Research Note

Treatment of Diatomaceous Earth to Obtain its Catalyst Support

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Treatment of diatomaceous earth with sulfuric acid reduces mineral and organic impurities, such as Fe_2O_3, Al_2O_3 and alkali metal oxides (CaO, MgO and Na_2O). In addition, wettability and porosity of the acid-treated diatomite are greatly enhanced. Acid-treated diatomite is suitable to be used as a siliceous support for catalysts, due to high silica content (> 90%), amorphous structure with low cristobalite and quartz phases, appropriate Brunauer-Emmett-Teller surface area, high absorptive capacity, good mechanical strength after calcinations and low cost of production. In the first part of this study, the influence of temperature, sulfuric acid concentration, acid-diatomite mass ratio and time of acid treating was investigated on one sample of diatomite obtained from one of the Khorassan Province mines (sample A). Then, the determined optimum ranges of the aforementioned parameters were tested on other samples of diatomite obtained from Tabriz and Khorassan mines (sample B) and the Persian Gulf seashore. Results confirmed the determined optimum conditions for acid treatment of diatomite.

INTRODUCTION

Diatomaceous earth is a siliceous, sedimentary rock consisting principally of the fossilized skeletal remains of diatom, a unicellular aquatic plant. Diatomaceous earth in land and marine resources is chalk like and is white, gray, pink, blue or green in color. The color depends on its impurities [1]. More than 60% of its world production is used for filtration and clarification of liquids, while the remaining 30% is used as filler and thermal insulating material [1-9]. Because of its unique properties, it can be utilized as a catalyst carrier and a chromatographic support [10-12].

Silica makes up the bulk of the chemical composition of commercial diatomites (usually 70-90%), the rest includes alumina (0.6-8%), iron (0.2-3.5%), alkali metal oxides, Na_2O and MgO (less than 1%), CaO (0.3-3%) and a minor amount of other impurities, such as P_2O_5 and TiO_2.

Sand, clay, carbonate and organic material are

typical common contaminants [1-3,7,8]. Organic material and carbonate decompose to CO_2, SO_2 and H_2O gases and leave the bulk of diatomite during the thermal operation, such as calcination [5,6,9].

Diatomite is divided into two broad categories: Centric and pennate. The centric type has circular, triangular and spherical shapes with radial symmetry. The pennate type has a large and a short axis with vertical symmetry along the large axis. Figure 1 shows different microscopic structures of diatomite [1,9]. These structures, apart from their biological importance, create higher surface area and porosity, which distinguishes diatomite from other siliceous minerals.

The silica of diatomite resembles opal or hydrous silica in composition ($SiO_2.xH_2O$) [1,9]. Diatomite is highly resistive against many chemical compounds. Only hydrofluoric acid and strong alkali solutions can affect it. Furthermore, diatomite has a low specific gravity ranging from 1.95 to 2.3. Although it has very low surface adsorption, diatomite possesses a high absorptive capacity, due to the presence of, most probably, mesopores, which create high capillary pressure (according to Laplace's equation). This feature makes it suitable for impregnation with catalytic active components. Diatomite has also an appropriate

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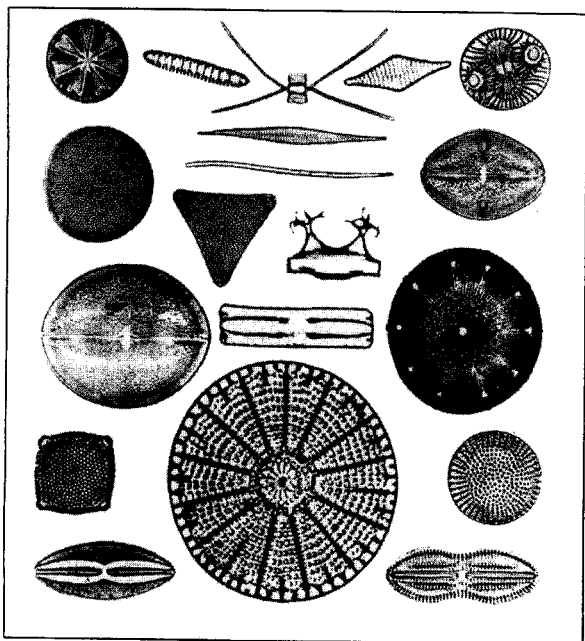
Figure 1. Microscopic structures of different types of diatomite.

surface area, $16 - 70 \times 10^4$ cm^2/g and a low heat of conduction [1-3,9].

