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PREPARATION AND CHARACTERIZATION OF ZEOLITE BETA SUPPORTED MONOMETALLIC AND BIMETALLIC CATALYSTS

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ABSTRACT : Biomass is an abundant renewable energy source and potentially produces hydrogen-rich gas by steam gasification. However, produced gas from this process usually contains unacceptable level of tars which can cause blockage and corrosion to the gasification system. Therefore, several catalysts have been investigated to counter this problem in addition to increase the overall efficiency of biomass conversion. In this study, Ni-Fe loaded on zeolite β has been prepared by incipient wetness impregnation method to be used as a catalyst in biomass conversion to H_2. The catalysts were characterized by physicochemical techniques such as Thermogravimetric Analysis (TGA), Powder X-Ray Diffraction (XRD), Brunauer-Emmett-Teller (BET) and Field Emission Scanning Electron Microscopy (FESEM). The strong interactions between Ni and Fe with zeolite β could control the reducibility of nickel oxide and prevent carbon deposition on the catalyst during steam gasification of biomass. The addition of Fe will help to stabilize the catalyst structure and provides partial protection against catalyst deactivation. As a result, tar free production of hydrogen-rich gas can be achieved.

KEYWORDS : Biomass gasification, catalyst, monometallic, bimetallic, zeolite β.

INTRODUCTION

Biomass is an unlimited renewable energy source, and its gasification to synthesise gas and hydrogen is an environmentally attractive method for energy production. The gases which mainly consist of H_2 content, CO, CO_2, CH_4 and various light hydrocarbons (Zhang *et al.*, 2007) can be potentially used either as a gaseous fuel for power generation or as a feedstock for clean transportation fuel such as methanol, Fisher-Tropsch oils or many other chemical related applications (Kimura *et al.*, 2006). Nevertheless, biomass derived gasification also produces several undesirable amounts of ash particle, char, volatile alkali metals and tar. Tar is a complex mixture of acids, aldehydes, ketones, alcohols, phenols and aromatic hydrocarbons (Uddin *et al.*, 2008)

Utilizing catalytic cracking to some extent in the biomass gasification is not only to accelerate reaction rate and lower reaction temperature but also to eliminate tar in the product (Hu *et al.*, 2006) and emphasize on the production of hydrogen-rich gas. In most cases, the catalyst deactivation due to coke deposition can be one of the critical problems which limit the catalyst activity. Coke is a solid carbon (char or tar) that can be deposited on the catalyst surface (Nakamura *et al.*, 2008) during gasification process.

Several studies have shown that three distinct groups of catalyst have been crucially investigated in the biomass gasification: non-metallic oxides such as dolomite and olivine, alkali metals and nickel based catalyst (Hu *et al.*, 2006; Sutton *et al.*, 2001). For non-metallic oxides, the activity of dolomite and olivine was more dependent on the Fe_2O_3 contents, which played an important role in lowering the rate of coke formation (Rapagna *et al.*, 2002).

Nickel-based catalyst is very active in tars elimination. However, the activity of the catalyst is sensitive to nickel loading and metal dispersion (Nakamura *et al.*, 2008) where the reaction is frequently accompanied by coke formation and sintering of Ni metal particles, leading to catalyst deactivation. According to previous studies, the addition of metal support such as SiO_2, Al_2O_3 (Sato & Fujimoto, 2007) are known to have been ineffective in obtaining a good interaction between Ni. This may be due to metallic particles that tend to migrate and form larger aggregates, reducing the dispersion of catalyst and consequently the catalyst activity (Rapagna *et al.*, 2002). In contrast, dolomite and olivine which contains Fe helps stabilize Ni in the support (Zhang *et al.*, 2007) and gives an important effect on precursor reducibility as well as catalytic properties.

Apart from that, commercially available alkali metal catalysts are also active in reforming hydrocarbon and diminish the tar content in the gas mixture. According to Nordgreen *et al.*, (2006), when metallic Fe is utilised as tar-depleting catalyst in the gasification of biomass, the product gas has significantly lower tar content. The capacity of Fe to diminish the tar content in the product gas is demonstrated to be in the range of the capability of dolomite. On the other hand, as Fe is used in the form of metal oxides, the effectiveness of the catalyst for tar reduction is reduced.

