A comparative study on the catalytic performance of SiO_2 and Al_2O_3 supported Ru nanoparticles prepared by chemical reduction and thermal decomposition in the sunlight-powered Sabatier reaction

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Introduction

Using sunlight to power the conversion of CO_2 and green H_2 to CH_4 simultaneously addresses two major challenges: the reduction of CO_2 emissions and replacement of fossil fuels with sunlight as a green and sustainable energy source. Recently, we have reported the use of an Al_2O_3-supported Ru nanocatalyst to promote the sunlight powered Sabatier reaction, which was prepared via impregnation of Al_2O_3 with $Ru_3(CO)_{12}$ and subsequent thermal decomposition of this carbonyl complex to form Ru nanospheres (TD). Here, similar catalytic performance for both Al_2O_3 and SiO_2 supported Ru nanocatalysts prepared via a chemical reduction technique using $RuCl_3$ as precursor (DP+CR) is reported. This demonstrates that the use of volatile and toxic $Ru_3(CO)_{12}$ as well as high temperatures can be avoided. Al_2O_3 as a carrier material is non-essential to the performance of this Ru nanocatalyst and can be replaced by SiO_2.

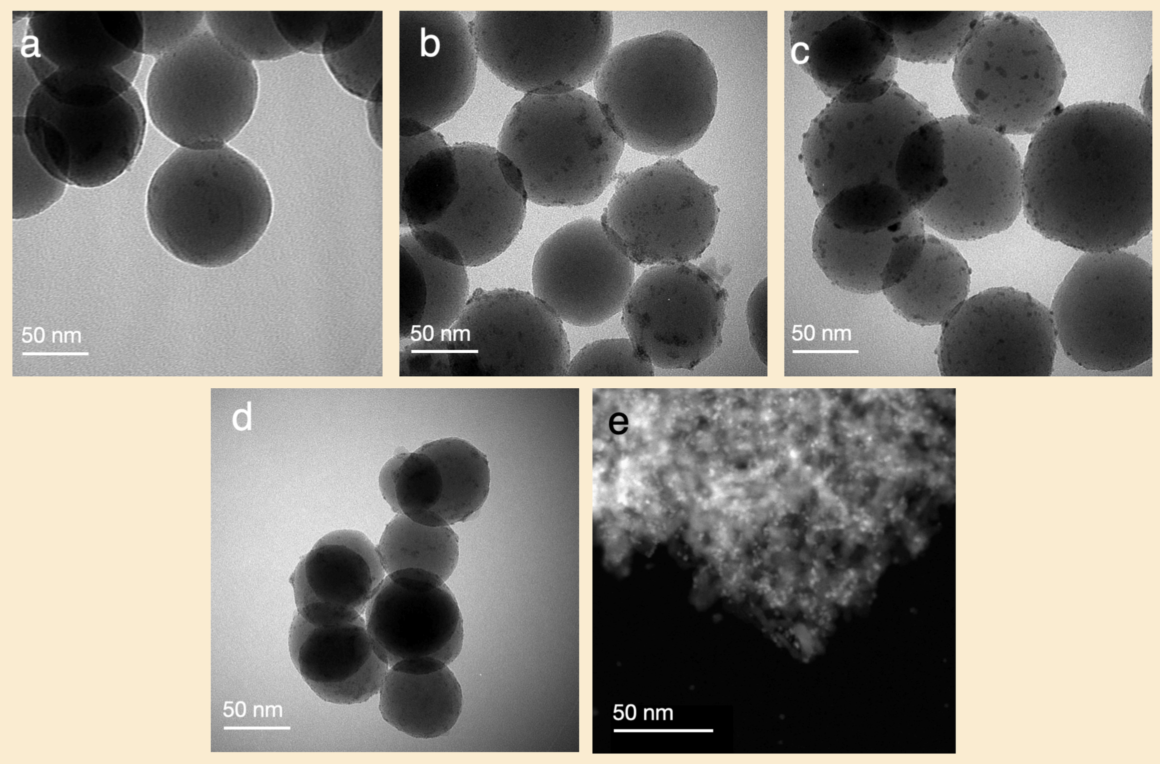
Catalyst nanoparticles

Deposition-precipitation with chemical reduction

- Put silica powder in urea solution, add $RuCl_3$ solution in HCl (0.02M), reflux it 5 hours at 80°C
- Add 0.01 M $NaBH_4$ solution and left for 30 minutes
- Filter and dry