DIATOMITE TREATMENT

Natural diatomite does not possess enough absorptive capacity and wettability, which are required for catalyst support. In addition, its mineral and organic impurities have a negative effect on the activity of the final catalyst. It is, therefore, necessary to remove these impurities.

In the present study, treatment of diatomite with sulfuric acid for utilization as a catalyst carrier was investigated. Acid-treated diatomite was also characterized by X-ray diffraction, Brunauer-Emmett-Teller specific surface area measurement and porosimetry methods, including chemical analysis. Acid treatment was implemented by suspending diatomite powder in a sulfuric acid solution, followed by homogenizing and heating. During treatment, acid reacts with the diatomite skeletal and dissolves alumina, iron and metal oxide impurities as sulfates. Through this operation, microscopic porosities (e.g. about 1×10^{-4} cm) were also opened up. Hence, the wettability and absorptive capacity of diatomite were enhanced.

EXPERIMENTAL SECTION

Materials

In this study, virgin diatomite, containing more than 75% by weight silica, was obtained from the mines

of Khorassan (two samples), Tabriz and the Persian Gulf seashore. The sulfuric and hydrochloric acid used for the acid treatment had 98% and 37% purity and were from the Razi Petrochemical and Merck Company, respectively.

METHODS AND INSTRUMENTS

Acid Treatment Instrument

In Figure 2, the system used for the acid treatment of diatomite is shown. This system includes an electrical heater and a magnetic agitator for heating and homogenizing slurry of diatomite with a sulfuric acid solution in a round bottom flask. This system is also equipped with a water condenser for refluxing water to the solution and a thermometer on the flask, which shows the slurry's temperature.

Acid Treatment Method

In the first part of the experiments, fifty grams of dry diatomite from the Khorassan mine (sample A) were sieved through 40-60 mesh particle size, which was refluxed with H$_2$SO$_4$ of 5% to 60% by weight concentration for 1 to 4 hrs. The slurry was cooled in air and filtered through Whatman No. 42 paper and a Büchner funnel. The filter cake was repeatedly washed with hot distilled water until the filtrate pH reached 6-7. The acid-treated sample was then dried at 110-120°C and weighed again.

In the second part, the determined optimum conditions for acid treatment were tested on the Khorassan
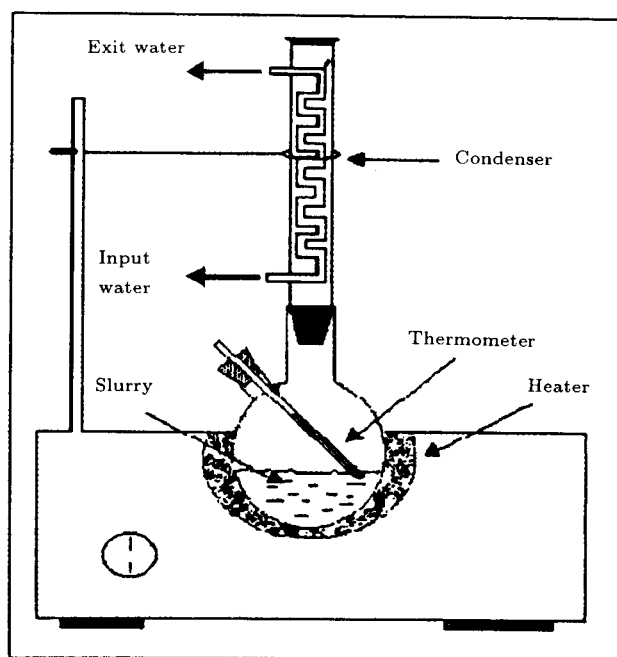

Figure 2. System used for acid treating of diatomite.

(sample B), Tabriz and the Persian Gulf diatomite with the same method and system.

Porosity Measurement

The pore volume of the diatomite samples was determined using the water porosimetry method. In this regard, 20 grams of dry diatomite powder were boiled with 100mL of distilled water in the system of Figure 2. After saturation of diatomite with water, the slurry was filtered through filter paper and exposed to ambient air to vaporize any surface water. The wet sample was weighed again and the pore volume was calculated through the following formula:

$$V_g = \frac{W_{wet} - W_{dry}}{\rho_{H_2O} W_{dry}}. \tag{1}$$

Total Acid-Soluble Matter of Diatomite

All alumina and iron impurities in siliceous skeletal of diatomite cannot be dissolved by mineral acid, because of their complex chemical compound. Total acid soluble matter represents the maximum impurities which may be leached by a strong acid. To determine this amount, 10 grams of dry diatomite powder were boiled for 30 minutes with 250 mL of 1:3 hydrochloric acid to water. The mixture was then filtered through filter paper and a Büchner funnel, weighed and the loss in weight was expressed as a percentage of the original sample.