Zeolites β are crystalline, microporous, hydrated aluminosilicates of alkaline or alkaline earth metals. The frameworks are composed of $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedral, which corner-share to form different open structures. Due to the excellent properties, zeolites β have been widely used in numerous technical applications as catalysts, adsorbents and ion exchangers (Rios *et al.*, 2009). Specifically, it is of interest to investigate the activity of metals supported on zeolites β for the development of a metal-based catalyst for the biomass gasification because of the remarkable catalytic performance of these solids in the reaction.

In order to eliminate most of the inconveniences encountered with the present catalysts in the biomass gasification processes, zeolite β supported monometallic and bimetallic Fe and Ni catalysts have been developed. A second metal component is introduced to form a bimetallic catalyst system with the intention of improving the anti-coking property of the catalyst.

In this study, bimetallic structures such as FeNi and NiFe in which Fe and Ni are compatible elements have been prepared. The strong interactions between the Fe and Ni elements included in the structure will limit the sintering of the active species as well as carbon build-up. Hence, combination of Fe and Ni active metals and zeolite β as support could mitigate the problems faced with current gasification catalysts.

MATERIALS AND METHODS

Catalyst Preparation

The catalyst preparation can be divided into two steps which is monometallic and bimetallic preparation. For monometallic preparation, 5 (wt%) metal loading of Ni and Fe based catalysts were prepared using incipient wetness impregnation method with zeolite β as the support.

In a typical preparation, zeolite β was calcined at 500 °C for 16 hrs before they were crushed and sieved to particles size between 250 – 750 µm prior to use. A required amount of $FeCl_3.6H_2O$ or $NiCl_2.6H_2O$ was dissolved in sufficient amount of deionised water. Then, 95 g zeolite β was added to the metal salt solution under continuous stirring. The slurry formed was impregnated for 4 hr under stirring and later dried at 120 °C for 16 hr. Finally, the dried samples were calcined at 500 °C for 16 hr.

For preparation of bimetallic catalysts, the metals was loaded into the support via a two-step impregnation method whereby the first impregnation method is the same as preparing the monometallic 5 % Fe and Ni catalysts. The second metal was introduced in the second impregnation step using another 5 wt% metals, yielding 5 % Fe 5 % Ni/zeolite β and 5 % Ni 5 % Fe/zeolite β catalysts which are designated as FeNi/zeolite β and NiFe/zeolite β, respectively where in AB/zeolite β, metal B was impregnated first, followed by metal A.

Catalyst Characterization

The prepared catalysts were characterized by typical characterization methods such as Thermal Gravimetric Analysis (TGA) to determine the weight loss of absorbed moisture and decomposition of metal salt in the catalyst, Powder X-Ray Diffraction (XRD) for crystalline phase and crystallite size identifications, Brunauer-Emmett-Teller (BET) for determination of total surface area, volume and also pore distribution and Field Emission Scanning Electron Microscopy (FESEM) to study the morphology of the catalysts.

RESULTS AND DISCUSSION

The TG analysis of monometallic and bimetallic catalysts (Figure 1) showed the weight loss steps of the catalyst samples prepared by wet impregnation method. Practically, absorbed moisture was fully removed after the calcinations process. But the result showed 13 % of absorbed moisture was still observed in the catalysts between room temperature and 120 °C. This indicates that the prepared catalysts especially zeolite β can easily absorbed the moisture from air. However, decomposition of metal salts was fully achieved after calcinations at 500 °C even Fe/zeolite β catalyst shows a slight degradation at this temperature.

