

Effect of Pt on Zn-Free Cu-Al Catalysts for Methanol Steam Reforming to Produce Hydrogen

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ABSTRACT: Steam reforming of methanol can be considered as an attractive reaction aiming at hydrogen production for PEM fuel cells. Although Cu/Al-contained catalysts are considerably evaluated in this reaction, further evaluation is essential to evaluate the impact of some promoters like Pt in order to find a comprehensively optimized catalyst. Pt promoter is employed with different methods in this study. Firstly, the amount of Cu loading in Cu/Al ratio is optimized via coprecipitation method. The sample containing 30% wt. of Cu exhibits better performance with methanol conversion of 70% and CO selectivity of 0.44%. Besides, impregnating a different amount of Pt onto Al₂O₃ reveals an inadequate potential for this reaction. In contrary, doping Pt into Cu/Al catalyst increases the methanol conversion as high as 81% and CO selectivity reaches to approximately zero at 270 °C. In addition, using a dual-bed reactor including Cu/Al and Pt/Al₂O₃ catalyst displays a relatively satisfactory performance by which the conversion and selectivity are found 83.7% and 1.5%, respectively. In this study, analyses of X-Ray Diffraction, Scanning Electron Microscopy, and BET surface area are used to characterize the synthesized catalysts.

KEYWORDS Methanol steam reforming; PEM fuel cells; Hydrogen; Dual-bed reactor; Pt; Cu/Al catalyst.

INTRODUCTION

Nowadays, developing green technologies is one of the main factors of resolving the environmental issues and in this way, hydrogen plays a pivotal role as an ideal and clean carrier especially for Proton Exchange Membrane Fuel Cells (PEMFCs) applications [1]. These systems can be regarded as one of the best candidates to be replaced with internal combustion engines. It, in turn, lead to gaining more effective systems and lower emissions in comparison with internal combustion engines [2]. PEMFCs require a CO-free hydrogen in the inlet stream to avoid deactivation of Pt-based electrodes.

An integrated system of PEMFC plus hydrogen production unit so-called fuel processor can, hence, be included reforming reaction unit, water gas shift reaction (high/low-temperature stages), and preferential oxidation of carbon monoxide (PrOx) units. The mentioned system provide an excellent condition to decentralize power and heat plants followed by economic applications in smaller scales [3,4].

Broadly consideration, there are various methods of hydrogen production like methanol steam reforming or other hydrocarbons associated with natural gas, gasoline and diesel fuel [5-7]. Nevertheless, methanol steam reforming

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1021-9986/2018/4/93-100 8\$/5.08

reaction represents some advantages like operating at lower temperatures (250-350 °C), higher conversion and lower CO amount (1000 to 10000 ppm) as well [8-12]. Cu-based catalysts normally display high activity and selectivity to perform a catalytic methanol steam reforming, and also are favorable in a low-temperature water gas shift [13-16], or a medium temperature shift reaction [17, 18]. These types of catalysts are prepared through various synthesis methods like impregnation, co-precipitation, and etc. [19, 20]. Typically, there are two approaches for investigation; I) using promoters II) employing different types of synthesis and preparation [21].

The Cu-based catalysts aside, catalysts of group 8-10 represent a promising performance for terms of both activity and stability. Of the latter, Pt/Al₂O₃ has been frequently used in various applications of fuel cell systems [22], catalytic combustion of hydrocarbons [23], and PrOx [24]. *Ma et al.* [1] studied the effect of promoters of Pt, Fe, Co, and Ni when using for SRM reaction. Their investigation showed which metal-doped molybdenum carbides exhibited better conversion and yielded more hydrogen than those of non-doped ones. In particular, the Pt-doped case represented approximately a full conversion even at as low as 200 °C and also revealed good stability for a long time at 200-400 °C. Likewise, *Brown et al.* [25] evaluated Pt-based catalysts for methanol decomposition reaction. This type of catalyst showed a higher H₂/CO selectivity than those of Cu-based types, although the conversion was relatively low. *Ito et al.* [26] indicated that Zn-promoted Pt/C catalyst represented higher activity and also CO₂ selectivity in comparison with only Pt/C catalyst in methanol steam reforming. Formation of Pt-Zn alloy provided another pathway where CO₂ would be produced through methyl formate over Zn-promoted Pt/C catalyst. This study aims at optimizing Pt over Cu-based catalyst in various steps. This research is to address the behavior of Pt affected by preparation methods and also to investigate the Pt role in different steps.

