

Nickel-tin alloy catalysts for liquid organic hydrogen carrier dehydrogenation

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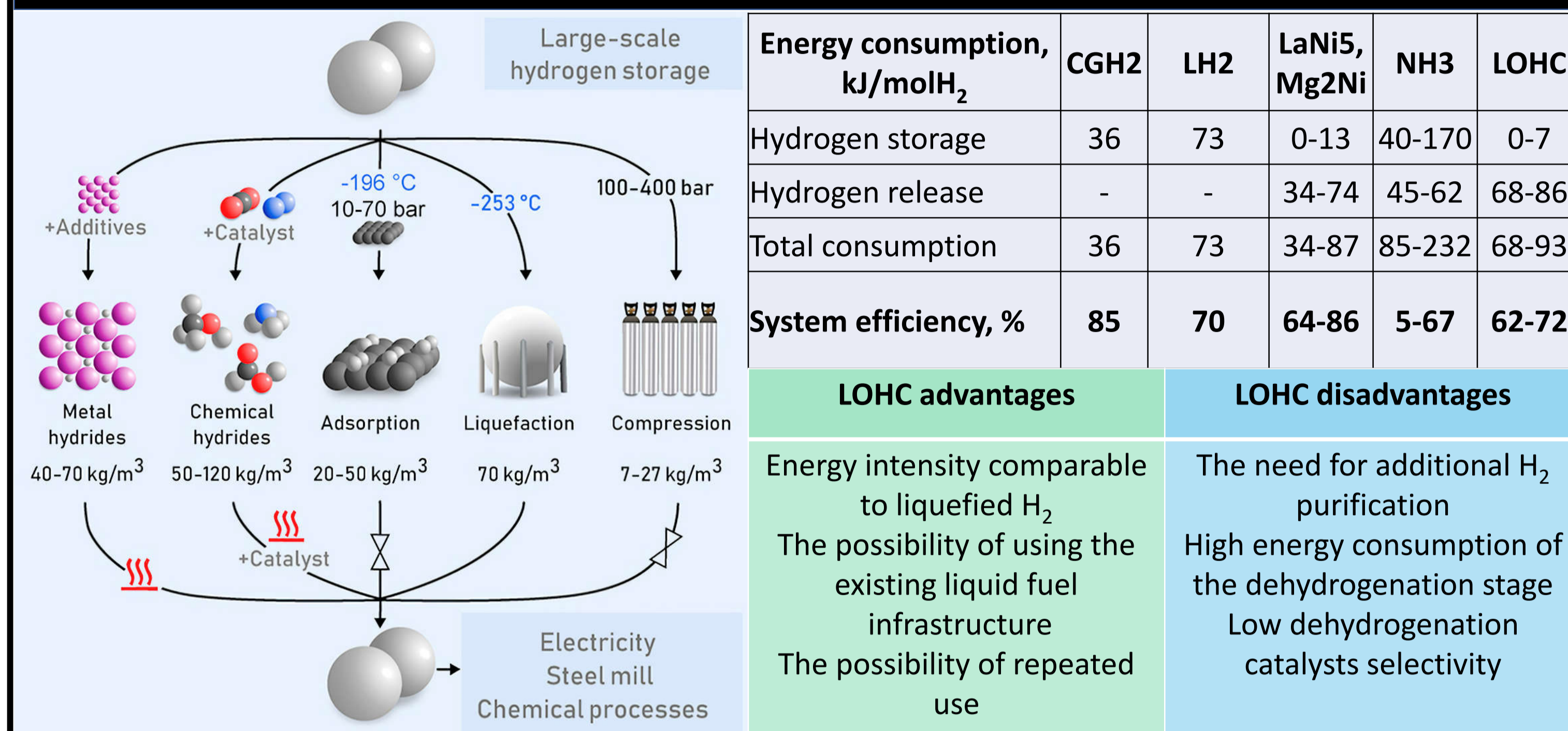
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Introduction

