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Demonstration of the photothermal catalysis of the Sabatier reaction using nickel nanoparticles and solar spectrum light†

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The promise of light-to-chemical energy conversion has led researchers to explore photo-thermal processes for chemical reactivity of nanoparticles. Previous work has examined particles as an element of a supported catalyst, but not as an unsupported nanopowder. We present a preliminary examination of a photo-thermal Sabatier reaction performed on suspended Ni nanoparticles. This new system performs a catalytic Sabatier reaction at lower bulk temperatures than reported for a standard reaction, driven by light. This result occurs only when the particles are suspended freely in a gaseous mixture; implying that particle isolation enhances photo-thermal catalysis.

Introduction

Heterogeneous catalysis is a critical step in many industrial processes, from the formation of ammonia to the conversion of CO₂ into methane.^{1,2} In academic research, such catalytic reactions use a variety of energy sources, including photocatalysts that use light through electron injection, as well as through traditional heating, *via* an oven or other external heat source.^{3,4} Both photocatalytic and thermal catalysts can perform CO₂ methanation. Many of these academically tested methods have limitations of efficiency, heat loss/transfer and cost that hinder industrial implementation. Moreover, innovation in these processes comes both from improvements in the catalysts and improvements in reactor conditions. In this report, we focus on a finding which shows potential has implications for reactor design. In thermal processes, energy is expended to maintain the reactor at an appropriate temperature, which can be mitigated by reducing mass of catalyst. In photocatalytic processes, thermal energy loss impacts both efficiency and reactor design.^{5,6} Recent research into photothermal heating of nanomaterials could have unique benefits for heterogeneous catalysis as it relates to reactor design. Photothermal heating offers high efficiency conversion from light to heat and high local temperatures at the catalytic surface, but low bulk temperatures of the system.^{7–13} In this communication we demonstrate that the photothermal heating of simple, ball-

milled nickel nanoparticles perform the Sabatier reaction *via* photothermal heating using broad wavelength solar spectrum light. The Sabatier process is the conversion of CO₂ and H₂ on the surface of a metal catalyst to form CH₄ and H₂O.^{3,14} The reaction occurs while the reactor temperature remains below those previously reported for this type of catalysis (see Table 2). This reduction in bulk heating is achieved by altering the reaction conditions – dispersing the nanoparticles throughout the reaction mixture *via* strong mechanical agitation. The particles become active while surrounded by reactant rather than resting on a support layer. We selected the Sabatier reaction as model reaction for the examination of this process due to (1) its well-studied kinetics and (2) its need for controlled heat in a heterogeneous reactor, and finally (3) its potential use in sustainable energy production. Other pioneering studies with supported particles have demonstrated the potential of a photothermal Sabatier process using Ru nanoparticles or supported Ni catalysts, but heat a catalytic bed.^{15,16} Another study constructed selectively absorbent nanosheets coated in single-Ni atoms, that prevented thermal energy from radiating out of the system.¹⁷ In contrast, the photo-thermal reactor performs reactions at reduced temperatures and the reaction only occurs when nanoparticles are dispersed throughout the reactant gas mixture. We report on the unique aspects and potential benefits of this photothermal catalysis. These include, (1) distinct product distributions of the Sabatier process which deviate other reports of heterogeneous Ni catalysts, (2) the contribution of heating in the particle bed *vs.* dispersed particles. From these observations, we hypothesize that particle isolation and the subsequent high heat gradients lead to a distinct reactivity profile. In addition, we report a rate of reaction for a batch process of 1.3 mmol h^{−1} production of methane, from total conversion of CO₂ to CH₄ in a small batch reaction illuminated by light with intensity of 12 kW m^{−2}, well within the range of

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† Electronic supplementary information (ESI) available: Detailed descriptions of experimental procedures and gas chromatography analysis, methane calibration curve and procedure, characterization of the particles by XPS and SEM, details of our estimation of active catalyst by way of a Beer's law curve for suspended Ni nanoparticles and BET surface adsorption data. See DOI: 10.1039/d0ra09939b



Table 1 Efficiencies of several experiments at different illumination levels. Table summarizes the experimental conditions, measured methane, and resulting efficiencies for variation in time and intensity of illumination and associated controls

Time (min)	Nickel (g)	Light intensity	mL methane	mmol methane	Unadjusted efficiency
20	10.0	12 kW m ⁻²	7.6	0.31	0.09 mmol h ⁻¹ g ⁻¹
180	10.0	2 kW m ⁻²	0.85	0.034	0.001 mmol h ⁻¹ g ⁻¹

current solar concentration technology.¹⁸ A simple approach to catalyzing this reaction at low temperatures with only sunlight has been successfully demonstrated and could provide the basis for further investigation of heterogeneous catalysis with unsupported nanoparticles (Table 1).

