# Kaolin and bentonite supported metallic catalysts for selective semi-hydrogenation reaction of phenylacetylene

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## ABSTRACT

Kaolin and Bentonite clays supported metal ions Ce, Pd and Pt, have been used to catalyze hydrogenation reaction of phenylacetylene. The purpose was to fabricate natural clay-based catalysts for selective hydrogenation of phenylacetylene to styrene. The reaction was performed into hydrogenation reactor connected to gas chromatography. Chemical composition of both clays was analyzed by atomic absorption spectroscopy and their particle size and BET surface area were measured. Both clays were found to be with high Si/Al ratios with Bentonite more Iron rich than Kaolin. Kaolin based catalysts showed higher catalytic activity and semi-hydrogenation selectivity compared to bentonite-based. Particularly, Pd/Kaolin exhibited a high conversion rate and styrene selectivity close to those reported for Lindlar catalysts.     © 2020 Knowledge Empowerment Foundation

## KEYWORDS

Bentonite; Kaolin; Sem-hydrogenation; Phenylacetylene; Styrene.

## INTRODUCTION

Clays are among the most widespread sedimentary rocks, which are mainly composed of clay minerals like kaolinite, illite, montmorillonite, etc[1]. Clays and clay minerals have gained considerable attention and subjected to intensive research. The importance of clays was gained from their wide and miscellaneous applications in the modern industry[2], energy conversion[3], and environmental applications[4]. The composition and morphology of clay play an important role in its properties that determines its application. Clays describe heterogeneously and a structurally complex assemblage of colloidal particles, having mean diameters ranging from a few microns down to a few hundredths of microns[5]. However, they are closely interrelated in terms of their basic crystal fine structures, and also in the characteristic physical and chemical properties resulting from their crystal chemistry[6]. Chemically, clay is an assemblage consists of a considerable quantity of hydrous Aluminum silicates, with lesser amounts of finely divided quartz, feldspars, carbonates, metal oxides, hydroxides, and organic matter[7].

Catalysis of chemical reactions and its impact on the environment currently represents a critical concern of the modern industry. The catalyst used must be

efficient, selective for a certain product, and finally does not add serious pollutants to the ecosystem. More than that, the catalyst should achieve economic anticipated profits. These requirements made natural clays as an excellent substitute for the traditional catalysts. Clays-based catalysts are environmentally green, inexpensive with endless resources, and of catalytic activity that can be manipulated and adjusted for specific reaction[8]. One of the most important catalytic reactions in organic chemistry is hydrogenation of unsaturated compounds, due to its industrial importance, especially with regards to the synthesis of petrochemical, pharmaceuticals and fine chemicals[9-11] Particularly, selective hydrogenation of alkynes to alkenes has gained a considerable attention. The more interesting of them, is the selective conversion of phenylacetylene to styrene. The hydrogenation of phenylacetylene may give two products; styrene and ethylbenzene (Scheme 1). The extent to which the two products are separated is expressed by the selectivity with which the intermediate styrene is formed.

Styrene is one of the important industrial monomer used in a variety of polymer products such as preparation of polystyrene, latexes, rubber, elastomers, thermoplastics, polyester resins, thermoset plastic, dispersions, resins, co-polymer and terpolymer[12]. For polymerization of styrene, pure styrene feedstock is needed for a longer catalyst life. Even very small amount of phenylacetylene (less than 10 ppm) in the styrene stream can deactivate the catalyst hence, styrene feed with very low concentration of phenylacetylene is mandatory[13]. Several catalysts have been used to convert phenylacetylene selectively to styrene, the important of them are those that are palladium based

catalysts. Hence, most of the research was concentrated to fabricate and test palladium catalysts formulations that achieve complete conversion of phenylacetylene and the highest possible selectivity for styrene[14-16]. Semi-hydrogenation of alkynes to alkenes requires the adsorption of monoene over the surface of the catalyst is weaker than alkynes, a condition that was experimentally observed with Palladium based catalysts[17]. Among our efforts to test natural Yemeni clays as catalysts for some selected industrial important reactions, we undertook the present work to study the fabricate catalysts using Yemeni Kaolin and Bentonite clays as supports for the metals, Ce, Pd, Pt for selective hydrogenation of phenylacetylene to styrene.

