



The Effect of Addition Method of Impregnation Solution on Catalytic Properties of Pd-Ag/Al₂O₃ catalyst

M. Takht Ravanchi*, S. Sahebdehfar, M. Rahimi Fard, H. Moosavi

Catalyst Research Group, Petrochemical Research and Technology Company, National Petrochemical Company, Tehran, Iran
m.ravanchi@npc-rt.ir

Abstract

The impregnation of alumina support with PdCl₂ precursor solution was investigated in batch and semi-batch modes of Pd addition using a recycle packed-bed impregnation reactor. UV-visible analysis was used to evaluate kinetic adsorption of Pd on alumina support. Transient data of palladium adsorption on alumina was studied. It was observed that Pd adsorption was very rapid completing within few minutes. Bi-metallic Pd-Ag/Al₂O₃ catalysts were synthesized by sequential impregnation. CO-chemisorption and CO-TPD were used to characterize synthesized bi-metallic samples and their performance were evaluated for tail-end acetylene selective hydrogenation process. It was observed that by batch-wise addition of Pd solution, a sample obtained with lowest amount of Pd dimmers that had highest ethylene selectivity.

Keywords: Recycle Reactor, Palladium, Acetylene Selective Hydrogenation.

Introduction

In petrochemical industries for acetylene removal from C₂ stream, acetylene selective hydrogenation process is used. Acetylene content must be reduced to 1-5ppm; as it is the poison of Ziegler-Natta catalyst in downstream polymerization unit. In commercial plants, acetylene selective hydrogenation process is performed either as “front-end” or “tail-end” configuration.

Generally palladium is used as active phase of catalyst. During the years, different researchers used various metals (such as Ag, Na, Ga, Au, Sn, Bi, Sb, B, Ni, Cu, Pb, Cr, and K) as promoter of this catalyst [1-3]. In recent years, Ag is used in commercial catalysts as promoter.

As Pd adsorption on alumina support is the determining step in catalyst synthesis, in the present research the effect of different modes of Pd addition was studied in detail and its effect on catalyst morphology and performance was evaluated for tail-end acetylene selective hydrogenation process.



Experimental

Chemicals

Spherical γ -alumina (2mm in diameter) supplied from Sasol Co. with 210m²/g surface area and 0.5cm³/g pore volume, after pre-treating, was used as catalyst support.

Palladium chloride (PdCl₂) and silver nitrate (AgNO₃) were used as Pd and Ag precursors, respectively. These precursors were of commercial grade, supplied from Padideh Sazan Shimi Co. and used without further treatment.

Acetylene-ethylene gas mix cylinder (with 1.5mol.% acetylene and 98.5mol.% ethylene), hydrogen (99.9mol.%) and nitrogen (99.9mol.%) were supplied from Dayan Gas Co. and used as reactant or diluent gases.

Catalyst synthesis

For kinetic study of palladium adsorption on alumina support, a double-wall tubular fixed bed quartz reactor accompanying two peristaltic pumps (with 40cm³/min flow rate) for circulation of impregnation solution was used. To ensure proper distribution of fluid flow, space below the alumina support was packed with 2mm glass inert balls. A schematic diagram of the experimental set-up is provided elsewhere [4]. For this reactor, height/diameter of support bed was 5.

The final target catalyst of the present research is Pd-Ag/Al₂O₃ catalyst. As the first step, Pd was impregnated on alumina support in the set-up described above at 40°C. In the second step, Ag was impregnated on Pd/Al₂O₃ catalyst in rotary equipment at 25°C. After each impregnation step, the samples were dried at 110°C for 12h and calcined in air at 450°C for Pd and 400°C for Ag.

In the present research, three different modes for the addition of Pd impregnation solution were considered, as below:

- Sample A: batch-wise impregnation in which Pd solution was added in one step to the circulating solution beaker containing DM water.
- Sample B: semi-batch impregnation in which Pd solution was added in four steps every 15mins to DM water inside the circulating solution beaker.
- Sample C: semi-batch impregnation in which Pd solution was added in a same batch in 32 steps every 1min to DM water inside the circulating solution beaker.

It is worth mentioning that for each sample, 40g support was loaded to the impregnation reactor.