Currently, there has been a significant increase in interest in alternative energy sources, primarily hydrogen, as a fuel with a zero-carbon dioxide emission [1]. The development of hydrogen energy, in addition to creating methods for H₂ production [2], implies the elaboration of methods for its efficient storage and transportation [3]. There is a wide range of developed technologies: storage of hydrogen in a compressed (CGH₂) [4], liquefied (LH₂) [5], and physisorbed state [6]. Hydrogen can also be stored in the composition of hydrides [7], ammonia, methanol, formic acid, and reversible liquid organic hydrogen carriers (LOHC) [8]. Among all these methods, the LH₂ technology is currently the most widely used. However, the use of expensive pressure vessels or cryogenic systems [3,9] and a capital-intensive liquefaction process (40–50% of capital costs) [10] is a key problem of this technology. According to a number of feasibility studies, LOHC technology is a promising alternative to LH₂ technology for large-scale storage and transportation of hydrogen [11]. Indeed, the use of the LOHC technology has a number of advantages: it provides energy-efficient reversibility of the hydrogen separation at its high specific content [12,13]. There is no need for additional purification of hydrogen from concomitant gases. It is possible to use the existing fuel storage and transportation infrastructure [13].

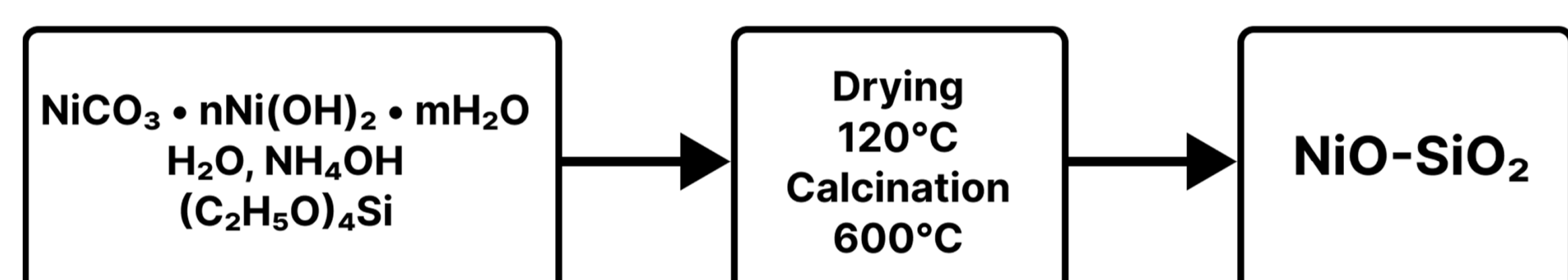
In this work, high-loaded nickel catalysts modified with Sn have been synthesized and tested in the dehydrogenation of methylcyclohexane (MCH) as a liquid organic hydrogen carrier. The catalyst composition and its reduction temperature were optimized which allowed to achieve high selectivity of the dehydrogenation. The genesis of the NiO-SiO₂ catalytic systems during their modification with Sn and reductive activation in hydrogen has been studied.

Hydrogen storage and transport technologies

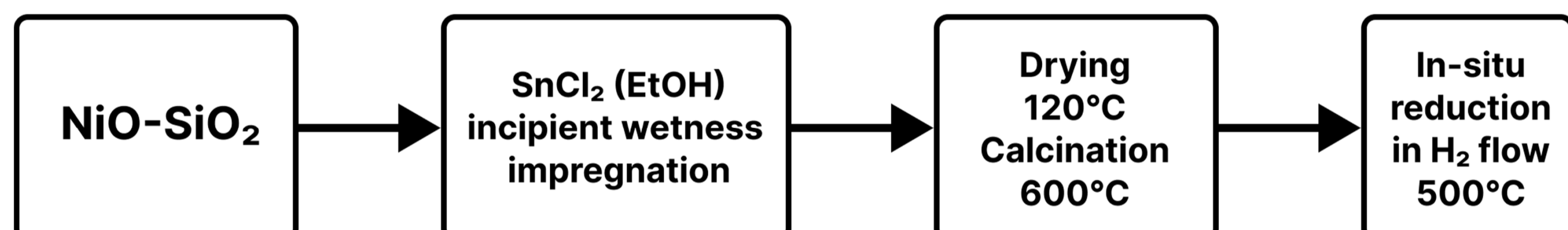


Synthesis of catalytic systems

The heterophase sol-gel technique [14] was used to prepare the NiO-SiO₂ ("Ni100") catalyst with SiO₂ as a stabilizing agent.

