Thesis abstract

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Title of the Thesis: **Exsolution Mediated *In Situ* Alloying in Engineered Hercynite: A Promising Approach to Develop Catalysts for Sustainable Dry Reforming of Methane**
Name of the scholar: **Monotosh Bhattacharjee**

The objective of the thesis is to design and synthesize some hercynite ($FeAl_2O_4$)-based catalysts, $(TM)_xFe_{1-x}Al_2O_4$ (where TM = Ni alone or in combination with other first row transition metals), capable of *in situ* alloying through co-exsolution, for sustainable dry (CO_2) reforming of methane (DRM) and provide a generalized idea for developing next generation DRM catalysts exploiting the 'exsolution mediated *in situ* alloying' technique.

DRM ($CH_4 + CO_2 \rightleftharpoons 2H_2 + 2CO$) is a thermocatalytic process that consumes two potent greenhouse gases, CO_2 and CH_4 to produce synthesis gas (also known as syngas, a mixture of H_2 and CO), a feedstock in the Fischer-Tropsch process. Additionally, this reaction has the required merits to be considered as a promising route for sustainable energy production. Despite its potential outcome, catalyst deactivation originating from sintering followed by carbon deposition are challenging issues for the commercialization of DRM process. Mostly explored catalysts are precious metals (Ru, Rh, Ir, Pd, and Pt), supported on a variety of materials, especially oxides. But their uses are limited because of scarcity and high cost. In this context, transition metals (mostly Ni) are viable substitution of the precious metals for DRM. Irrespective of high activity of Ni in DRM, there is a hurdle of interrelated issues viz., sintering and coking, as demonstrated by many researchers that over a threshold particle size of Ni, carbon formation is evident. The design and development of Ni-based catalysts with anti-sintering, anti-coking ability includes addition of other metal(s) (in various forms) as promoter. Alloying is a form of adding another metal to improve the electronic behaviour of Ni, which eventually assists in enhancing the performance of Ni-based catalysts in DRM. For alloying, reduction of the catalyst, particularly with H_2 is a common practice. In that case, dealloying of active phases in the DRM environment may hinder its applicability. To avoid the consumption of H_2 in prior reduction process and to prevent dealloying, 'exsolution mediated *in situ* alloying' may be effective for availing a hassle-free DRM. In this regard, hercynite, which is always challenging to synthesize in its pure phase, has purposefully been chosen for some judicial chemical tailoring towards robust DRM activity using Ni and other transition metals in different proportions which are discussed in various chapters of the thesis.

Chapter 1 provides a concise overview based on the literature survey on sustainable DRM taking into consideration the limiting issues of Ni-catalyzed DRM with a special featuring on alloying.

Chapter 2 enunciates at first the beauty of facile solution combustion synthesis (SCS) method utilized to prepare the different catalysts. The wide range of modern sophisticated characterization techniques are summarized that have been explored to observe the physicochemical nature of the catalysts and to provide comprehensive idea about structure-property relationship. These techniques include powder X-ray diffraction (PXRD), BET surface area measurement (S_{BET}), H_2-temperature programmed reduction (H_2-TPR), CO_2-temperature programmed oxidation (CO_2-TPO), inductively coupled plasma-atomic emission spectroscopy (ICP-AES), Chemical (CHNS) analysis, Raman spectroscopy, high resolution transmission electron microscopy (HRTEM), high-angle annular dark-field scanning tunneling electron microscopy (HAADF STEM),

Monotosh Bhattacharjee.
27.08.2025

Arup Gayen
27/08/2025

Dr. Arup Gayen
Professor
Department of Chemistry
Jadavpur University
Kolkata-700032

Parthasarathi Bera

वैज्ञानिक / SCIENTIST
पृष्ठीय अभियांत्रिकी प्रभाग
SURFACE ENGINEERING DIVISION
सीएसआईआर राष्ट्रीय वांतरिक्ष प्रयोगशालाएं
CSIR-National Aerospace Laboratories
बेंगलूरु/Bengaluru-560 017

thermogravimetry-differential thermal analysis (TG-DTA) and X-ray photoelectron spectroscopy (XPS). The gas-solid heterogeneous catalyst testing protocols have been discussed at the end of this chapter.

