

An Egg-Shell Pd-Ag/ α -Al₂O₃ Catalyst for Tail-End Acetylene Selective Hydrogenation

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Abstract

In the present research, egg-shell Pd-Ag/ α -Al₂O₃ catalysts prepared by impregnation method using self-improved spherical alumina support with BET 13.34m²/g and pore volume 0.36cm³/g were used for the hydrogenation of acetylene in the presence of a large excess of ethylene (tail-end cuts) and their activity-selectivity patterns were compared with the commercial one. All of the synthesized catalysts were tested under 60 °C, 10bar, space velocity 6500h⁻¹ and H₂/C₂H₂ ratio 1.5 (mol/mol) which is the same as an industrial plant.

The effect of impregnation operating parameters, such as pH of the impregnation solution and impregnation type, on palladium penetration depth and palladium uptake was investigated. pH 1.5 is best for impregnation solution. Catalytic performance tests showed that for Pd-Ag/ α -Al₂O₃ catalysts, sequential impregnation was a suitable method for the active metal. By controlling the synthesis condition, the best Pd-Ag/ α -Al₂O₃ sample was an egg-shell one in which Pd was loaded evenly in a layer with thickness 20-30 μ m. This sample gave ethylene selectivity of 100% and acetylene conversion of 58% which is higher than the commercial one.

Keywords: Acetylene, Selective Hydrogenation, Palladium, Impregnation

1. Introduction

Ethylene, mainly produced by steam cracking of naphtha, usually contains 0.1-1% of acetylene as an impurity, which must be removed to less than 5ppm because it poisons the catalyst in ensuing ethylene polymerization processes and eventually degrades the quality of the produced polyethylene. Acetylene impurities are usually removed by two methods that are adsorption with zeolite and conversion to

ethylene by selective hydrogenation using palladium (Pd) catalyst[1-4], the latter is more commonly used and is the subject of the present research.

Originally nickel, iron and cobalt containing catalysts were used in the selective hydrogenation of acetylene but sulphur compounds had to be added to minimize ethylene losses[5-7].

In the 1950s, palladium was proved to be the most active and selective metal in the

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hydrogenation of acetylene. About 20 years later a new catalyst type was commercially used containing 0.04wt.% palladium impregnated on Al₂O₃ pellets. After 10 years, bimetallic catalyst systems and especially Pd-Ag/Al₂O₃ catalysts were established in the industry and are still used today [8-11]. In bi-metallic catalysts, charge redistribution in Pd-Ag alloy was observed which enhanced its selectivity. This enhancement was obtained by decreasing the quantity of hydrogen adsorbed and reducing its rate of diffusion from bulk to the surface. On the other hand, the presence of a promoter at the surface and in the bulk produced a change of the relative adsorption strength of acetylene and ethylene which resulted in an increased reactivity for acetylene and a decreased reactivity for ethylene. A brief summary of some researchers' findings in this field is tabulated in Table 1.

The catalyst carrier may be any low surface area carriers such as α -alumina since it possesses relatively low specific surface area and low acidity compared to other "transition" alumina. To qualify as a "low surface area" carrier, it must have a surface area 5-20m²/g. The pore volume of the carrier is preferably greater than 0.3cm³/g. The carrier, if at all possible, should be a spherical one with a diameter of 1-3mm [19, 20].

These catalysts are characterized by an egg-shell distribution of palladium and silver over the catalyst pellet to reduce the influence of mass transfer resistance. In egg-shell catalysts, the active phase is distributed only on a thin external surface layer of the support spheres, allowing quick migration of ethylene away from the active sites, which will promote the ethylene selectivity for selective hydrogenation of acetylene.

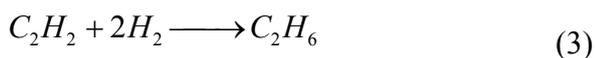
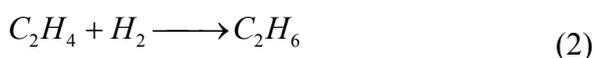
Table 1. Catalytic performance of various Pd catalyst used for acetylene selective hydrogenation.

