



Collective photothermal effect of Al₂O₃-supported spheroidal plasmonic Ru nanoparticle catalysts in the sunlight-powered Sabatier reaction

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Plasmon catalysis is an interesting technology concept for powering chemical processes with light. Here, we report the use of various Al₂O₃-supported Ru spheroidal nanoparticles as catalyst for the low-temperature conversion of CO₂ and H₂ to CH₄ (Sabatier reaction), using sunlight as energy source. At high loadings of Ru spheroidal nanoparticles (5.9% w/w), we observe a sharp increase in the rate of the sunlight powered reaction when compared to the reaction in dark at the same catalyst bed temperature. Based on our results we exclude plasmon coupling as cause, and attribute the rate enhancement to collective photothermal heating of the Al₂O₃-supported Ru nanoparticles.

Driven by the global aspiration to achieve a CO₂-neutral society, the conversion of CO₂ to the energy carrier CH₄ via the Sabatier reaction has recently experienced its renaissance.^[1] This reaction offers the prospect of a reduction of anthropogenic CO₂ emissions and long-term storage of renewable energy, producing the safe and easy-to-handle energy carrier methane that possesses a high gravimetric storage density. Conventionally, the Sabatier reaction (CO₂ + 4 H₂ → CH₄ + 2 H₂O)^[2] is performed in dark and catalysed by supported metal nanoparticles (e.g. Ni, Ru, Rh on supports such as alumina), and requires thermal activation at temperatures between 300 °C and 500 °C.^[3] Instead of conventional heating, sunlight would be an appealing and sustainable alternative for powering this process. To pave the way to shift from conventional thermally activated processes to sustainable, solely sunlight-powered ones, plasmon-enhanced chemical reactions have very recently become a topic of intense research.^[4] Plasmon catalysis makes use of the localized surface plasmon resonance (LSPR) of metal nanocatalysts for light harvesting. Upon illumination of a plasmonic nanocatalyst a coherent electron oscillation occurs in these particles, which dephases and generates hot electrons.^[5] These can then either transfer into an electron accepting orbital of a nearby adsorbate, or thermalize resulting in an increased temperature of the catalyst. Because of the electronic oscillation, the plasmonic catalyst may also behave as an electromagnetic dipole and emit light coherently at the same frequency.^[4a] While part of this emitted light is scattered to the far field, the other is concentrated at the metal surface. *Ergo*, plasmonic nanoparticles can be efficient sources of electrons, heat and light, and as such boost the activity of chemical reactions, influence their selectivity and/or provide a tool for spatial and temporal control. Depending on their type of metal, size, and shape, plasmonic nanocatalysts can harvest a particular part of the sunlight spectrum.^[6] Combining plasmonic nanoparticles with several sizes and shapes within a single catalyst could be exploited to harvest the energy from the entire solar spectrum reaching the earth's surface.

For the Sabatier process, Liu and co-workers showed that the plasmonic properties of TiO₂-supported Rh nanospheres enable methanation of CO₂ at low temperature (<250 °C) through use of the entire solar spectrum, and claim a combination of photothermal and hot electron contribution to explain their increased activity upon illumination.^[7] Further-

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more, the groups of Corma^[8] and Ye^[9] have reported supported Ni and group 8 nanocatalysts, respectively, for photomethanation of CO₂. Corma and co-workers propose a non-thermal contribution to explain their increased activity,^[8] and Ye *et al.* applied a high intensity light source to promote their catalyst to a temperature of approx. 300 °C (bulk photothermal heating).^[9] Very recently, Dai and Sun reviewed the research performed on 'the reduction of carbon dioxide on photoexcited nanoparticles of VIII group metals', and detailed all claims with respect to photothermal and hot electron contributions made for 47 different catalyst systems.^[10] Recently, Lee and co-workers proposed that direct photoexcitation of CO₂, when adsorbed to the surface of Ru nanoparticles, is possible with visible light.^[11] They observed a linear relationship between the rate of the Sabatier reaction and the intensity of their light source. They claim that for silica supported Ru nanoparticles of a size between 2.6 nm and 17.1 nm the observed increase in CO₂ conversion is not related to light absorption of the nanocatalyst, but to the decreased HOMO-LUMO gap of adsorbed CO₂. They supported their claim by DFT calculations showing that the HOMO-LUMO gap decreases from 8.5 eV to 2.4 eV upon adsorption to the Ru surface, and exclude photothermal heating, albeit without measurement of the catalyst bed temperature.^[11] To the best of our knowledge, this is the only study to date claiming direct photoexcitation of CO₂ as cause for the observed rate enhancement of a metal nanoparticle catalyzed, light-powered Sabatier reaction.