EXPERIMENTAL SECTION

Catalysts preparation

Different amount of Cu/Al catalyst (Cu: 5, 10, 20, 30 and 40% wt.) were prepared with the co-precipitation method. The aqueous solutions (0.5 M) containing Cu(NO₃)₂.4H₂O (Loba Chemie, 99.9%) and

Al(NO₃)₃.9H₂O (Loba Chemie, 99.9%) was prepared. Another aqueous solution of Na₂(CO₃) as a precipitating agent was also prepared. These solutions were slowly added dropwise to 200 ml of D.I. water at 70 °C under strongly stirring condition. After the precipitation, the suspension was aged for 2 h at the same conditions and then was washed by distilled water to separate the rest of the Na⁺ ions. Then drying at 110 °C for 12 h was performed followed by calcination at 400 °C for 4 h. To synthesize the PtCuAl, the same synthesis method of Cu/Al preparation was repeated and moreover, H₂PtCl₆.4H₂O precursor was also added to the co-precipitation beaker. These steps were completed with drying and calcination as adopted before. Besides, to synthesis Pt/Al₂O₃ catalyst, the prepared boehmite sol, was calcined at 550 °C for 2 h to form γ-alumina. Then, the prepared alumina powder was strongly mixed with D.I water and after a while, a certain amount of H₂PtCl₆.4H₂O solution was added to this powder. In the end, the mixture was aged followed by drying for 12 h and also calcination at 500 °C for 4 h.

Catalysts Characterization

The BET surface area analysis was used by which all data were obtained from N₂ adsorption-desorption data at the boiling temperature of nitrogen (-196 °C) using an automated gas adsorption analyzer (Tristar 3020, Micromeritics). The samples were purged with nitrogen gas for 2 h at 200 °C using a VacPrep 061 degas system (Micromeritics). Temperature Programmed Reduction (TPR) was also utilized to characterize the reducibility of the catalyst by a Micromeritics Chemisorb 2750 equipped by a Thermal Conductive Detector (TCD). Each sample was pretreated at 200 °C for 1 h under a constant argon flow rate. It was reduced by increasing the temperature to 350 °C at a rate of 5 °C/min with a stream of 10% H₂/Ar, (30 mL/min). After cooling to the room temperature, the produced water was trapped using a 3A molecular sieve; hydrogen consumption was monitored using a TCD.

X-Ray Diffraction (XRD) analysis was performed using an X-ray diffractometer (PANalytical X'Pert-Pro) with a Cu-K_α monochromatized radiation source and Ni filter in the range with 2θ = 5 to 70. Scanning Electron Microscopy (SEM) analysis was also performed with VEGA TESCAN operated at 30 kV.

Catalytic Evaluation

The SRM tests with 0.5 g of catalyst loading were done in a quartz fixed bed reactor (inner diameter of 10 mm) as reported in [27]. They were then located in an electrical furnace equipped via thermal programmed capability. Prior to the test, the catalyst was reduced at room temperature to 300 °C, 5 °C/min rate, for 2 h under a constant rate of 10 mL/min and 40 mL/min for hydrogen and argon, respectively. All the tests were carried out at 230-270 °C. For all of the experiments, argon (flow rate= 40 ml/min) was used as carrier gas. The catalytic investigation was performed in GHSV of 18000 h⁻¹ and S/C of 1.3/1 for all the catalysts. The output stream was imported to a cold-trap to separate the unconverted methanol-water mixture from the gas products. Then, the produced gases were injected to a gas chromatograph apparatus equipped with a Hyesep-Q column. During the analysis, only H₂, CO, and CO₂ gases were detected. To calculate methanol conversion and CO and CO₂ selectivity, a carbon balance was calculated, and also some correlations are expressed below:

$$X(\%) = \frac{F_{in,MeOH} - F_{out,MeOH}}{F_{in,MeOH}} \times 100 \quad (1)$$

$$S_{CO}(\%) = \frac{F_{CO}}{F_{CO} + F_{CO_2}} \times 100 \quad (2)$$

$$S_{CO_2}(\%) = \frac{F_{CO_2}}{F_{CO} + F_{CO_2}} \times 100 \quad (3)$$

$$S_{H_2}(\%) = \frac{F_{H_2}(\text{out})}{\Delta F_{H_2O} + \Delta F_{CH_3OH}} \times 100 \quad (4)$$

Where X, F_{in}, and F_{out}, represent the methanol conversion, the inlet methanol concentration and the outlet methanol concentration, respectively. Likewise, terms of S_{CO}, S_{CO₂}, and S_{H₂} indicate the selectivity of CO and CO₂, and H₂, respectively. The defined compositions of each catalyst are illustrated in Table 1.

RESULTS AND DISCUSSION

Cu-Alumina catalysts

Firstly, the Cu-Alumina catalysts (x%CuAl) with various Cu loading (5-40% wt.) were evaluated. As shown in Fig. 1, the methanol conversion

increased with further loading of Cu up to 30% wt., while since then, an obvious falling occurred. It might be attributed to the increase in catalytic active sites until loading of 30% wt., while further Cu loading probably causes a particle agglomeration and an inadequate dispersion. Meanwhile, employing more Cu into the catalyst could reveal less CO in the output because Cu particles drive the WGS equation toward the right side thereby consuming more CO during the reaction. Since the SRM is an endothermic reaction, both methanol conversion and CO selectivity also raised with increase in operating temperature (see Fig. 1). Moreover, the Reverse Water Gas Shift reaction (rWGS) and Decomposition of Methanol (DM) are intensified with increasing the temperature. The 30CA, in between, showed methanol conversion nearly 70% and CO selectivity 0.44% at 270 °C.

As shown in Fig. 2, the XRD patterns including 30 and 40% wt. of Cu loading exhibited approximately amorphous structure with broad peaks of CuO at around positions of 2θ= 38.76, 48.74 and 67.98 (monoclinic, ICPDS: 01-080-1268). It, in turn, represents more capability of the methanol adsorption due to its microcrystal structure. Based on the patterns, increasing Cu content from 30 to 40% resulted in stronger peaks implying more crystallinity in the same direction. Scherrer's equation was used to confirm the growth of crystalline size from 30 to 40% of Cu loading by which the average crystallite size of 15.6 and 25.4 nm were calculated for 30Cu and the 40Cu, respectively.

Furthermore, the SEM image of 30CA is illustrated in Fig. 3. Besides, the BET analysis showed a relatively high surface area of 235 m²/g for 30Cu which was probably due to low-temperature calcination, aging time, appropriate pH, or using Na₂CO₃ as a precipitate agent. Likewise, pore volume and pore size were achieved 0.98 cm³/g and 15.5 nm, respectively.

As shown in Fig. 4, the 30CA catalyst displays a mesoporous structure with diameters of mainly 5-25 nm. According to the adsorption/desorption isotherms, see Fig. 4, they are regarded as type 3 hysteresis loop and classified as H₃ type in the IUPAC categorization. This category exhibits agglomerated structures (containing blade and cubic-like plates), non-homogenous in shape and size.

Table 1: Overview of the synthesized catalysts code definition.

