



Partial Acetylene Hydrogenation over Commercial Pd-Ag/ α -Al₂O₃ Catalyst Promoted by Ionic Liquid

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ABSTRACT

The 1-butyl-3-methyl imidazolium hydroxide ionic liquid (BMIIm[OH]) is loaded on commercial low surface area Pd-Ag/ α -Al₂O₃ solid catalyst to enhance its selectivity in acetylene partial hydrogenation. Different experimental techniques such as atomic absorption spectroscopy, BET and gas chromatography have been utilized to characterize chemical, structural and catalytic properties of the catalyst. Additionally, FT-IR spectra are collected to study the synthesized ionic liquid. The selectivity and activity of the fresh and used catalysts are compared for both ionic liquid free sample and loaded one. Results revealed that the 13.7% Ethylene to Ethane ratio improvement over commercial catalyst is achievable successively through 0.2 Wt.% of BMIIm[OH] ionic liquid loading.

1. INTRODUCTION

Alumina supported palladium has been successively developed for acetylene removal in excess ethylene feed. This is essential for keeping ethylene polymerization to be proceeded by Ziegler-Natta catalyst [1-3].

Economically, selective partial hydrogenation of acetylene is the favored reaction toward acetylene elimination as well as higher ethylene yield at the same time. Feeding of CO or addition of some metals such as Ag or Ga to the palladium particles have been employed in industry to improve the selectivity [4-7].

However, because of high activity and exothermic nature of the reaction, it is accompanied by the thermal runaway of the adiabatic reactor or creation of hot spots [8]. All attempts are towards high activity and selectivity with low local temperature rise due to the exothermic reactions.

Nowadays ionic liquids (IL) with astonishing characteristics are being utilized to enhance the superlative catalytic properties. Fundamentally, ionic liquids are organic salts with low melting point and negligible vapor pressure [9, 10].

Many transition metal complexes dissolve readily in ionic liquids, which enable them to be used as solvents for transition metal catalysis [10-12].

The non-nucleophilic and weakly co-ordinated nature of ionic liquids can maintain an inert reaction medium which extends the lifetime of a catalyst.

Ionic liquids and solid catalysts can be integrated to approach a solid catalyst with the behavior of homogenous type catalyst. Solid catalyst with an ionic liquid layer (SCILL), which is composed of dissolved active species in an IL film [12-14], is a well-known system for highly selective homogenous catalyst with large interaction area and ease of product separation [15-18].

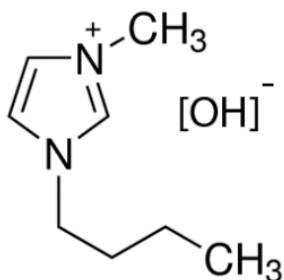
Among the various classes of ionic liquids, those containing N-heterocyclic cations are the most common types. Imidazolium salts are the most prominent subclass of this group and a number of them are commercially available.

Their solvent properties such as melting points, solubility and viscosity can be tuned easily in a wide range by varying the substituents at the nitrogen atoms as well as by varying the counter-ions [19-21].

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Recently, Hermman et al. investigated the BMIm[DCA]² and DMIm[MeHPO₃]³ ILs in selective hydrogenation. It is assumed that the negative contributions of limited hydrogen solubility and diffusion-limited regime in ILs are less-effective than its consumption rate resulting in decrease of reaction rate and increase in the selectivity [22]. In another work by J. Palgunadi et al. ionic liquids are used to separate acetylene from ethylene. In comparison to ethylene and ethane, acetylene is a weak acid because of SP hybrid orbital, and this improves its solubility in comparison to ethane especially in basic mediums [17].

We have succeeded to introduce hydroxyl functionalized butyl-3-methylimidazolium or BMIm[OH] ionic liquid as a promoter to improve the selectivity of acetylene partial hydrogenation reaction in excess ethylene feed. The chemical structure of utilized ionic liquid is shown in Scheme 1. This type of IL has been characterized as a basic ionic liquid and used instead of traditional bases such as NaOH, K₂CO₃, NaHCO₃, NaOAc. In our previous report, BMIm[OH] was loaded on high surface area γ -Al₂O₃ supported palladium catalyst and the selectivity in partial hydrogenation was maintained over long time catalytic reaction [13]. Here the effect of BMIm[OH] loading on low surface area commercial catalyst is investigated to provide higher ethylene yield.



Scheme 1. Structure of BMIm[OH].

2. MATERIALS AND METHODS

2.1. Chemical and structural properties

Pd concentration and structural properties were evaluated by flame atomic absorption spectroscopy (GBC-906) and BET (micromeritics-tristar 3020), respectively.