Also our group demonstrated an efficient sunlight-powered Sabatier reaction, driven by the LSPR of alumina-supported Ru nanorods.^[12] We have demonstrated that individual Ru nanorods efficiently harvest sunlight based on their broadband LSPR. For this Ru nanorod catalyst, we identified a large 'nonthermal' contribution at a slightly elevated sunlight intensity of 8.5 kW m⁻² (8.5 sun), resulting in a high photon-to-methane conversion efficiency (PTM) of 55%^[12] over the whole solar spectrum. The PTM is the quotient of the increase in reaction rate upon illumination and the rate of incident photons.^[12] It carries the same definition as the so-called 'apparent quantum yield' introduced by Liu and coworkers,^[7] and quantifies the 'nonthermal' share of the reaction. In contrast to nanorods, the LSPR of spheroidal Ru nanoparticles is positioned in the UV.^[12,13] Because the catalyst was capable of harvesting UV light only, the PTM achieved with spheroidal particles (5% w/w Ru at a reactor temperature 150 °C and light intensity of 8.5 sun) was much lower than for rods (same loading and conditions).^[12] The difference in PTM under these conditions was 41.5%.^[12]

It is an intrinsic limitation of plasmon catalysis that catalytically highly active metal nanospheres for CO₂ methanation display only a weak plasmon resonance, typically positioned in the UV.^[12,13] Strong plasmonic metals like Ag, Au and Al, on the other hand do not catalyse methanation of CO₂. Here, we report plasmonic Al₂O₃-supported Ru spheroidal nanoparticles (d ~ 1 nm) as catalyst for the low-temperature conversion of CO₂ and H₂ to CH₄. At high loadings of Ru spheroidal nanoparticles (5.9% w/w), we observe an increase in the ratio of reaction rate upon illumination vs. in dark at the same catalyst bed temperature. Based on our results we consider photothermal heating

as main contributor. We rule out plasmon coupling as cause for the observed increase in the ratio of reaction rate upon illumination vs. in dark at high Ru loadings, and attribute this phenomenon to collective photothermal heating of the Al₂O₃-supported Ru nanoparticles.

To validate whether collective effects, viz. plasmon coupling and/or collective photothermal heating, play a role in the sunlight-powered Ru-catalysed Sabatier reaction, we prepared Al₂O₃-supported catalysts with various loadings of Ru nanospheres. For this purpose, we impregnated pre-calcined γ -Al₂O₃ with Ru₃(CO)₁₂, and heated the resulting material to 450 °C in a tube furnace under N₂ atmosphere (SI S1). Using this preparation method, we prepared three catalysts with a Ru loading of 3.6% w/w, 4.9% w/w and 5.9% w/w, as determined by inductively coupled plasma – optical emission spectroscopy (ICP-OES, SI S2). The size and shape of the Ru nanoparticles has been analysed using high angle annular dark field scanning transmission electron microscopy (HAADF-STEM, Figure 1)

In the HAADF-STEM analyses, for all three catalysts small, non-agglomerated spheroidal Ru nanoparticles (nanospheres or faceted) can be observed, that are randomly distributed over the Al₂O₃ support. The average radius of the spheroidal Ru nanoparticles was similar for all three catalysts, with a diameter of 0.8 ± 0.2 nm (3.6% w/w), 1.0 ± 0.3 nm (4.9% w/w) and 1.1 ± 0.1 nm (5.9% w/w). The average interparticle distance cannot be determined from these images, because the HAADF-STEM image is a 2D projection of the 3D catalyst (SI S3). XRD analysis indicates the presence of crystalline Ru nanoparticles on the crystalline γ -Al₂O₃ support, although peak broadening due to the small diameter of the Ru particles makes interpretation of the XRD difficult (SI S4).