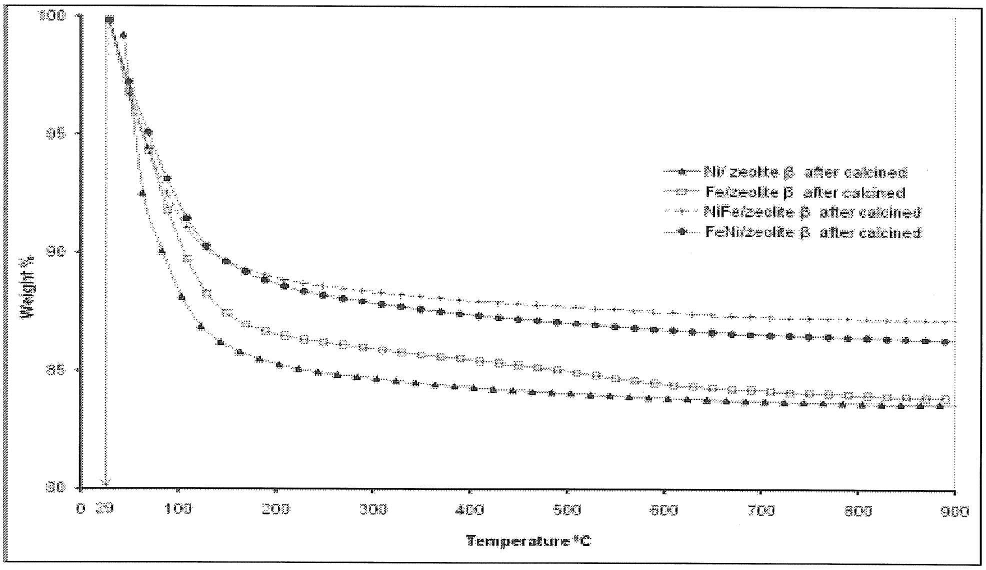

Figure 1. *The TGA profile of the monometallic and bimetallic catalysts after calcinations at 500 °C*

The removal of the moisture and decomposition of metal salt is significant in catalyst preparation in order to enhance the productivity and effectiveness of the catalyst.

Characterization by XRD analysis of Fe and Ni loaded on zeolite β in Figure 2 showed the appearance of both active metals as two diffraction peaks which is corresponding to hematite, Fe_2O_3 (at 2θ = 33.0° and 35.5°) and bunsenite, NiO (at 2θ= 37.1° and 43.2°) respectively. The strong interactions between these two elements in bimetallic catalysts allow for a better control of the degree of reduction of the catalyst, preventing the oxidation of metallic Ni sites, and provide partial protection against catalyst deactivation (Rapagna *et al.*, 2002). The dominant peaks for zeolite β were at 2θ = 8° and 22.5°. (The intensity of zeolite β diffraction peaks was high and quite broad illustrating that the peaks containing Si and Al which is more than one element). Most of the Al are tetrahedral (two different Al tetrahedral sites), and a small amount of Al^{3+} and Al_2O_3. However, when both Fe and Ni were incorporated with zeolite β and monometallic catalysts in order to form bimetallic, the intensity of zeolite β peak becomes lower and shifted due to removal of one Al tetrahedral site and is probably associated with the ions metal that occupied the lattice site. Referring to the values reported from International Centre for Diffraction Data (ICDD) the prepared catalysts had hexagonal structure (SS-NNNN 89-5416) for Fe_2O_3 and cubic structure (SS-NNNN 47-1049) for NiO, respectively.