Catalyst Characterization

In order to determine palladium concentration in impregnation solution, UV-Visible (T90, PG Instruments Limited Co.) apparatus was used. By taking different Pd concentration, calibration curves were constructed in two different ranges as below:

$$0.024-0.3 \text{ mmol}_{\text{Pd}}/\text{L}_{\text{solution}}: y=0.3798x+0.00019 \quad (1)$$

$$0.3-2.4 \text{ mmol}_{\text{Pd}}/\text{L}_{\text{solution}}: y=0.28359x+0.03829 \quad (2)$$

where x is Pd concentration and y is its absorbance.

For kinetic experiments, Pd concentration in impregnation solution was determined by recycling the solution to the quartz cell and measuring the absorbance at 432nm against the reagent blank (appropriate amount of HCl in H₂O).



In order to determine Pd dispersion in catalyst samples, CO chemisorption analysis was performed. At first, the catalyst was pre-treated in a reactor with 50ml/min hydrogen at 400°C for 15min. Afterwards, the reactor was connected to BELCAT apparatus (type A) and cooled down to 50°C with the aid of 50ml/min helium. Then, a pulse of 1.009ml CO was introduced to the reactor which was repeated every 1min. A TCD detector recorded CO-signals. It is worth mentioning that CO is selectively chemisorbed on Pd.

For CO temperature-programmed desorption (CO-TPD), the catalyst sample was loaded to the reactor of BELCAT A apparatus, reduced at 150°C for 2h by hydrogen, and purged with helium at 150°C for 1h to remove adsorbed H₂ from the Pd surface. Afterwards, the catalyst was exposed to CO at 40°C and temperature was raised from 40°C to 700°C at a rate of 10°C/min in helium.

Reaction Study

The synthesized samples were evaluated for acetylene selective hydrogenation (tail-end) in a high pressure set-up, the detailed explanation of which is provided elsewhere [5].

In each test, 4g catalyst diluted with the same size quartz was loaded. At first, the catalyst was reduced in situ with hydrogen at GHSV of 500h⁻¹ and temperature of 150°C. Afterwards, the reactor was cooled down by nitrogen to reaction temperature (60°C). Each catalyst was evaluated in the presence of 1mol.% C₂H₂, 1.5mol.% H₂, 30mol.% N₂ and C₂H₄ as balance (as feed) at 10bar and GHSV of 4000h⁻¹. For analyzing the components of feed and product streams, an on-line gas chromatograph (Varian-CP-3800), equipped with FID and TCD detectors, was used.

Acetylene conversion and ethylene selectivity are parameters used for catalyst performance evaluation.

Results and discussion

Catalyst Characterization

Kinetic adsorption of Pd on alumina support for all synthesized samples (in the first stage of Pd/Al₂O₃ catalyst) is depicted in Figure 1. As it is obvious, palladium adsorption on alumina support used in the present research is very rapid and high. As it is observed in Figure 1 for sample A, within less than 20min, Pd is totally adsorbed and after that time no more Pd was observed in circulating solution. When Pd solution was added in a stepwise manner (samples B and C), a high concentration of Pd persists for longer time in impregnation solution (Figure 1, samples B and C) and the support is contacted with the Pd precursor gradually.

Palladium dispersion and Pd active sites for Pd-Ag/Al₂O₃ synthesized samples were tabulated in Table 1. As it is observed, when Pd was added in four portions (i.e. sample B), highest Pd dispersion was obtained which is equivalent to lowest Pd particle size. Moreover, this sample had highest Pd active sites.

Table 1- Pd dispersion and Pd active sites for Pd-Ag/Al₂O₃ catalysts

Sample	Pd dispersion (%)	Pd active sites ($\times 10^{17}$ site/g _{catalyst})
A	54.45	8.61
B	62.13	9.84
C	52.26	8.26