In our previous work we have observed a strong rate enhancement for Al₂O₃-supported Ru nanorods when the catalyst bed temperature reached approximately 200–220 °C resulting from a combination of the reactor temperature of 150 °C and photothermal heating upon illumination with artificial sunlight.^[12] To determine the activity of our three prepared catalysts in the sunlight-powered Sabatier process, the catalysts were tested at a catalyst bed temperature of

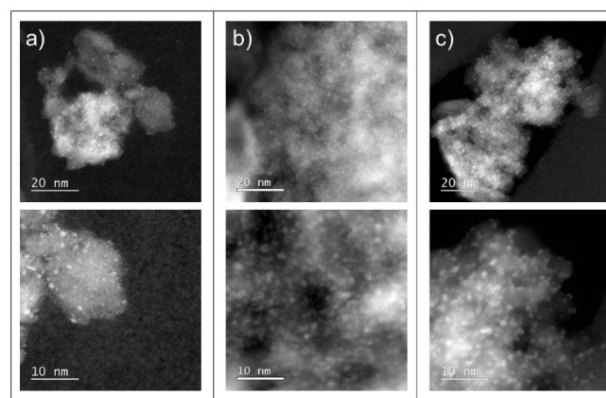


Figure 1. HAADF-STEM of Ru nanoparticle catalysts with a Ru loading of (a) 3.6% w/w, (b) 4.9% w/w and (c) 5.9% w/w, as determined by ICP-OES.

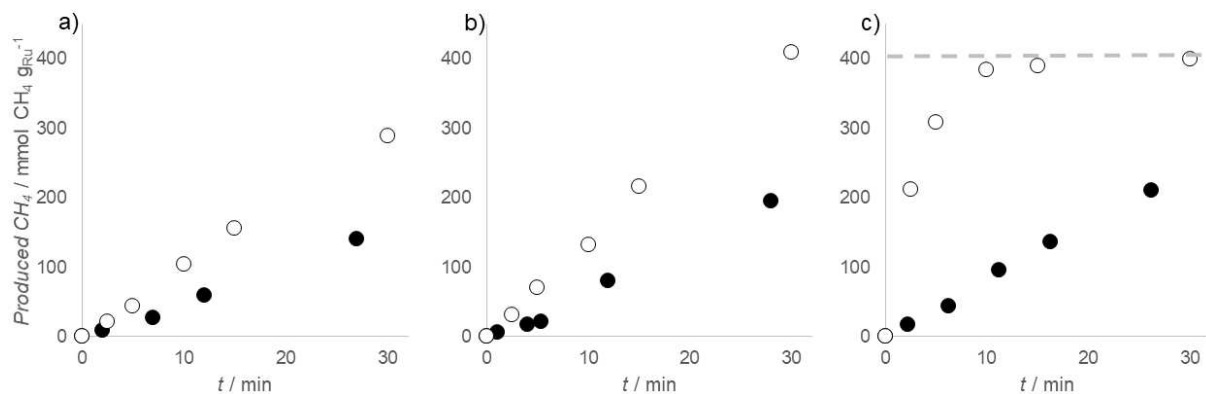


Figure 2. Conversion-time profiles for solar methanation at 6.2 suns (o) vs methanation in dark (•) using a catalyst with (a) 3.6% w/w Ru [max. production approx. 620 mmol CH₄g_{Ru}⁻¹], (b) 4.9% w/w Ru [max. production approx. 470 mmol CH₄g_{Ru}⁻¹] or (c) 5.9% w/w Ru [max. production denoted by dashed line approx. 400 mmol CH₄g_{Ru}⁻¹]. Reaction conditions for all experiments: reaction mixture of H₂/CO₂/N₂ (5:1:1)^[12] at 3.5 bar pressure, 300 mg of Ru/Al₂O₃ catalyst, catalyst bed temperature approximately 220 °C.

approximately 220 °C, realised either through conventional heating of the reactor to this temperature, or through combined heating and illumination. In the latter case, a solar simulator was applied for illumination of the catalysts, using a light intensity of 6.2 suns (for spectrum see SI S5, Figure S7). Additional heating of the reactor was applied to increase the measured catalyst bed temperature to approximately 220 °C in all three cases. This comparative study of the reaction in dark and under illumination with sunlight clearly shows that illumination yields a higher catalytic activity (Figure 2).

The reaction rate upon illumination with 6.2 suns, all at a measured catalyst bed temperature of approx. 220 °C, increased from 0.63 mol CH₄ g_{Ru}⁻¹h⁻¹ (3.6% Ru w/w) and 0.77 mol CH₄ g_{Ru}⁻¹h⁻¹ (4.9% Ru w/w) to 5.09 mol CH₄ g_{Ru}⁻¹h⁻¹ (5.9% Ru w/w). The ratio between the reaction rate upon illumination and in dark also increased from 2.2 (3.6% Ru w/w) and 1.8 (4.9% Ru w/w) to 12.3 (5.9% Ru w/w). Based on these results, we conclude that there is a collective effect of the Ru nanoparticles which causes this boost in activity.

