Production of Hydrogen and Carbon Nanotubes using Ni SBA-15 Catalyst

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ABSTRACT: Thermo Catalytic Decomposition of Methane Using Ni/SBA-15 catalyst was tested in a fixed bed reactor to simultaneously produce hydrogen and carbon nanotubes. SBA-15 nano catalysts were successfully been synthesized using p123, tetraethyl ortho silicate and Ni $(NO_3)_2.6H_2O$ as template, silica source and Nickel nano particle precursors respectively under acidic hydrothermal conditions. The BET surface area, pore size distribution and low angle X-ray Diffraction (XRD) studies revealed that the retention of hexagonally ordered behaviour in the catalysts. Wide angle XRD study divulged the crystalline behaviour of Nickel oxide species and these Nickel oxide species are in nano range. The catalytic activity experiments were preceded by blank tests intended to ascertain that the reaction did not take place to an appreciable extent in the absence of the catalyst. With SBA-15 alone and Ni alone reaction has not been taken place. Even with 50Ni-SBA-15 and 70Ni-SBA-15 catalysts reaction was not occurred. Only low loading Ni-SBA-15 catalyst was found to be active towards the conversion of methane into the corresponding hydrogen. Among all other catalysts, 30Ni-SBA-15 we observed to produce high yield of hydrogen produced 20% to 50% of H_2 at a moderate temperature of 1123 K (850ºC) and the catalytic activity of the catalyst remains stable for 5hrs.

KEYWORDS: Thermo catalytic decomposition, methane, hydrogen, carbon nanotubes, Ni/SBA-15.

1 INTRODUCTION

Hydrogen is expected to become an important energy carrier for sustained energy consumption with reduced impact on the environment. A hydrogen-based energy system is regarded as a viable and advantageous option for delivering high-quality energy services [1]. Traditionally, hydrogen is synthesized through steam reforming and/or partial oxidation of methane. Methane decomposition into hydrogen and carbon is of current interest as an alternative route of hydrogen production [2, 3]. Methane decomposition produces hydrogen only as a gaseous product. It is well known that supported Nickel (Ni) catalyst is one of the most effective among the catalysts tested so far [4-6]. We have already examined the catalytic performance of Ni catalysts supported on different supports and obtained the highest yields of hydrogen. The catalyst decomposed methane actively at the early period of the reaction. However, the activity of the catalyst decreased gradually with time on stream and finally the catalyst was deactivated completely. Thus, the catalysts having a longer life should be explored. In addition, the supported Ni catalysts cannot decompose methane efficiently at temperatures higher than 923K because of a very rapid deactivation after contact with methane, while they are very active for the reaction in the temperature range from 773 to 873K [7].

SBA-15, discovered as an ordered mesoporous silica a few years ago, presents some advantages as a catalyst support, such as high surface area (600-1000 m2/g) and a hexagonal structure of mesopores with size 4.6–30 nm and thicker walls (3.1-6.4 nm) [8]. Unfortunately, few investigations of Ni/SBA-15 catalysts prepared with the deposition precipitation method were reported [9]. Therefore, it is interesting to employ SBA-15 as a support in combination with advantages of deposition precipitation method for preparing highly active methane decomposition catalysts with high dispersion, narrow particle distribution and high thermal stability. A series of Ni/SBA-15 catalysts have been prepared by the deposition precipitation method and used to produce COx-free hydrogen from methane decomposition in the present work.

SBA-15 materials have been prepared in acidic conditions with poly (alkaline oxide) tri-block co-polymers. They usually have wider pores than MCM-41, with the reported SBA-15 pore diameters up to 300A. Both solids have periodically ordered structures, which consist of two-dimensional hexagonal arrays of uniform mesoporous.

SBA-15 is a far the largest pore size mesoporous material with highly ordered hexagonally arranged meso channels, with thick walls, adjustable pore size from 3 to 30nm, and high hydrothermal and thermal stability. SBA-15, which possesses larger pores, thicker walls and higher thermal stability as compared other mesoporous silica may be used a promising catalyst support, particularly for reactions occurring at high temperatures. The base mesoporous materials have often been modified by adding noble metals or metal oxides in order to improve their physical and chemical properties. Recently, there are various studies carried out by using SBA-15 as support.