Results and discussion

In previous work, we determined that photothermal heating of CO₂ capture fluids with carbon black nanoparticles was sufficient to release CO₂, achieving reactivity normally observed at 120 °C at bulk temperatures of 60 °C.¹⁹ In this work, we extended this idea to heterogeneous catalysis. To simplify our test system, we selected a gaseous reaction to minimize thermal transfer to the medium. We selected the Sabatier reaction for its utility – conversion of CO₂ into methane and its well documented thermal reaction profile – the production of CO and CH₄ as a function of bulk temperature. We wanted to examine if the local heating we observed in CO₂ capture solutions, could be translated to the activation of CO₂ for catalytic conversion and how the lower bulk-temperatures might alter the product distribution.

In our initial experiments, we designed a simplified reactor which consisted of (1) a light source with variable intensity from 1 to 20 kW m⁻², (2) a stoichiometric mixture of Sabatier reactants (H₂/CO₂ 4 : 1), and (3) nickel nanoparticles dispersed within the sealed, stirred vessel (Fig. 1). In our initial test system, 10.0 g of nickel nanoparticles (99.5%, 300 nm, Sky-Spring Nanomaterials) were placed in a 40 mL gas sample vial. Absorbance and BET analysis of particles was performed, data

available in ESI†. The vial was purged three times with a stoichiometric reactant mixture (H₂ : CO₂ 4 : 1), with the end result being a vial filled with 0.7 mmol CO₂ and 2.8 mmol H₂. During the reaction, a positive pressure of either hydrogen or additional reactant mixture was applied *via* balloon. No CO was detected in these experiments, with an instrumental detection limit of 0.25% (see ESI† for details).

After screening different illumination levels, we observed that at an intensity of 4 kW m⁻² nanoscale heating achieved the highest CH₄ production. At these conditions, the reactor vial temperature as measured by thermocouple never rose above 90 °C (see ESI† for details). This temperature is more than 100 °C below temperatures observed for Sabatier reactions with Ni.^{16,20} While the conversion and efficiency are not optimized in this system, this result demonstrates the possibility of running this reaction with low bulk-temperatures. Further optimization and reactor design would be required to generate an efficient system using this approach if it is even possible at all.

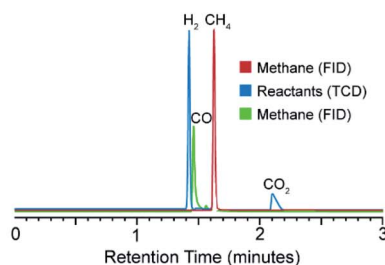
This surprising result led us to examine if photothermal heating of the particles was responsible. To do this, we performed several control experiments. We first tested if the bulk temperature of the reaction could be responsible on its own by heating a particle/gas mixture *via* an oil-bath without light. An oil bath was set at a temperature of 105 °C and a vial was covered in aluminum foil to prevent light from entering. The system was then held in equilibrium at the max temperature for the equivalent time as the test reaction. Methane production was compared to identify the difference in reactivity. We observed that the bulk temperature alone was insufficient to account for the conversion we observed (Fig. 2, -light control).

Table 2 Comparison of our observed efficiencies and recent literature for methanation. Compares efficiency considering our estimate of active catalyst mass, see ESI for estimation details. Note, the high temperature trial was evaluated using a different gas chromatography system with a different calibration

Source	Catalyst temperature (°C)	Light intensity (kW m ⁻²)	Catalyst	Selectivity	Catalyst efficiency mmol (g h) ⁻¹
This publication	170	20	Nickel nanoparticles	At least 99.9%	0.09
This publication	100	2	Nickel nanoparticles	At least 99.9%	0.001
Sastre <i>et al.</i> 2019 (ref. 21)	230	10.1	Ruthenium		52
O'Brien <i>et al.</i> 2018 (ref. 15)	150	2.47	Ruthenium film on inverted silicon opal crystal		2.8
Jantarang <i>et al.</i> 2018 (ref. 22)	285	300 W Xe lamp	Ni on Ce _x Ti _{1-x} O ₂ supports	Not reported	17
Jelle <i>et al.</i> 2018 (ref. 23)	170	22	Ruthenium on TiO ₂ nanoparticles		4.4
Meng <i>et al.</i> 2014 (ref. 24)	365	300 W Xe lamp	Ruthenium on alumina support	99.22	18.16



Gas Chromatography Trace with Analyte Peaks



Experimental Diagram

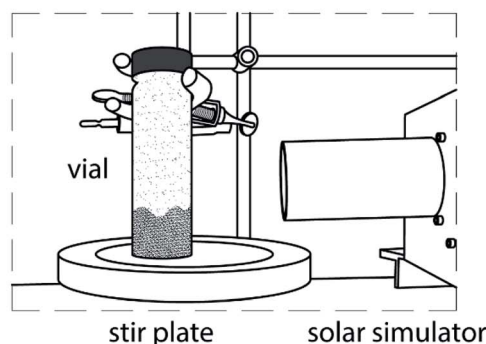


Fig. 1 Photo-thermal Sabatier reaction powered by solar spectrum light with corresponding reactant and product species. On the left is a set of example Gas Chromatography (GC) traces and on the right a symbolic diagram of the reaction set-up. The three GC traces show the peaks that were used to identify reactants, products, and to check for CO as a possible side-product. Traces for both the Flame Ionization Detector (FID) and the Thermal Conductivity Detector (TCD) are shown. The experimental diagram shows the standard set-up for the experiments that follow, the green in the vial indicates where the "active" dispersed particles are in the system.