Loss on Ignition (LOI)

2 grams of dry diatomite were placed in a porcelain crucible and ignited at 960 °C for 2 hours in the furnace (Carbolite S30 2AU). The hot sample was cooled in a desiccator and weighed again. Weight loss percent is 'loss on ignition' and is related to organic matter, carbon dioxide, combined water and sulfur compounds.

Chemical Analysis

A Shimaodzo 3100S atomic absorption spectrophotometer was used for determination of SiO_2, Al_2O_3 and Fe_2O_3 content in each diatomite sample.

X-Ray Diffraction

X-ray difractograms were obtained using Siemens D5000 equipment, using Cu Kα line ($\lambda = 1.5406$ Å) for virgin, as well as acid-treated diatomite.

Surface Area

Surface area was determined by adsorption-desorption of nitrogen at 77°K using Quantachrome,

Autosorb-1. Surface area was calculated using the Brunauer-Emmett-Teller specific surface area measurement method.

Microscopic Structure

A Vanox AH-3 microscope, equipped with a color video camera, was used for observation of the diatomite microscopic structure.

RESULTS AND DISCUSSION

The criteria for evaluating acid-treated diatomite were selected as the amount of weight loss and whiteness of treated diatomite. By using the experimental design method and varying treatment parameters, such as temperature, acid concentration, time of treatment and acid-diatomite mass ratio, the optimum values of these parameters for sample A were determined as follows.

Temperature

At temperatures between 95-110°C, maximum removal of impurities occurs. At lower temperatures, there is no considerable removal of iron and alumina impurities, as indicated by the color of the slurry.

Sulfuric Acid Concentration

Acid concentration is the most important parameter in treatment. Acid concentration between 15-25% by weight, equal to 5-7 normal, is the range at which more than 80% of the total acid soluble impurities are removed.

Time of Operation

The optimum range of this parameter is determined to be 3-4 hrs. In order to obtain this, several experimental runs at different run times were carried out. In other words, shorter times of 1-4 hours and longer times of 4-5 hours were attempted. At the end of each period of time, weight loss percent for each diatomite sample was measured. Comparison of obtained results shows that the purity of diatomite constantly increases with increasing treatment time from 1 to 4 hours and reaches a maximum between 3-4 hours. Longer treatment time (i.e. 4-5 hours), however, shows no noticeable difference compared to shorter times, leading the authors to conclude that after 4 hours, the thermodynamic equilibrium is established between diatomite and the acid solution.

Acid-Diatomite Mass Ratio

The best ratio for this parameter is between 3 to 5. At ratios less than 2 or 3, a paste-like material instead

Table 1. Characteristics of three types of diatomite used.

Parameter		Khorassan (Sample B)	Tabriz	Persian Gulf
Microscopic Structure		Pennate diatom	Centric diatom	Pennate diatom
Initial Color		White	Yellowish white	Pinkish white
Total Acid-Soluble Matter (%)		11.98	16.2	10.65
Water-Soluble Matter (%)		4.75	10.5	5
Pore Volume	Before Treatment	1.1	1.22	1.197
	After Treatment	1.52	1.52	1.56
Color After Calcination for 2 hrs at 700°C	Treated Diatomite	White	Light creme	White
	Virgin Diatomite	Creme	Orange	Creme
LOI (%) at 960°C for 2 hrs.		4.466	7.202	3.8
Density (g/cm³)	Loose	0.375	0.46	0.21
	Packed	0.5	0.597	0.407

of slurry is formed because of the water absorption of diatomite. Moreover, higher mass ratios are not economical.

The determined optimum conditions for sample A were tested on the Tabriz sample B and Persian Gulf diatomite. It is to be noted that samples A and B from the Khorassan mine were different in composition and color.

In Table 1, the complete characteristics of these three types of diatomite are given. Figure 3 also shows different microscopic structures.