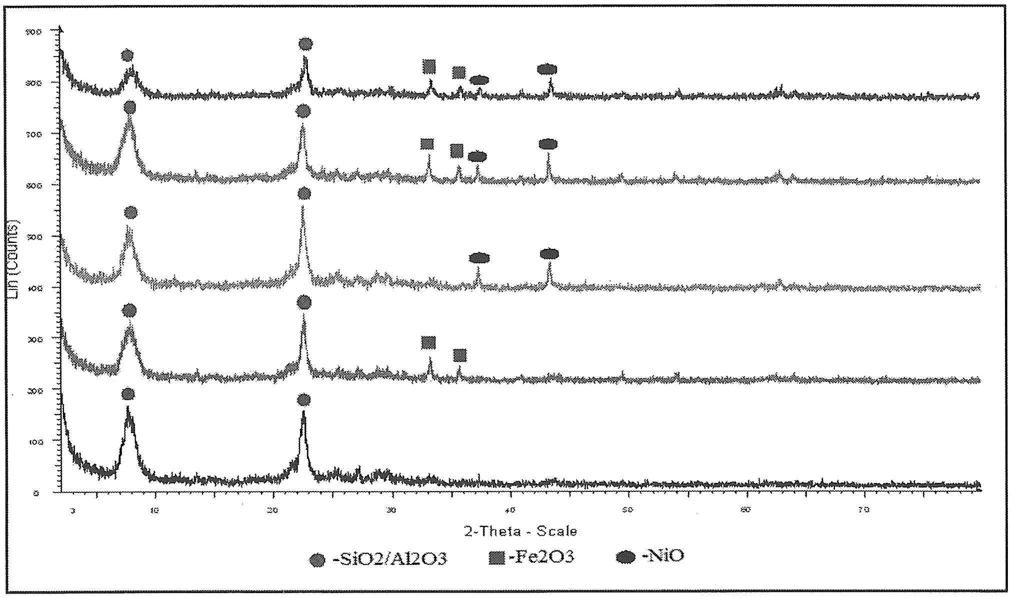

Figure 2. *XRD patterns for Fe and Ni loaded on zeolite β (a) zeolite β, (b) Fe/zeolite β, (c) Ni/zeolite β, (d) FeNi/zeolite β, (e) NiFe/zeolite β*

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The result can be proved by estimating the crystallite size of the catalysts based on the basis of line broadening analysis using Scherer's formula. Referring to Table 1, the crystallite size value of bimetallic is not as high as compared to monometallic catalysts since it depends on the metal loaded into the zeolite β instead of agglomeration between the metals. In fact, when second metal was impregnated with the monometallic catalysts the second metal has higher crystallite size value.

Table 1. Crystallite size of the catalysts

Catalyst	Crystallite size (nm)
Fe/zeolite β	96.92926
Ni/zeolite β	74.76854
FeNi/zeolite β	
Fe	95.41263
Ni	94.00173
NiFe/zeolite β	
Fe	70.05418
Ni	74.22434

The morphology of the prepared catalysts was examined by FESEM and the images are displayed in Figure 3. From Figure 3, the zeolite β which is a conventional catalyst has fine particle size with indistinct features and do not seem to have any changes when impregnated with the first metal for monometallic preparation. This occurred because only a small amount of metal 5 % was added and as a result, the metals were packed into the particles. However, when the particles or monometallic catalysts were incorporated with the second metal particle, the prepared catalysts revealed a crystalline structure instead of indistinct features. This is illustrated in more detail by Figure 3 (d) and (e). The Fe was shown in hexagonal structure meanwhile Ni in a cubic structure as confirmed in the XRD measurement. This is as a result of the metal tendency to agglomerate when the second impregnation occurred.