| Catalyst | Acetylene Conversion (%) | Ethylene Selectivity (%) | Operating Conditions | Reference |
|--|--------------------------|--------------------------|----------------------------|-----------|
| Pd/nano α -Al ₂ O ₃ | 90 | N.R. ^(a) | 4000h ⁻¹ | [12] |
| Pd-Ag/ α -Al ₂ O ₃ | 50 | N.R. | 50°C, 2000h ⁻¹ | [13] |
| Ti-Pd/PHSN ^(b) | 70 | 50 | 40°C, 1bar | [14] |
| Pd-Ag/Al ₂ O ₃ | 70 | 78 | 35°C, 10bar | [15] |
| Pd/ α -Al ₂ O ₃ | 70 | 82 | 40°C, 10000h ⁻¹ | [8] |
| Pd/Al ₂ O ₃ | 18 | 90 | 30°C, 1bar | [16] |
| Pd/PHSN ^(b) | 20 | 80 | 30°C, 1bar | [16] |
| Pd-Ag/Al ₂ O ₃ | 15 | 100 | 50°C, 16bar | [17] |
| Pd-Cu/Al ₂ O ₃ | 60 | 80 | 60°C | [18] |
| Pd-Ag/Al ₂ O ₃ | 15 | 78 | 60°C | [18] |

(a) N.R.: not reported

(b) PHSN: porous hollow silica nanoparticles

The catalysts investigated in the present research are used in a process called tail-end C₂ selective hydrogenation. A requirement of this process is the separation of the C₂ hydrocarbons; acetylene, ethylene and ethane, from the cracked gas of the steam cracker. The necessary hydrogen for the removal of acetylene has to be added into the reactor where the following four reactions take place:



Reaction (1) is the desired one whereby acetylene is selectively hydrogenated to ethylene. Simultaneously ethylene is hydrogenated to ethane in reaction (2), which leads to an unwanted reduction of the ethylene selectivity of the process. Moreover, the formation of heavy hydrocarbons from acetylene and hydrogen is illustrated in reaction (4). The reactions (2)-(4) should be prevented to obtain high selectivities to ethylene. Butadiene is proposed to be involved in this formation of heavy hydrocarbons. These heavy hydrocarbons are composed of liquid and solid parts. The liquid part is usually called "green oil" which predominantly consists of olefins and paraffins but also to a minor extent of diolefins and aromatics. Green oil is generally accepted as the precursor for the solid coke.

The coke is deposited on the active sites of the catalyst leading to an activity decrease. Therefore, several regenerations have to be carried out during the life time of the catalyst[21-23].

The objective of the present study is to design and synthesize a bimetallic Pd-Ag/ α -Al₂O₃ catalyst and determine its properties in terms of dispersion, metal loading and metal distribution over the support. This catalyst is suitable for tail-end C₂ selective hydrogenation.

2. Materials and methods

2-1. Chemicals

Commercial spherical γ -Al₂O₃ (BET: 210.13m²/g and pore volume: 0.53cm³/g) supplied from Sasol Co. after calcination at 1100°C for 180min was used as support. Palladium chloride (PdCl₂), palladium nitrate (Pd(NO₃)₂·2H₂O) and silver nitrate (AgNO₃) purchased from Merck Co. were used as palladium and silver precursors, respectively. Hydrochloric acid (HCl) and ammonium hydroxide (NH₄OH) supplied from Merck Co. were used as PdCl₂ solvent and pH adjustor, respectively. These precursors were of analytical grade and used without further purification. Cylinders of acetylene-ethylene gas mix (containing 1.5mol.% C₂H₂ with C₂H₄ as balance), ethane (with purity 99.9mol%) and hydrogen (with purity 99.9mol.%) were supplied from Pars Havaye Alborz and used as reactant gases.

2-2. Catalyst preparation

Mono-metallic egg-shell Pd/Al₂O₃ catalysts (namely Pdx for which x=1, 2, ..., 5) were prepared by impregnation method with weight (%) of Pd approximately 0.03%. The

catalysts were subsequently dried at 110°C for 12h and calcined in air at 450°C for Pd.

The egg-shell Pd-Ag/Al₂O₃ catalysts (namely A, B and C) were prepared by sequential and co-impregnation method with weight (%) of Pd approximately 0.03% and that of Ag approximately 0.18%. The catalysts were subsequently dried at 110°C for 12h after each impregnation step and calcined in air at 450°C for Pd and 400°C for Ag.

Commercial Pd-Ag/Al₂O₃ catalyst (namely D) was supplied by SÜD-CHEMIE and contained 0.03 wt.%Pd and 0.18 wt.% Ag.