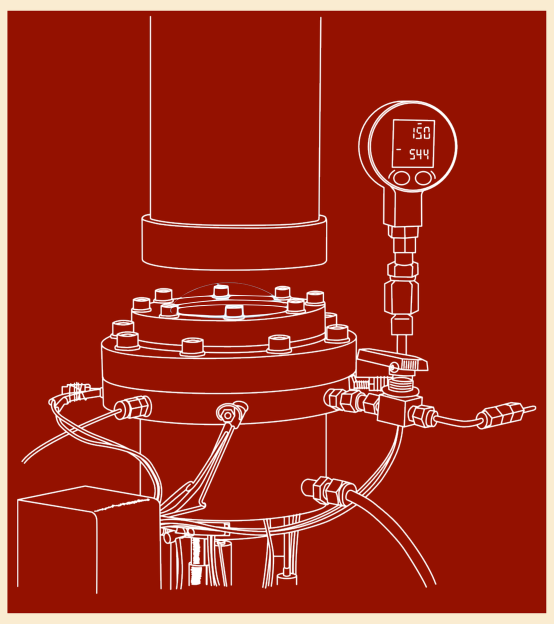
Thermal decomposition

- Dissolve $Ru_3(CO)_{12}$ in THF
- Disperse silica in Ru solution and remove THF via vacuum evaporator
- Put material in the oven: N_2 atmosphere, heating ramp 5°/min till 300°C, keep at 300°C for 2 hours



TEM of Ru nanoparticle catalysts on SiO_2 and Al_2O_3 (DP+CR) with a Ru loading on silica of (a) 0.98% w/w, (b) 2.05% w/w, (c) 3.34% w/w and (d) 3.88% w/w and HAADF STEM (e) on alumina of 3.89% w/w, as determined by ICP-OES.