According to the IUPAC notation, a mesoporous material can be disordered or ordered in a meso structure. The first mesoporous material, with a long-range order, was synthesized in the late 80s/ early 90s, by a research group of the former Mobil Oil Company .Since then, research in this field has steadily grown. Notable examples of prospective applications are catalysis, sorption, gas sensing, optics, and photo voltaics. Mesoporous materials are those with pores in the range 20-500Å in diameter. They have huge surface areas, providing a vast number of sites where sorption processes can occur. These materials have numerous applications in catalysis, separation and many other fields. The synthesis of these materials is of considerable interest and is constantly being developed to introduce different properties.

In this paper we discuss about the hydrogen production on various Ni/SBA-15 catalysts using thermo catalytic decomposition of methane. Among all, 30Ni-SBA-15 catalyst showed highest percentage of Hydrogen as 50%. Ni/SBA-15 catalysts were characterized by BET surface area, pore size distribution, X-ray diffraction (XRD) and scanning electron microscopy (SEM).

2 EXPERIMENTAL

2.1 MATERIALS

All the chemicals used for this work are purchased from Ni $(NO_3)_2.6H_2O$ (98wt% purity; M/s Fenar Reagents, India); Conc. HCl (35 wt. %; Make: M/s Qualigens, India), Tetra ethyl ortho silicate (TEOS), Tri block co-polymer (Sri Sudhi Chemicals, Hyderabad) and deionized water.

Gases: Nitrogen and Methane (Purity: 99 vol %) from BOC India Ltd.

2.2 CATALYST PREPARATION

2.2.1 SBA-15 SYNTHESIS

SBA-15 support has been prepared in accordance with the literature reports [10]. In a typical synthesis, approximately 20g of tri block copolymers (P123) was dispersed in 460ml of deionized water in a 1000ml glass beaker at ambient temperature for 4-6h. About 102 g of 35% hydrochloric acid was added under constant stirring. Stabilizing the reaction temperature at 35 - 45ºC, 44g of silica source, i.e., tetraethyl orthosilicate (TEOS) was added drop by drop within a single stretch of 10min under continuous stirring. The color of reaction mixture changed into milky white with certain suspension within a half hour time. The reaction is continued for a period of 12h for the completion of TEOS hydrolysis. The hydrolyzed gel was transferred to an autoclave and subjected to heat treatment (aged) in an oven at 100ºC for 12h. Latter on the white precipitate that formed was separated by filtration under reduced pressure in hot condition followed by drying at 100ºC for 12h. This dried white powder is generally called as 'as made SBA-15'. The occluded P123 template in the as made SBA-15 was removed by calcination using a muffle furnace under static air condition by gradual increase of temperature from ambient to 550ºC with a heating rate of 1ºC/min and maintained the constant temperature of 550ºC for 8 h.

2.2.2 NI-SBA-15 SYNTHESIS

Ni-SBA-15 synthesis is prepared by pH adjustment method. In this method tri block copolymer, P123 was used as a structure directing agent, TEOS as a Si source, Nickel nitrate taken as a Ni precursor and HCl as an acidic media. First 20gm of P123 polymer was taken in to 1L beaker and then 390ml of distilled water was added and stirred at RT (30ºC) for 3-4 h until attainment of clear solution. Latter on 9ml of HCl (35%) was added and stirred for one hour and then required quantity of TEOS was added at 40ºC in different molar ratios. This solution was stirred at 40ºC for 12h. Then the mixture was aged at 100ºC for overnight without stirring and then obtained solid product was washed and dried for 12h at 100ºC. Finally the

catalysts were calcined at 550ºC in air for 6h for complete removal of template. The Ni-SBA-15 catalyst samples were designated as xNi-SBA-15 (x refers to the mole percent of Ni in SBA-15).