Experiments were then performed at 105°C, with an acid-diatomite mass ratio of 4, an operation duration of 3 hours and with sulfuric acid concentration varying from 0 to 40% by weight. Figure 4 shows
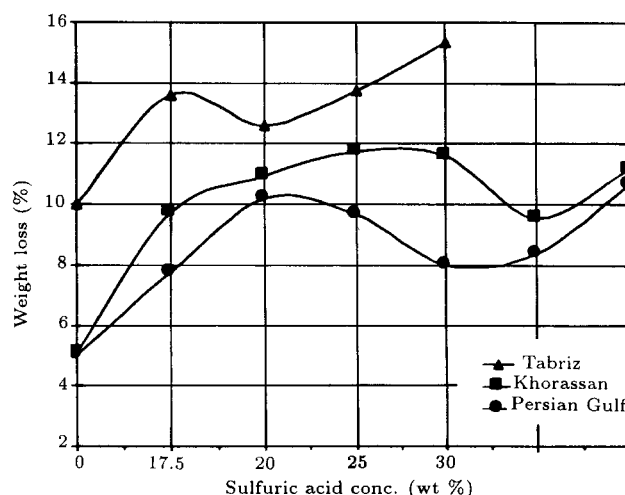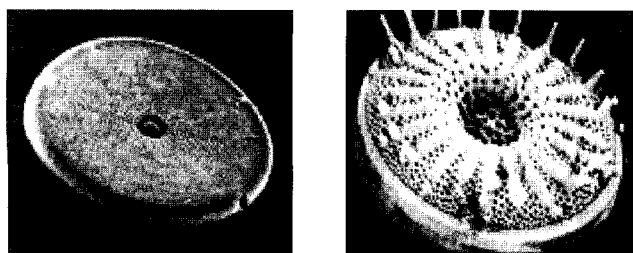

Figure 4. Treatment of Tabriz, Khorassan (sample B) and Persian Gulf diatomites with sulfuric acid at 105°C for 3 hours and acid-diatomite mass ratio of 4:1.

(a) Khorassan and Persian Gulf diatomites (pennate type)

(b) Tabriz diatomite (centric type)

Figure 3. Microscopic structure of three types of diatomite used.

results according to which, under the aforementioned conditions, a relative maximum for weight loss percent occurs in an acid range of 15-25%. This relative maximum is at 20%, 25% and 17.5% of sulfuric acid for the Persian Gulf, Khorassan sample B and Tabriz diatomite, respectively. At this relative maximum, 84-98% of the total acid soluble matter of the diatomite is leached out, which is sufficient for the purpose of acid treatment.

Chemical analysis of these diatomites, before and after treatment, is given in Table 2. According to analysis, the Persian Gulf diatomite has less impurities and a higher silica content (90.5%) in comparison with the others. Chemical analysis indicates that acid treatment increases silica content and leaches out organic and inorganic impurities, especially iron and alumina. Besides this, the loss in ignition percent of the treated sample, which is mainly related to

Table 2. Chemical analysis of diatomites before and after treatment.

Weight Percent	Before Treatment			After Treatment		
	Khorassan Diatomite (Sample B)	Tabriz Diatomite	Persian Gulf Diatomite	Khorassan Diatomite (Sample B)	Tabriz Diatomite	Persian Gulf Diatomite
SiO_2	84.16	76.39	90.51	93.91	85.09	93.77
Al_2O_3	4.89	8.47	2.34	2.30	5.24	2.32
Fe_2O_3	1.46	2.26	0.56	0.15	0.62	0.16
Free Moisture*	2.33	3.16	1.00	1.40	1.63	0.57
LOI	4.47	7.20	3.80	2.80	6.53	3.22

* Amounts of water vaporized after heating at 110-120°C.

thermally decomposable compounds, is less than the virgin diatomite at all acid concentrations (Figure 5).

Increase of pore volume and wettability is another important effect of acid treatment. This increase is from 1.197 to 1.570 cm³/g for the Persian Gulf diatomite, from 1.220 to 1.570 cm³/g for the Tabriz diatomite and 1.150 to 1.780 and 1.100 to 1.520 cm³/g for samples A and B of the Khorassan diatomite, respectively.

X-ray diffraction data are given in Figure 6 and Table 3. The Persian Gulf diatomite was selected for this study because of its high silica (SiO_2) content. According to chemical analysis of the two diatomite samples, for which the X-ray diffraction spectra is also displayed, silica is the major component (> 90 wt%).
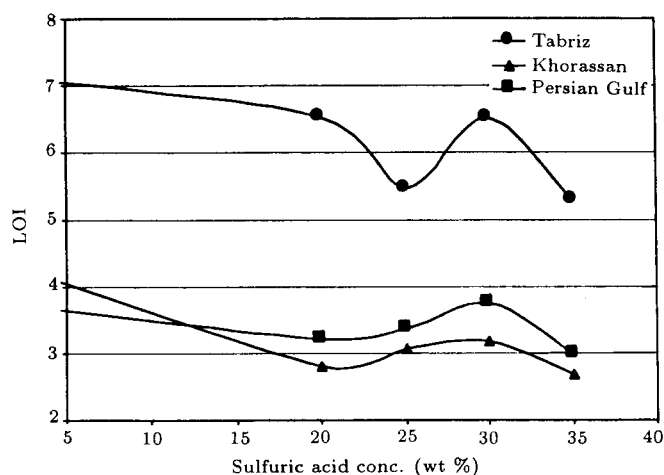

Figure 5. LOI of treated diatomite versus acid concentration used for acid treating.

