

Novel Methanation Catalysts Discovered by Computational Screening

Anne Mette Frey¹, Claus Hviid Christensen^{1*}, Arkady Kustov¹, Kasper Emil Larsen², Jens Sehested², Thomas Bliigaard³, Martin P. Andersson³, Jens K. Nørskov³.

¹Center for Sustainable and Green Chemistry, Department of Chemistry, Technical University of Denmark, Building 206, DK-2800, Lyngby, Denmark

²Haldor Topsøe A/S, Nymøllevvej 55, DK-2800 Lyngby, Denmark.

³Center for Sustainable and Green Chemistry, Department of Chemistry, NanoDTU, Technical University of Denmark, DK-2800 Lyngby, Denmark.

*chc@kemi.dtu.dk

Introduction

The methanation reaction was discovered almost 100 years ago by Sabatier and Senderens [1]. However, the preferred industrial catalyst, Ni/Al₂O₃, has remained largely unchanged since then despite of numerous attempts to find new catalysts. Methanation catalysts are used industrially on a large scale in ammonia synthesis plants to remove traces of carbon oxides that would otherwise poison the ammonia synthesis catalyst [2]. Other applications for the methanation reaction are found in the purification of hydrogen in refineries and hydrogen plants, and for CO removal in caprolactam plants [3]. Recently, an impressive experimental high-throughput screening study was performed to identify new catalyst leads. Shortly thereafter, a computational screening study based on density functional theory calculations was performed. From this work it was found that Ni-Fe alloys should be more active than the monometallic Ni catalyst [4]. This indicated that the catalyst could be interesting for industrial applications since it should not only be more active but also less expensive than the current industrial used monometallic Ni catalyst. Interestingly, Fe-Ni alloy catalysts were not identified in the high-throughput screening study, and had therefore not been investigated before. The superior activity of Ni-Fe alloys was then verified in CO hydrogenation experiments [4] but to be useful industrially, it is central that the improved performance is also found for CO₂ hydrogenation as well [5]. Thus, in the present study simultaneous CO and CO₂ hydrogenation are investigated with supported nickel and iron catalysts, and with a number of alloy catalysts.

Materials and Methods

The catalysts were prepared by incipient wetness impregnation of the support materials, alumina Al₂O₃, with aqueous solutions of the respectively metal nitrates to achieve the desired metal concentrations. The impregnated catalyst precursors were calcined in air and activated in the catalytic reactor by reduction immediately prior to testing. The simultaneous CO and CO₂ hydrogenation was tested at temperatures from 220-330°C with 150 mg of catalyst (0.25-0.50 mm) and a total flow of 6 l (STP) /h of a gas mixture containing 2% CO and 2% CO₂ in 96% H₂. The reaction rates were calculated from GC analyses of the exit gases. Selected catalysts were characterized by elemental analyses, BET surface areas, XRD and TEM.

Results and Discussion

The simultaneous CO and CO₂ hydrogenation experiments show that the activity for hydrogenation of both CO and CO₂ is increased for the alloy catalysts compared to the

monometallic catalysts. This is illustrated in Figure 1, where it is shown how the rate of CO₂ hydrogenation is significantly increased over the nickel-iron alloy catalysts compared to the pure nickel catalyst. It is found that the best catalysts have a Ni/Fe ratio above 1 and that the pure iron catalyst is much less active than the pure nickel catalyst. Thus, the activity pattern can be described as a volcano curve in agreement with previous studies conducted with a range of pure metal catalysts [6]. This work is a new example of the applicability of the interpolation concept [7] in catalyst discovery. It illustrates that the use of computational screening provides an interesting alternative to high-throughput screening and can provide new catalyst leads even for reactions that have been known for about a century. In the light of these promising results other bimetallic alloys have been investigated as catalysts for the methanation reaction too.

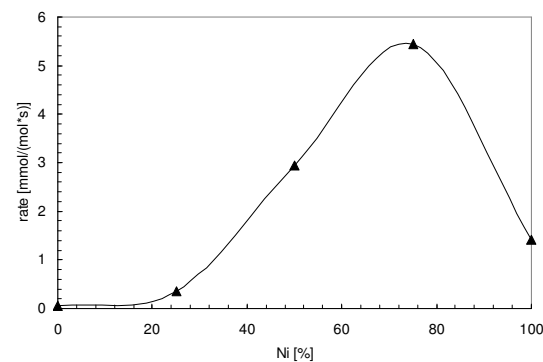


Figure 1. The figure shows the rate of CO₂ hydrogenation at 330°C for a series of Ni-Fe catalysts as a function of the nickel content. It is clear that the Ni-Fe alloys are much more active than the pure nickel catalyst.

Significance

We have designed and investigated several new methanation catalysts, which are both more active and cheaper than the industrially used Ni based catalyst for CO and CO₂ hydrogenation.

References

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