Research Article

Enhancing Activity of Pd-Based/rGO Catalysts by Al-Si-Na Addition in Ethanol Electrooxidation in Alkaline Medium

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The article presents modified Pd-based catalysts supported on reduced graphene oxide (rGO), used in the electrooxidation reaction of ethanol in alkaline medium. When NaBH_4 reducing agent was used, the random presence of Na was found out. According to this result, Na was used as a promoter of Pd-based catalyst. Consequently, the Al-Si-Na addition not only assisted active phase Pd nanoparticles to disperse homogenously on graphene support, but also contributed to increase catalytic activity in the reaction. This value, $16138 \text{ mA} \cdot \text{mg}^{-1}_{\text{Pd}}$, is about 1.5 times higher than that of the catalyst modified by Al-Si. Moreover, the stability of the catalyst is enhanced more. The electrochemical stability of PASGN.N catalyst was relatively good: after 500 scanning cycles, the current density diminished 32% compared with the highest peak current density of the 15th cycle, which was chosen as a reference. These significant improvement results in electrooxidation of ethanol have opened up the high potential application of these catalysts in direct-ethanol fuel cell.

1. Introduction

Nowadays, the direct ethanol fuel cell (DEFC) is one of the potential options for use in portable electronic devices, storage, and small electrical appliances. DEFC has high energy efficiency, remarkable efficiency in energy conversion, low temperature in operation, and considerable poison gas emissions. Moreover, producing ethanol from agricultural products and biomass fermentation process on a large scale is widely carried out [1, 2]. However, in DEFC, noble metal-based catalysts, despite their good activity, are highly costly and easily poisoned by the adsorption process of the intermediate compounds formed during electrooxidation of ethanol. In addition, the electrode kinetics are sluggish [3, 4].

In the noble metal group, Pd and Pt had similar structure and electrochemical properties. However, for the electrooxidation of ethanol, Pd showed more advantages in comparison with Pt by the better resistance in alkaline

medium, faster anionic film exchange capacity, and higher possibility of combination with other metals or transition metal oxides.

Some Pd-based catalysts such as Pd-Co [5], Pd-Ni [6–8], Pd-Ni-Sn [9], Pd-Ru-Ni [10], Pd-Cu [11], Pd-Au [12], Pd-Ag [13], or Pt-Pb [14] have been studied to minimize Pd content and poisoning effect in high electrochemical activity of remaining Pd. According to various researches, the presence of transition metals such as Co and Ni, provided $\text{M-ROH}_{\text{ads}}$ or formed M-(ROH)_x species (where M is the metal atom, ROH are methanol or ethanol), which changed the ethanol adsorption ability and enhanced the adsorption process of intermediate CHO_{ads} , CO_{ads} , limiting the poisoning process and thus improving the catalytic activity [5–7, 9, 10].

On the other hand, choosing the support for Pd-based catalyst is an important factor that affects the electrochemical activity of catalyst. Carbon nanotubes (CNTs) and carbon black (Vulcan XC-72) are commonly used as support [15–18]. Recently, graphene materials have been attracting a

high attention because of their advantages of physical and chemical properties such as electrical conductivity and a very high surface area ($\sim 2630 \text{ cm}^2\text{-g}^{-1}$) [19]. And, more especially, graphene enhances the dispersion of active metal particles.

In a recent research of Tan and colleagues [20], it was observed that the combination of Pd and Ni on graphene remarkably augmented catalytic activity of electrooxidation of ethanol in alkaline medium in comparison with PdNi/C and Pd-Ni catalysts. Liu et al. [21] obtained similar results at the same conditions of the catalytic test for catalyst of MnO_2 -promoted Pd supported on graphene oxide (GO) and multiwalled carbon nanotubes. This was explained by the few-layer structure, a high conductivity, and the large accessible area of GO which enhanced the interaction and dispersion of the Pd-active phase on graphene surface. In addition, GO also contains oxygen-functional groups which are the combination site of metal ions, thereby increasing catalytic stability in the electrolyte medium.