## MATERIALS AND METHODS

### Preparation of clays samples

The chemicals that were used in this work and their suppliers are given in TABLE 1. All chemicals were used as received without further purification.

Two types of clays were used throughout the work; kaolin (a sample was obtained from Geological and mineral agency, Yemen) and was used without further purification, and Bentonite (a sample brought from Hadramout region, Yemen) and subjected to purification as follows: Mozelyhydrocylone (2 inches) was used for separation of the undesired non-clay materials. The feed (Bentonite) plus the dispersing agent (sodium hexametaphosphate) were mixed with water and passed through 0.50 mm sieve. They introduced to the hydrocyclone through the inlet pipe under pressure of 25 bar. As a result of the high centrifugal forces, the coarse particles move downward and discharged
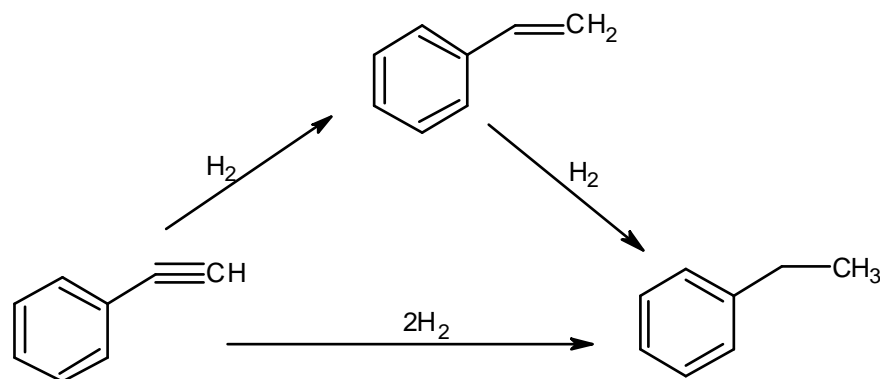


Scheme 1: Reaction pathway for hydrogenation of phenylacetylene

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| Chemical | Supplier |
| --- | --- |
| Sodium hexameta phosphate | J.C.L.E |
| Methanol, HPLC | Baker Analyzed |
| Phenyl acetylene | Ferak Laboral |
| Styrene | Fluka Chemica |
| Platinum (IV) Chloride | Janssen Chimica |
| Palladium (II) Bromide | Ferak Laboral |
| Cerium (III) Nitrate, $Ce(NO_3)_3.6H_2O$ | Fluka–Garantie |
| Cyclohexane | M & B laboratory chemical |
| Hydrochloric Acid 36.5% - 38% | Baker Analyzed |
| Nitric Acid 69-72% | BDH Chemical Ltd |
| Compressed air | Arab Supply Co. |
| $H_2$ Gas | Arab Supply Co. |

through the vortex finder pipe (overflow 8 mm). The overflow was collected and left to dry in air. Thereafter, the two types of clays were crushed, milled using a steel ball mill, and then they were sieved using $\leq 63\ \mu m$ sieve (mesh No. 230). The clays particle with size $\leq 63\ \mu m$ were taken and used later.

## Elemental analysis

About 0.20 g of crushed and acid untreated Kaolin and Bentonite clays was weighed and put into 100 ml plastic bottle: (5 ml of 40% HF, 2.5 ml of 25% HCl and 2.5 ml of 25% $HNO_3$) were added. The mixture was left for 2 hrs in a water bath at 70C° with shaking, 50 ml of Boric acid (39 g/L) was added and 40 ml of distilled water were added; then 10 ml of the solution were taken and 67 diluted to 100 ml so that to get a (10% V/V) solution. The analysis of these elemental was made by using (Pye Unicam SP9) Atomic Absorption Spectrophotometer.

## Particle size analysis and surface area

About 1 g of the clay was placed in relatively large test tube which was half-filled with distilled water. A dispersing agent (Sodium hexameta phosphate) was added; then the whole mixture was shaken and left for two days to insure complete dispersion. The grain size analysis was carried out using the (Fritsch Particle – Size Analyzer 20). Surface area measurements were carried out using BET method using $N_2$ adsorption.

