Promotion of unsupported nickel catalyst using iron for CO_2 methanation

*Dharmendra Pandey [a],[1], Koustuv Ray [b],[1], Rahul Bhardwaj [c], Sreedhar Bojja [d], K.V.R. Chary [e], Goutam Deo [b],***

[a] Department of Chemical Engineering, Birla Institute of Technology Mesra, Mesra 835215, India
[b] Department of Chemical Engineering, Indian Institute of Technology Kanpur, Kanpur 208016, India
[c] Advanced Imaging Centre, Indian Institute of Technology Kanpur, Kanpur 208016, India
[d] Inorganic and Physical Chemistry Division, Indian Institute of Chemical Technology, Hyderabad 500607, India
[e] Catalysis Division, Indian Institute of Chemical Technology, Hyderabad 500607, India

ARTICLE INFO

ABSTRACT

To facilitate the understanding of the Ni-Fe bimetallic system, unsupported nickel, iron and a series of Ni-Fe catalysts were synthesized, characterized and tested for the CO_2 methanation relevant for power to gas technology. Characterizations revealed the formation of various types of Ni-Fe alloys in the reduced catalysts. The activity results revealed that Ni-Fe catalysts with weight ratio of Ni:Fe > 1 showed a significantly improved rate (~2–5 times) of CO_2 conversion and CH_4 formation compared to Ni and Fe due to the formation of suitable nickel-rich Ni-Fe alloy. A change in surface morphology of these alloy catalysts was also detected. The Ni-rich Ni-Fe alloy formed in 90Ni10Fe and 75Ni25Fe differed from each other. The former was the most active due to the absence of unalloyed Fe, in contrast to the presence of unalloyed Fe in the later. Such observations would be helpful to design better performing Ni-Fe catalysts.

Introduction

Nickel-iron based catalysts are used for several reactions where hydrogen is a reactant or a product [1]. Furthermore, supported Ni-Fe catalyst produce enhancement in catalytic activity for the reactions like methane decomposition [2], steam reforming of acetic acid [3] and electrochemical water splitting [4]. In the supported catalysts the properties of Ni and Fe appear to combine in such a way that the activity and selectivity of certain reactions are enhanced [5,6]. In these reactions the improvement in activity has been attributed to various factors. These factors include the formation of alloys, change in reducibility, stabilization of the Ni phase and homogeneous distribution of the metals. However, the support may also play a role in the promotion of the catalytic reaction. To determine the role of the Ni-Fe bimetallic system independent of the support it would be worthwhile to study unsupported Ni-Fe bimetallic catalysts, though it is apparent that the unsupported catalysts would posses lower activity compared to their supported counterparts due to the limited active surface area. An increased understanding of the

unsupported Ni-Fe catalyst will have a significant effect on improving the performance of these catalysts.

Unsupported Ni-Fe bimetallic systems have also been used for several catalytic reactions. These reactions include the hydrodechlorination of trichloroethylene to hydrocarbons [7], decomposition of hydrous hydrazine [8,9], hydrolysis of ammonia-borane [10], and low temperature carbon nanotube growth [11]. In some of these supported and unsupported Ni-Fe based catalysts the Ni to Fe ratio has an effect on the catalytic activity and selectivity [8,9]. In contrast, an unsupported Ni-Fe catalyst with a Ni to Fe ratio of 2:1 was able to grow carbon nanotubes at a lower temperature compared to the pure Ni, Fe and other Ni to Fe ratios [11]. These unsupported Ni-Fe catalysts were primarily characterized by (low and wide angle) X-ray diffraction (XRD) [10], X-ray photoelectron spectroscopy (XPS) [8] and high resolution transmission electron microscopy (HRTEM) [8,10,11]. For supported Ni-Fe catalysts various other characterization techniques have been used [1,5,12—17]. Thus, to effectively investigate unsupported Ni-Fe catalysts of various Ni to Fe ratios it would be necessary to synthesize and characterize the corresponding samples, and then test the samples for a particular reaction. One such important catalytic process is the hydrogenation of CO_2 to CH_4.

The catalytic hydrogenation of CO_2 to CH_4 is also called the Sabatier reaction and has a wide range of applications, which include those related to energy. The energy related Power to Gas technology (also referred to as P2G or PtG) [18—20] has gained considerable attention. During the P2G process hydrogen is produced from electricity that is available from renewable sources or when there is a supply-demand difference. The hydrogen so produced can react with CO_2 to store energy as synthetic natural gas (methane). This provides a route to produce CO_2 neutral fuel by using H_2 [20]. The synthetic natural gas can be then be used as a fuel to generate power during power shortfalls or at regions having shortage of electricity. The synthetic natural gas when used as a fuel will produce CO_2, which can then be recycled [21]. Some of the other applications include the production of syngas, and the conversion of Martian CO_2 to CH_4 (fuel) and H_2O (life support) [22].