Sample code	Composition	Description	synthesis
(i)CA	(i)% Cu(100-i)% Al	i=5, 10, 20, 30, 40	coprecipitation
(i)P/A	(i)% Pt/100% Al ₂ O ₃	i=0.5, 0.7, 1	impregnation
0.5P30CA	0.5%Pt30%CuO70%Al ₂ O ₃	i=0.5, j=30	doping
0.5P/A+30CA (Dual-bed)	30%CuO70%Al ₂ O ₃ +0.5%Pt/Al ₂ O ₃	i=0.5, j=30	-

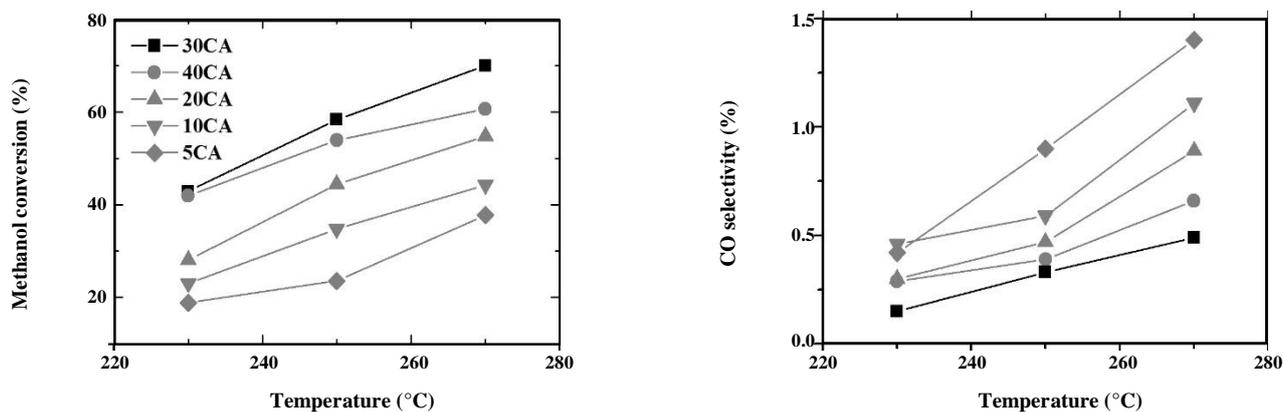


Fig. 1: Optimization of Cu/Al ratio via coprecipitation method in SRM reaction.

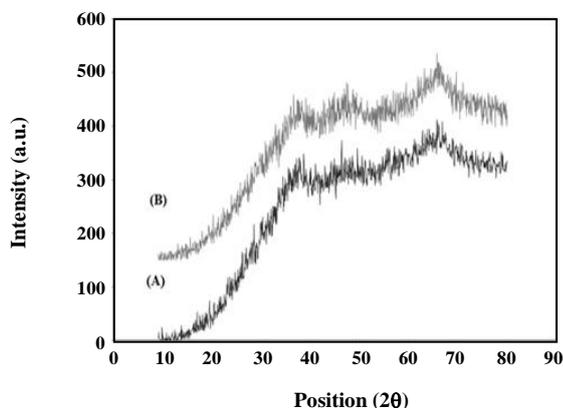


Fig. 2: XRD patterns of synthesized catalysts of a) 30CA b) 40CA.

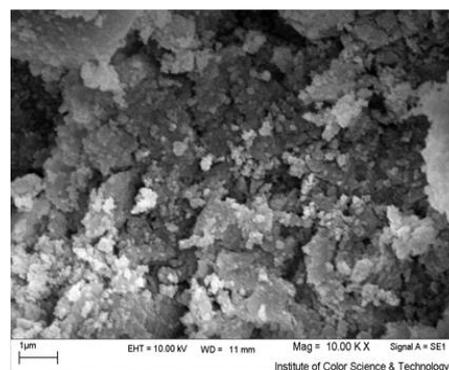


Fig. 3: SEM image of synthesized 30CA catalyst.