## Acid treatment

A hydrochloric acid solution of pH = 4 was prepared and used in the acid washing of the clays. about 100 g

of each clay was taken and put in a large flask; then, the acid solution was added to it and the mixture was shaken. The mixture, was left overnight and the clay was filtered under vacuum. The clay was then washed with distilled water. The clays were acidified and then dried overnight in an oven at 70 C°.

## Impregnation

Appropriate concentrations of salt solution of $PtCl_4$, $PdBr_2$, $Ce(NO_3)_3.6H_2O$ were prepared and used to impregnate 9.5 g samples of (Bentonite and Kaolin). The mixture was shaken well and was left to dry overnight in the oven at 70 °C.

## Cation exchange

An appropriate concentration of $Ce(NO_3)_3.6H_2O$ solution was prepared and used for the cation exchange of Bentonite and Kaolin; they were immersed in the solution and left for overnight to insure complete exchange. Then the clay was filtered, washed with distilled water and left to dry in the oven at 70 C°.

## Reduction

All acid washed, impregnated clays was subjected to reduction treatment. A glass fixed –bed flow reactor was used for Calcination and reduction of the catalysts. Calcination was performed by placing the catalyst in the reactor, which was heated using a tubular Pyrex electric oven. The temperature measurements were performed by a thermocouple thermometer inserted in the thermowell located at the bottom of the reactor. The temperature was controlled by adjusting the input voltage of the electric oven using a variable AC transformer. Flow –rate of gases was controlled by (Matheson) four-channel manual flow meter controller. The air flow was at the rate of 45 ml / min at 500 °C for 1.5 h. Helium was then introduced followed by introduction of hydrogen at a flow rate of 100 ml/min through the catalyst-bed for 2 hrs at the same temperature used for Calcination. The catalyst was then cooled to room temperature in a Helium atmosphere.

## Hydrogenation reactions

A stock solution of phenylacetylene in cyclohexane (1:9 v/v) was prepared, then 0.50 g sample of the catalyst with a 20.0 ml solution were transferred into a 100 ml reaction bottle. The hydrogenater was evacuated; then

filled with hydrogen to 40 psi (gauge pressure); the reaction was carried at room temperature. A simple hydrogenater (similar to the parr-hydrogenater) consists of a hydrogen reservoir (500 ml) with a pressure gauge (0-100 psi) connected to a thick – wall glass reaction bottle (100 ml) by a tygon pressure tubing, this is connected with a stainless-steel tubing passing, through a rubber stopper, into the reaction bottle. The reaction bottle was placed in a mechanical shaker. The reaction progress was monitored by pressure drop measurements, the reaction was stopped at $\Delta p(H_2) = 2$ psi intervals.

Samples were then taken and analyzed using a Gas Chromatograph (Pye- Unicam) with an FID detector and 1.5 m, 6 mm stainless steel column, packed with 10 % PEGA (polyethylene glycol adipate) and supported on acid washed Diatomite " C " mesh No. 2. The carrier gas flow rate was 24 ml/min. An electronic integrator (spectra- physics, Data jet) was connected to the chromatograph for data collection. The reaction was continued until hydrogenation was completed then the reaction was stopped and a sample was analyzed. Another run was done each catalyst for 8 minutes only for activity measurements. Also another hydrogenation reaction was carried, which is the hydrogenation of phenylacetylene and styrene mixture in cyclohexane (1:1:18 v/v). The tested catalysts in this hydrogenation reactions are shown in TABLE 2.

## RESULTS AND DISCUSSION

The compositions of the two clays obtained from elemental analysis are presented in TABLE 3. In general, the used clays were of high silica/alumina ratio. The Kaolin content of alumina was higher than that of bentonite while iron was higher in bentonite. The BET surface area of Bentonite and Kaolin were of 200 $m^2/g$ and 15 $m^2/g$, respectively, and particle size analysis of both clays showed that 100 % of particles were < 63 µm.

