Alumina Supported Iron Catalyst for Hydrogen Production: Calcination Study

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Abstract—Production of clean hydrogen from thermal decomposition of methane was studied over impregnated 30%Fe/Al2O3 catalysts in a micro-activity fixed-bed reactor. The reactant gases comprising CH4 and N2 in the ratio of 1.5 to 1 were passed through reactor at a flow rate of 25 mL/min. Moreover, effect of calcination was investigated as well. The catalytic activity results indicated that calcination temperature had a significant impact on the performance of 30%Fe/Al2O3 catalyst. The catalyst calcined at 450°C, having CH4 conversion as well as H2 yield over 70%, showed better activity as compared to all other calcination temperatures.

Keywords—Hydrogen, Iron, CH4.

I. INTRODUCTION

WELCOME Hydrogen, a clean energy fuel, can be taken as a demanding alternative to conventional fossil fuels in order to reduce CO2 emissions [1-3]. Fossil fuels are generally accepted as a source for hydrogen production in the near future. Hydrocarbon reforming has been widely used so far for the production of hydrogen using metal based catalysts including Ni, Cu and Co but reforming leads to CO2 generation which needs to be captured to make the reforming process clean [4-8].

Hydrogen production near to its utilization place through small to medium decentralized installations would minimize the risks involved in hydrogen transport. Hydrogen production via methane reforming in these installations may significantly increase the cost of hydrogen production as CO2 needs to be transported to sink. Therefore, catalytic decomposition of methane (CDM) to hydrogen gas and solid valuable carbon can be considered a very interesting alternative to methane reforming [9].

Several factors including active metal, support, preparation method, calcination and activation temperatures significantly affect the catalytic performance during CDM. Pudukudy et al [10] studied the Thermocatalytic decomposition of methane as an alternative route for the production of COx-free hydrogen and carbon nanomaterials. They used bimetallic catalysts that include iron supported over mesoporous SBA-15. The results showed that the bimetallic catalysts were highly active and stable for the reaction at 700°C even after 300 min of time on stream (TOS). Formation of bimetallic alloys is related to the catalytic stability. Ibrahim et al. [11] investigated the decomposition of methane by iron catalyst to produce hydrogen and carbon. The catalysts were calcined at 700°C and reduced with pure H2 at 650°C. The reaction was carried out at 700°C. The study involved the use of different iron loadings supported on alumina catalysts obtained by co-precipitation technique. The catalyst characterization revealed the formation of multiwalled nanotubes from alumina supported iron catalyst. Alternatively, time on stream tests of the supported catalyst for about 4 h at 700°C showed the relative profile of hydrogen production and hydrogen yield increased as the % loading of Fe was increased. A maximum H2 yield of 77.2% was obtained using 60% Fe/Al2O3 catalyst. Higher Fe loadings decreased the surface area of the catalyst.

In this paper, we have investigated the effect of calcination temperature over impregnated 30%Fe/ Al2O3 catalysts. Catalyst characterizations have been employed to study the behavior of catalyst before and after reaction. Moreover, a short description related to effect of activation temperature over impregnated 30%Fe/ Al2O3 catalyst has been added as well.

II. EXPERIMENTAL AND PROCEDURES

A. Catalyst Preparation and Testing

The wet-impregnation method was used to prepare the catalysts and the total Fe loading with all catalysts were fixed at 30 wt % with respect to Al2O3 support. In a typical wet-impregnation process, the solution having a stoichiometric amount of iron nitrate nona-hydrate [Fe(NO3)3·9H2O] was prepared using double distilled water. Afterwards respective supports were added to the solution with constant stirring at 85 °C. Then catalysts were dried at 120 °C for about 13 h, followed by calcination at different temperatures i.e., 50, 500, 550 and 600 °C in atmospheric air for 3h.