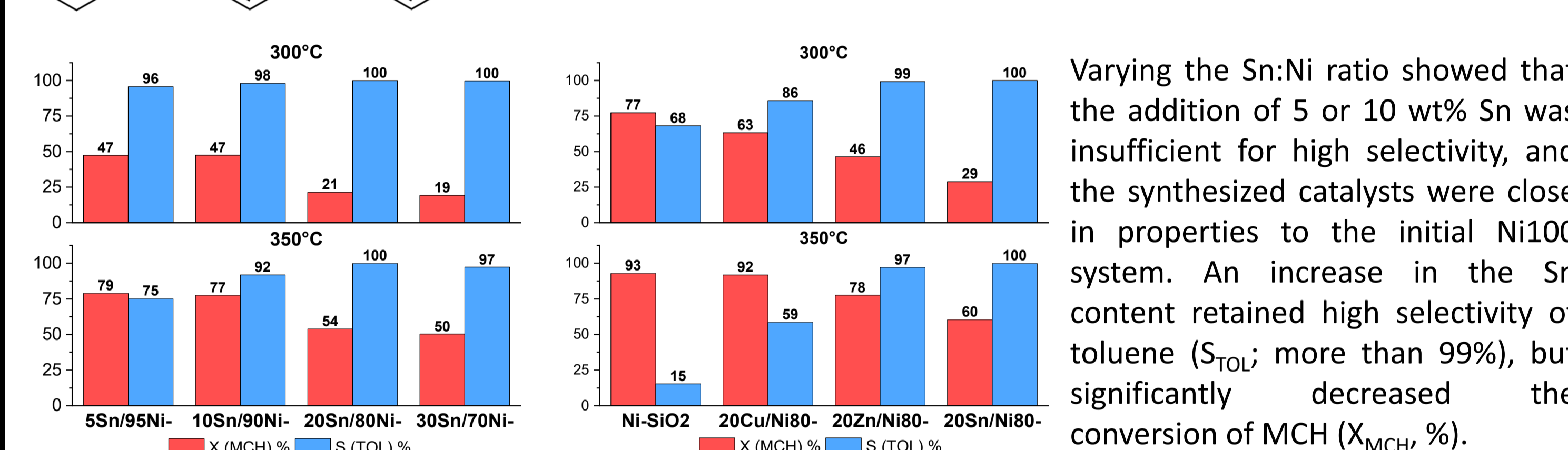


5Sn/95Ni, 10Sn/90Ni, 20Sn/80Ni, and 30Sn/70Ni mixed oxide catalysts (SnOx/NiO-SiO₂) were obtained by wetness impregnation of the NiO-SiO₂ sample with a solution of tin (II) chloride in ethanol followed by heat treatment.