In our paper [22], Si-Al was a very good bimetallic promoter phase in modified catalyst based on Pt/rGO in methanol electrooxidation. The results in this paper showed that modified Pt-rGO with 7% Si-Al was the best catalyst which had the highest activity in methanol electrooxidation with more than $1700 \text{ mA}\cdot\text{mg}^{-1}_{\text{Pt}}$ current density. The Al and Si compounds obtained in the catalyst exist as pseudo-boehmite (AlOOH) and silica (SiO_2), and they improve dispersion of the active phase on GO surface.

In this article, the preparation of Pd/rGO-based catalysts modified by promoters such as Al, Si, Al-Si, and Al-Si-Na and reduced by NaBH_4 and ethylene glycol (EG) was reported. These catalysts are intended to be used as an anode catalyst for DEFC. These catalysts modified by promoters exhibited high activity in electrooxidation of ethanol in alkaline medium, and a highly improved resistance against poisoning of intermediary compounds in comparison with non-modified Pd/rGO catalysts.

2. Materials and Methods

2.1. Chemicals. Exfoliated graphite was provided by SGL Carbon GmbH (GFG). Tetraethyl orthosilicate (TEOS) 99%, aluminum tri-isopropoxide 99.9%, CH_3COONa 99%, NaOH 98.8%, H_2SO_4 96%, and ethanol 99.9% were purchased from Merck. And, Nafion® solution (whose mass fraction is 5%), ethylene glycol (EG), sodium borohydride (NaBH_4), isopropanol (IPA) 99.5%, and PdCl_2 99% were purchased from Sigma Aldrich. The nitrogen gas of high purity (99.95% (Air Liquide)) and deionized water were used in all experiments.

2.2. Catalyst Preparation and Characterization. GO slurry synthesized by the modified Hummers' method [23] was diluted to the content of $5 \text{ mg}\cdot\text{mL}^{-1}$. Several catalysts based on graphene-supported palladium modified by metallic promoters were prepared in this study.

Sample of 28.57% Pd by active metal loadings (theoretically calculated, denoted as PG.E) and sample of 26.40% Pd-7.60% Na (PNG.E) made from GO, EG, CH_3COONa ,

and PdCl_2 were synthesized in the similar way of preparation of 40% Pt/rGO following a procedure described in [22].

In this catalyst, theoretical total mass fraction of Al and Si was 4.76% and mass fraction of Pd was 27.21%. The PdAlSiNa/rGO catalyst was reduced by EG as PASG.E catalyst with the addition of CH_3COONa precursor (whose mass fraction of Na is 7.26%) during the synthesis (denoted as PASNG.E).

The PdAl/rGO and PdSi/rGO catalysts reduced by EG (PAG.E and PSG.E) were synthesized in the similar way of preparation of PASG.EG catalysts but in absence of Si or Al precursors during synthesis, respectively. The theoretical elemental composition is 4.76 wt% of Al and 27.21 wt% of Pd in PAG.E catalyst, and 4.76 wt% of Si and 27.21 wt% of Pd in PSG.E catalyst.

All catalysts reduced by NaBH_4 are Pd/rGO, PdNa/rGO, PdAlSi/rGO, and PdAlSiNa/rGO, respectively, were denoted as PG.N, PNG.N, PASG.N, and PASGN.N. The PASGN.N catalyst synthesis process was performed as follows: a precursor mixture of 18.8 mL of PdCl_2 0.01 M and 10 mL of the solution GO $5 \text{ mg}\cdot\text{mL}^{-1}$ was mixed and ultrasonicated for 2 min before adding 8.2 mg Al-isopropoxide, 2 mL IPA, 20 μL TEOS, and 34 mg CH_3COONa . The obtained mixture was sonicated by probe ultrasonic for 2 min. Then, 20 mL of NaBH_4 0.15 M was slowly added into the mixture for 15 min. The reaction mixture was continuously stirred for 15 h before being washed with distilled water. The final product was dried by using a vacuum oven at 80°C for 2 h. The PG.N, PNG.N, and PASG.N catalysts were synthesized by the same method as above with the addition of corresponding precursors.