2-3. Catalyst characterization

The X-ray diffraction (XRD) pattern of the Al₂O₃ support was carried out using an X-ray diffractometer (Model GNRMPD 3000) with CuK α radiation at 40kV and 30mA within the range $5 < 2\theta < 110^\circ$. The mean crystal size of Al₂O₃ support was estimated from the half-width of the corresponding XRD peaks using Scherrer equation.

The BET surface area of the Al₂O₃ support was measured by N₂ physisorption using a Quantachrome Nova 2200 apparatus.

The analysis of metal penetration depth was performed with scanning electron microscope (SEM) using VEGA II TESCAN apparatus. Each spherical pellet was polished on the top surface whereby half of the active Pd-egg shell was revealed. Afterwards, the pellet was covered with Au layer and transferred into the microscope. The measurements were carried out under high vacuum and with an electron beam having a voltage of 15kV. The depth of the Pd-layer was read out from SEM pictures.

The metal content of the catalysts was determined by ICP (ICP-OES simultaneous

Instrument, Model: VISTA-PRO, Varian).

CO chemisorption was used to determine the dispersion of active metal. The catalyst samples were pretreated in glass reactor with a flow of 50ml/min hydrogen and 400°C for 15min. Then the reactor was connected to the chemisorption apparatus (BELCAT, type A) and cooled down to 50°C in a 50ml/min flow of helium. At the beginning of the measurement a pulse of 1.009ml CO was introduced in the glass reactor which was repeated every 1min. A thermal conductivity detector (TCD) recorded the CO-signals, which were lowered as CO was chemisorbed on the sample. CO is chemisorbed on palladium only and not on silver. Palladium dispersion was estimated from the amount of CO chemisorbed assuming a stoichiometry of CO/Pd=1 [8].

UV-Vis apparatus (T90, PG Instruments Limited Co.) was used to determine palladium concentration in impregnation solution.

2-4. Reaction study

A schematic diagram of the high-pressure set-up used was depicted in Figure 1. The performance of catalysts for tail-end selective hydrogenation of acetylene was tested with a high pressure reactor made of stainless steel (SS316) that has an internal diameter of 14.5mm, a wall thickness of 1.5mm and a length of 610mm. A thermocouple was placed in the center of the reactor tube. The temperature of the reactor was adjusted by a heating jacket. 2g spherical catalyst diluted with the same size quartz was used in each performance test. Prior to the start of each experiment, the catalyst was reduced *in situ* with hydrogen (GHSV of

500h⁻¹) for 4h by heating from room temperature to 150°C. Then the reactor was purged with nitrogen and cooled down to the reaction temperature 60°C. The reactants with composition of 1.19% C₂H₂, 10.01% C₂H₆, 1.81% H₂ and C₂H₄ as balance at GHSV of 6500h⁻¹ were introduced through mass flow controllers (BROOKS instrument SLA 5850). The reaction pressure was kept at 10bar by a back pressure regulator (BROOKS instrument series 5866). The feed and products were analyzed by an on-line gas chromatograph (RGA Agilent- 6890N) equipped with FID and TCD detectors. Acetylene conversion (Eq. (5)) and ethylene selectivity (Eq. (6)) were used to evaluate the behaviour of the catalysts.

3. Results and discussion

3-1. Support pre-treatment

The α -Al₂O₃ supports used for preparation of the catalysts were obtained by calcining γ -Al₂O₃ (calcination temperature 1100°C and holding time 3h). The XRD patterns of Al₂O₃ are shown in Fig. 2. The broad peak means poor crystallization of the sample and the sharp ones indicate a well-crystallized sample and the sintering effects of the sample as well as relatively bigger crystalline size. The sharp peaks of α -phase indicate the relatively large grain sizes and well-defined long-range order in corundum, which signifies the collapse of the porous structure characteristic of the low-temperature phases and the consequent diminishment of the powder surface area[24].

$$\text{acetylene conversion} = \frac{\text{mol of acetylene in feed gas} - \text{mol of acetylene in effluents}}{\text{mol of acetylene in feed gas}} \quad (5)$$

$$\text{acetylene selectivity} = \frac{\text{mol of ethylene in effluents} - \text{mol of ethylene in feed gas}}{\text{mol of acetylene in feed gas}} \quad (6)$$