Comparative tests of catalyst performance

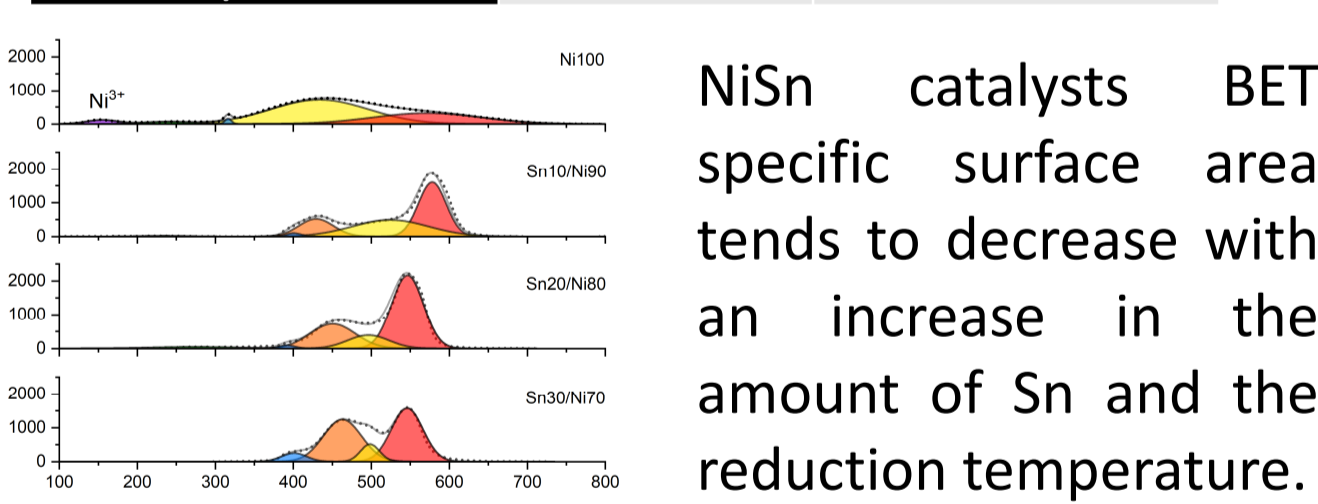
The dehydrogenation process was performed in a fixed-bed continuous flow reactor in a temperature range of 250–350°C under ambient pressure.



The Sn-modified catalyst reduced at 500 °C (20Sn/80Ni-500) showed the highest toluene selectivity (>99%)