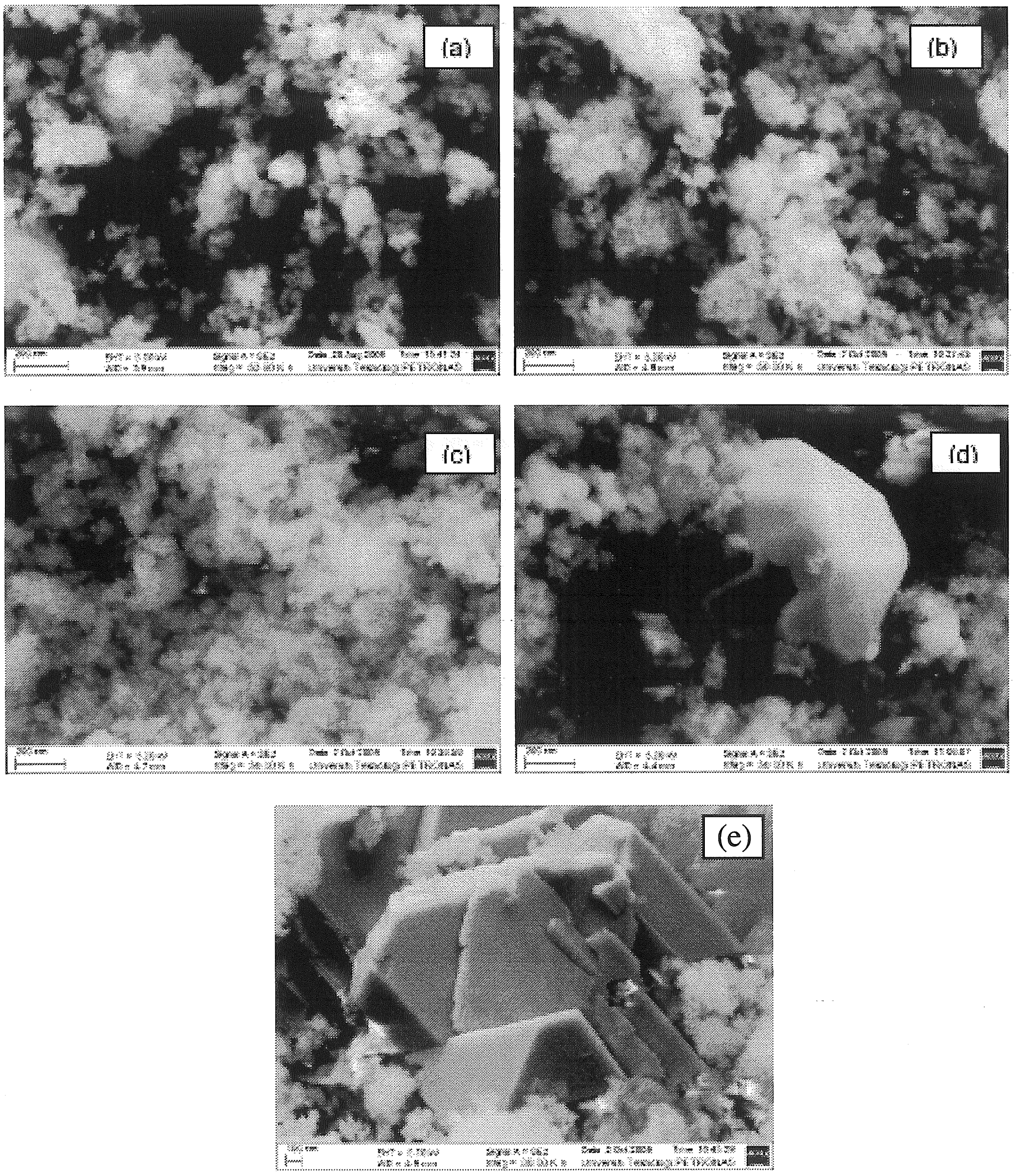
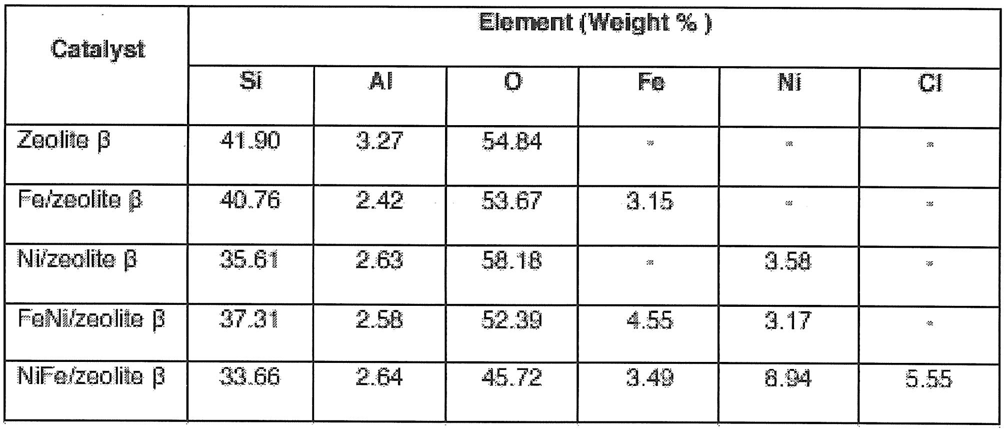


Figure 3. *FESEM images of synthesized catalysts (a) Zeolite β, (b) Fe/zeolite β, (c) Ni/zeolite β, (d) FeNi/zeolite β, (e) NiFe/zeolite β*

EDX data of the prepared catalysts are taken to study the elemental analysis. Table 2 shows that, Fe and O have been detected which verifies the prepared catalyst in the form of hematite, Fe_2O_3 phase which agrees well with the XRD analysis. Meanwhile Ni and O verified that the catalyst is in the form of nickel oxide NiO phase and Si-Al is in the form of zeolite β. When the Fe and Ni were impregnated together with zeolite β, it shows that both phases were present in the bimetallic catalysts. The atomic percentage of metal for monometallic catalysts is 3.15 % for Fe/zeolite β and 3.58 % for Ni/zeolite β, respectively. The measured element ratio of metal has a close agreement with the starting materials which is 5 %.