The CO_2 hydrogenation is thermodynamically favorable ($\Delta G_{298K} = -130.8$ kJ/mol). However, the reduction of the fully oxidized carbon to CH_4 requires a catalyst to achieve an acceptable rate and selectivity [23]. Hydrogenation of CO_2 to CH_4 has been studied over a number of catalysts based on group VIII metals supported on various oxides [22,24—29]. Of these different systems supported Ni catalysts remain the most widely studied material [30]. Furthermore, supported Ni-Fe catalysts have been successfully used for the hydrogenation of CO_2 to form CH_4 [5,6,31]. However, to the best of our knowledge unsupported Ni-Fe catalysts have not been considered for the CO_2 hydrogenation reaction. Thus, examining the catalytic activity of characterized unsupported Ni-Fe samples of different Ni to Fe ratios for the CO_2 hydrogenation reaction is a worthwhile investigation, and can provide more detailed information that can be useful to understand and improve upon the design and development of supported Ni-Fe catalysts.

In the present study unsupported Ni-Fe bimetallic catalysts were synthesized and characterized by ultraviolet and visible (UV—vis) spectroscopy, temperature programmed reduction using hydrogen (H_2-TPR), XRD, Scanning electron microscopy (SEM) with energy dispersive X-ray (EDX) mapping, XPS, Mossbauer spectroscopy, HRTEM and high angle annular dark field-scanning transmission electron microscopy (HAADF-STEM). The surface area of the catalysts was also determined by N_2 adsorption at 77 K. The catalysts were then probed by the CO_2 hydrogenation reaction to examine changes in catalytic activity. Physical mixtures of reduced Ni and Fe of the same ratio as those of catalysts were also tested for the CO_2 hydrogenation reaction for comparison.

Experimental

Catalyst synthesis

Unsupported Ni, Fe and Ni-Fe catalysts of varying Ni to Fe ratio were synthesized for the study. A mixture of Ni and Fe precursors of required Ni to Fe ratio was taken in a crucible and gradually heated in a muffle furnace from room temperature to 773 K and finally calcined at 773 K for 6 h. Nickel (II) nitrate hexahydrate (Sigma-Aldrich) and Iron (III) nitrate nonahydrate (Sigma-Aldrich) were used as precursor solution for Ni and Fe, respectively. The catalysts were referred to as xNi-yFe, where x and y were the wt.% of the Ni and Fe in the bimetallic sample. The unsupported single metal samples were referred to as 100Ni-0Fe and 0Ni-100Fe.

Catalyst characterization

The surface area of the reduced samples was determined using an Autosorb iQ (Quantachrome Instruments) surface area analyzer. All the samples were degassed at 423 K for 1 h prior to the measurement. The UV—vis—NIR spectra of the synthesized samples were obtained using a Cary 5000 instrument, which was equipped with a Praying Mantis and diffuse reflectance accessory (Harrick Scientific) [32]. The ambient spectra of the samples were collected using $BaSO_4$ as the reference.

The H_2-TPR profiles of all samples in the temperature range of 323—1223 K were obtained using a dedicated setup (Altamira AMI-200). The degree of reduction of the samples was also obtained for the samples reduced at 773 K for 4 h, which was the condition used for the catalytic runs. The detailed procedure in this experiment has been described elsewhere [33]. The amount of H_2 consumed was used to calculate the % degree of reduction which was determined from the H_2-TPR profile along with the calibration amounts of H_2 in Ar. For the Ni-Fe bimetallic catalysts, the total uptake of H_2 was assumed to be equally distributed between the Ni and Fe oxide phase according to the Ni:Fe molar ratios in each catalyst. Similar calculation procedures for determining the degree of reduction during TPR have been used previously [34]. Furthermore, to calculate the % degree of reduction the initial state of Ni and Fe oxide in the calcined samples was required. The initial state of Ni and Fe oxide were taken as those detected from the XRD patterns and UV—vis spectra of the calcined samples.

The XRD patterns of the calcined and reduced samples were obtained on a 180 Debye Flex-2002 X-ray Diffractometer. This instrument used Ni filtered K_α radiation from a Cu target ($\lambda = 1.541841$ Å) [35] and the diffraction patterns of all the