2.3 EXPERIMENTAL SET UP

2.3.1 CATALYTIC ACTIVITY MEASUREMENT

The stainless steel reactor is filled with ceramic beads of size 5mm X 5mm up to the centre of the reactor. A thin bed of quartz wool is created on the top of ceramic beads. 2.5g of various Ni wt% supported on SBA-15 [x Ni-SBA-15, where x = 10, 30, 50 and 70 wt%] has been placed on quartz wool to make 2g of x Ni-SBA-15 catalysts. NiO can be completely reduced to Ni by treating it with methane at 998K [12, 13]. The metal reactor is heated up to the nickel oxide reduction temperature of 998K under nitrogen flow rate of 54cm3 (STP/min). The nitrogen is slowly replaced with high purity methane (99.99 vol %) on the attainment of 998K and the flow is maintained at 54cm3 (STP/min). The reduction process is carried out for 15min. Methane reduces NiO to Ni as per the following reaction [19]

$$4NiO + CH_4 \rightarrow 4Ni + CO_2 + 2H_2O \qquad (1)$$

After 15min, methane gas is replaced with nitrogen and the reactor temperature has been raised to 1123K. On the attainment of reaction temperature (1123K), nitrogen is once again replaced with methane. The methane gas flow rate is set at 54cm^3 (STP/min) (VHSV: 1.62 L/hr g) using rota meter. The initial gas samples have been collected immediately after 5min in a 1L Teddlar bag. By maintaining the methane flow rate at 54cm^3 (STP/min) and reactor temperature at 1123K, reactor effluent gas samples have been collected in Teddlar bags at an interval of 1h for 4h. The initial gas sample and gas samples collected at the end of each hour in 4h duration have been analyzed for methane decomposition products using Agilent Gas chromatography (GC) equipped with thermal conductivity detector (Oven Temperature: 80ºC; Detector Temperature: 100ºC; Injector Temperature: 100ºC) and porpak Q column. Nitrogen has been used as carrier gas. The calibrated data of hydrogen and methane have been obtained using the standard gases, hydrogen (99.99 vol%, BOC India Ltd) and methane (99.99 vol%, BOC India Ltd). AIMIL GC data sheet has been used in the analysis of GC data. The concentrations of hydrogen and methane in gas samples have been determined using the calibrated data. In all the experiments no methane decomposition products other than hydrogen and unconverted methane have been detected in the effluent gas.

2.4 CATALYST CHARACTERIZATION

The Catalysts were thoroughly characterized by different techniques such as Brunauer-Emmett- Teller (BET) surface area, Barrett-Joyner-Halenda (BJH) Pore size distribution, X-ray diffraction (XRD), Scanning Electron Microscopy (SEM).

The N$_2$ BET surface area measurement has been carried out after catalytic test using surface area analyzer SMART SORB93 by pre-treating the samples at 473K for 2h under nitrogen purging. Nitrogen adsorption/desorption isotherms obtained at 77K have been used to calculate BET surface area. Total pore volume (PV) has been estimated according to the BJH method from the adsorption data [14].

XRD patterns of all the catalysts in this study were obtained on a Rigaku Miniflex X-ray diffractometer (M/s. Rigaku Corporation, Japan) using Ni filtered Cu K$_\alpha$ radiation.

The Surface morphology of 30Ni-SBA-15 catalysts after the catalytic activity has been analyzed using Hitachi S-3700 variable vacuum SEM at an accession voltage of 15.0KV, using a carbon conducting tape adhered on aluminum stub.

The initial gas sample and gas samples collected at the end of each hour in 5h duration have been analyzed for methane decomposition products using GC equipped with thermal conductivity detector (Oven temperature:80ºC; Detector temperature:100ºC; Injector temperature: 100ºC) and porpak Q column. Nitrogen has been used as carrier gas. The calibrated data of hydrogen and methane have been obtained using the standard gases, hydrogen (99.99 vol%, BOC India Ltd) and methane (99.99 vol%, BOC India Ltd). AIMIL GC data sheet has been used in the analysis of GC data. The concentrations of hydrogen and methane in gas samples have been determined using the calibrated data.