Table 2. EDX data for monometallic and bimetallic catalysts



Catalyst	Element (Weight %)					
	Si	Al	O	Fe	Ni	Cl
Zeolite β	41.90	3.27	54.84	-	-	-
Fe/zeolite β	40.76	2.42	53.67	3.15	-	-
Ni/zeolite β	35.61	2.63	58.18	-	3.58	-
FeNi/zeolite β	37.31	2.58	52.39	4.55	3.17	-
NiFe/zeolite β	33.66	2.64	45.72	3.49	8.94	5.55

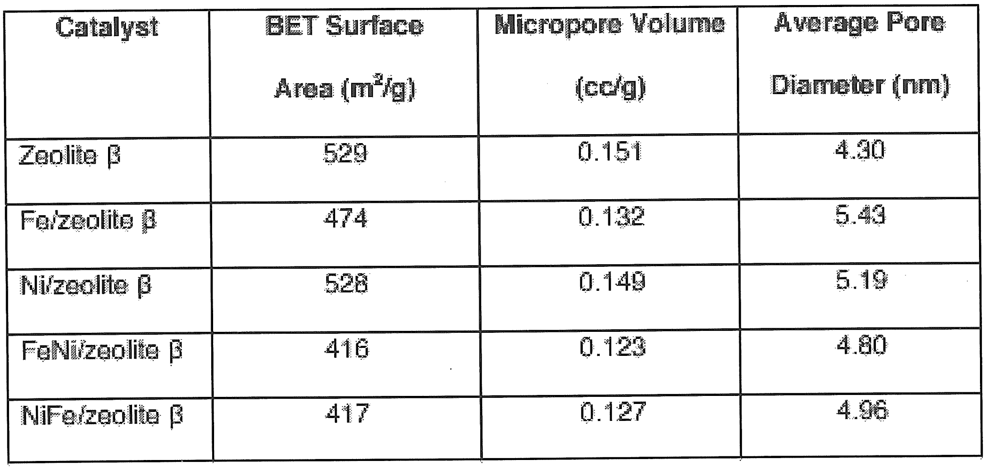
For bimetallic catalyst, the atomic percentage for both metal are different where the first metal loading with support has less percentage compared to the second metal. This is because the second metal has covered the first metal during the impregnation. Additionally, the presence of 3.45 % Cl as an impurity was detected in NiFe/zeolite β decomposition of Fe and Ni during calcinations. This has resulted the atomic percentage of Ni element to be larger than 5 %.

Pore structure is equally crucial to material performance since porosity can increase the available surface area from a few to literally hundreds of square meters per gram. Accessibility of this surface area via pore tortuosity and opening size determines material performances which have a great influence on production rates. Limiting the pore size allows only molecules of desired sizes to enter and leave. Materials with more available surface area are generally more active, more adsorptive, sintered at lower temperature and exhibit more catalytic activity (Webb & Orr, 1997).

Table 3 shows that the surface areas of the samples are varied widely where fresh zeolite β has bigger surface area compared to the prepared catalyst. Once zeolite β is incorporated with Fe and Ni, the surface area is reduced. The effect becomes more significant for the bimetallic systems. The influence is so pronounced in some instances that Fe and Ni has occupied the zeolite β pore which resulted in the surface area reduction. The reduction of the surface area for bimetallic catalysts should be twice than the monometallic. However, the results showed less surface area which could be due to the overlapping of the metals, reduction instead of occupying sites in the zeolite β. In addition, the surface area of the catalyst is identical with the volume where the size of volume is reduced when more metals were impregnated with zeolite β. Based on the data; the prepared catalysts have a greater surface area and smaller volume.

On the other hand, the average pore diameter for fresh zeolite is 4.30 nm smaller than the synthesized catalyst ranging from 4.8 to 5.4 nm. This happened due to the acidic nature of the metal salts used for impregnation which attack the support pore opening leading to a bigger pore size and deformation of some of the continuous surface into smaller non-continuous surface.