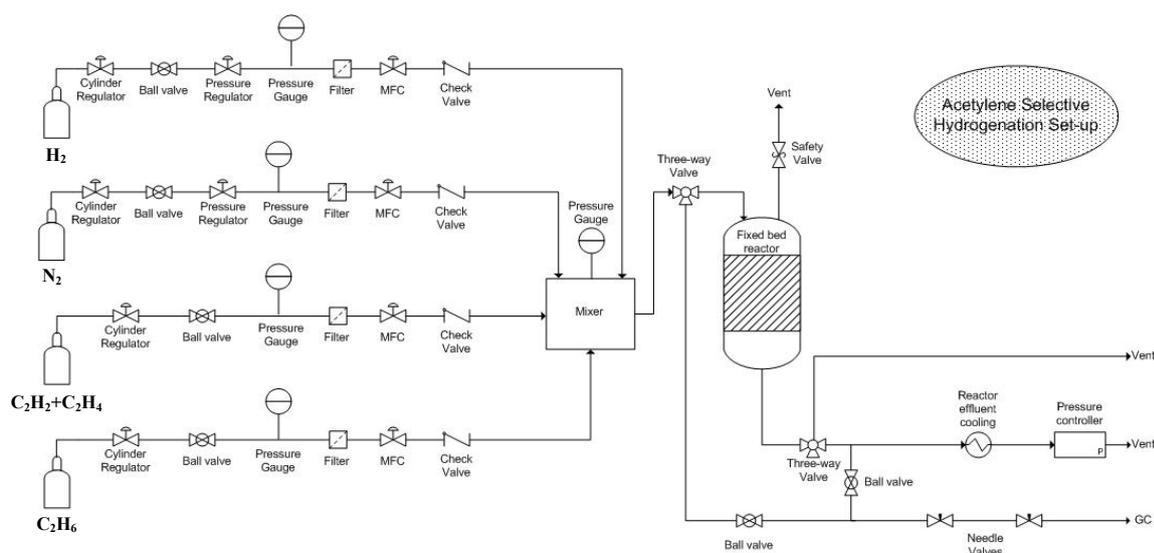


Figure 1. A schematic diagram of the high-pressure set-up used.

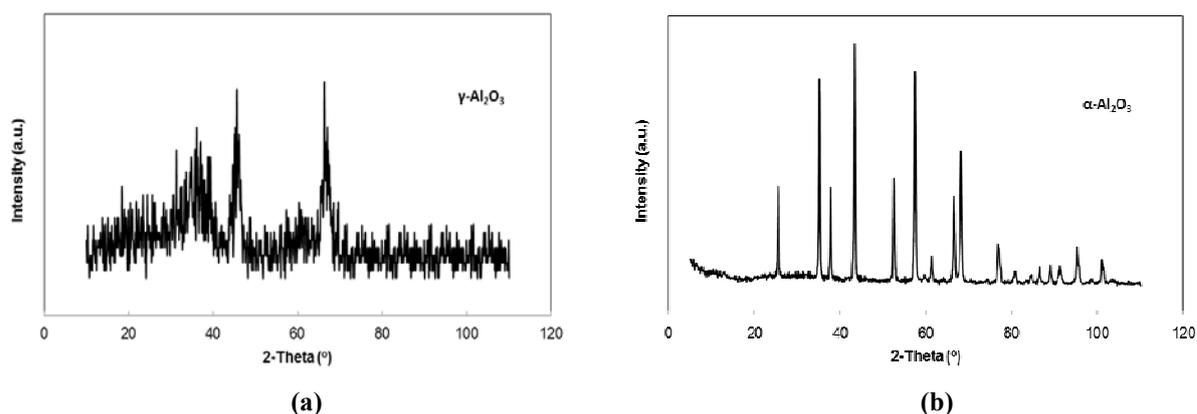


Figure 2. XRD patterns of Al_2O_3 supports before (a) and after (b) pre-treatment by calcinations.

Table 2 summarizes the physical properties of supports. It can be seen that with increasing calcination temperature, the surface area of the samples decreased from $210.13\text{m}^2/\text{g}$ (γ phase) to $13.34\text{m}^2/\text{g}$ (α phase) and corresponding pore diameter increased from 100\AA to 1070\AA . This phenomenon may have resulted from the destruction of some small micropores and reconstruction of large macropores by the sintering process. Data of support calcined at 1100°C indicate that most micropores are destroyed and reoriented at high temperature which confirmed the collapse of pore structure. This finding is consistent with what was reported by other researchers [16].

