

different platinum loadings (5 and 10% in weight). The latter one could achieve complete conversion under the 24 h mark, while the 5% loaded catalyst reached 83.2% of the conversion at the end of the 3-day experiment. Although this is a clear result towards a high loading-high activity conclusion, other factors might influence in a non-linear way the amount of metal used. Besides the economic cost increase, a different type of support might not get benefited from larger amounts of metal. Indeed, the benchmark only has a 3% weight platinum loading and performs 6× faster (around 240 min).

There are other factors that affect the catalyst activity that were not considered in this work. For example, variations in the adsorption and desorption of products and byproducts on the catalyst's surface may lead to differing availability of the active surface, and thus the catalytic activity.^[26]

Conclusions

We have reported a fast and efficient protocol for heterogeneous catalyst testing in the back-conversion reaction of a QC to NBD isomerization pair. This will be key in the development of realistic MOST closed-cycle systems in the future, as the back-conversion reaction is much less explored than photochemical isomerization. Also, this protocol can be easily adapted to related reactions or catalysts when there is no competing absorption between both isomers in the MOST system. Similarly, after conducting a thorough examination of a set of commercial catalysts and analyzing key features that impact the rate of the back-conversion reaction, the privileged role of platinum as the metal core and the importance of a relatively small particle size catalyst with carbon-based support was demonstrated, providing catalyst Pt/C #14-1 as the best performing catalyst for this transformation among the 27 catalysts tested. This highlights the necessity of a multi-variant analysis comparison that can consider the influence of different parameters simultaneously to design the optimal catalyst for this MOST system.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

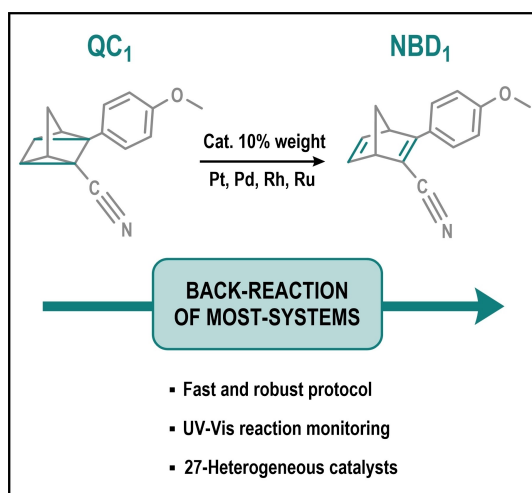
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Developing compounds that store and release solar energy is crucial for overcoming its intermittent nature. In Molecular Solar Thermal (MOST) systems, a high-energy photoisomer captures and releases energy. While photoisomerization is well-studied, back-conversion using catalysts is

underexplored. We compare 27 catalysts in a Norbornadiene/Quadricyclane MOST system, offering insights for effective catalyst development and testing, highlighting the efficiency of Pt based heterogeneous catalyst.

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