We have studied the catalyst with 5.9% w/w Ru in more detail, through investigating the activity at a similar catalyst bed temperature of 210 °C, achieved with different combinations of conventional heating and solar illumination (Figure 3). Reactions were performed in dark, and for the combinations 190 °C reactor temperature + 1.3 suns, 172 °C reactor + 3.7 suns and 150 °C reactor + 6.2 suns. With an increasing share of solar illumination in the combination, the reaction rate at 210 °C catalyst bed temperature increased from 0.43 mol CH₄ g_{Ru}⁻¹h⁻¹ in dark to 5.09 mol CH₄ g_{Ru}⁻¹h⁻¹ for the combination with 6.2 suns.

Upon further increase of Ru loading on our catalyst we observe an increase in Ru particle size (SI S1 and S3). Due to the increase in particle size the catalysis results using the catalyst with higher loading are not directly comparable to the results achieved with Ru loading of up to 5.9%. However, similar trends are observed; i.e. the catalyst bed heats up upon illumination, the ratio between the reaction rate upon illumination and in

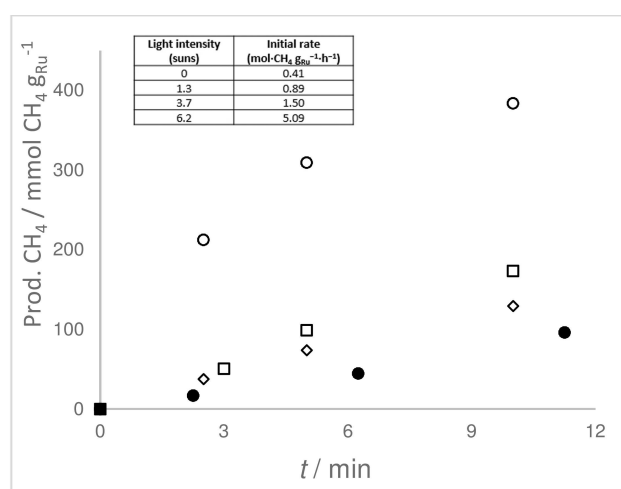


Figure 3. Conversion-time profiles and initial rates for the solar methanation using a catalyst with 5.9% Ru loading. Reaction conditions: reaction mixture of H₂/CO₂/N₂ (5:1:1) at 3.5 bar pressure, 300 mg of Ru/Al₂O₃ catalyst, catalyst bed temperature approximately 210 °C, various mixes of reactor temperature and solar illumination, viz. 215 °C reactor temperature + 0 sun (●), 190 °C reactor temperature + 1.3 suns (◊), 172 °C reactor temperature + 3.7 suns (□) and 150 °C reactor temperature + 6.2 suns (○).

dark is higher than 2, and a non-linear dependency of reaction rate on the light intensity is observed (SI S7).

To determine the cause for the collective effect upon illumination and at the higher catalyst loading (in this series 5.9% w/w Ru), we studied the optical properties of the catalyst using UV-vis-NIR spectrophotometry. For that purpose, freshly prepared Al₂O₃-supported Ru catalysts powder (d ~ 1.8 nm, 2.0%, 5.9% and 7.8% as determined by ICP-OES, SI S9) was dispersed in diethylene glycol, and transmission (T) measurements were performed on the resulting stirred slurries for the wavelength range of 200 nm to 800 nm (Figure 4, displayed as relative absorption of Ru/Al₂O₃ vs. absorption of Al₂O₃). With the catalysts, we prepared slurries of the same concentration Ru, viz. 0.252 mg ml⁻¹. These transmission measurements clearly show that the LSPR is positioned in the UV for all Ru loadings.

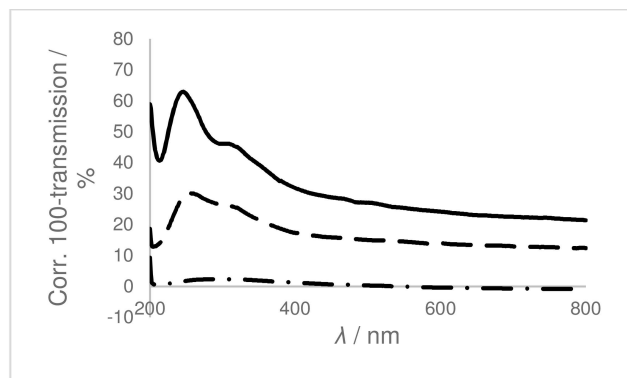


Figure 4. 100-transmission spectra of Ru/Al₂O₃ vs. Al₂O₃. As determined for each sample against an adjusted concentration of pure Al₂O₃ as reference, all in diethylene glycol. UV-vis spectra (100%-T) obtained from slurries of Al₂O₃-supported Ru nanocatalysts at a constant concentration of 0.252 mg Ru ml⁻¹ solvent, and for Ru loadings of 2.0% (long dash dot line), 5.9% (long dash line) and 7.8% (continuous line).