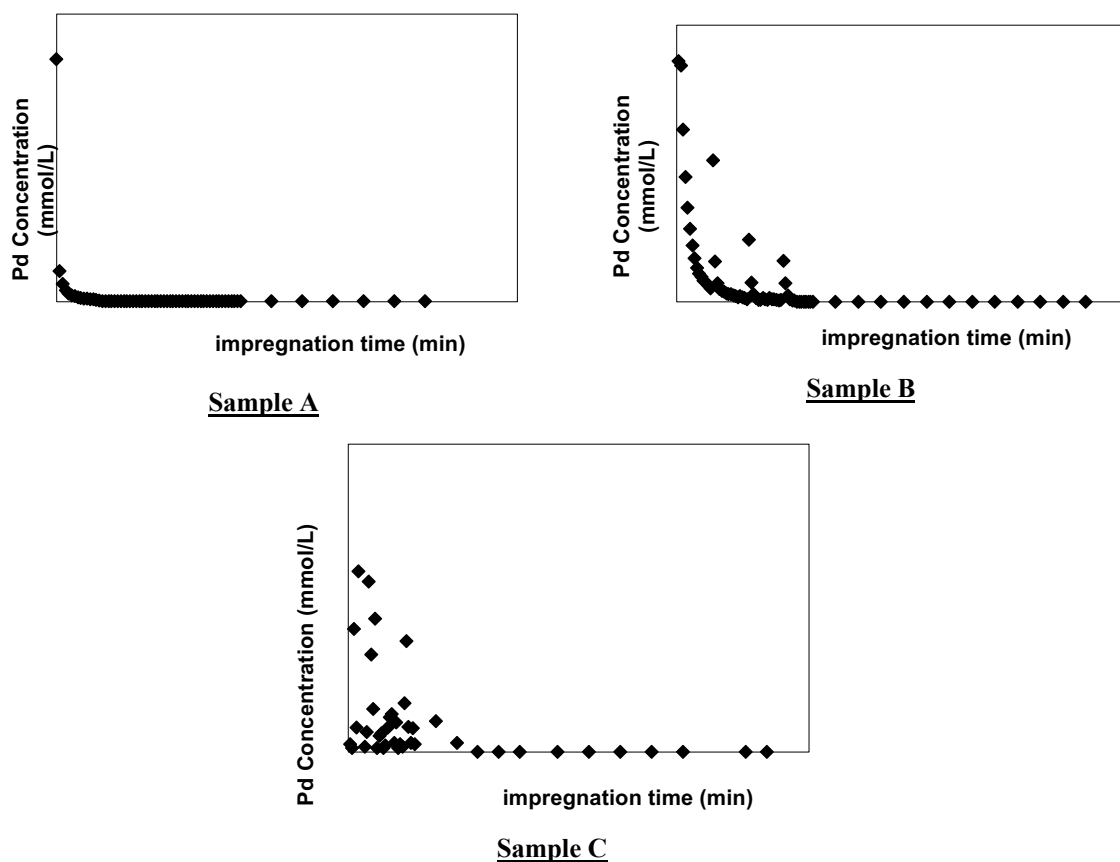


Figure 1- Transient adsorption of Pd on alumina support

TPD-CO results for Pd-Ag/Al₂O₃ synthesized samples were presented in Table 2 and Figure 2. All samples showed three desorption peaks characterizing different palladium adsorption sites. When Pd solution was added in a stepwise manner to DM water (samples B and C), in comparison to single-step manner (sample A), the first peak shifted to higher temperature which showed a stronger adsorption of CO on the related Pd atoms. It is predicted that adsorption strength of unsaturated hydrocarbons on Pd would be increased and consequently, ethylene selectivity would be decreased. Among these stepwise modes of Pd addition, when Pd was added in high volume (sample B), this shift in temperature of the first peak was higher; consequently, the resultant sample has strongest Pd sites.

According to Table 2, sample A has lowest CO consumption on 2nd and 3rd peak, which is equivalent to lowest amount of Pd dimmers on this sample. As 2nd and 3rd peaks are attributed to Pd dimmers which are responsible to bridge adsorption sites, their lower amount is equivalent to higher ethylene selectivity for that sample. Hence, it is predicted that sample A would have highest ethylene selectivity.

Table 2- CO consumption of Pd-Ag/Al₂O₃ catalysts.