The plots for the progress of Hydrogenation of phenylacetylene using various Kaolin and Bentonite supported catalysts are shown in Figures (1-8). As can

be seen, hydrogenation of phenylacetylene results in two products; styrene which results from semi-hydrogenation, and ethylbenzene from complete hydrogenation. When the two clays samples were used as treated without the addition of any metallic materials, the reaction was not initiated. This is due to the absence of the metal active sites which are responsible for the hydrogen and alkynes adsorption. This indicates that the parent calys cannot be used as catalysts for this reaction. However, enhanced rates of the reaction were observed when the metal ions were added to the clay supports. Cerium ion was added by ion exchange, did not produce any significant rise in the rate of the reaction, whereas platinum and palladium ions could derive the reaction to occur to a great extent. The enhancing magnitude was dependent on the type of clay support and type of metal ion. Kaolin supported catalysts were found to be more active and showed higher semi-hydrogenation selectivity than Bentonite based catalysts. In comparing Figures 1 and 2, we can observe that the time needed for 100% Conv. is about 5 minutes when Pd/Kaolin was used and more than 15 min with Pd/Bentonite. Moreover, an exceptional high selectivity was observed with Pd/Kaolin. As can be shown in Figure 1, the amount of styrene reached 96% within the time needed to reach maximum conversion (100% Conv.). Ethylbenzene started to form only after phenylacetylene

**TABLE 2: Catalysts used in the hydrogenation reaction**

| Catalyst | Catalyst treatment |
|---|---|
| 5% Pt on Bentonite | Reduced |
| 5% Pt on Kaolin | Reduced |
| 5% Pd on Bentonite | Reduced |
| 5% Pd on Kaolin | Reduced |
| 5% (Pt-Ce) on Bentonite | Reduced |
| 5% (Pt-Ce) on Kaolin | Reduced |
| 5% (Pd-Ce) on Bentonite | Reduced |
| 5% (Pd-Ce) on Kaolin | Reduced |
| Ce-cation exchange with Bentonite | Reduced |
| Ce-cation exchange with Kaolin | Reduced |
| Clays alone | Reduced |

**TABLE 3: Chemical analysis of major components in the Yemeni clays**

| %Component | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | NiO | MgO | $K_2O$ | $TiO_2$ | CaO | $Na_2O$ |
|---|---|---|---|---|---|---|---|---|---|
| Kaolin | 65.93 | 23.38 | 1.74 | 0.16 | 0.21 | 1.13 | 1.79 | 0.44 | 4.6 |
| Bentonite | 70.80 | 13.19 | 7.93 | 0.34 | 0.095 | 2.07 | 1.24 | 0.24 | 1.52 |

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was consumed completely. When compared with the maximum selectivity of Lindler catalyst with a maximum of 98%[18], Pd/Kaolin catalyst of this work can be considered asof competing performance. Hence, Pd/ Kaolin catalyst has proven to be of potential use and can be used to produce styrene from phenylacetylene with high conversion rate and a minimum amount of the reactant impurity.

The mechanism by which Pd catalysts control hydrogen selectivity still uncertain. The most common depends on that hydrogen adsorbs in two phases; hydrogen poorly α and rich β-phases. Suppression of Hydrogen β-phase formation leads to semi-hydrogenation selectivity. The Suppression of hydrogen β-phase can be achieved by increasing the dispersion of catalyst particles[9]. Increasing electronic density of

Pd *d-band* using metallic promoters or changing the geometry of particles may also contribute to selectivity enhancement[19]. Therefore, the better selectivity of Kaolin based catalysts compared to Bentonite based ones can be attributed to that the structure of Kaolin offers better dispersion medium than Bentonite and it also may contain specific types of trace metals that act as promoters. Similarly, Pt/ Kaolin showed better performance than Pt/ Bentonite either in activity and semi-hydrogenation selectivity. Surprisingly, samples that contain cerium in addition to Pd and Pt showed substantial declination in ether activity and selectivity (Figures 1-8). Ismail and Imad reported that Ce incorporation into Pd-Pt/$Al_2O_3$ used to catalyze the same reaction, increased the rate of conversion of phenylacetylene but did not alter styrene selectivity[20].
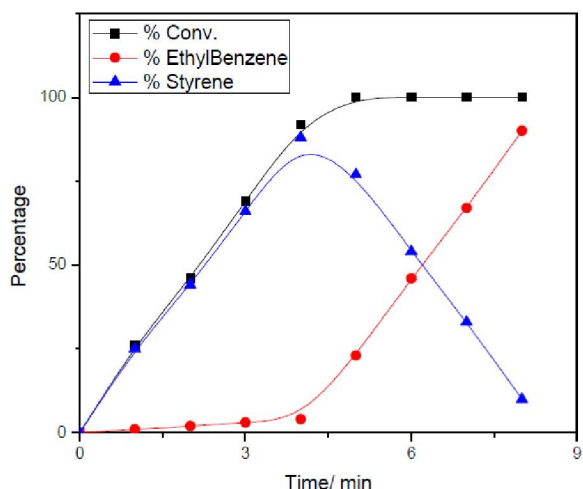