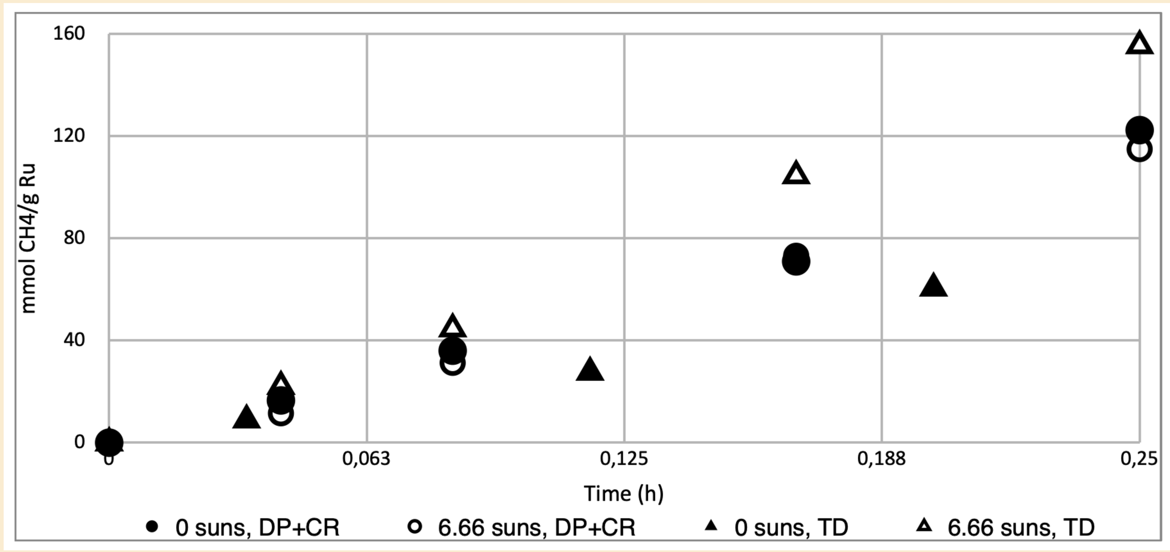
Photoreactor



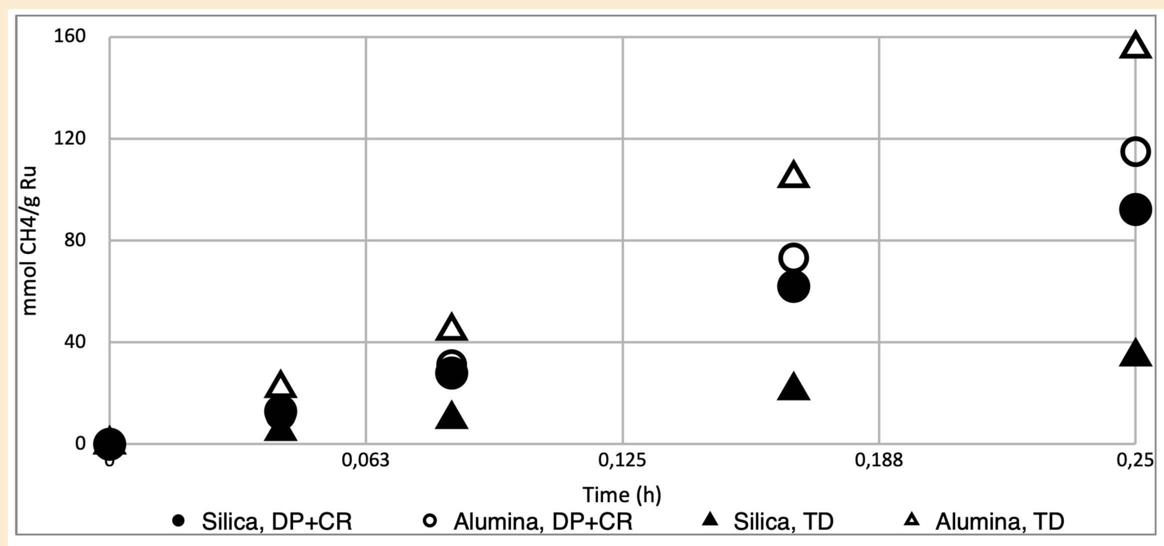
For the photomethanation experiments a custom-build photoreactor equipped with a solar simulator and reaction cell with quartz window was used. The temperature was stabilized at the desirable point with the internal heater. After temperature stabilization, the reactor was filled with the reaction mixture of gases. Gas samples (5 to 7 mL) were taken every 2,5 or 5 minutes from the upper part of the reactor using a gas tight syringe and directly analyzed by gas chromatography.

Catalysis

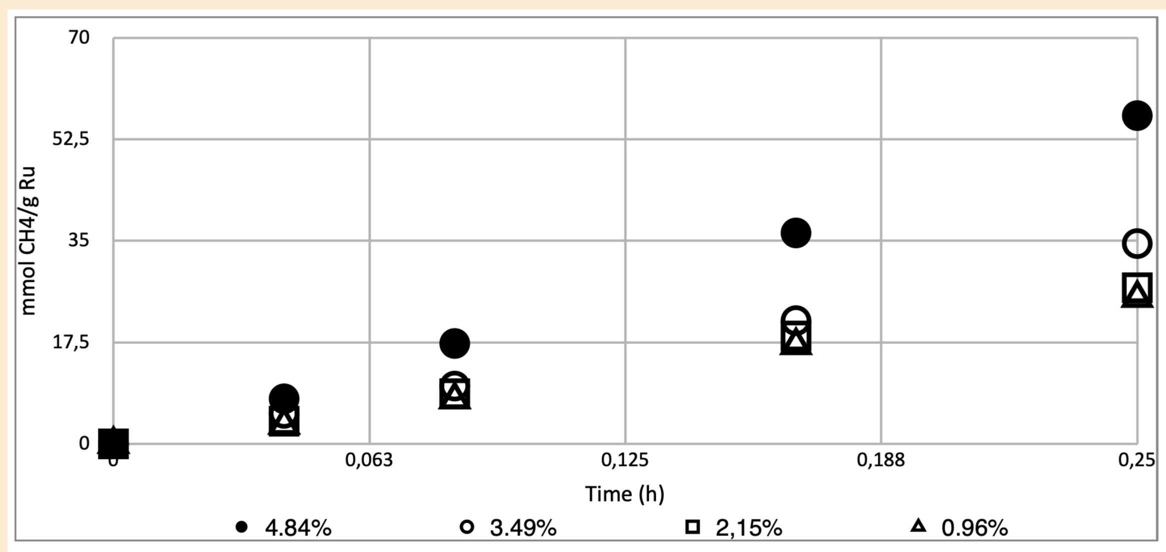
For both way of synthesis of Al_2O_3-Ru, CH_4 was produced as sole reaction product with a slightly lower quantity for Ru/Al_2O_3 (DP+CR) for the light and dark reaction. A comparison between two carrier materials - silica and alumina - under identical reaction conditions and synthesis methods revealed that for thermal decomposition method the choice of carrier makes a difference, whereas there is no such difference for deposition precipitation followed by chemical reduction way.