Sample	CO consumption (mmol/g)		
	First peak	Second peak	Third peak
A	0.034	0.058	0.076
B	0.111	0.098	0.150
C	0.094	0.110	0.131

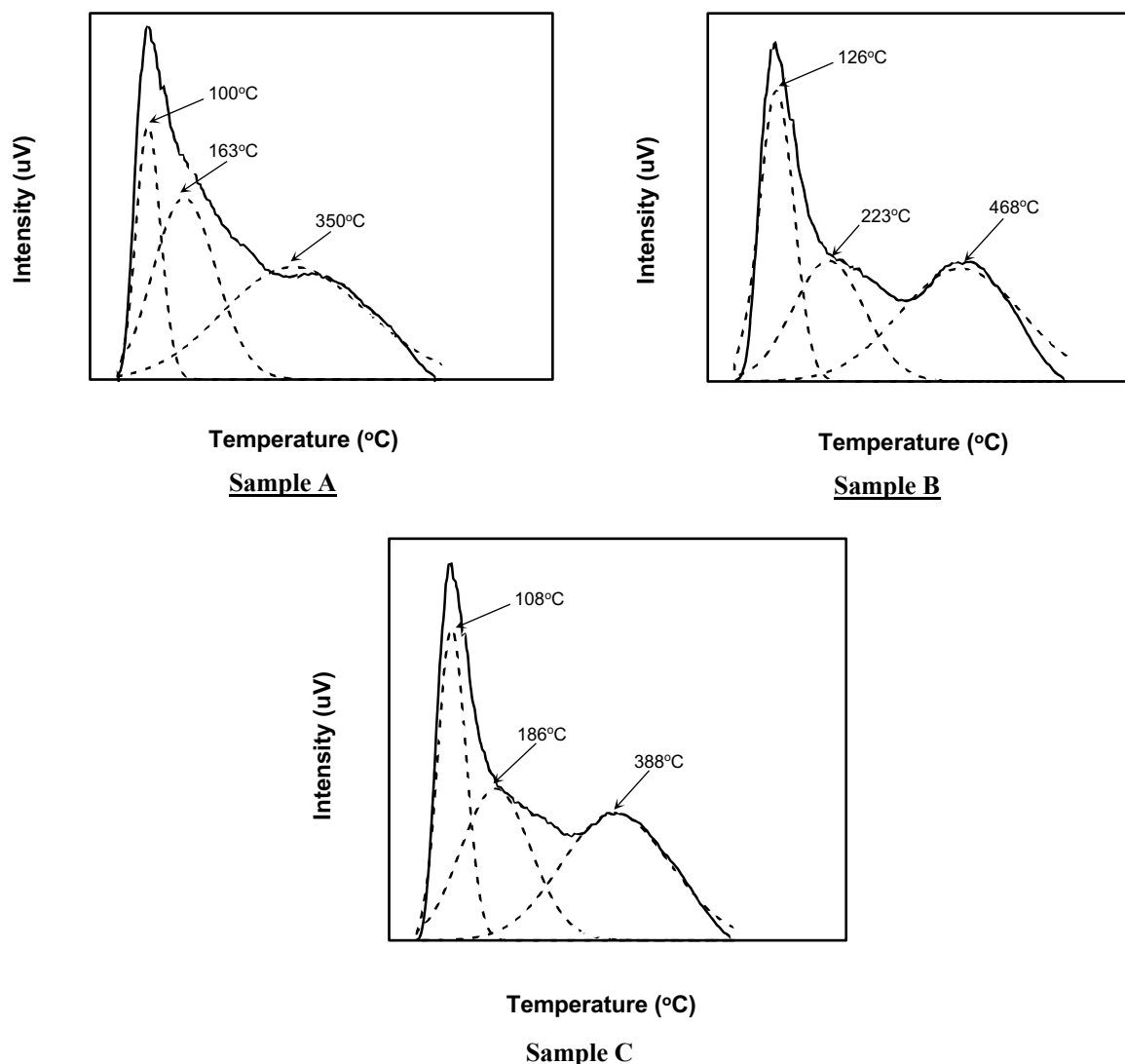


Figure 2- TPD-CO graphs of Pd-Ag/Al₂O₃ catalysts

Catalyst Performance

Catalytic performance of the synthesized samples is presented in Figure 3. Among the synthesized samples, sample C had lowest initial C₂H₄ selectivity. This sample had lowest dispersion as well (Table 1). Lowest dispersion is equivalent to highest Pd particle size which is not suitable for acetylene selective hydrogenation reaction; as they shift the reaction to ethylene hydrogenation pathway by which ethylene selectivity is reduced.