Transmission electron microscope (TEM) JEOL JEM 2010 and scanning electron microscope (SEM) in a S-4800 microscope (Hitachi, Japan) were used to investigate the morphology and microstructure of catalysts. A LabRam HR (Horiba Jobin Yvon) spectrometer was operated to record Raman spectra. A KRATOS Axis Ultra DLD spectrometer was applied to perform the XPS analyser. The ICP-OES analyses were performed after pretreatment of the samples, in an ICP-OES ACTIVA (Horiba Jobin Yvon). The infrared spectrum of the samples, in the wavelength range of $400\text{--}4000 \text{ cm}^{-1}$, was measured on a Tensor 27-Bruker FTIR spectrometer. XRD patterns of the catalysts were measured on a D8 Advance (Bruker) apparatus. The process of these measurement preparations was clearly presented in [22].

2.3. Electrochemical Measurement. Electrochemical measurements were performed on a PGS-ioc-HH12 Potentiostat/Galvanostat electrochemical workstation (Institute of Chemistry—Vietnam Academy of Science and Technology). All experiments were conducted in a three-electrode system at room temperature: a glassy carbon working electrode (whose diameter is 5 mm), a platinum counterelectrode, and an Ag/AgCl reference electrode. The procedure of preparing catalyst ink was similar to the one described in [22]. The catalyst ink was prepared by dispersing 2 mg of the catalyst powder in a mixture containing 0.9 mL ethanol and 0.1 mL Nafion solution 5 wt % under sonication for 30 min.

Electrochemical active surface area (EASA) measurements were carried out in 0.5 M NaOH aqueous solutions at a scan rate of $50 \text{ mV} \cdot \text{s}^{-1}$, in the potential range of -0.8 V to 0.5 V .

Cyclic voltammetry was carried out in (NaOH 0.5 M + $\text{C}_2\text{H}_5\text{OH}$ 1 M) aqueous solutions at a scan rate of $50 \text{ mV} \cdot \text{s}^{-1}$, in the potential range of -0.8 V to 0.5 V . The chronoamperometric curves for the catalysts were recorded in a (NaOH 0.5 M + $\text{C}_2\text{H}_5\text{OH}$ 1 M) solution at a constant potential value of -0.25 V (vs. Ag/AgCl) for 4000 s.

3. Results and Discussion

Cyclic voltammograms and chronoamperometry curves in a (NaOH 0.5 M + $\text{C}_2\text{H}_5\text{OH}$ 1 M) solution at a room temperature for ethanol electrooxidation on Pd/rGO-based catalysts modified by different metals in ethylene glycol environment were introduced in Figure 1 and Table 1.

From the catalytic activity evaluation results for catalysts reduced by EG during synthesis, Pd-based catalyst that is nonmodified (PG.E) clearly showed a lower electrooxidation activity of ethanol than Pd-based catalyst modified by metal (see Figure 1(a)). Specifically, in alkaline medium, the activity of the catalysts is in ascending order as follows: PG.E ($5369 \text{ mA} \cdot \text{mg}^{-1}_{\text{Pd}}$) < PAG.E ($5374 \text{ mA} \cdot \text{mg}^{-1}_{\text{Pd}}$) $\approx$ PSG.E ($5574 \text{ mA} \cdot \text{mg}^{-1}_{\text{Pd}}$) < PASG.E ($7822 \text{ mA} \cdot \text{mg}^{-1}_{\text{Pd}}$) (see Table 1).