3 RESULTS AND DISCUSSIONS

The Hydrogen production is observed in only in 10Ni-SBA-15 and 30Ni-SBA-15 catalysts. With SBA-15 and Nickel we did not observed any hydrogen production and also in high Ni metal loading of 50Ni-SBA-15 and 70Ni-SBA-15 catalysts also did not produced any hydrogen. Among 10Ni-SBA-15 and 30Ni-SBA-15 catalysts, 30Ni-SBA-15 catalyst produced high hydrogen production. Because of this reason 30Ni-SBA-15 catalyst is used for further study.

The catalytic activity of 30Ni-SBA-15 catalysts is as follows: The initial hydrogen production within a 15min is 20% of H_2; for 1hr, it has been slightly decreased to 18% of H_2; again from 2hr to 5hr, it has been increased to 30% H_2, 45% H_2, 48% H_2 and 50% H_2 is observed.

3.1   CATALYST CHARACTERIZATION

3.1.1   BET SURFACE AREA

The BET surface areas of different Ni-SBA-15 catalysts were shown in Table 1. As the molar composition of Ni increase in/ on SBA-15 from 10 to 70, there is a gradual decrease in surface area was observed. The decrease in surface areas with increased loading of Ni prepared by direct synthesis method may be due to diminishing of mesoporous silica ratio particularly at higher loading Ni-SBA-15 catalysts.

Table 1: BET surface areas Ni-SBA-15 catalysts

S.No	Catalyst	BET Surface Area (m^2/g)
1	10Ni-SBA-15	726.98
2	30Ni-SBA-15	668.99
3	50Ni-SBA-15	515.32
4	70Ni-SBA-15	415.83

N_2 adsorption–desorption isotherms for Ni-SBA-15 catalysts were shown in Fig. 1: All the nitrogen adsorption-desorption isotherms are found to be of Type IV in nature as per the IUPAC classification and exhibited a H1 hysteresis loop, which is typical of mesoporous solids. The adsorption branch of isotherm obtained for 10Ni-SBA-15 showed a sharp inflection. This is a characteristic of capillary condensation within uniform pores. The position of the inflection point is clearly related to a diameter in the mesopore range, and the sharpness of these steps indicates the uniformity of the mesopore size distribution. There is a small deformation in shape of the hysterosis loops, which is an indication of the partial collapse in the hexagonal mesoporous ordering. This kind of behavior is seen in higher Ni loading catalysts.
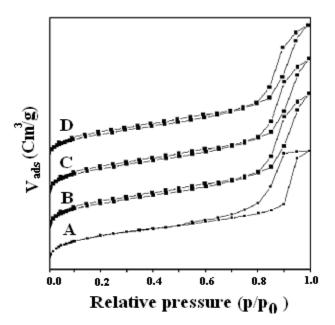

Fig.1. N_2 adsorption-desorption isotherms of different Ni- SBA-15 catalysts. (A) 10Ni-SBA-15, (B) 30Ni-SBA-15, (C) 50Ni-SBA-15, (D) 70Ni-SBA-15
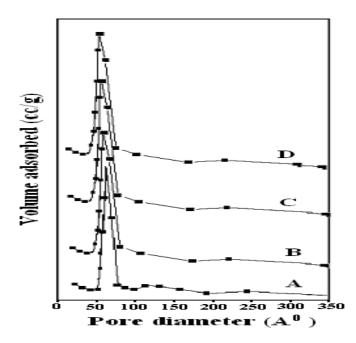
Fig.2. Pore size distribution of different Ni- SBA-15 catalysts. (A) 10Ni-SBA-15, (B) 30Ni-SBA-15, (C) 50Ni-SBA-15, (D) 70Ni-SBA-15

The pore size distribution curves of all the Ni-SBA-15 catalysts are shown in Fig. 2, which shows an average pore size of about 70Å for all the catalysts. Furthermore, a narrow pore size distribution is observed for all of the catalysts. Interestingly, an increase in the mesopore size is noticed with an increase in Ni loading. Such a trend may correspond to a decrease in wall thickness of the crystallized samples with an increase in Ni loading. These results indicate that the Ni-substituted SBA-15 could be crystallized without any decrease in mesopore size via a direct synthesis approach under hydrothermal conditions.