The FT-IR (Perkin Elmer 2000) spectra were employed to study structural features of synthesized ionic liquid. For this purpose, 32 scans were measured in the range of 400 to 4000 cm^{-1} wavenumbers with a spectral resolution of 2 cm^{-1} . Self-supporting thin pellet of analytical grade NaCl was prepared as a support and the relative spectra were collected before and after ionic liquid addition to the pellet.

²1-butyl-3-methyl imidazolium dicyanamide

³1,3-dimethyl imidazolium methyl phosphonate

2.2. Catalyst preparation

Low surface area commercial Pd-Ag/ α -Al₂O₃ (Olemax® Series) catalyst was employed to investigate the effect of ionic liquid loading on the acetylene hydrogenation reaction with front end composition. The catalyst was cylindrical shaped tablets (4×4 mm), and the cross section shown in Figure 10. illustrates its eggshell type with 67 μm of shell thickness. According to the result of atomic absorption spectroscopy, the total Pd content of the catalyst was 200 ppm and hence the Pd concentration of the outer shell is calculated to be approximately 0.8 Wt.%. Palladium concentration was in accordance with the commercial data released by the manufacturing company.

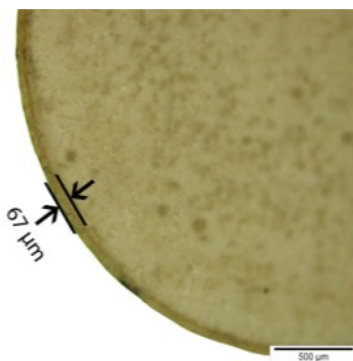


Figure 1. Cross section of the commercial Pd-Ag/ α -Al₂O₃ eggshell type catalyst.

To synthesize the ionic liquid, 1-butyl-3-methylimidazolium-bromide was prepared by mixing 1-methylimidazole and excess 1-bromobutane being refluxed for 24 h at 60 °C and evaporated in rotary evaporator at 80 °C for 24 hours. Then KBr was precipitated and removed by adding stoichiometric amount of KOH in CH₂Cl₂ solvent. The prepared 1-butyl-3-methylimidazolium-hydroxide was purified by evaporating the solvent at 90 °C for 12 h. Then obtained BMIm[OH] was impregnated by 0.2 wt.% of the total catalyst pellets using acetone as the solvent, followed by drying at 150 °C. Impregnation was carried out in a rotary evaporator at 65 °C to eliminate the solvent.

2.3. Catalyst performance evaluation setup

1 ml of catalyst was grinded and meshed between 0.25-0.6 mm to be loaded in a U-shaped quartz reactor with the diameter of 10 mm to avoid channeling effect. The catalyst containing reactor was heated in the bath filled with silicon oil as heating medium just like our previous report [13] as shown in Figure 1. Temperature was controlled by two thermocouples, one fixed inside the reactor in contact with the catalyst and the other one nearby the reactor to measure the oil temperature. In addition to these thermocouples, the heating bath had its own temperature indicator and controller. A mechanical agitator was utilized to homogenize the oil temperature throughout the bath.

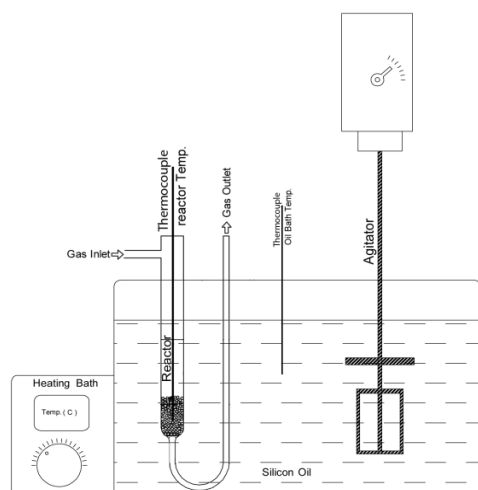


Figure 1. Catalytic test setup.

Before gas feeding, the catalyst was reduced in hydrogen atmosphere at 150 °C for 2 hours to remove any trace amount of palladium oxides. After cooling down the catalyst, the feedstock was introduced into the reactor with the gas composition as specified in **Error! Reference source not found.** The total flow was 75 mL/min at ambient pressure and the flow of gases were separately controlled by Mass Flow Controllers (MFC). The outlet gas composition was analyzed by YL-6100 Gas Chromatograph (GC) equipped with a thermal conductivity detector and a Carboxen1010 capillary column. The Gas Hourly Space Velocity (GHSV) of inlet gas in the test was 4500 h⁻¹. Acetylene conversion was calculated by Equation (1). Selectivity was assessed using the ratio of volumetric percentage of ethylene to volumetric percentage of ethane in the outlet gas as given in Equation (2).

$$Con_{C_2H_2} (\%) = \frac{F_{in} X_{C_2H_2}^{in} - F_{out} X_{C_2H_2}^{out}}{F_{in} X_{C_2H_2}^{in}} * 100 \quad (1)$$

$$S_{C_2H_4} = \frac{X_{C_2H_4}^{out}}{X_{C_2H_6}^{out}} \quad (2)$$

TABLE 1. Feedstock composition.