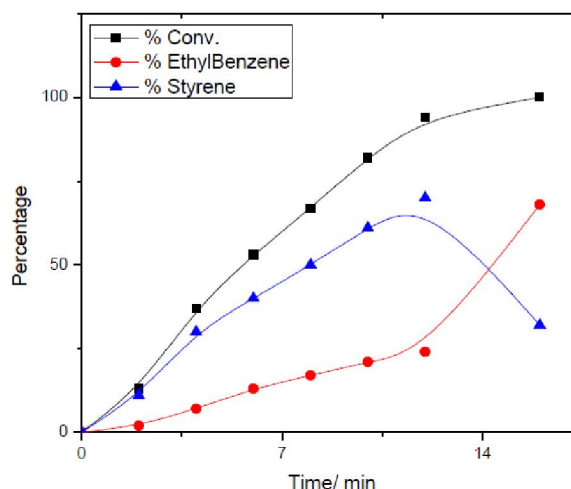**Figure 1: Hydrogenation of phenylacetylene over 5 % Pd/ Kaolin**



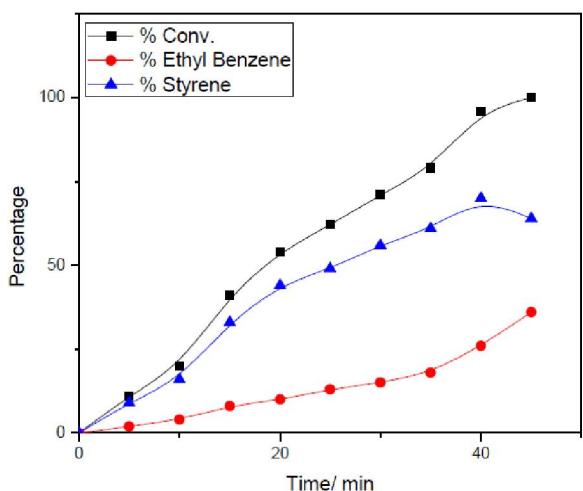**Figure 2: Hydrogenation of phenylacetylene over 5 % Pd/ Bentonite**



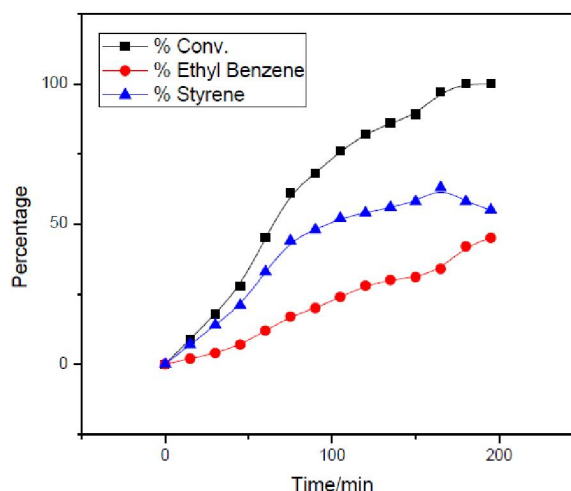**Figure 3: Hydrogenation of phenylacetylene over 5 % Pt/ Kaolin**