Next, we sought to test if the particle isolation was responsible for the conversion. In this control, the reaction vial was setup in an identical fashion, but not stirred. In this control, at intensities of 4–12 kW m^{-2} , the unstirred particle control did not produce methane at measurable levels. At intensities above 12 kW m^{-2} , results were inconsistent. The reactor occasionally produced comparable amounts of methane to the light-free thermal controls and other times none. These two controls leave the most reasonable explanation for the high conversion and unique product distribution as the result of the agitated particles being heated beyond the temperature of the reaction vial during their agitation. From these experiments we conclude that photo-thermal heating of the particles can perform a Sabatier reaction without bulk heating of the reaction.

While the low bulk temperature provides an interesting example for a new design of the catalytic process, for a Sabatier process, high catalytic efficiency is often considered a critical factor when comparing between systems. This system is only an experimental demonstration. It remains far from optimized and only a small portion of the particles are even being used for

catalysis at any given time. We've done rudimentary analysis of the effective dispersed density of the particles when stirred, by comparing the reduction in illumination in the vial to a derived Beer's law curve (see ESI†). It does show how a reactor employing photo-thermal heating might operate and thus explored an a lower-limit of what might be possible with these processes. In most photo-catalytic processes, high efficiency results from high intensity and subsequent high bulk-temperatures of the catalyst bed. To determine the efficiency of photothermal particle dispersions, we examined the reactivity by increasing the illumination to 12, then 20 kW m^{-2} . These experiments show how photothermal heating of particles might be applied in a large-scale catalytic process, where bulk temperatures already rise to above 200 $^{\circ}\text{C}$ from the exothermic nature of the reaction and increased intensity. A summary of these results, as well as a comparison to our decoupled lower intensity systems, is shown in Table 2.

While this process remains unoptimized, to provide context for the reader we compared our process with reported efficiency values for photocatalytic systems. Table 2 includes a summary of our experimental efficiencies from our systems along with reported values from recent literature.

Low Illumination 3 Hour Light/Heat Decoupling

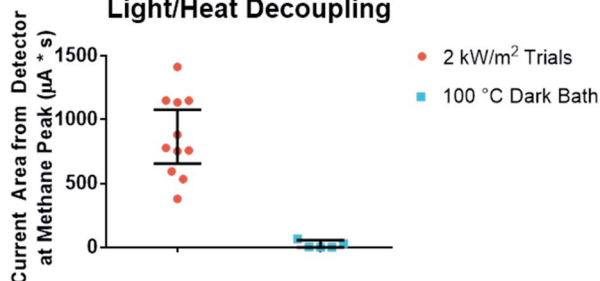


Fig. 2 Comparison of low illumination experimental results and dark heat control. The illuminated trials were compared to a comparable heat control, and the current area used to indicate methane production was compared system to system. The 95% confidence intervals for each treatment are graphed, and the means were determined to be significantly different *via* unpaired *t*-test.

Conclusions

In conclusion, we identified photothermal heating of nanoparticles as a method for heterogeneous catalysis processes that require high temperatures. Our test system uses the Sabatier reaction on nickel nanoparticles. By tuning the illumination level, we controlled the bulk temperature and reactivity of our system. In low irradiance, reactivity derives predominantly from nanoscale heating. At higher irradiances closer to focused light applications, high overall efficiency was achieved over a thermal only control – indicating improved yield from photo-thermal catalysis.

The study represents the first example of using suspended nanoparticles to achieve high temperature reactions while



maintaining low bulk temperatures – suggesting that photo-thermal heating of nanoparticles might hold promise as a method for heterogeneous catalysis. In addition, the specific Sabatier reaction shown here compares well with other published methods indicating its potential use in CO₂ reduction or methane production. This study is preliminary, and further examination of catalyst stability and reusability is necessary to quantify industrial viability. Regardless, we are excited by the potential that this new approach to photo-thermal catalysis might offer for reactor design and new process design. Reactions such as ammonia synthesis, ethylene epoxidation, or any number of other carbon fixing reactions are all excellent candidates for localized high-temperature reactions.

Finally, there is tremendous opportunity for further optimization of this system. The need for the particles to be suspended means that only a small fraction of particles is active at any given time. Advances in reactor design could allow for constant use of almost all particles, increasing efficiency and potentially allowing photothermally-driven heterogeneous catalysis to be competitive or improve on other modern methanation processes.

Conflicts of interest

There are no conflicts to declare.

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