For acetylene selective hydrogenation, the pore size of the support affects catalyst selectivity, since a secondary process of complete hydrogenation takes place in their

fine pores due to steric hindrances in the removal of reaction products. Under conditions of the purification of the ethylene-ethane fraction from acetylene impurities, the hydrogenation of acetylene to ethane thus occurs in fine pores. Therefore, according to this reaction characteristic, $\alpha\text{-Al}_2\text{O}_3$ would be a suitable support. Specifications of $\alpha\text{-Al}_2\text{O}_3$ reported in Table 2 are in accordance with what was reported in literature [19, 25].

3-2. Palladium penetration depth

As selective hydrogenation catalyst must be an egg-shell one, palladium penetration depth is a detrimental factor in selecting impregnation condition. Impregnation type and pH of the impregnation solution are two critical parameters that affect palladium penetration depth in the support.

Table 2. Physical properties of alumina support.

| Sample | α -phase (%) | BET Surface Area (m^2/g) | Pore Volume (cm^3/g) | Pore Diameter ($^\circ\text{A}$) | Crystallite Size (nm) ^(a) | |
|--------------------------------|---------------------|--|--|------------------------------------|--------------------------------------|-----------------|
| | | | | | γ -phase | α -phase |
| $\gamma\text{-Al}_2\text{O}_3$ | 0 | 210.13 | $0.53^{(b)}$ | $100^{(b)}$ | 16.11 | 0 |
| $\alpha\text{-Al}_2\text{O}_3$ | 100 | 13.34 | $0.36^{(c)}$ | $1070^{(c)}$ | 0 | 23.82 |

(a) calculated from XRD results

(b) based on BJH method

(c) calculated from water displacement method

In order to investigate the effect of impregnation type, three Pd/Al₂O₃ samples were prepared for which the effect of impregnation type on palladium adsorption was reported in Table 3 and that of palladium penetration depth was depicted in Fig. 3. Palladium content of these samples was reported in Table 3, as well.

According to SEM graphs reported in Fig. 3, penetration depth for these samples is as follows: sample Pd1: 16-22 μ m, sample Pd2: 28-36 μ m, sample Pd3: 30-42 μ m.

As it is obvious in Table 3 for wet impregnation, the best type is for sample Pd1 which has the highest palladium adsorption. On the other hand, Fig. 3 confirmed that for wet impregnation, by increasing impregnation volume, palladium penetration depth is increased as well. Decreasing the volume of impregnation solution caused its concentration to be increased, thus palladium molecules have more interaction with surface hydroxyl groups and penetration depth

decreased.

In order to investigate the effect of pH, wet impregnation was used to prepare Pd/Al₂O₃ catalyst samples. The volume of impregnation solution is 4 times that of support pore volume. pH of the impregnation solution was adjusted in range 1-4 by using hydrochloric acid and ammonium hydroxide. The effect of pH on palladium adsorption was reported in Table 4 and that of palladium penetration depth was shown in Fig. 4. Palladium content of these samples was reported in Table 4 as well.

From Table 4, it is obvious that the highest palladium adsorption is obtained at pH 1.5. Increasing pH caused palladium penetration depth to be increased (Fig. 4). This phenomenon is due to decrease in alumina surface charges because of increase in pH.

According to SEM graphs reported in Fig. 4, penetration depth for these samples is as follows: sample Pd1: 16-22 μ m, sample Pd4: 10-25 μ m, sample Pd5: 32-42 μ m.