Pt-Alumina catalysts

The x%Pt/Al₂O₃ (x containing 0.5, 0.7 and 1% wt.) was evaluated. As can be seen in Fig. 5, the methanol conversion is rather low in comparison with Cu-based catalysts while CO is relatively higher in the output. However, both methanol conversion and CO production were relatively raised by increasing loading of Pt from 0.5 to 1% wt. It reached to the maximum conversion of 28% for 1.0P/A while the CO selectivity

was nearly 52%. The Pt might tend to affect the methanol decomposition reaction rather than the main reaction of SRM [28]. As expected, the CO concentration increased with raising the temperature because water gas shift reaction much prefers lower temperatures. In this way, the catalyst containing 0.5% wt. of Pt resulted in better performance for PEMFC, with the conversion of nearly 20% and CO selectivity about 46% (0.185 volumetric).

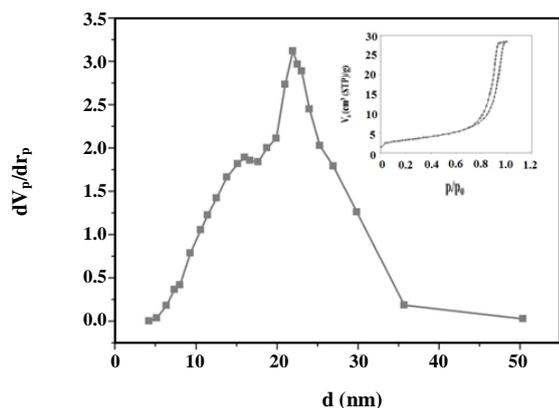


Fig. 4: Pore size distribution size and adsorption/desorption isotherm of 30CA catalyst.

The effect of Pt on Copper-Alumina

As explained, to apply Pt on CuAl two methods of doping and impregnation were chosen. Although the impregnation method is much preferred for noble metals [29, 30] doping of them also shows a good activity for both SRM and OSRM [31]. Doping Pt into 30CA led an enhancement in methanol conversion from approximately 70 to 81% compared to those of impregnated ones. The amount of Pt loading varied from 0.5 to 1.0% wt. for both doping and impregnation. According to the latter, methanol conversion decreased from 22.63 to 18.67% with an increase in Pt loading. This falling might be seemingly due to Pt deposition on the catalyst's active sites. It consequently prevents the reactants to properly interact with CuO species. Thanks to employing doping method, the SRM was significantly enhanced, as shown in Fig. 6.

It was also found that this method resulted in CO selectivity nearly zero. Besides, the doping method resulted in a homogenous dispersion of Pt into 30CA and consequently a close contact with CuO species. On the other hand, the CO formation was relatively stronger for the impregnated Pt onto 30CA in comparison with those of 30CA alone and doped one in which displayed the selectivity of 31.29% for 0.5P/CA at 270 °C. As proposed in some SRM and OSRM studies, the adsorption associated with H atoms and intermediates requires two kinds of sites on CuO/ZnO-based catalysts [32]. Copper species play a vital role in splitting and adsorption of H atoms in order to transform the intermediates. The noble metals like Pt might play a similar role like that of

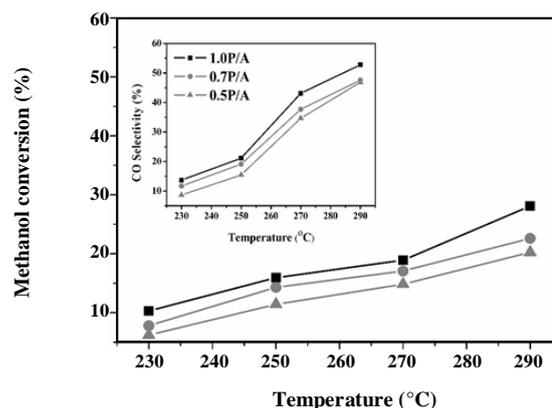


Fig. 5: Effect of Pt loading on Al for Pt/Al₂O₃ catalyst; methanol conversion and CO selectivity.