On the other side, the forward scanning peak current density (or called anodic current density)— I_F —means current density of ethanol electrooxidation on the electrode surface. And, the reverse scanning peak current density (or called cathodic current density) means current density in reduction of the oxygen group on the electrode surface. If I_F/I_R ratio and I_F are higher, ethanol electrooxidation on electrode surface will happen more completely [24–27]. Therefore, in alkaline medium, the Pd-based catalysts modified by monometallic such as Al and Si showed only a slight improvement of catalytic activity in comparison with PG.E (see Table 1). Meanwhile, the one modified by bimetallic Al-Si (PASG.E) showed a significant increase in activity, which indicates a positive synergistic effect with Pd of two metals.

Some intermediate species such as CHO_{ads} and CO_{ads} formed during the ethanol electrooxidation poisoned the catalysts, which explained why all catalysts display an initial fast current decay in the chronoamperometry test (see Figure 1(b)). It is noted that the PASG.E catalyst exhibited better activity and resistance against poisoning by intermediate compounds in comparison with other catalysts reduced by EG during synthesis. After 4000 s of working, the current density of the PASG.E catalyst was $104.4 \text{ mA} \cdot \text{mg}^{-1}_{\text{Pd}}$, significantly higher than that of PG.E catalysts ($21.6 \text{ mA} \cdot \text{mg}^{-1}_{\text{Pd}}$), PAG.E ($48.1 \text{ mA} \cdot \text{mg}^{-1}_{\text{Pd}}$), and PSG.E ($34.35 \text{ mA} \cdot \text{mg}^{-1}_{\text{Pd}}$). These remarkable results may be explained by the presence of pseudoboehmite (AlOOH) and silica (SiO_2) that preferentially prevented the adsorption of toxic intermediate and/or formed products on the surface of catalyst, leading to the increase in the number of available catalytic site for reactants.

Thus, the addition of the metal as promoter phase in general, and the bimetallic phase Al-Si in particular, increased the electrochemical activity and also significantly improved resistance against poisoning of intermediate compounds of Pd/rGO catalysts reduced by EG agent.

The content of noble metals and other elements in the catalysts was determined by the ICP-OES characterization and shown in Table 2. It is interesting to note that the mass fraction of Pd found in most catalysts is approximately 10%, compared to the theoretical value of Pd ranging from 25% to 28%. The mass fraction of other metals was measured from 0.2% to 2.7%. The Pd loading of the catalysts reduced by NaBH_4 is higher than that reduced by EG. Especially, the ICP-OES measurement showed the presence of Na in all catalysts reduced by NaBH_4 .

The valence state and surface composition of PASG.N catalyst were determined by X-ray photoelectron spectroscopy (XPS) measurements (see Figure 2). Figure 2(a) presents the XPS spectrum included the characteristic peaks of C 1s, O 1s, Al 2s, Al 2p, Si 2s, and Si 2p. Accordingly, Al and Si existing at the Al and Si compounds obtained in the catalysts exist as pseudoboehmite (AlOOH) and amorphous silica (SiO_2) [22]. In addition, a characteristic peak of Pd 3d is also observed on the spectrum. Especially, the random appearance of Na 1s and Na KLL that corresponds with the ICP results may be an important factor to augment activity of PASG.N catalyst.

Moreover, an intense peak of the C 1s core level was observed in the XPS spectrum of rGO (see Figure 2(c)). After the deconvolution, two major peaks were identified and assigned as $\text{sp}^2 \text{ C}=\text{C}$ at 284.4 eV (due to the graphitic carbon), $\text{sp}^3 \text{ C}-\text{O}$ at 285.8 eV and 289.4 eV (due to the hydroxyl and epoxy groups with graphene framework) [28].