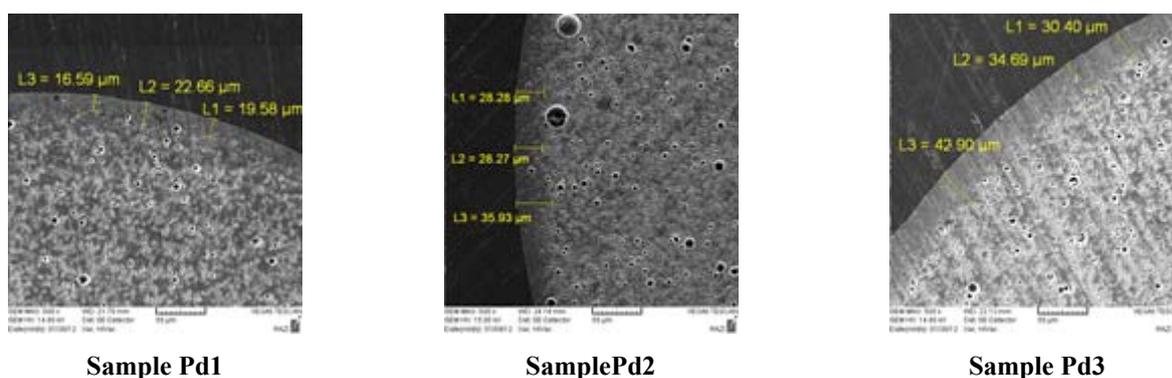


Figure 3. The effect of impregnation type on palladium penetration depth (obtained from SEM).

Table 3. Effect of impregnation type on palladium adsorption.

| Sample | Impregnation Condition ^(a) | | Palladium Content (wt.%) ^(b) | Palladium Adsorption (%) |
|--------|---------------------------------------|------------------------|---|--------------------------|
| | Type | Volume of Solution | | |
| Pd1 | wet | 4 times of pore volume | 0.03 | 97 |
| Pd2 | wet | 5 times of pore volume | 0.03 | 90 |
| Pd3 | dry | pore volume | 0.03 | 100 |

(a) all impregnation solutions were prepared at pH 1.5

(b) obtained from ICP

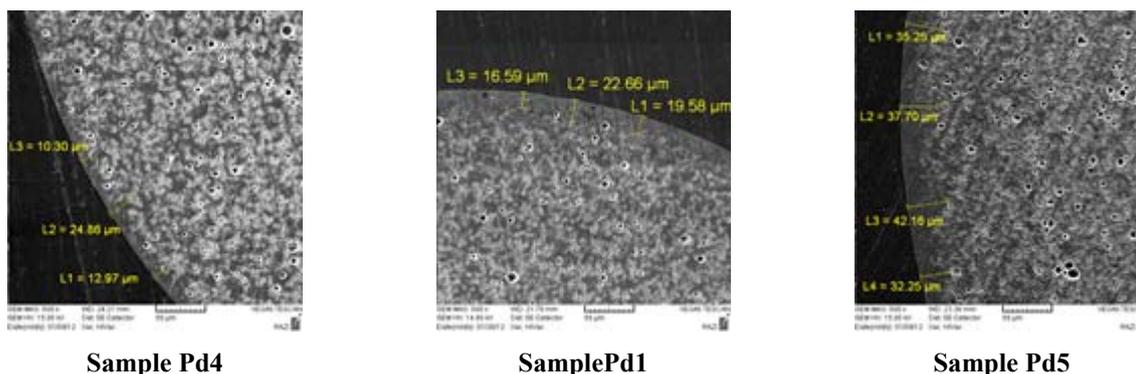


Figure 4. The effect of pH on palladium penetration depth (obtained from SEM).

Table 4. Effect of pH on palladium adsorption.

| Sample | pH of the Impregnation Solution | Palladium Content (wt.%) ^(a) | Palladium Adsorption (%) |
|--------|---------------------------------|---|--------------------------|
| Pd4 | 1.1 | 0.03 | 75 |
| Pd1 | 1.5 | 0.03 | 97 |
| Pd5 | 4.0 | 0.03 | 92 |

(a) determined by ICP

For palladium adsorption, there is an optimum value for pH that would be 1.5 (Table 4). Above this optimum pH value, palladium adsorption was decreased. This is due to a decrease in surface hydroxyl groups. On the other hand, by increasing pH to values near iso-electric point of alumina, palladium adsorption is not increased drastically; because near point of zero charge (PZC) the driving force for palladium adsorption is decreased as well. Moreover, it was reported that [26] at pH above 2, approximately 40-50% of PdCl_4 is hydrolyzed to $\text{PdCl}_3(\text{H}_2\text{O})^-$ which caused some adsorption limitations due to its larger sizes.

As palladium is a precious metal, its adsorption content is the detrimental parameter in the selection of pH values. Hence pH 1.5 is selected for catalyst synthesis.

From Figs. 3 and 4, it can be concluded that any change in pH of the impregnation solution and impregnation type cannot cause the penetration depth of palladium to be more than 40 μm . As the palladium content of the catalyst is rather low (0.03wt.%) and there are a large number of alumina surface sites available, palladium molecules do not have time to penetrate inside the alumina support.

