Modification of the methane dry reforming reaction mechanism during visible light illumination of the Ni/CeO_{2-x} catalyst

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Significance and Relevance

Illumination of the nickel-ceria catalyst by visible light of about 7 sun intensity converts CH_4 and CO_2 beyond the thermodynamic equilibrium, while the energy efficiency reaches 33 %. The reaction is sustained in a purely photocatalytic mode without external heating, yielding CH_4 and CO_2 rates of 0.21 and 0.75 mmol/g_{cat}*min, respectively. This contribution analyzes the light-induced alteration of the methane dry reforming reaction mechanism and paves the road for non-thermal and highly efficient methane and CO_2 valorization under non-thermal conditions.

Preferred and 2nd choice for the topic: (1) Photocatalysis and solar energy utilization, (2) Fundamental advances in understanding catalysis
Preferred presentation: Oral only

Introduction and Motivations

Visible light-assisted conversion of CO_2 and methane into syngas (methane dry reforming reaction, DRM) over suitable (photo)catalysts is an emerging pathway for producing fuels and chemicals with minimized involvement of fossil fuels. Illumination of the catalyst enables non-thermal energy input in the form of hot carriers, thus unlocking new reaction channels. Consequently, reaction rates can be significantly accelerated, selectivity can be steered and conversions beyond the thermodynamic equilibrium can be achieved.[1,2] The DRM reaction is under thermally driven conditions troubled by fast carbon accumulation which can be overcome by nanosized (≤5nm) nickel particles. However, such small Ni entities sinter quickly under harsh reaction conditions (temperatures above 700°C). Also, the H_2/CO selectivity increases sharply as the operating temperature exceeds 700°C, which justifies the high operating temperatures. In this research, new insights into the light-driven DRM pathways were acquired, which will enable us to better understand the photocatalytic reactions and perform energy demanding chemical conversions with higher rates and selectivity under mild conditions.

Materials and Methods

The CeO_2 nanorods were synthesized according to Zabilskiy[3] and decorated with 0.5-4 wt.% of nickel. Different *in-situ* spectroscopies (UV-VIS, DRIFTS and XAS), HRTEM, XRD and wavelength- and irradiance-dependent photocatalytic experiments were performed, and the differences in the working state of the catalysts under dark and illuminated conditions were thoroughly analyzed.[4]

Results and Discussion

TEM analysis revealed the CeO_2 is in the shape of nanorods, supporting nickel particles of about 6 nm. The *in-situ* UV-Vis DRS showed that upon heating in reductive atmosphere, the bandgap values of Ni/CeO_{2-x} samples decreased more than the thermal contribution: the change is dominated by chemical change (reduction) of the catalysts (Figure 1A).

Simulation of electromagnetic properties of CeO_2 decorated with 6 nm Ni particles showed negligible absorption for wavelengths longer than 400 nm over fully oxidized CeO_2. However, partly reduced CeO_{2-x} shows remarkable extinction in the visible part of the light spectrum. The maximum near field enhancement in the region around the contact point between Ni particle and CeO_{2-x} support is almost two orders of magnitude larger than the average value over the particle surfaces.

During photo-thermal DRM using white light, the CH_4 and CO_2 conversions were greatly increased compared to the thermo-catalytic tests at identical catalyst temperatures. In the light-assisted mode, the 2Ni catalyst produced syngas with the H_2/CO ratio of 0.61 and 0.47 at 460 and 362 °C, respectively. These values are substantially higher than the maximum values predicted by the thermodynamic equilibrium. The apparent activation energies (Ea) in the thermo-catalytic mode (90-130 kJ/mol) decreased to 30-55 kJ/mol in the light-assisted mode. The effect of wavelength on light-assisted DRM activity was tested at a constant irradiance of 300 mW cm^{-2} using different bandpass filters. The highest rate acceleration was observed between 450 - 550 nm, which correlates with the wavelength dependence of the near-field electromagnetic intensity enhancement.

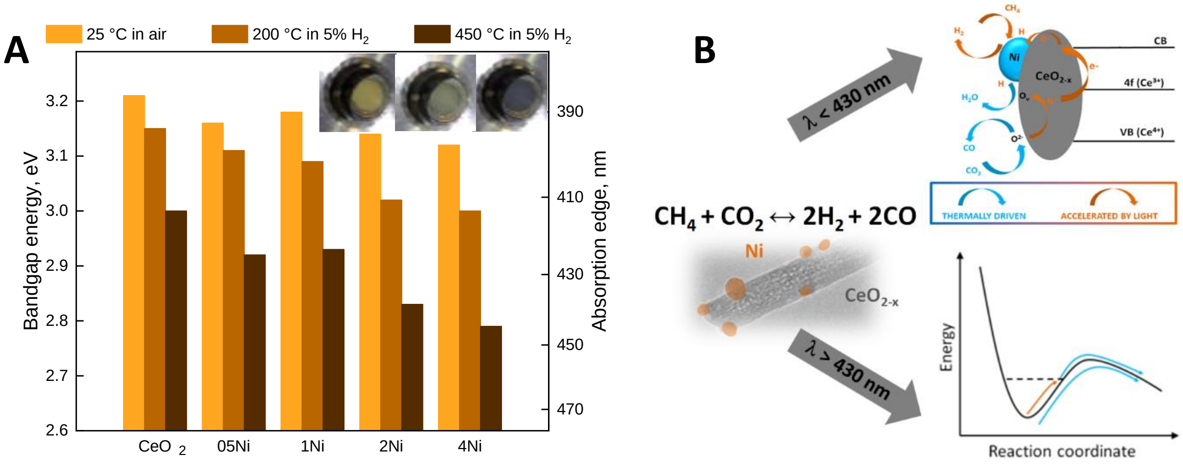

Figure 1. A) Bandgap energies for Ni/CeO_2 catalysts containing 0-4 wt. % Ni in air at 25 °C and 200 °C and 450 °C in 5 % H_2/N_2 atmosphere. Inset shows the 2Ni catalyst at mentioned temperatures and atmospheres. **B**) Proposed DRM mechanisms depending on the irradiation wavelength.

Conclusions

Based on the characterization, theoretical and photocatalytic data, we can postulate the light-assisted DRM mechanisms over Ni/CeO_{2-x} (Figure 1B).

Upon excitation with photons having energy higher than CeO_{2-x} bandgap, electron transfer from partly reduced ceria to nickel occurs, helping with C-H bond activation. Remaining hot holes on the ceria help with its re-oxidation, by incorporating oxygen from dissociated CO_2.

Upon excitation with photons having energy lower than the bandgap of ceria, the near field enhancement induces resonant and vibrational energy transfer into the Ni-CH_x bond of methane adsorbed on nickel, causing its destabilization.

References

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Acknowledgements

Slovenian Research and Innovation agency (ARIS) is acknowledged for funding via projects N2-0265 and P1-0418.