It is observed (Figure 3) that when Pd solution was added in stepwise manner in its lowest amount (sample C), highest acetylene conversion was obtained. From another viewpoint, highest acetylene conversion was obtained by the sample that has lowest Pd dispersion.

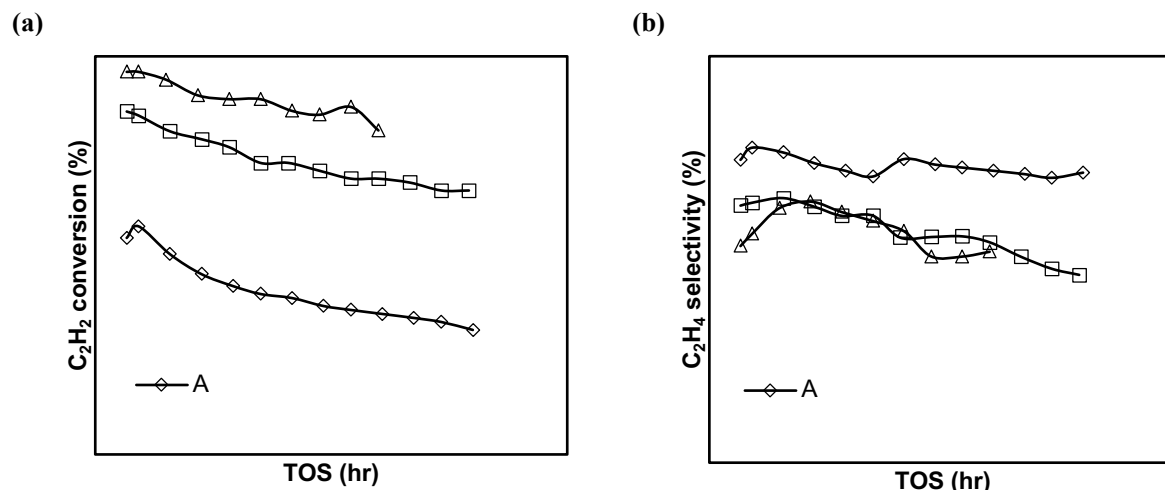


Figure 3- Catalytic Performance of the synthesized samples

Conclusions

The effect of addition method for Pd solution on catalytic performance of Pd-Ag/Al₂O₃ was investigated. It was observed that in batch-wise addition of Pd solution, palladium was immediately and completely adsorbed on alumina support and the obtained sample had highest ethylene selectivity.

Reference

- [1] Takht Ravanchi, M., Sahebdehfar, S. and Komeili, S., "Acetylene selective hydrogenation: a technical review on catalytic aspects", *Rev. Chem. Eng.*, 34, 215-237 (2018).
- [2] Komhom, S. Mekasuwandumrong, O., Praserttham, P. and Panpranot, J., "Improvement of Pd/Al₂O₃ catalyst performance in selective acetylene hydrogenation using mixed phases Al₂O₃ support", *Catal. Commun.*, 10, 86-91 (2008).
- [3] Kim W. J. and Moon S. H. "Modified Pd catalysts for the selective hydrogenation of acetylene", *Catal. Today*, 185, 2-16 (2012).
- [4] Takht Ravanchi, M., Abedini, A., Sahebdehfar, S., Mehrazma, Sh. and Seyyed Shahabi, S., "Mathematical modeling of platinum and chlorine distributions within Pt-Sn/Al₂O₃ catalyst prepared by impregnation", *Sci. Iran. C* 22, 981-991 (2015).
- [5] Takht Ravanchi, M., Sahebdehfar, S., Rahimi Fard, M., Fadaeeraeyeni, S. and Bigdeli P., "An Experimental and Modeling Investigation on Catalyst Deactivation for Pd-Ag/ α -Al₂O₃ for Acetylene Selective Hydrogenation", *Chem. Eng. Tech.*, 39, 301-310 (2016).