As a concluding remark, according to the economic value of the active component, i.e. palladium, in selective hydrogenation catalyst, in the present research, pH 1.5 for impregnation solution and volume of impregnation solution equal to 4 times that of support pore volume is selected as optimum impregnation condition.

3-3. Catalyst synthesis

In order to investigate the influence of

impregnation method on catalyst performance, three bi-metallic samples were synthesized. The metal content of these samples was reported in Table 5. As it is observed, all the synthesized samples have the required metal content.

The metal penetration depth of all samples was determined by SEM (Fig. 5). It is obvious that all synthesized samples are egg-shell catalysts. Moreover, as it is illustrated in Fig. 5, the penetration depths of all samples are in the same range (sample A: 20-30 μ m, sample B: 27-33 μ m, sample C: 20-23 μ m and sample D: 24-33 μ m). Hence, the catalytic performance of these samples

cannot be interpreted by diffusion path as a limiting parameter.

The CO chemisorption results such as Pd active sites and Pd dispersion (%) were summarized in Table 6. The reason for higher dispersion of samples A and C in comparison with sample B is that sequential impregnation gave a catalyst sample with higher palladium dispersion and active sites. The use of PdCl₂ as a precursor and wet impregnation method for Pd resulted in higher dispersion and consequently higher hydrogenation activities. This finding is in accordance with what was reported by other researchers[27-30].

Table 5. Metal content and impregnation method of commercial and synthesized catalysts.

| Sample | Metal Content (wt.%) ^(a) | | BET Surface Area (m ² /g) | Pore Diameter (°A) | Impregnation Method | Palladium Precursor Source |
|--------|-------------------------------------|------|--------------------------------------|--------------------|---------------------------|----------------------------|
| | Pd | Ag | | | | |
| A | 0.03 | 0.18 | 9.34 | 1000 | Sequential ^(b) | chloride |
| B | 0.03 | 0.18 | 9.56 | 960 | Co-impregnation | nitrate |
| C | 0.03 | 0.18 | 9.45 | 975 | Sequential ^(c) | chloride |
| D | 0.03 | 0.18 | 27.82 | 133 | commercial | --- |

(a) obtained from ICP

(b) palladium was impregnated by wet method

(c) palladium was impregnated by dry method

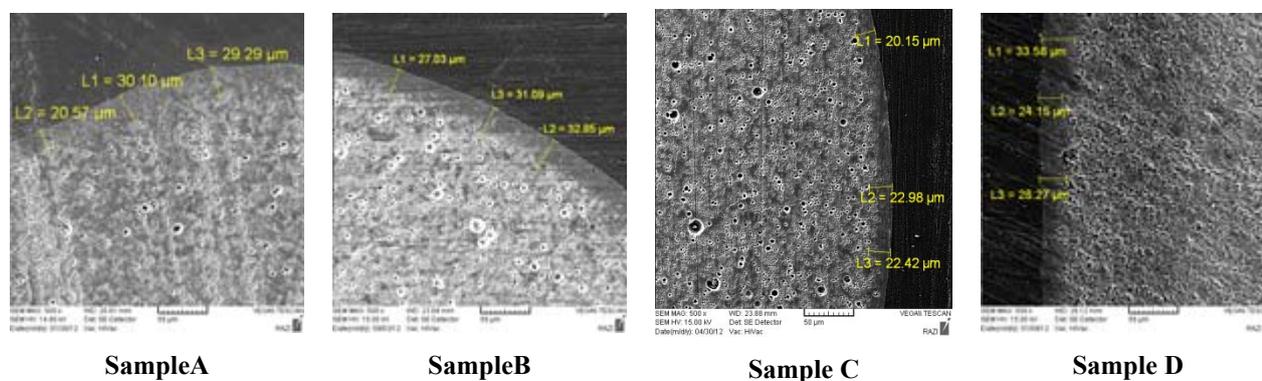


Figure 5. Palladium penetration depth in commercial and synthesized catalysts obtained from SEM.

