

Preparation and characterization of Ni-Ag surface alloy catalysts

Anh H. Dam¹, H. M. Wang¹, Roya Dehghan², John Walmsley², Anders Holmen¹ and Chen De^{1*}

¹Department of Chemical Engineering, Norwegian University of Science and Technology, N-7491 Trondheim, Norway

²Department of Physics, Norwegian University of Science and Technology, N-7491 Trondheim, Norway

*chen@chemeng.ntnu.no

Introduction

Hydrogen production is a matter of great importance, both in refinery and clean fuel production. Steam reforming of CH₄ is the largest and generally the most economical way to produce H₂ [1-3]. Nickel-based hydrotalcite-like (HT) materials have properties that make them suitable for preparing promising steam reforming catalysts. We have reported the preparation of highly dispersed and stable Ni/HT catalysts which were successfully applied in CH₄ steam reforming [4]. However, deactivations of Ni-loaded catalysts caused by coking, sintering or oxidation of the active metal species have been frequently reported.

Bimetallic catalysts are known to have higher activity and/or selectivity for various catalytic reactions than the pure metal catalysts. It has also been suggested that the addition of noble metals to a Ni catalyst may reduce coke deposition and therefore provide stability [5-8].

In this study, we report on preparation of bimetallic Ni(Ag)/HT catalyst using the redox reaction method to precisely control the surface composition. The advantage of this method is that Ag selectively associates on the surface of Ni nanoparticles instead of on/in the support. The work will deal with preparation and characterization of catalysts with various Ag/Ni ratios on the surfaces of Ni nanoparticles. A relationship between surface composition and kinetic performance was addressed.

Materials and Methods

Monometallic Ni/Mg(Al)O catalysts were prepared by using the co-precipitation method. Bimetallic Ni-Ag catalysts were prepared by redox reaction of the reduced monometallic Ni catalysts with an aqueous solution containing AgNO₃. Certain amount of Ni/Mg(Al)O catalyst was first added into a AgNO₃ aqueous solution. Then, a redox reaction occurred between Ag⁺ ions and Ni metal. The Ni²⁺ ions were gradually formed and Ag⁺ ions were reduced to Ag atoms which were deposited only on the surface of nickel particles. After the reaction, the product was passivated with 1vol% O₂/Ar and dried in air at 373 K. Subsequently the sample was calcinated at 873 K.

The mono and bimetallic catalysts were studied by different characterization techniques such as: Temperature programmed reduction (TPR), H₂-chemisorption, N₂-adsorption (BET), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Transmission electron microscopy (TEM) to obtain information about the structure and morphology of the catalysts.

Results and Discussion

We prepared particles of Ni(Ag)/Mg(Al)O by reducing NiO/Mg(Al)O mixed oxide and dipping it in an aqueous solution of Ag⁺ nitrate. From XRD results, during this treatment, reconstruction of Mg–Al hydrotalcite took place by a “memory effect”, and simultaneously Ag

was incorporated on the surface of Ni particles by replacement of the Ni site, resulting in the formation of highly dispersed Ni(Ag) bimetal supported catalysts.

After dipping Ni/Mg(Al)O mixed oxides in Ag⁺ nitrate aqueous solution, XRD observations clearly showed the formation of Mg–Al hydrotalcite. The surface areas and pore volumes of Ni(Ag)/Mg–Al hydrotalcite were drastically decreased comparing with Ni/Mg(Al)O mixed oxides. After the recalcination at 873 K, the Ni(Ag)/Mg(Al)O sample recovered the high surface area and mixed oxide structure of Ni/Mg(Al)O. The Ni catalysts derived from hydrotalcite precursors have pores distributed around 3 nm and 23 nm. But after redox reaction in the aqueous solution pore distribution was very different, which is only uniformly distributed around 3 nm. The changes in structures of the catalysts in different preparation steps were further studied by TEM to gain the insights of the changes at a nanometer level.

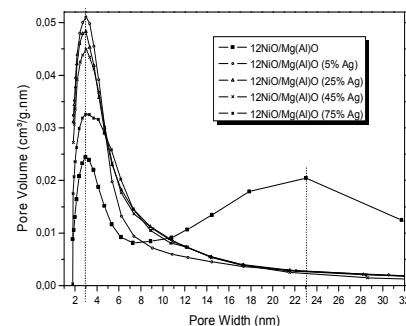


Figure 1. Pore size distribution of NiO/Mg(Al)O and NiO(Ag)/Mg(Al)O (%Ag: mol Ag/ mol Ni_{surface}).

The addition of Ag on Ni caused a decrease in the reduction temperature of Ni and a decrease in the amount of H₂ uptake on the Ni over the catalyst. In addition, XPS study confirmed the surface alloy formation of Ni-Ag. Therefore, it can be concluded that the surface redox reaction is a powerful tool to precisely introduce surface alloying of the Ni catalysts, confirmed by combined techniques such as TPR, Chemisorption, XPS, and TEM.

Effects of the surface alloy of Ag with Ni catalysts were further investigated in the CH₄ steam reforming reaction in a fixed bed reactor. It was found that surface alloying of Ag with Ni decreased the activity and increased activation energy, and that these changes were the function of the surface Ag/Ni ratio.

References

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