Gas	H ₂	C ₂ H ₂	C ₂ H ₄	C ₂ H ₆	sum
Concentration (% Vol.)	10	5	68	17	100
Gas flow (mL/min)	7.5	3.75	51	12.75	75

3. RESULT AND DISCUSSION

The results of evaluated chemical and structural properties of the commercial catalyst are given in Table 2. The N₂ adsorption and desorption isotherms over the catalyst are also shown in Figure 3.

As shown in Figure 4. FT-IR spectra of the synthesized imidazolium based ionic liquids show contributions between 2800 cm⁻¹ and 3000 cm⁻¹, which can be clearly referred to the -C-H stretching band of CH₂ and CH₃ vibrations of the alkyl groups located at the nitrogen

atoms of the imidazolium ring [23] besides 1100-1200 Cm⁻¹ which is designated to the original -C-C-N part of imidazolium ring [24]. FT-IR spectra show that BMIm[OH] is synthesized successfully.

TABLE 2. Structural and chemical properties of the utilized catalyst.

Sample	Pd-Ag /α-Al ₂ O ₃	
Shape	Cylindrical	
Type	Eggshell	
Dimension	d=3.9 , h=3.9	(mm)
Total Pd	200	(ppm)
Surface Area	3.91	(m ² /g)
Pore Volume	0.005	(cm ³ /g)
Average Pore width	0.0054	(nm)

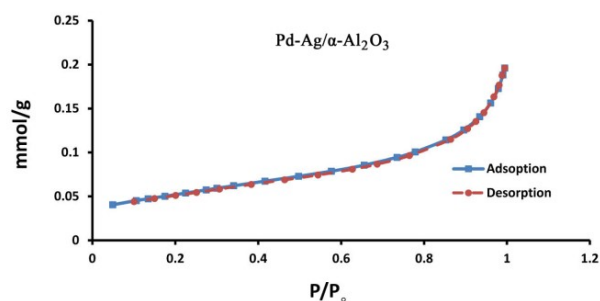


Figure 3. N₂ adsorption and desorption isotherms of commercial Pd-Ag/α-Al₂O₃ catalyst.

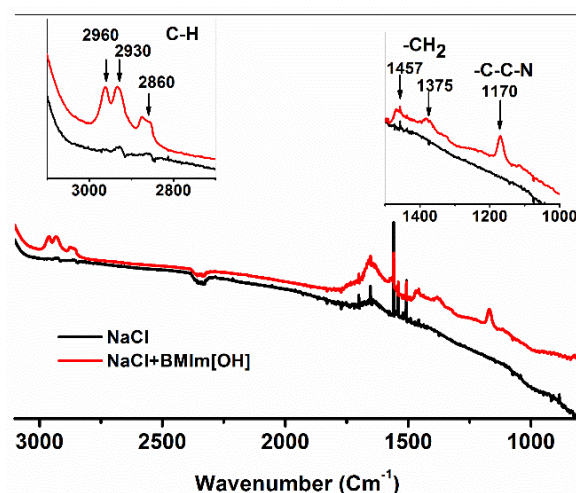


Figure 4. FT-IR spectra of bare NaCl (black) and BMIm[OH] ionic liquid loaded one (red).

3.1. Catalytic performance

Catalytic activities of the samples at different temperatures from room temperature up to 180 °C are shown in **Error! Reference source not found.** Gas chromatography analyses of the outlet gas have been done by two injections within 20 minutes of being stable at the evaluating temperature. Selectivity can be assessed

considering hydrogen consumption and ethylene to ethane ratio. Higher ethylene to ethane ratio with less hydrogen consumption rate shows more ethylene yield or more selectivity in acetylene partial hydrogenation. Following this rule, as shown in **Error! Reference source not found.** 13.7 % selectivity improvement was achieved by increasing the Ethylene to Ethane ratio from 3.28 to 3.73 through the ionic liquid loading. Selectivity fall at temperatures that acetylene elimination occurs, is due to ethylene hydrogenation to ethane in absence of acetylene, which is also reported in numerous reports [25-27]. The IL loading decreases the H_2 consumption even after acetylene elimination at high temperatures, which shows its effectiveness in selectivity improvement especially at temperatures with high conversion rates. This feature of ionic liquid might be due to lower adsorption of reactants on palladium surface in presence of an ionic liquid layer, which needs more investigation via further experimental and theoretical studies [13].