If this silica had a crystalline form, a sharp related peak should have been observed by the diffractometer for both the fresh (untreated) and treated samples. Combining all these together, it may be concluded that treated and untreated diatomites are principally amorphous and acid treatment may not create any appreciable crystalline form of it. It is noteworthy that a small part of this silica is in the form of quartz, cristobalite and feldspar being represented in the range of $20 < 2\theta < 30$ in the X-ray diffraction spectra, with relatively low line intensities (i.e. in counts per second or cps). Feldspar is a silica-aluminate which contains Mg and Na as the main components. Quartz and cristobalite are siliceous crystalline. According to the respective X-ray diffraction data (Table 3), the line intensities of these three crystalline phases increased through acid treatment, which is the direct result of impurity removal.

The results of the surface area measurement for the Persian Gulf diatomite are shown in Figure 7. According to these results, the surface area of untreated and treated diatomite is 13.6×10^4 and 15.7×10^4 cm²/g, respectively, which indicate, firstly, that diatomite has a moderate surface area and, secondly, that acid treatment has increased this surface area.

The average pore sizes calculated by the Saito-Foley method [13] are also 34.1×10^{-8} and 34.2×10^{-8} cm for these two samples, which demonstrates that diatomite has mesoporosites. Mesopores are responsible for most of the surface area and, together with macropores, create approximately 95% of the total related Brunauer-Emmett-Teller surface area.

The combination of surface area and pore size

Table 3. X-ray diffraction data for Persian Gulf diatomite.

Crystal	After Treatment				Before Treatment			
	2θ	d	Line Intensity	(%)	2θ	d	Line Intensity	(%)
Quartz	26.553	3.354	84.20	71.14	26.596	3.349	74.35	78.71
Cristobalite	21.909	4.054	117.07	98.93	21.925	4.051	94.46	100.00
Feldspar	27.830	3.303	118.34	100.00	27.907	3.194	70.88	75.04