the copper one [31]. To further investigation, a dual-bed reactor was employed to simultaneously integrate both Pt/Al and 30CA. This reactor consisted of a bed loaded by 30CA catalyst and another bed by 0.5P/A located 1 cm away. As shown in Fig. 6, the methanol conversion increased as the temperature was raised. The methanol conversion reached 83.7%, a better performance for the dual-bed type in comparison with those of other cases. Besides, its CO selectivity was lower than that of the impregnated catalysts although it was a bit higher than that of the doped samples. In this case, the selectivity was 1.5% at 270 °C. Increasing temperature can develop both reactions of steam reforming and methanol decomposition in the first bed due to having endothermic nature. Regarding steam reforming of methanol in the first bed by 30CA, the un-reacted feedstock passing through the first bed is then decomposed in the 0.5P/CA bed. This scheme was proposed by Jacobs et al. [33], who reported that SRM over Pt catalyst indicated a low methanol conversion of 20% at 320 °C. Moreover, the DM process, the formation of hydrogen, and also carbon monoxide from methanol were studied by Brown et al. [25]. It is, therefore, proposed that Pt catalyst much prefer to do the DM reaction compared to the SRM when both methanol and water are the reactants. Details of the performance of the catalysts are listed in Table 2. The hydrogen selectivity for the cases in Table 2 indicate that 30CA with hydrogen selectivity of 77% is more favorable for SRM reaction. In contrary, the other cases might tend to be done in DM reaction rather than SRM.

Table 2: Overview of the catalysts performance.

Sample code	Preparation method	T (°C)	Conversion (%)	S _{CO} (%)	S _{H₂} (%)
30CA	CP	270	70	0.49	77
0.5P/A	IM	270	20	46	69
0.5PCA	Precursor Mixing	270	80	0.06	63
0.5P+CA (Dual-bed)	CP,IM	270	84	1.5	57

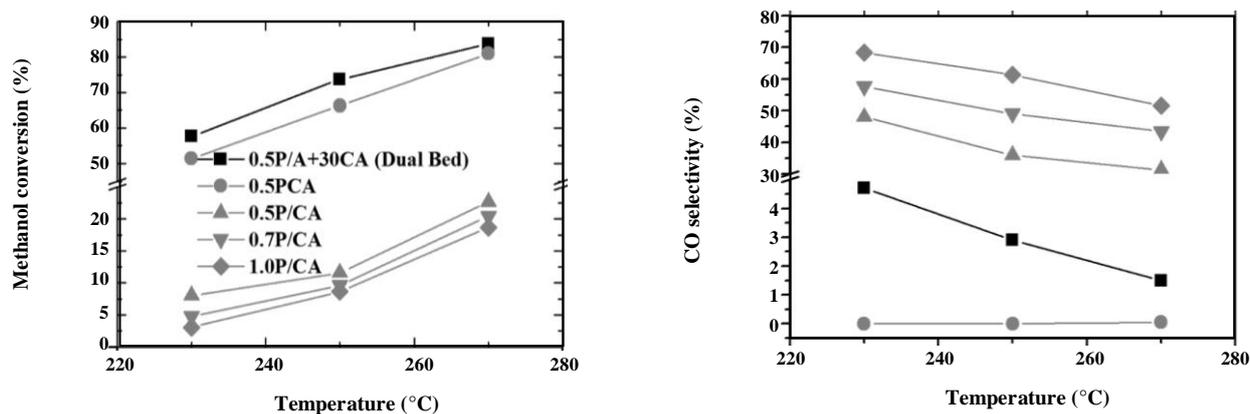


Fig. 6: Effect of Pt loading over 30CA; methanol conversion and CO selectivity.