The prepared catalysts were tested in a micro-activity fixed bed tubular reactor (10 mm ID) coupled with K-type thermocouple using 0.3 g of the catalyst at different reaction temperatures and space velocities. Prior to CDM reaction, each catalyst was first reduced under H2 flow (40 mL/min) at 500°C for 90 min. The products of the reactor were analyzed by using an online GC (Varian Star 3400 cx; Ar as carrier) equipped with a thermal conductivity detector and a gas sampling valve.

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2.2. Catalyst Characterization

The specific surface area of the catalysts was determined from N2 adsorption-desorption data at -196°C by using a Micromeritics Tristar II 3020 surface area and porosity analyzer. For each analysis, 0.3 g of catalyst was degassed at 300°C for 3 h to rid the catalyst surface from moisture content and other adsorbed gases.

The TPR measurements were completed on a chemisorption apparatus (Micromeritics Auto Chem II apparatus) using 70 mg for each sample. The samples were pretreated with high purity Argon (Ar) flowing at 150°C for 30 min, followed by cooling to room temperature and then heating in a furnace up to 1000°C with a constant heating rate of 10°C/min using a H2/Ar mixture flowing at a rate of 40 mL/min (volume ratio, 10/90). The signal of H2 consumption was monitored by a thermal conductivity detector (TCD).

III. RESULTS AND DISCUSSIONS

The calcination step perhaps has the most influence on the properties of the prepared catalyst. Selection of proper calcination temperature is of extreme importance in the preparation methods of catalysts. Fig.1 shows the N2 partial pressure adsorption during the measurements of surface area for 30%Fe/Al2O3 catalyst at different calcination temperatures. The quantity of the gas adsorbed increases with the increase of the partial pressure for all calcination temperatures. However, the catalyst calcined at 600°C adsorbs the most amount of N2 and hence gives the highest surface area (BET), but the catalyst calcined at 500°C indicated relatively the highest BET instead of that calcined at 600°C.

IV. UNITS

Fig. 2 displays the TPR curves of 30%Fe/Al2O3 catalysts calcined at 450, 500, 550 and 600°C. TPR patterns for different calcined catalysts are rather alike to each other stipulating that catalysts have experienced thoroughly similar reduction behavior. The response of temperature scans using hydrogen as reducing agent provides three peaks in the TPR profiles. Their signals appear around 250-460, 484-810, 835-945°C with maximum peaks centered at 400, 710 and 898°C respectively. These regions of temperature obviously identify that catalytic methane decomposition follows three mechanisms that are predominant at different temperatures. The first peak is ascribed to the transformations of FeOOH → Fe2O3 while the second peak is attributed to the reduction of Fe2O3 → Fe3O4, and third peak is assigned to Fe3O4 → Fe. Here, again the response peaks of 450°C calcined catalyst are clearly mostly shifted to lower temperature reduction showing easiest reduction behavior. While the catalyst calcined at 550°C indicates the strongest metal support interactions and therefore its response appears fairly at highest reduction temperature.

On the other hand, Fig. 3 exhibits the time on stream methane conversions of 30%Fe/Al2O3 catalysts prepared by impregnation method, calcined at 450, 500, 550 and 600°C and operated at 700°C. It is evident that the conversion increases and remains constant after an hour. The catalysts calcined at 450°C gives the best performance of conversion and stability. The trend of conversion is similar to that of Fig. 3. However, the stability of the best catalyst, catalyst calcined at 450°C, becomes constant after 90 minutes. Fig. 4 shows the time on stream against hydrogen yield for 30%Fe/Al2O3 catalysts prepared by impregnation method, calcined at 450, 500, 550 and 600°C and operated at 700°C. Catalyst calcined at 450°C tops in yield and stability than all other catalysts right from the initial period.
Clean hydrogen production from methane decomposition reaction was investigated over impregnated 30%Fe/Al$_2$O$_3$ catalyst. Furthermore, effect of calcination temperature was studied as well. The catalytic performance results showed that catalyst calcined at 450°C exhibited better activity, in terms of CH$_4$ conversion as well as H$_2$ yield, as compared to the rest of the catalysts.

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REFERENCES