There are no red-shifted peaks resulting from plasmon coupling observed in the spectra.

Furthermore, optical simulations indicate that plasmon coupling does not occur for this size Ru particles at these edge-to-edge distances (SI S10). Nonetheless, the relative absorption spectra display that the UV-vis-NIR absorption increases with increasing Ru loading on Al₂O₃, in spite of the constant Ru concentration in the measurements. This means that at higher Ru loadings on Al₂O₃, the catalyst absorbs sunlight more efficiently, and harvests more solar energy for powering the Sabatier reaction.

Since we observe an increase of the catalyst bed temperature upon illumination, we conclude that photothermal heating contributes to the reaction. In case of a photochemical process, either via hot electron transfer into an electron accepting orbital of a nearby adsorbate or via direct photoexcitation of CO₂, a linear relationship between light intensity and reaction rate is expected.^[13,14d] This is clearly not the case in our study (Figure 3).

All obtained results can be explained by a collective photothermal effect, a working mechanism which was recently proposed by Baffou *et al.*^[14d] Baffou *et al.* propose that, upon illumination of an ensemble of metal nanoparticles in a 3D sample, the most important optical characteristic of the plasmonic nanocatalyst is not the individual absorption cross section, but rather the absorption of the entire sample. It is stated that, if the nanoparticle density is sufficiently high, a temperature increase will be observed. This is spread across the entire sample, and continuous without nanoscale features (photothermal collective heating). Plasmonic coupling, which can merely take place at interparticle distances in the range of the particle diameter, is not required to obtain this effect. The temperature increase experienced by a nanoparticle results from its own heat generation and the heat generated by the other nanoparticles under illumination. For a 2D distribution of nanoparticles, the ratio between the local and collective

temperature increase (ζ_{2D}) is defined by the following equation [Eq. (1)].

$$\zeta_{2D} \sim \frac{p}{3R\sqrt{N}} \quad (1)$$

Herein, p is the interparticle distance, R is the particle radius and N the number of illuminated particles. As can be derived from Equation 1, the contribution of the collective temperature increase rises when ζ_{2D} is lower, *i.e.* with decreasing interparticle distance, increasing particle radius and increasing number of illuminated nanoparticles. For our Ru nanocatalyst system with 3.6% w/w, 4.9% w/w and 5.9% w/w, the estimated ζ_{2D} values are 2.1×10^{-9} , 2.2×10^{-9} and 2.3×10^{-9} , respectively (SI S11). Such small values ($\ll 1$) indicate a dominant collective photothermal effect.

In conclusion, we have successfully prepared Al₂O₃-supported spheroidal Ru nanoparticles for the sunlight-powered Sabatier reaction. We varied the Ru loading of these catalysts between 3.6% w/w and 5.9% w/w, whilst retaining a similar Ru particle size ($d \sim 1$ nm). We have determined the composition, structural and optical properties of these catalysts, and validated their performance in the hydrogenation of CO₂ to CH₄. We observed that the activity of the catalysts upon illumination with sunlight increased from 0.63 mol CH₄ g_{Ru}⁻¹ h⁻¹ (3.6% Ru w/w) to 5.09 mol CH₄ g_{Ru}⁻¹ h⁻¹ (5.9% Ru w/w). The ratio between the reaction rate upon illumination and in dark at the same catalyst bed temperature increased accordingly from approximately 2 to 12. This superlinear increase in activity with Ru loading indicates a collective effect. In absence of plasmonic coupling, given the fact that sunlight absorption increases with increased Ru loading, that the ratio between local and collective photothermal heating is very low for our catalyst system ($\ll 1$, between 2.1×10^{-9} and 2.3×10^{-9}), and the observed non-linear dependency of the reaction rate on the light intensity the obtained results are likely caused by collective photothermal heating.

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Conflict of Interest

The authors declare no conflict of interest.

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