(a) Before acid treatment

(b) After acid treatment
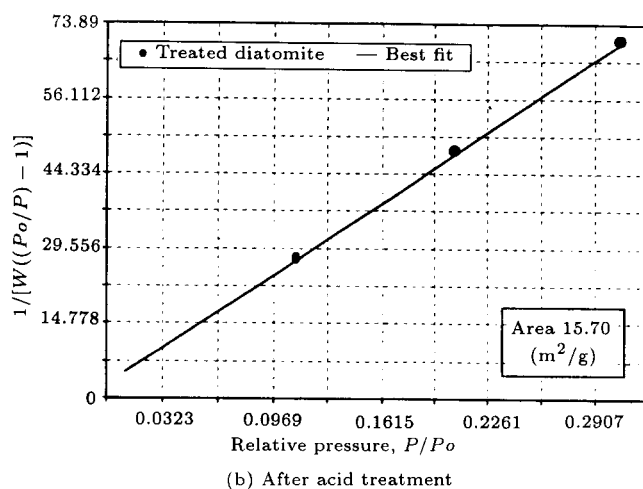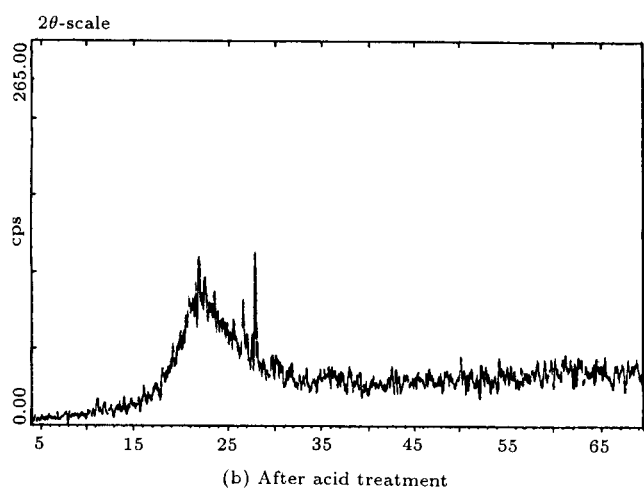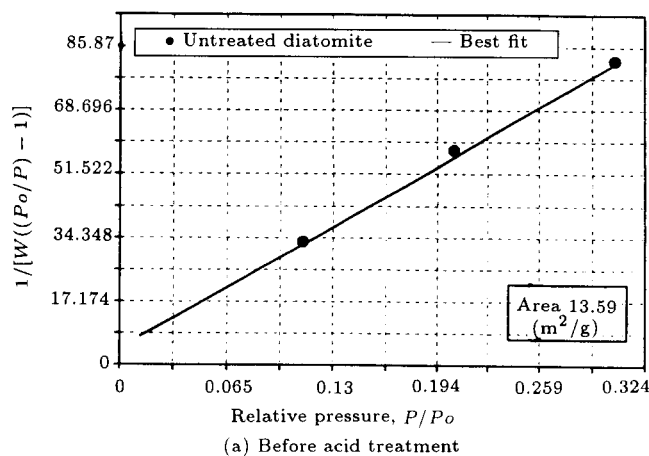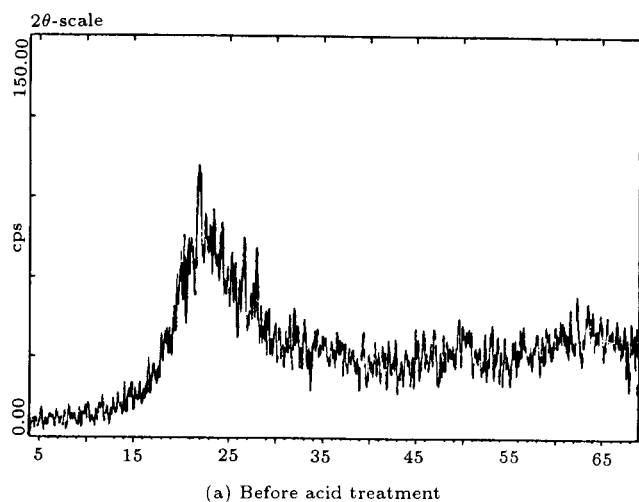
Figure 6. XRD data of Persian Gulf diatomite.

(a) Before acid treatment

(b) After acid treatment

Figure 7. BET surface area of Persian Gulf diatomite.

data, emphasizes the idea that pore structures remain unchanged by acid treatment while blocked pores are opened.

CONCLUSION

In this study, optimum conditions for the acid treatment of diatomite were determined and then tested on three different samples of diatomite. According to the results, the optimum conditions are:

1. Temperature: 95-110°C,
2. Sulfuric acid concentration: 15-25% by weight,
3. Time of operation: 3-4 hrs,
4. Acid-diatomite mass ratio: 3-5.

Acid-treated diatomite was also characterized by X-ray diffraction, Brunauer-Emmett-Teller surface area measurement and water porosimetry methods. Results indicated that diatomite has an amorphous structure, a high surface area $(13-16 \times 10^4 \text{ cm}^2/\text{g})$ and 40-60% porosity, which make it suitable for utilization as a catalyst carrier, according to the following:

i) Acid-treated diatomite is an inert support and resistive against many chemical compounds,

ii) Diatomite has a high absorptive capacity, a good feature for impregnation with catalytic active components,

iii) Acid-treated diatomite has a high Brunauer-Emmett-Teller surface area, which causes catalytic active components to be dispersed in such a way that high catalytic activity may be obtained and, moreover, sintering be reduced,

iv) The presence of alumina (even after treatment) increases the mechanical strength of the prepared catalyst after calcination,

v) Diatomite is an inexpensive source of amorphous hydrated silica with a low cristobalite, quartz and feldspar crystalline phase,

vi) The natural pores and meshlike openings of diatomite particles reduce the need for porosity producing agents during the catalyst preparation;

vii) Due to the diatomite structure, a relatively low abrasion loss may be sustained.

NOMENCLATURE

d	interplane spacing ($\overset{\circ}{\text{A}}$)
V_g	pore volume of diatomaceous earth (cm^3/g)
W_{dry}	weight of dry diatomite (g)
W_{wet}	weight of wet diatomite saturated with water (g)
ρ_{H_2O}	density of water (g/cm^3)
θ	Bragg angle in X-ray diffraction data (degree)

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