CHAPTER II

EXPERIMENTAL

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II.1. Catalyst preparation

Several catalysts were prepared by loading of Pt and Ni with different percentage over different supports as SBA-15 and AlSBA-15 through wet impregnation technique.

II.1.1. Synthesis of the support

(a) **Siliceous SBA-15** material was synthesized according to the procedure described by Zhao et al. ,[48] using Pluronic P123 triblock copolymer ($EO_{20} - PO_{70} - EO_{20}$; Aldrich) as template. In a typical synthesis: 4 g of pluronic 123 was dissolved in 30 g of distilled water and 120 g of 2 M HCl solution with stirring at 40 °C. 8.50 g of tetraethyl othosilicate (TEOS; Aldrich) was added into that solution with stirring at 40 °C for 20 h, followed by aging at 80 °C over night without stirring. The solid product was recovered by filtration, washed several times with distilled water, and air-dried at room temperature for 24 h. the template was removed from the as-synthesized mesoporous material by calcination at 500 °C for 6 h (Heating rate = 1 °C min^{-1}). This calcined support was denoted as SBA-15.

(b) **AlSBA-15 material** was prepared by direct synthesis method using aluminum isopropoxide (AIP; Aldrich) as aluminum source following the published procedure described by Vinu et al.[90] in a typical synthesis: 4 g of P123 was added to 30 ml of distilled water. After stirring for a few hours, a clear solution was obtained. Thereafter, 70 g of 0.28 aqueous HCl was added and the gel formed was stirred for another 2 h at 40 °C. Then, 9 g of tetraethylortho silicate (TEOS; Aldrich) and the required amount of aluminum source were added to obtain n_{Si}/n_{Al} ratio (5, 7and 14). Then the resultant mixture was stirred for 24h at 40 °C and finally heated to 100 °C for 48 h without stirring. The solid product was recovered by filtration, washed with distilled water for several

times, and dried overnight at 100 °C. Finally; the product was calcined at 540 °C to remove the template. The molar gel composition of the gel was1TEOS:0.02–0.15 Al_2O_3:0.016 P123:0.46 HCl: 190 H_2O. The samples were denoted as AlSBA-15(x) where x refers to the n_{Si} / n_{Al} molar ratio.

II.1.2. Loading of metallic part

SBA-15 support was loaded with (0.3 and 0.6 wt%Pt) and (5, 10 and 15wt% Ni).While AlSBA-15 (5, 7 and 14) supports were loaded with (0.3 and 0.6 wt%Pt) and (2.5 and 7.5 wt %Ni).

(a) Loading of platinum

The supports were impregnated with 0.002 M solution of $H_2PtCl_6.6H_2O$.The calculated volumes of impregnating solution were added to the supports in order to obtain 0.3 and 0.6 wt%Pt in the final catalysts. The slurry was stirred for few minutes and dried at 110 °C for 16h and calcined at 450 °C for 2h.

Calcination before reduction is important because it removes the water molecules still contained in pores of the support and allows the stabilization of active sites. Without this treatment the Pt (IV) ions will be very mobile in presence of water at high temperature leading thereby to agglomeration of metallic Pt particles.[129] The obtained samples in oxide form were reduced at 350 °C in a steam of dry and clean hydrogen gas with a flow rate 100 mL /min for 4h to obtain Pt/support catalysts.

(b) Loading of nickel

The supported samples were prepared by impregnating the required amount of the support with proper concentrations of Ni $(NO_3)_2.6H_2O$ aqueous solution (viz., 5, 10, 15 wt% Ni/SBA-15 ‹ 2.5 and 7.5 wt% Ni/AlSBA-15). The obtained slurry was stirred vigorously for 15 min and dried at 110 °C for 16 h. The dried samples were calcined at 200 °C for 4 h in a stream of air for decomposition of the impregnated salts to the corresponding metal oxide. The calcined samples were heated in H_2 atmosphere at 350 °C for 4h to obtain Ni/support catalysts.

II.2.Catalyst characterization

II.2.1. X-ray diffraction analysis (XRD)

X-ray diffraction patterns of mesoporous samples were collected on a PAN analytical X' Pert Pro diffractometer Using Cu K_α (λ= 0.1542 nm). The differactograms were recorded in the 2θ range of 0.5-70° with a 2θ step size of 0.02 Å and a step time of 0.60 s. Computer file storage made it possible to compare the obtained differactograms to that of known compounds taken from JCPDS (the Joint Committee on Powder Diffraction Standards) index.