Operating conditions for 0.5PCA

GHSV effect

Fig. 7 displays the effect of Gas Hourly Space Velocity (GHSV) on the catalytic performance of 0.5PCA. The GHSVs of 9000, 12000, 18000, 27000, and 36000 (h^{-1}) per 0.5 g of catalyst were chosen. The methanol conversion and the CO concentration in the outlet reduced with increasing methanol space velocity. According to the results, this reduction might be attributed to a reduction in contact time of the reactants on the catalytic active sites when passing through the bed. Consequently, it, in turn, results in a decrease in the amount of CO in the output. The methanol conversion varied from approximately full conversion to 74.4% with an increase in the GHSV, from 9000 to 36000 h^{-1} , meanwhile, the CO selectivity decreased from 1.6 to nearly zero.

Catalyst stability

In order to evaluate the catalyst stability during the SRM reaction, the continuous operation was carried out at 270 °C for 0.5PCA during 17 h. As can be seen in Fig. 8, no strong deactivation can be found during the time of operation. The methanol conversion stays almost constant throughout this period. The CO selectivity remains steady roughly less than 0.1% during the time of operation.

CONCLUSIONS

To supply required hydrogen of PEM fuel cells, a series of catalysts were synthesized and evaluated in steam reforming of methanol. Taking Pt promoter into consideration, three different procedures of synthesis were used. Pt species were impregnated onto both Al and CuAl structures in which they both displayed an unsatisfactory performance with maximum methanol conversion of 28% for 1.0P/A while the CO selectivity of nearly 52% did not meet the requirements. However, doping Pt into CuAl catalyst enhanced the methanol conversion as high as 81% at 270 °C and CO selectivity reached to approximately zero. Homogenous distribution of Pt into the catalyst structure was probably the key to reach a satisfactory performance in SRM. Furthermore, adopting a dual-bed reactor including Cu/Al and Pt/Al₂O₃ catalyst indicated a relatively satisfactory performance by which the conversion and selectivity were found 83.7% and 1.5%, respectively. The case of 0.5PCA was undergone different GHSVs in which the conversion and the CO selectivity varied from nearly 100% and 1.6% to 74.4% and nearly zero, respectively, as the GHSV changed from 9000 to 36000 h^{-1} . Moreover this sample

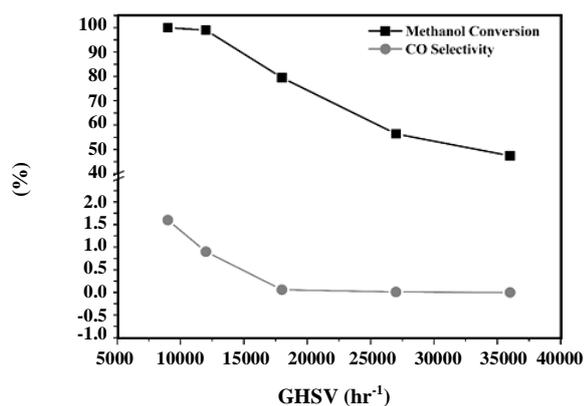


Fig. 7: Effect of GHSV over 0.5PCA catalyst.

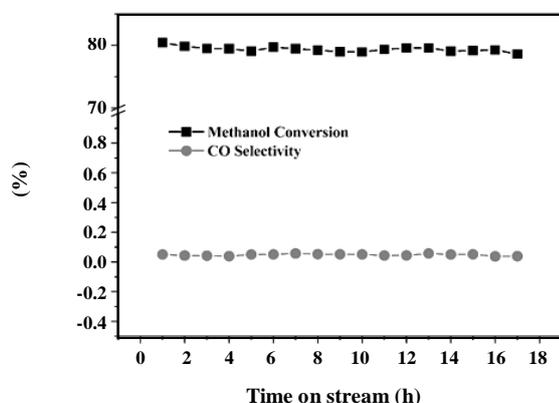


Fig. 8: Time on stream performance of 0.5PCA catalyst.

(0.5PCA) remained active and worked non-stop for 17 h without significant deactivation.

Acknowledgment

This work was financially supported by Iran Renewable Energy Organization (SUNA). The authors gratefully acknowledge the support of this organization.

Received : Aug. 29, 2015 ; Accepted : Nov. 20, 2017

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