Table 3. Textural properties of the catalyst prepared



Catalyst	BET Surface Area (m^2/g)	Micropore Volume (cc/g)	Average Pore Diameter (nm)
Zeolite β	529	0.151	4.30
Fe/zeolite β	474	0.132	5.43
Ni/zeolite β	528	0.149	5.19
FeNi/zeolite β	416	0.123	4.80
NiFe/zeolite β	417	0.127	4.96

Comparison between adsorption and desorption isotherms often indicates pore complexity. Figure 5 shows the adsorption and desorption isotherms for Fe/zeolite β and corresponding to all catalysts since each isotherms plot classified as Type IV. The isotherms rise comparatively rapidly at intermediate relative pressure and show a wide hysteresis loop. This behaviour is typical of mesoporous catalyst which corresponds with the average pore diameter of the prepared catalysts of greater than 2 nm. The initial rise in the curve is due to adsorbing molecules interacting first with the most energetic areas of the catalyst surface and then with the less energetic areas. The rise of the curve diminishes as these areas are occupied. By the midpoint of the curve, the attachment of additional gas molecules layer proceeds on the sites that were already occupied. While, the abrupt rise at the end is due to the adsorbing gas at the beginning of bulk condensation to a liquid (Webb & Orr, 1997). Theoretically, the exact shape of the loop varies from one adsorption system to another but the amount adsorbed is always greater at any given relative pressure along the desorption than along the adsorption (Gregg & Sing, 1982).

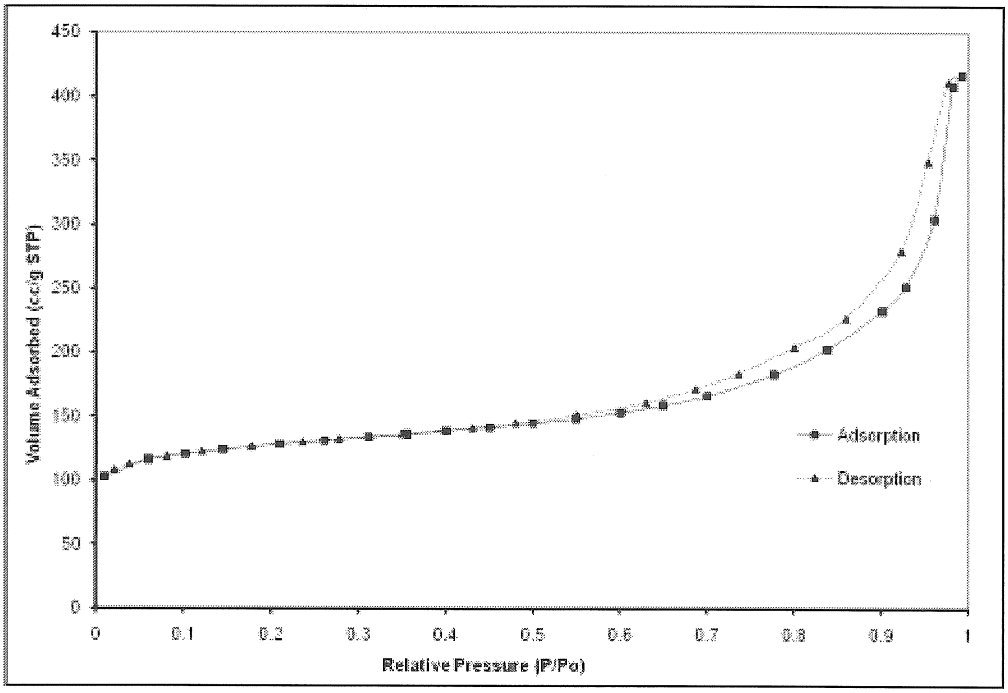


Figure 5. *Adsorption and desorption isotherms for Fe/zeolite β*

CONCLUSION

Monometallic and bimetallic catalysts with zeolite β as supports have been prepared with an impregnation technique and fully characterised in relation to their structure. XRD characterization revealed that both active metals Fe and Ni corresponds to Fe_2O_3 and NiO. The strong interactions between these two elements in bimetallic catalysts can play an important role in minimising the formation of coke thus ensure longer catalyst lifetime during the catalytic steam gasification reaction. For FESEM characterization, the morphology of bimetallic catalyst was improved by revealing a crystalline structure compared to monometallic with indistinct features. Characterization by means of BET indicates that the prepared catalysts were mesoporous and has a bigger surface area which has a good dispersion, more active and exhibit more catalytic activity in the gasification application.

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