Conversion-time profile for a Sabatier reaction carried out in dark and light conditions with a Ru catalyst on Al_2O_3 prepared via thermal decomposition (TD) (3.6% w/w) and deposition-precipitation with chemical reduction (DP+CR) (3.89% w/w) methods. Total methane production for each sample is 372.3 (•), 449.4 (o), 290.04 (▲) and 630.36 (△) mmol CH_4 g_{Ru}^{-1}.



Conversion-time profile for a sunlight-powered Sabatier reaction with a Ru catalyst on SiO_2 and Al_2O_3 prepared with thermal decomposition (TD) and deposition-precipitation with following reduction (DP+CR) methods. Ru loadings are 3.88% (•), 3.6% (△), 3.89% (o) and 3.49% w/w(▲).

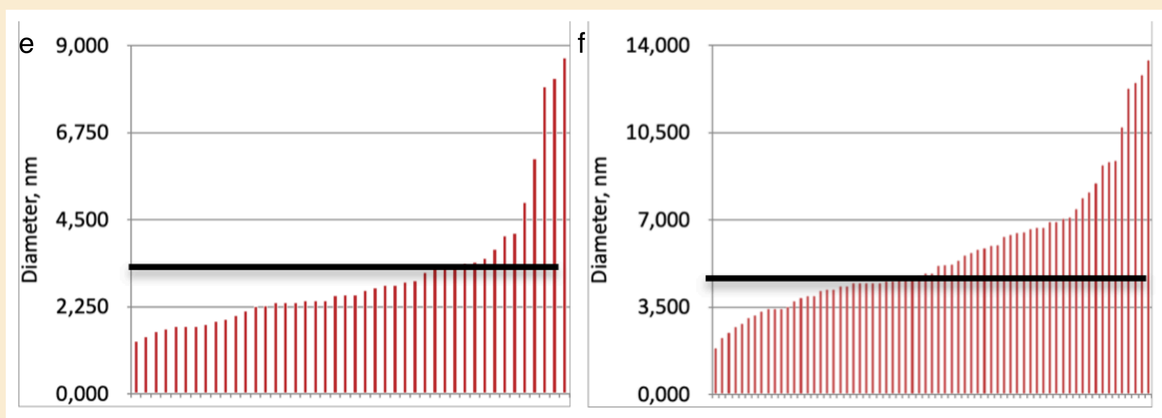


Conversion-time profile for a sunlight-powered Sabatier reaction with a Ru catalyst on SiO_2 (thermal decomposition) with a Ru loading of (a) 0.96% w/w, (b) 2.15% w/w, (c) 3.49% w/w and (d) 4.84% w/w.