Table 6. Physicochemical properties of commercial and synthesized catalysts.

| Sample | Pd Active Sites (*10 ⁻¹⁷ CO molecule / g _{cat}) | %Pd, Dispersion |
|--------|---|-----------------|
| A | 2.03 | 12.78 |
| B | 0.75 | 4.76 |
| C | 1.55 | 10.03 |
| D | 4.18 | 26 |

The higher dispersion of sample D in comparison with samples A, B and C is due to higher surface area of commercial support in comparison with the support used for synthesis of samples A, B and C.

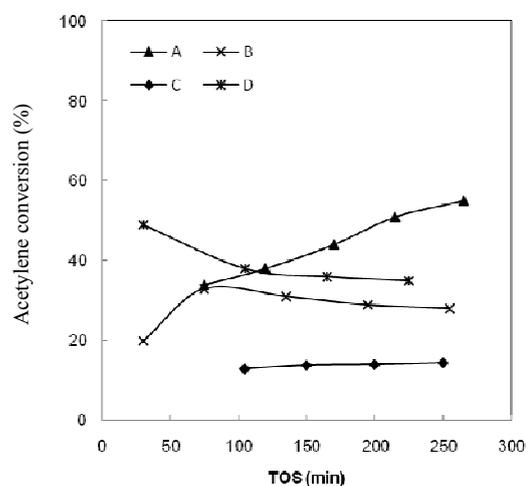
3-4. Catalyst performance

The catalytic performance of these samples is depicted in Fig. 6. The higher activity of sample A in comparison with samples B and C is because of its higher dispersion and active sites, as both of them have the same support with equal physical characteristics such as equal diffusion length and equal pore diameter. On the other hand, due to small pore diameter, commercial sample has more diffusion constraints[2]. Because of the positive overall reaction order[31, 32], although commercial sample has higher dispersion, it has lower activity.

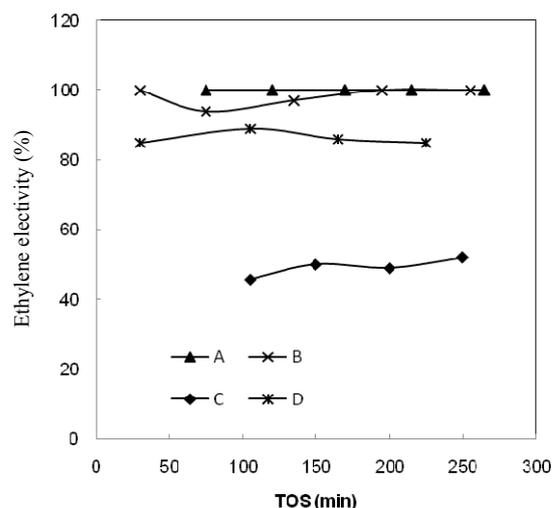
Higher selectivity of samples A and B is due to better interaction between palladium and silver molecules and reduction of large palladium ensembles. Moreover, smaller pore diameter of commercial sample caused the residence time of ethylene molecule to be increased and consequently catalyst selectivity is decreased.

According to Table 5, samples A and C have the same palladium precursors. Their only difference is in palladium impregnation method. Dry impregnation for Pd is not a

suitable method as it gave a sample with poor acetylene conversion and ethylene selectivity.



(a)



(b)

Figure 6. Catalytic performance of synthesized and commercial catalyst; (a) acetylene conversion, (b) ethylene selectivity.

Overall, as acetylene conversion and ethylene selectivity are two determining factors for catalyst performance evaluation, sequential impregnation is the preferred method for catalyst synthesis. Moreover, the support introduced in the present research has physical properties that are more suitable for decreasing diffusion resistances and increasing activity and selectivity of catalyst.

4. Conclusions

The effect of two impregnation parameters (i.e. pH of the impregnation solution and impregnation type) on palladium penetration depth and palladium uptake was investigated. It was observed that by changing these parameters, palladium penetration depth cannot be increased to more than 40 μ m, due to the presence of large number of surface hydroxyl sites and low palladium content. Egg-shell Pd-Ag/Al₂O₃ catalysts were prepared by impregnation method using a self-improved spherical alumina support. Palladium was distributed in an egg-shell layer with average thickness of 20-30 μ m. When applied in the selective hydrogenation of acetylene, the bimetallic Pd-Ag/Al₂O₃ prepared by sequential impregnation method with wet Pd impregnation showed better performance than the commercial one. From the viewpoint of precursor source, palladium chloride is better than palladium nitrate as its catalyst has better catalytic performance.

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