Determining the specific surface area, pore volume, and pore size distribution, as well as the surface properties. The adsorption isotherm provides an enormous amount of information about the surface properties. There are six types of isotherms possible, but only five apply to materials.

Type I isotherms indicate micropores. Neither type II nor type III isotherms contain hysteresis loops. These designate macroporous solids. Type IV and V isotherms possess hysteresis loops and are indicative of mesoporous solids.

The pore size distribution of a material is usually determined via the Barrett Joyner, and Halenda (BJH) method. The BJH method utilizes an algorithm that depends on the accuracy of the relation between pore size and capillary condensation/evaporation pressure, the correct t-curve(s), and the aptness of the adsorption/desorption curves.

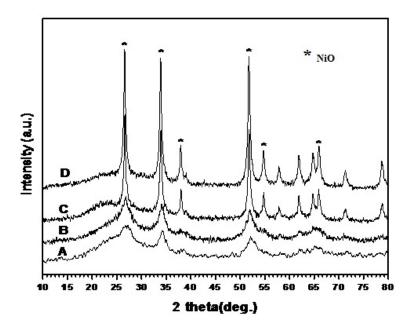**3.1.2 POWDER X-RAY DIFFRACTION ANALYSIS (XRD)**

Fig.3. X-ray diffraction patterns of different Ni- SBA-15 catalysts. (A) 10Ni-SBA-15, (B) 30Ni-SBA-15, (C) 50Ni-SBA-15, (D) 70Ni-SBA-15

The XRD patterns of different Ni-SBA-15 catalysts are shown in Fig. 3. Poorly resolved XRD reflections were observed for the low Ni loaded samples, viz., 10Ni-SBA-15, and 30Ni-SBA-15 catalysts. The crystalline behavior of casseterite phase of Nickel oxide was clearly seen from the Fig. 3. There is a sequential enhancement in the Nickel oxide phase from lower to higher loadings of Ni. Except Nickel oxide phase, no other phases of Ni oxides or metallic Nickel were observed. i.e., phase purity is the importance of this direct hydrothermal synthetic route, particularly for the synthesis of Ni-SBA-15 catalysts. XRD patterns of all the catalysts in this study were obtained on a Rigaku Miniflex X-ray diffractometer (M/s. Rigaku Corporation, Japan) using Ni filtered Cu K_{α} radiation.

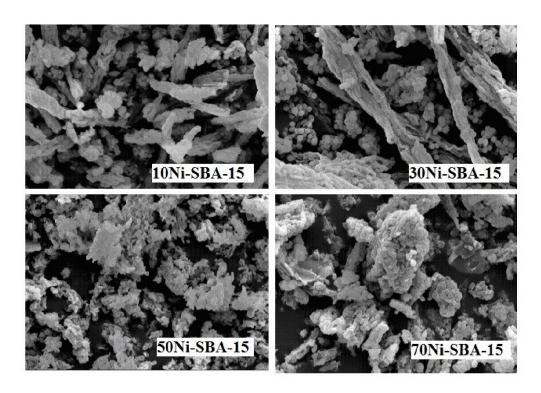### 3.1.3 SCANNING ELECTRON MICROSCOPY (SEM) ANALYSIS

Fig.4. SEM Images of different Ni- SBA-15 catalysts. (A) 10Ni-SBA-15, (B) 30Ni-SBA-15, (C) 50Ni-SBA-15, (D) 70Ni-SBA-15

Scanning electron microscopic images are shown in Figure 4; these SEM images of mesoporous materials with different loading of Ni have different morphologies. 10Ni-SBA-15 and 30Ni-SBA-15 catalysts are more less having the morphology of original SBA-15. As the loading of Ni increases, mesoscopic order has been diminished. Only the aggregate of Ni is seen in both 50Ni-SBA-15 and 70Ni-SBA-15catalysts.