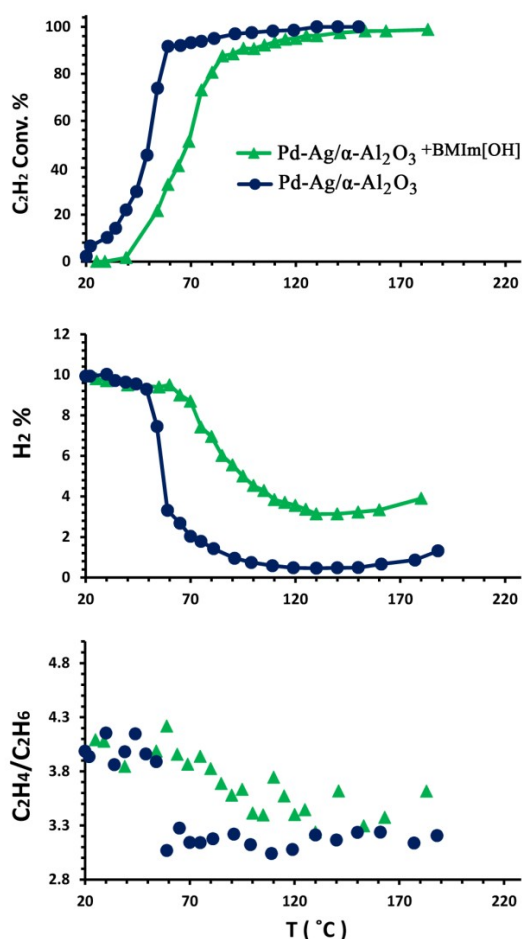


Figure 5. C_2H_2 Conversion, $H_2\%$ and ethylene to ethane ratio of IL free and IL loaded $Pd-Ag/\alpha-Al_2O_3$.

3.2. Catalytic stability

Stability under reaction conditions for a long time is an important factor determining the catalytic performance. Selectivity

maintenance over time along with longstanding of the catalyst, are critical in catalytic reactions. In this work, the stability was evaluated considering catalyst activity shift as a function of time-on-stream for 48 h at 150 $^{\circ}C$. This temperature is selected due to the complete acetylene removal. The activities of fresh and used catalysts for both ionic free and ionic loaded- $Pd-Ag/\alpha-Al_2O_3$, are shown in Figure 6. Approximately 20% conversion degradation is occurred in both commercial $Pd-Ag/\alpha-Al_2O_3$ and $BMIm[OH]$ loaded catalyst but the selectivity has been improved in both systems. Activity drop can be attributed to presence of Ag in Pd lattice limiting the subsurface active hydride phase formation. Ionic liquid loading has further effect on decreasing the activity through limiting the solubility of the reactants and hence their adsorption on the Palladium surface, which needs further theoretical studies to be investigated [28].

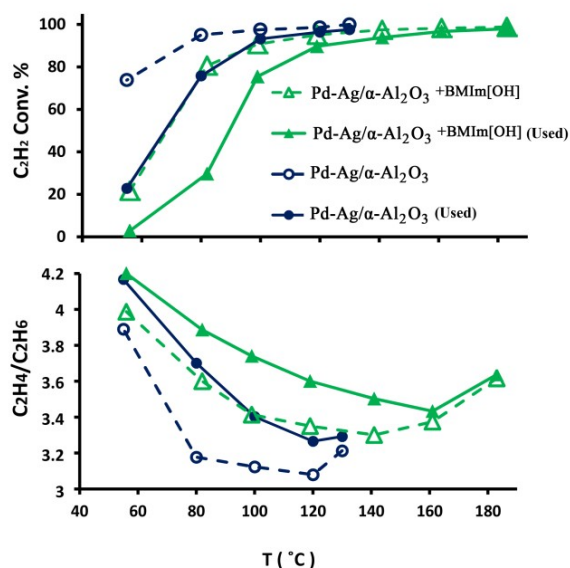


Figure 6. The activity and selectivity of fresh and used catalysts.

4. CONCLUSIONS

$BMIm[OH]$ ionic liquid can be utilized as a promoter for selectivity improvement in acetylene partial hydrogenation over low surface area commercial alumina supported palladium catalyst. As an approach, the ethylene to ethane ratio in catalytic hydrogenation of acetylene with front end feed composition was improved by 13.7% at higher temperatures of complete acetylene removal. Activities diminish as a function of time, which is the characteristic behavior of the commercial catalyst and it was also observed in the catalysts loaded by ionic liquid.

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Appendix

X_r^{in}	Volumetric percentage of reactant r in inlet feed gas	%
X_r^{out}	Volumetric percentage of reactant r in outlet gas	%
F_{in}	Total inlet gas flow	ml/min
F_{out}	Total outgas gas flow	ml/min

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