II.2.2. Nitrogen physisorption

Nitrogen adsorption-desorption isotherms at -196 °C were obtained with a NOVA 3200 Unit, USA apparatus, using volumetric technique. The samples were previously out-gassed under vaccum at 250 °C for 4 h to remove the moisture and other impurities. Surface areas were calculated with Brunauer Emmett and Teller (BET) equation from nitrogen uptakes at relative pressure (P/P^o) ranging from 0.05 to 0.35. The total pore volume derived from the amount of nitrogen adsorbed at the relative pressure close to unity by assuming that all the accessible pores had been filled with condensed nitrogen in the normal liquid state. Whereas pore size distributions were determined by Barrett, Joyner and Halenda (BJH) method applied to the adsorption branch of the isotherms. The adsorption branch was favored over the desorption branch in order to avoid the Tensile Strength Effect (TSE) artifact which very often complicates the PSD determination in mesoporous systems.[130]

II.2.3.Thermal Analysis

Thermogravimetric measurements (TGA) and Differential Scanning Calomitery (DSC) were performed in N_2 gas flow at a flow rate100 mL min^{-1} on SDTQ-600 (TA-USA) thermobalance instrument. About 6 mg of sample was heated up to 600 °C, with a heating rate (10 °C min^{-1}).

Thermodynamic functions as enthalpy, heat capacity (Cp, cal /g.deg) and entropy change (ΔS, cal /g.deg) were calculated from DSC curves for all samples according to:

$$\mathbf{Cp} = \Delta H / \Delta T .^{131}$$

Where $\Delta T = T_2 - T_1$ ($\mathbf{T_1}$ is the temperature at which the DSC peak begins to leave the base line, whereas $\mathbf{T_2}$ is the temperature at which the peak lands) and **ΔH** (is the measure of the intensity of the resulted DSC peak).

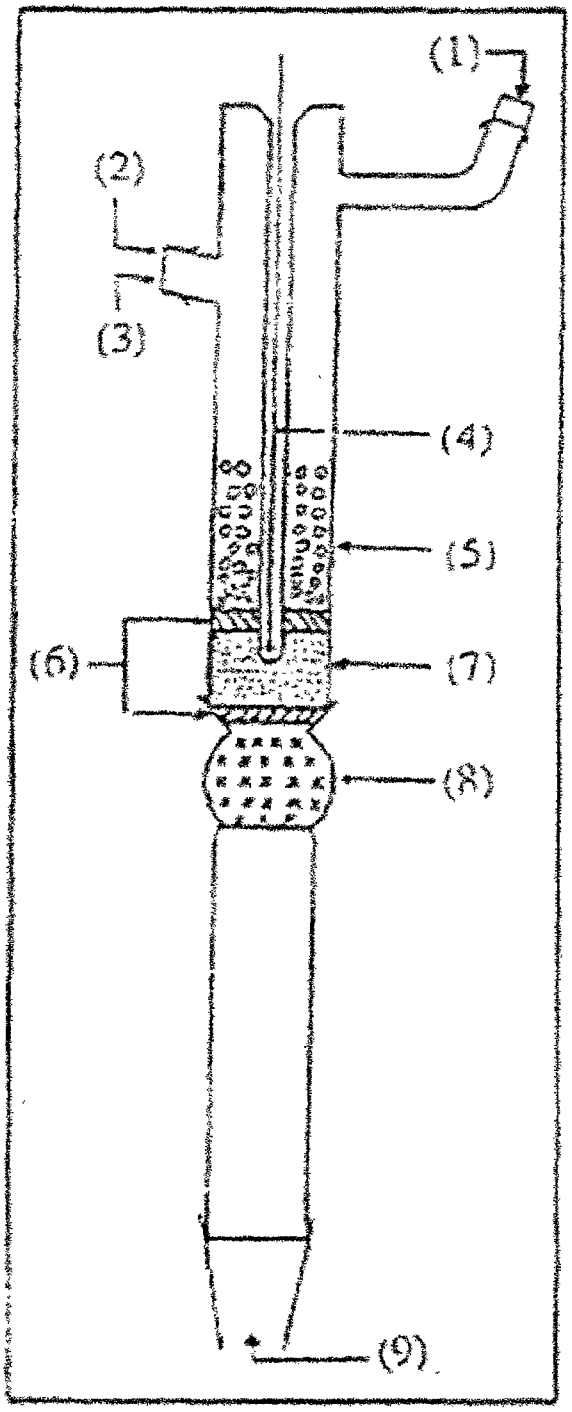
$$\mathbf{\Delta S} = 2.303\ Cp \log (T_2 / T_1).^{131}$$

II.2.4.Catalytic activity

Catalytic activities of the prepared catalyst samples were tested through cyclohexane dehydrogenation and n-hexane hydroconversion (hydroisomerization and hydrocracking) as two model reactions using a micro catalytic pulse technique.

The reaction was carried out under atmospheric pressure and temperature range250-450 °C. Hydrogen carrier gas flow rate was kept constant at 50 mL/min and dried over 5 Å molecular sieves before entering the reactor. Prior to catalytic activity test, the investigated catalyst samples were activated by heating in H_2 atmosphere at 450 °C for 2 h. Few doses of reactants were injected first to reach a steady state of the activity.