The catalytic activity of Ni-SBA-15 catalysts can be seen from the Table 2. The catalytic activity experiments were preceded by blank tests intended to ascertain that the reaction did not take place to an appreciable extent in the absence of the catalyst. With SBA-15 alone and Ni alone reaction has not been taken place. Even with 50Ni-SBA-15 and 70Ni-SBA-15 catalysts reaction was not occurred. Only low loading Ni-SBA-15 catalysts were found to be active towards the conversion of methane into the corresponding hydrogen.

Table 2: The Catalytic Activity of different Ni-SBA-15 catalysts

S.No	Catalyst	H_2 Production (%)
1	SBA-15	Nil
2	Nickel	Nil
3	10Ni-SBA-15	10
4	30Ni-SBA-15	20
5	50Ni-SBA-15	Nil
6	70Ni-SBA-15	Nil

High hydrogen production is observed in 30Ni-SBA-15 catalyst among all other catalysts. Because of this 30Ni-SBA-15 is selected for further study.

Table 3: The Catalytic Activity of 30 Ni-SBA-15 catalysts

Time	H_2 Production (%)
15min	20
1 hr	18
2 hr	30
3 hr	45
4 hr	48
5 hr	50

The catalytic activity of 30Ni-SBA-15 catalysts is as follows: The initial hydrogen production within a 15min is 20% of H_2; for 1hr, it has been slightly decreased to 18% of H_2; again from 2hr to 5hr, it has been increased to 30% H_2, 45% H_2, 48% H_2 and 50% H_2 is observed. The catalytic activity of 30Ni-SBA-15 for H_2 production is shown in figure 5. The graph is plotted between Time and Hydrogen Production (%); where on X-axis Time is plotted and on Y-axis Hydrogen Production (%)
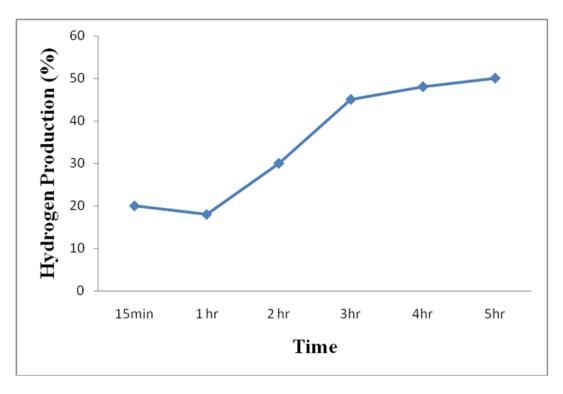

Fig.5. Catalytic Activity of 30 Ni- SBA-15 catalyst for H_2 Production

4   CONCLUSION

SBA-15 nano catalysts were successfully been synthesized using p123, tetraethyl ortho silicate and Ni $(NO_3)_2.6H_2O$ as template, silica source and Nickel nano particle precursors respectively under acidic hydrothermal conditions. The BET surface area, pore size distribution and low angle XRD studies revealed the retention of hexagonally ordered behavior in the catalysts. Wide angle XRD study divulged the crystalline behavior of Nickel oxide species and these Nickel oxide species are in nano range. The catalytic activity experiments were preceded by blank tests intended to ascertain that the reaction did not take place to an appreciable extent in the absence of the catalyst. With SBA-15 alone and Ni alone reaction has not been taken place. Even with 50Ni-SBA-15 and 70Ni-SBA-15 catalysts reaction was not occurred. Only low loading Ni-SBA-15 catalysts were found to be active towards the conversion of methane into the corresponding hydrogen. Among all other catalysts, 30Ni-SBA-15 we observed high percentage of hydrogen production.

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