Structural studies of the 20Sn/80Ni-SiO₂ system

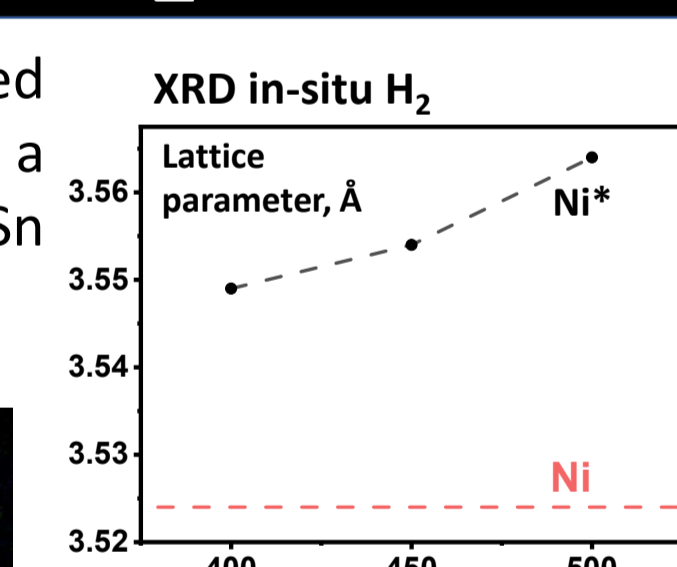
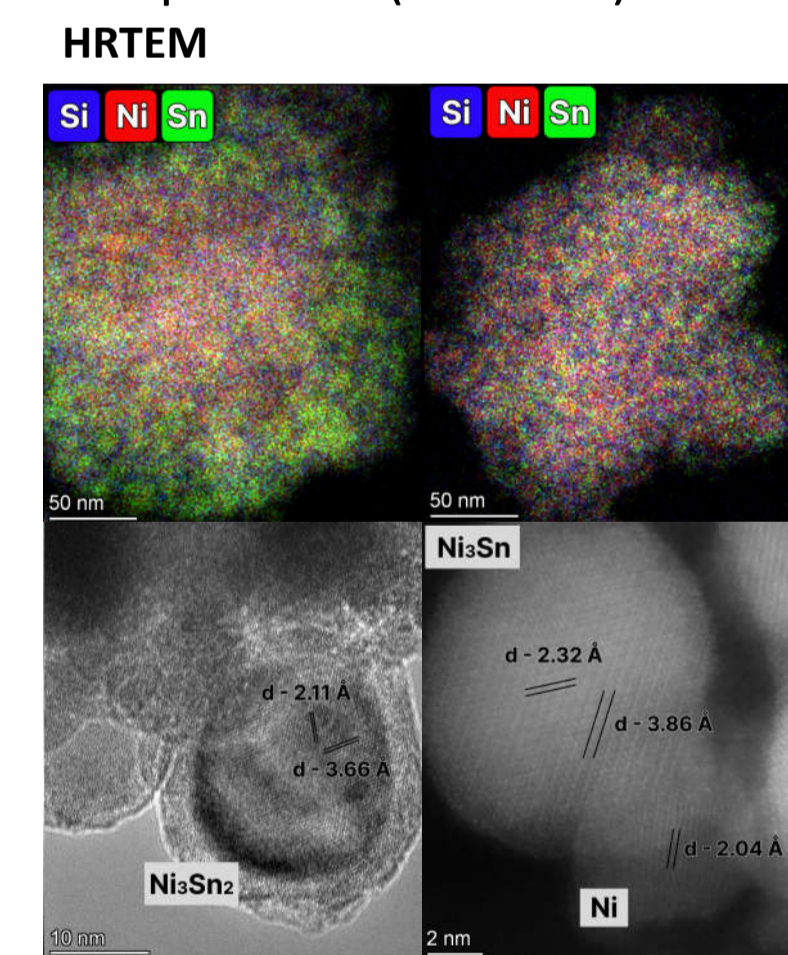
Catalysts	BET SSA, m ² ·g ⁻¹	CO uptake, μl·g ⁻¹
Ni100-400	310	555
Ni100-500	294	742
10Sn/90Ni-500	169	470
10Sn/90Ni-600	150	382
20Sn/80Ni-500	167	350
20Sn/80Ni-600	153	274
30Sn/70Ni-500	124	208
30Sn/70Ni-600	111	158