Chapter 3 deals with investigation about the effect of chemical tailoring through simultaneous doping of Ni and Cu in the hercynite spinel. A series of nanodimensional (10–14 nm) hercynites has been synthesized following SCS method and the optimized sample, $Ni_{0.08}Cu_{0.07}Fe_{0.85}Al_2O_4$ (named as NCFAO8), is reported to exhibit noteworthy coke-free conversions of 97% and 99% for CH_4 and CO_2, respectively, with H_2/CO ratio of ~0.80 at a gas hourly space velocity (GHSV) of ~34000 mL g^{-1} h^{-1} at 800 °C. True potential of the catalyst has been evaluated over a range of temperatures and varying GHSVs. Additionally, this investigation highlights the structural evolution of the hercynite-based catalyst during time-on-stream activity behavior. Thorough characterization of the aged (after catalytic test for a prolonged duration of 100 h) vis-à-vis the as-prepared catalyst suggests *in situ* co-exsolution of the doped metal ions (Ni and Cu) and a certain portion of Fe from the catalyst leading to formation of NiCuFe trimetallic alloy and is accompanied by the formation of γ-Al_2O_3 along with the retention of pristine hercynite phase. Alloying of the active component Ni with Cu, the two dopant ions, and host Fe in presence of the spinel ($FeAl_2O_4$ and γ-Al_2O_3) is shown to be beneficial in circumventing the difficulties of Ni-only catalysts in DRM. Interestingly, the residual carbon, present initially in the catalyst prepared with SCS method gets diminished in the course of reaction. Instead of coke deposition, substantial removal of the residual carbon in the DRM environment suggests NCFAO8, a promising next generation catalyst for DRM with sustainable coke resistant ability, which can be further extrapolated to simulated bio-gas reforming.

Chapter 4 discusses the study of DRM over the SCS-made Ni-doped hercynites, with general formula $Ni_xFe_{1-x}Al_2O_4$ (where, x = 0.2–0.5). All these catalysts show stable conversion behavior towards moderate temperature DRM reaction. It has also been noted that $Ni_{0.40}Fe_{0.60}Al_2O_4$ exhibits the highest DRM activity amongst all, after 20 h of continuous reaction without loss of activity. The catalyst shows nearly similar DRM activity up to 50 h run time of DRM. After the reaction, the aged phase of the catalyst has been recovered and found to contain the signature of NiFe alloying along with the retention of original hercynite phase. *In situ* alloying of the doped metal with host is again proved to be an effective way for entailing a sustainable moderate temperature DRM.

Chapter 5 comprises of the chemical tailoring of hercynite through simultaneous doping of Ni, Cu, Co, and Mn at the Fe-site using the ultra-fast SCS method followed by their activity test in catalytic DRM. No additional peak in the PXRD pattern of as-prepared catalyst confirms the structural flexibility of the hercynite in incorporating several transition metals into the spinel framework. The general formula of the catalysts is $(NiCuCoMn)_xFe_{1-x}Al_2O_4$ (x = 0.2 and 0.4). All these catalysts are shown to be very promising with respect to both conversions (CH_4 and CO_2) as well as H_2/CO ratio. Moreover, the diffraction pattern of 30 h aged catalyst clearly indicates the presence of *in situ* formed alloy.

Finally, the key research findings have been summarized in **Chapter 6** followed by highlighting certain significant insights in a conclusive manner. The plausible future directions have also been pointed out which are generalized in true sense in the crucial and developing field of "exsolution mediated *in situ* alloying" for sustainable DRM. The thesis is concluded with the briefing of research works that are underway and discussing of necessity of detailed investigations by high-end instruments and cutting-edge technologies, which may be availed in near future through collaborative research.

Monatosh Bhattacharjee
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Arup Gayen
27/08/2025

Dr. Arup Gayen
Professor
Department of Chemistry
Jadavpur University
Kolkata-700032

Parthasarathi Bera

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