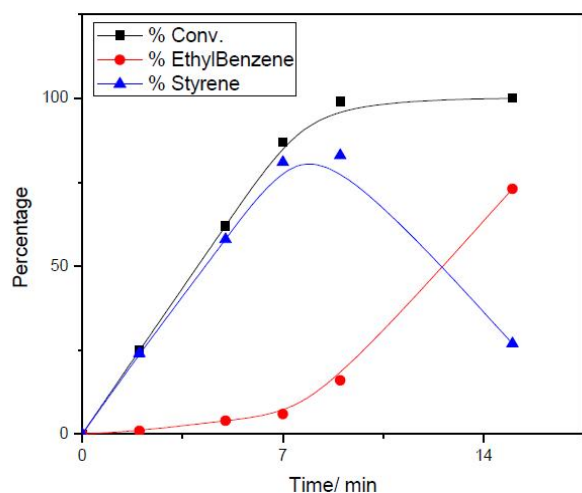**Figure 4: Hydrogenation of phenylacetylene over 5 % Pt/ Bentonite**

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**Figure 5: Hydrogenation of phenylacetylene over 5 % (Pd-Ce) / Kaolin**
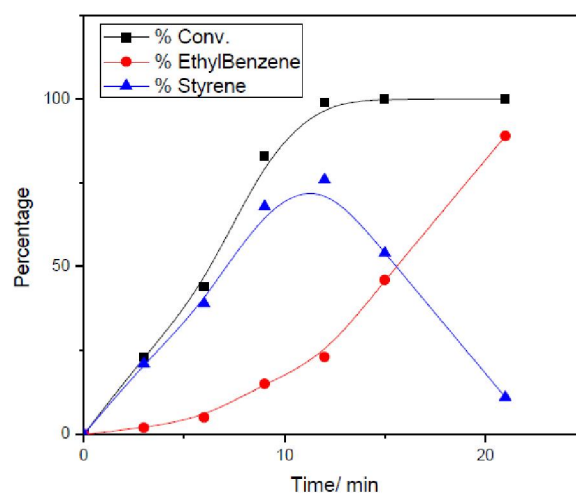


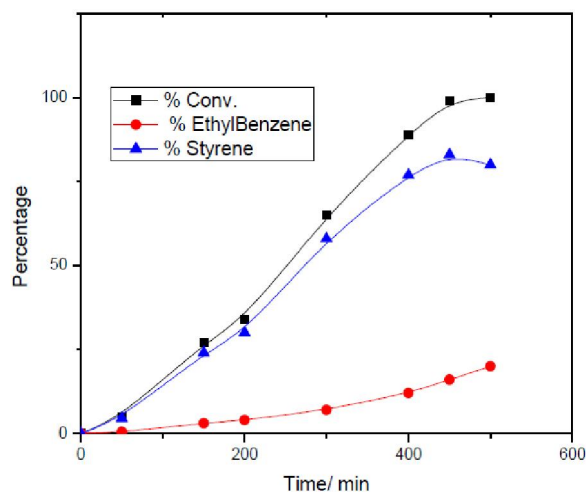**Figure 6: Hydrogenation of phenylacetylene over 5 % (Pd-Ce)/ Bentonite**