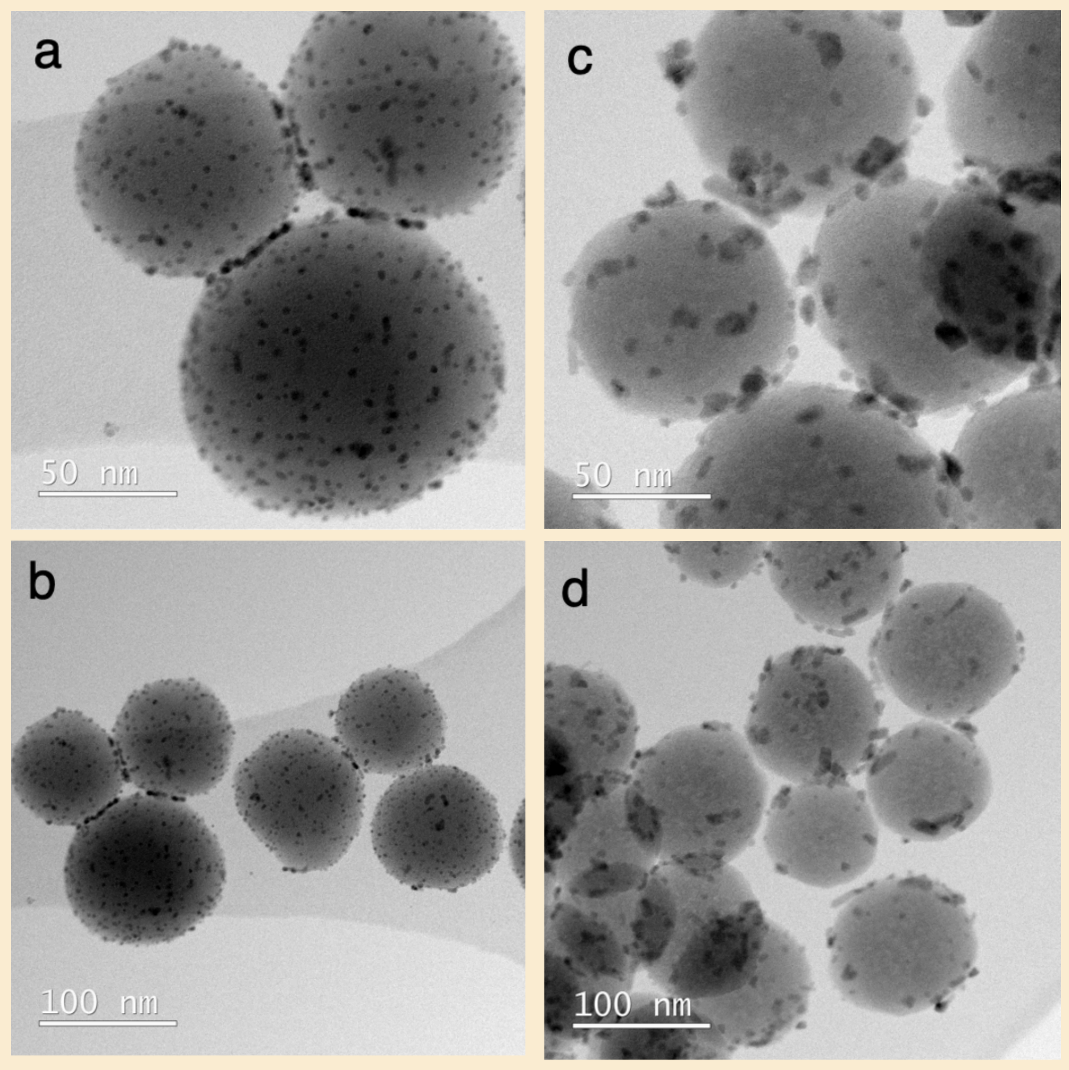
Loading (theor), %	6	4	2,5	1
Loading (real), %	4.84	3.49	2.15	0.96
Reaction 1	241.5	135.1	117.7	103.7
Reaction 2	226.5	146.1	297.1	90.3
Reaction 3	234.9	136.4	348.7	92.1

Methane production (mmol $CH_4 \cdot h^{-1} \cdot g^{-1}$ Ru) for a sunlight-powered Sabatier reaction with a Ru catalyst on SiO_2 (thermal decomposition) with a Ru loading of (a) 0.98% w/w, (b) 2.05% w/w, (c) 3.34% w/w and (d) 3.89% w/w.

To found out the cause of this phenomenon thorough TEM characterization was done for samples before after catalytic process. For the samples synthesized with thermal decomposition the mean diameter particles before and after catalytic reaction was calculated (using only single particles) and percentage of agglomerates. We observed an increase of a mean diameter about 1.3 times (2.47 nm vs 3.14 nm) and an increase in number of agglomerates from 7% to 52.8% (number of agglomerates was counted by analyses of each TEM pictures for each sample, listed in a table and then determined the limit in diameter for single particle and agglomerate).



Comparison of mean diameter of Ru nanoparticles and numbers of agglomerates before (e) and after (f) reaction.



TEM of Ru nanoparticle catalysts on SiO2 (thermal decomposition) with a Ru loading on silica of 3.49% w/w before (a), (b) and (c), (d) after sunlight-powered Sabatier's reaction.

Conclusion

In conclusion, we have successfully prepared alumina- and silica-supported Ru nanoparticles for the sunlight-powered Sabatier reaction using two completely different methods: solution-based deposition precipitation with chemical reduction and impregnation with following thermal decomposition. All the samples showed good effectiveness and catalytic activity coupled with extremely high selectivity in the hydrogenation of CO_2 to CH_4. For the chemical reduction method both carrier materials are good enough and show close initial reaction rate with the total methane production, for the thermal decomposition method alumina is more preferable as a carrier material, but as we still want to find a more sustainable solution, chemical reduction is preferred. Which leads us to the following statement, that chemical reduction way of production of Ru catalyst on different support materials is more favorable for several reasons as reproducibility, stability, easier up-scaling and less energy costs for production and neutralizing sides chemicals.

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