Workshop Summary

ALBA II - Workshop on present and future perspectives of catalysis

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Title:

Thermo-photo catalytic production of H_2: Insights from in-situ/operando spectroscopy

Short Abstract:

Thermo-photo-catalysis is an exciting new field of research which attempts to combine thermal and light energy sources. The combination of the two energy sources may find attractive application in order to mitigate the main problems for thermal (high energy consumption) or photo (low efficiency) alone processes. Thus it could be an attractive path to provide useful (catalytic) alternatives to a significant number of chemical processes of industrial interest (1).

In this contribution we analyze the potential of ($M/CeO_x/TiO_2$) titania-based catalysts promoted by metals (ruthenium or platinum) and cerium oxide in the gas-phase thermo-photo catalytic reforming of methanol to generate hydrogen (2,3). Series of samples having different contents of the promoters were synthesized using a combined microemulsion, for oxide-based components, followed by a chemical reduction method to introduce the

metallic components. Optimum activity was measured quantitatively using reaction rate and quantum efficiency observables. The best $M/CeO_x/TiO_2$ materials can exceed the sum of the corresponding additive combination of thermo and photo processes by more than 50 %. The origin of the activity boost is analyzed using a complete in situ/operando analysis. Micro X-ray absorption spectroscopy was utilized to follow the behavior of the catalytic solids under reaction conditions while the interaction of the reactants and the solids was evaluated using infrared spectroscopy. Combination of spectroscopies uncovers several beneficial effects connected with the reaction mechanism and kinetics. Hydrogen boost appears as a complex light-heat combination triggered by the metal or ceria components and affecting specific oxidation/decarbonylation steps of some carbon-containing intermediates coupled with the water gas shift reaction.

Describe the technique/probe to solve the grand challenge

Establishment of activity-structure relationships appears as the most significant challenge in heterogeneous catalysis. A key tool in this quest corresponds to the combination of *operando* spectroscopies able to render surface and bulk information of the catalytic solid and process. Implementation of operando schemes reaches high complexity when energy for the process comes from the combination of light and heat sources. In this case a fine turning of the experimental set-ups and procedures are required in order to provide insightful information, concerning exclusively the illuminated part of the catalyst.

Provide supporting literature, if appropriate or necessary:

1 V. Nair, M. Muñoz-Batista, M. Fernández-García, R. Luque, J.C. Colmenares. Thermo-Photocatalysis: Environmental and Energy Applications. ChemSusChem 12 (2019) 2098-2116. https://doi.org/ 10.1002/cssc.201900175

2 U. Caudillo-Flores, G. Agostini, C. Marini, A. Kubacka, M. Fernández-García. Hydrogen thermos-photo production using Ru/TiO2: Heat and light synergistic effects. Applied Catalysis B: Environmental 256 (2019) 117790. https://doi.org/10.1016/j.apcatb.2019.117790.

3 U. Caudillo-Flores, I. Barba-Nieto, M.J. Muñoz-Batista, D. Motta-Meira, M. Fernández-García, A. Kubacka. Thermo-Photo Production of Hydrogen using Ternary Pt-CeO2-TiO2 Catalysts: a Spectroscopic and Mechanistic Study. Chem. Eng. J. 425 (201) 130641. https://doi.org/10.1016/j.cej.2021.130641