**Figure 7: Hydrogenation of phenylacetylene over 5 % (Pt-Ce)/ Kaolin**
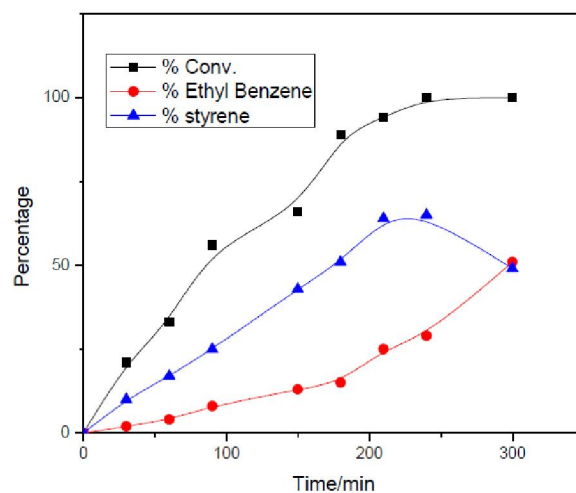


**Figure 8: Hydrogenation of phenylacetylene over 5 % (Pt-Ce)/ Bentonite**

**TABLE 4: Activity and selectivity for the catalysts used in the hydrogenation reactions of phenylacetylene**

| Catalyst | Activity (M min$^{-1}$ g$^{-1}$) | Styrene Sel.[a] | Ethylbenz. Sel.[b] |
|---|---|---|---|
| Pd/ Kaolin | $4.4 \times 10^{-1}$ | 96 | 4 |
| Pd / Bentonite | $9.8 \times 10^{-2}$ | 68 | 32 |
| Pt/ Kaolin | $3.7 \times 10^{-2}$ | 73 | 27 |
| Pt / Bentonite | $1.3 \times 10^{-2}$ | 65 | 35 |
| (Pd-Ce) Kaolin | $1.1 \times 10^{-1}$ | 84 | 16 |
| (Pd-Ce)/ Bentonite | $1.1 \times 10^{-1}$ | 77 | 23 |
| (Pt- Ce)/ Kaolin | $2.7 \times 10^{-3}$ | 84 | 16 |
| (Pt-Ce) / Bentonit | $1.0 \times 10^{-2}$ | 69 | 31 |

[a]Styrene Selectivity $= \dfrac{\% \text{ Styrene}}{\% \text{ Conversion}} \times 100\,\%$;    [b] Ethylbenzene Selectivity $= \dfrac{\% \text{ Ethylbenzene}}{\% \text{ Conversion}} \times 100\,\%$

When looking again to the %Conv. curves in Figures 1-8, we observe that these curves tend to be linear during the pre-maxima segments. The linearity of the curves suggests zero-order kinetics which agrees with the expected behavior of heterogeneous catalysis at these conditions[21,22].

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Hence the rate constants of the hydrogenation reactions performed using different catalysts are the slopes of these curves. The activities of catalysts were calculated from the rate constant values divided by the used quantity of the catalyst (g), and added to TABLE 4, along with the selectivities at maximum conversion for each of the styrene and the ethylbenzene.

To obtain a more significant parameter for comparing semi-hydrogenation selectivity of different catalysts, they were used to activate hydrogenation reaction of phenylacetylene and phenylacetylene/styrene mixtures. Then the slopes of curves of phenylacetylene consumption and styrene/ethylbenzene production were calculated and used for calculating C=C/C-C ratios. These values are given in TABLE 5, and show that, in terms of styrene selectivity, the catalysts used in this work can be arranged as in the following order; Pd/ Kaolin > Pd- Ce/ Kaolin > Pd-Ce/Bentonite > Pt-Ce/ Kaolin > Pt/ Kaolin > Pd/ Bentonite > Pt / Bentonite > Pt- Ce/ Bentonite.

**TABLE 5: The slopes of the consumption of phenylacetylene and the production of styrene and ethylbenzene in the phenylacetylene / styrene mixture.**

| Catalyst | $PhC=C-H$ | $PhCH=CH_2$ | $PhCH_2-CH_3$ | Ratio of C=C/C-C |
|---|---|---|---|---|
| Pt / Bentonite | -1.00 | 0.74 | 0.26 | 2.8 |
| Pt/ Kaolin | -1.00 | 0.82 | 0.20 | 4.1 |
| Pt- Ce/ Bentonite | -1.00 | 0.74 | 0.27 | 2.7 |
| Pt-Ce/ Kaolin | -1.00 | 0.91 | 0.15 | 6.1 |
| Pd/ Kaolin | -1.00 | 0.94 | 0.06 | 15.7 |
| Pd- Ce/ Kaolin | -1.00 | 0.93 | 0.09 | 10.3 |
| Pd-Ce/ Bentonite | -1.00 | 0.90 | 0.13 | 6.9 |
| Pd/ Bentonite | -1.00 | 0.75 | 0.25 | 3 |

## CONCLUSION

It is concluded that the Kaolin and Bentonite clay samples can be used as supports for metal ions, specially, Palladium, to fabricate catalysts for the production of styrene with a minimum amount of phenylacetylene. Among the catalyst used in this work, Pd/Kaoline was the most efficient; it results in a high conversion rate of phenylacetylene with high selectivity toward styrene that is comparable to those reported for the common Lindlar catalysts. Platinum-based catalysts did not prove to be as active as those of Palladium based. Ce-(Pd or Pt)/Kaolin or Bentonite showed declined activity and lower semi-hydrogenation selectivity compared to Ce free.

## ACKNOWLEDGMENT

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