NiSn catalysts BET specific surface area tends to decrease with an increase in the amount of Sn and the reduction temperature.

All the Sn/Ni-SiO₂ catalysts, despite the weaker binding particles to the support (TPR-H₂ data), demonstrate low CO absorption. An increase in the T_{red} leads to a further decrease in the volume of adsorbed CO because of sintering and more uniform distribution of Sn particles on the nickel surface.

The samples consist of rounded submicron agglomerates is a SiO₂ matrix with included NiSn nanoparticles (5-10 nm)

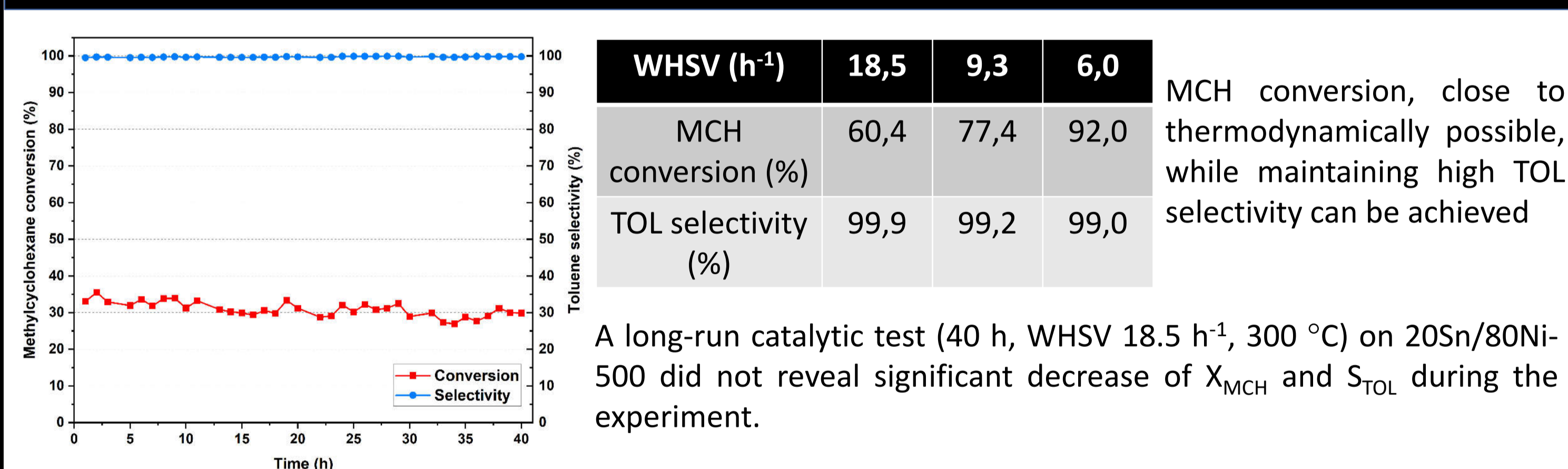


The XRD in situ data confirm the HRTEM data. With an increase in reduction T, the Sn distribution becomes more uniform. The formation of Sn-Ni alloys provides increased selectivity of the catalyst

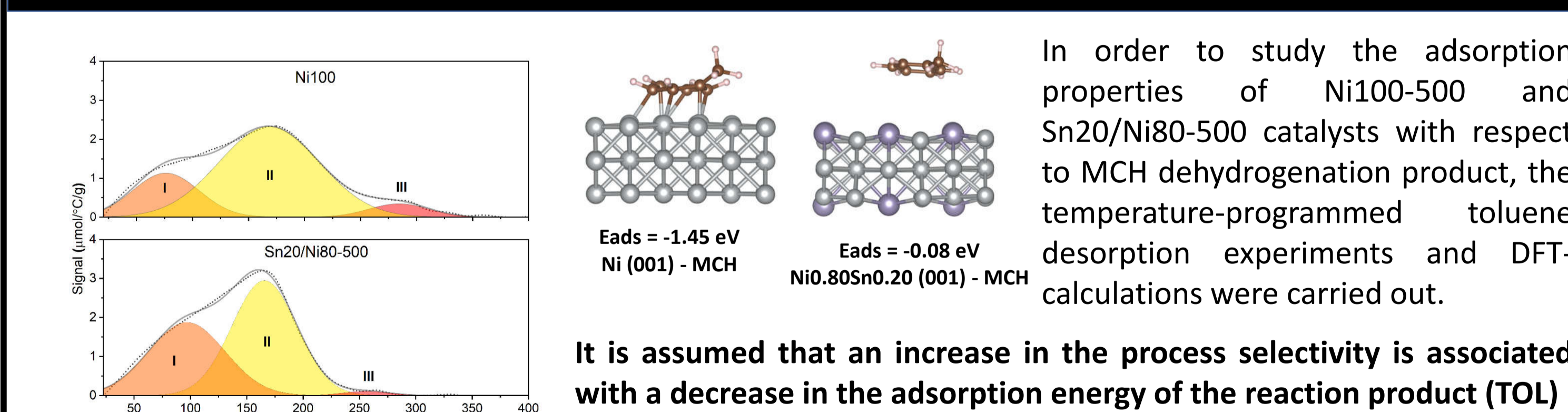
Conclusions

It was shown that the NiSn catalyst with optimal composition (atomic Ni:Sn ratio 5:1) reduced at 500 °C provides the selectivity of the dehydrogenation over 99.9% and the conversion of MCH of 87.4% at WHSV = 6.2 h⁻¹ and temperature 350 °C. The achieved selectivity exceeds the selectivity of all the previously studied Cu- and Zn-modified analogs based on NiO-SiO₂ and is comparable with selectivity of Pt-based catalysts. The high selectivity of the bimetallic NiSn-based catalyst is due to the formation of NiSn solid solutions.

In-depth catalyst performance test



The origin of enhanced selectivity



Acknowledgement

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