Micro catalytic unit (Fig.7), is manually constructed, assembled and calibrated at the catalysis department, Egyptian Petroleum Research Institute (EPRI). This unit is mainly composed of a Pyrex micro reactor directly attached to a gas chromatographic analysis system in order to provide immediate analysis of reactor effluents. The micro reactor was filled with 0.25g of the tested catalysts and the reactants were injected in micro quantities (2μL) by micro syringe in the form of pulses. The reactor is heated in a furnace controlled by proportional band- pyrometer. This control system renders the reactor



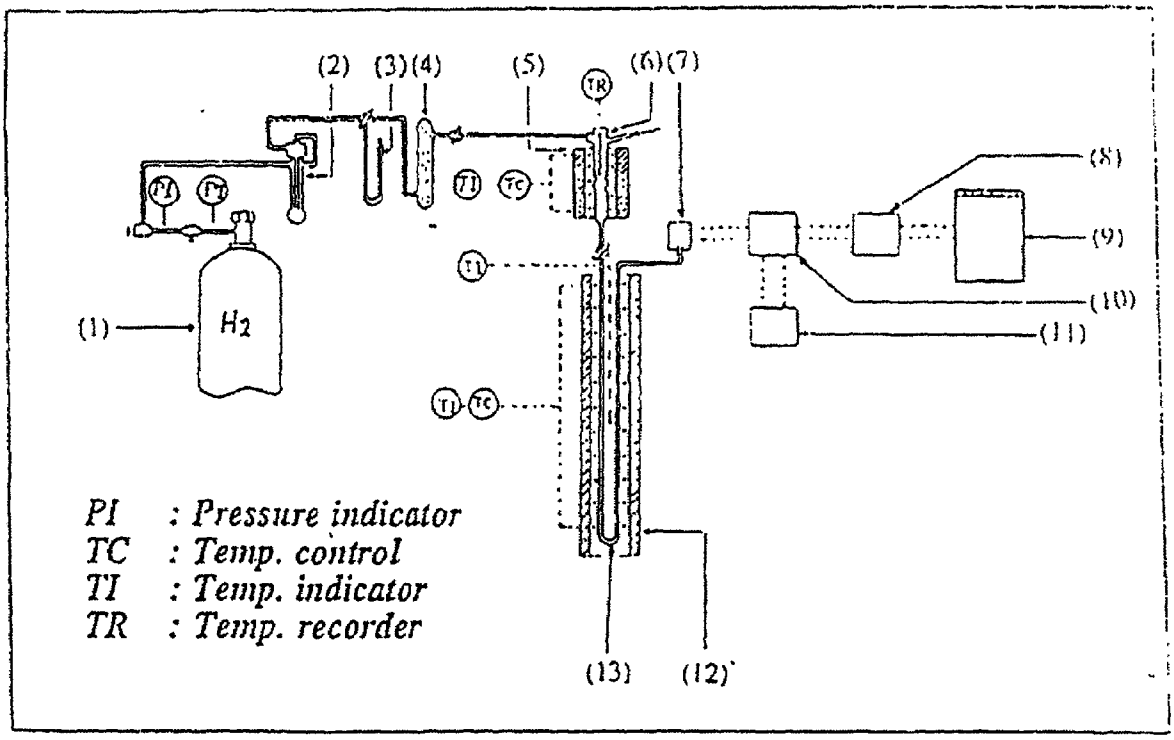
(1)Carrier gas inlet
(2)Reactants inlet
(3)Injector port
(4)Ni /Ni-Cr thermocouple
(5)Glass beads
(6)Thin quartz layer
(7)Catalyst bed
(8)Glass wool
(9)To chromatographic column

Fig. 7 : Micro Catalytic Reactor

temperature at a maximum fluctuation of ±1°C. Reactor temperature is measured and recorded, using a Ni-Ni Cr thermocouple, placed in the center of the catalyst bed (Fig. 7).

Chromatographic part (Fig.8) is mainly composed of a chromatographic column and a detector. The Chromatographic column has u form with 0.3cm internal diameter and 200 cm length. It is placed in a 1.5-meter vertical tube furnace controlled by an on-off electronic pyrometer and its temperature was adjusted and controlled at 40 °C. The column was packed with acid washed PW chromsorb (60-80 mesh size) loaded by 15% by weight squalane.

The chromatographic detector is a flame ionization type, [132] which is locally designed and constructed. The chromatograph is attached to a data station to calculate the weight percent of the effluent products. The main electric power entering the unit (220 V A.C.) was stabilized by voltage stabilizer (isolated by 220/220V isolating transformer) in order to stabilize the unit and protect it from external noise.



(1) H_2 cylinder (2) Flowmeters (rotometers) (3) Manometer
(4) 5Å Molecular sieve drier (5) Reactor Furnace (6) Reactor
(7) H_2 Flame ionization detector (8) Electronic integrator (9) Chart recorder
(10) Flame ionization circuit (11) D. C. source (12)Chromatographic oven
(13) chromatographic column

Fig.8 : Pulse Micro Catalytic Unit