Figure 2(b) shows the Pd 3d core level XPS spectrum of PASG.N catalyst which is resolved into $3d_{5/2}$ and $3d_{3/2}$ doublets caused by spin-orbital coupling [28]. The Pd 3d signals for catalysts can be deconvoluted into two pairs of doublets, which can be attributed to metallic Pd (0) and Pd (II). The deconvolution energies for Pd (0) and Pd (II) were at 335.7 eV and 340.9 eV , and 336.7 eV and 342.6 eV , respectively. Metallic Pd phase was proved to be the major contribution as the intensities of Pd (II) were quite lower than those of Pd (0). It means that reducing from Pd (II) to Pd (0) reaction has happened successfully.

Besides, the relative signal intensities of Pd (0) and Pd (II) of PASG.N catalyst were different, 53.56% and 37.81%, respectively. In addition, the Pd weight density on the catalyst surface was 8.23%, while that of Al, Si, and Na was 2.38%, 3.44%, and 2.19%, respectively, which are similar to ICP results. It means that Pd nanoparticles were dispersed evenly both inside and outside of the catalyst. Moreover, the ratio between Pd (0) and Pd (II) PASG.N in XPS result of PASG.N, approximately 1.41, is higher than that of PASG.E, approximately 1.01. This may be a cause of the different electrochemical activity of these catalysts.

In fact, when the agent NaBH_4 was used instead of EG, the catalyst presented more catalytic activity and resistance against poisoning of intermediate compounds. Specifically, with the bimetallic Al-Si promoter phase, catalyst reduced by

FIGURE 1: CV (a) and CA curves (b) of (A) PG.E, (B) PAG.E, (C) PSG.E, and (D) PASG.E catalysts in a (NaOH 0.5 M + C₂H₅OH 1 M) solution at a scan rate of 50 mV·s⁻¹.

TABLE 1: CV results of Pd/rGO-based catalysts after 15 scanning cycles in a (NaOH 0.5 M + C₂H₅OH 1 M) solution at a scan rate of 50 mV·s⁻¹.

Catalyst	I_F (mA·mg ⁻¹ _{Pd})	I_R (mA·mg ⁻¹ _{Pd})	I_F/I_R
PG.E	5369	3915	1.37
PAG.E	5374	3799	1.41
PSG.E	5574	4010	1.39
PNG.E	6988	5273	1.33
PASG.E	7822	6111	1.28
PASNG.E	8800	4367	2.02
PG.N	7457	3967	1.88
PNG.N	8357	4687	1.78
PASG.N	10705	5531	1.94
PASGN.N	16138	7949	2.03

NaBH₄ (PASG.N) showed 1.4 times higher activity than by EG (PASG.E) (see Table 1). In addition, after 4000 s of working, the current density of the PASG.N catalyst was 6.5

times higher than that of PASG.E. Furthermore, both electrochemical activity and the ratio of the forward scanning peak current density to the reverse scanning peak current density, (I_F/I_R) of the PASG.N catalyst (1.93), were also higher than those of the PASG.E catalyst (1.28). Consequently, NaBH₄ could be a better agent for Pd-based catalyst reduction than EG.

Na presence may cause increasing adsorption of oxygen and fuel on surface of the catalyst [29], which brings out increase of catalytic activity. To evaluate the role of Na, the electrochemical activity of catalysts with and without addition of Na during synthesis for both EG and NaBH₄ reducing agents was investigated (see Figure 3(a) and Table 1). It is obvious that whatever reducing agents were used during synthesis (EG or NaBH₄), all Na-doped catalysts showed significantly higher electrocatalytic activity compared with the non-Na-doped catalysts. Therefore, the role of promoter of Na was completely independent of the effect of the

TABLE 2: ICP-OES results of Pd/rGO-based catalysts reduced by EG and NaBH₄.

Catalysts	Elemental mass fraction by ICP-OES measurement		Theoretical elemental mass fraction	
	Pd (%)	Other metal (%)	Pd (%)	Other metals (%)
PG.E	8.53	—	28.57	—
PNG.E	7.51	2.52 (Na)	26.40	7.61 (Na)
PAG.E	8.03	2.33 (Al)	26.40	7.61 (Al)
PSG.E	7.86	2.54 (Si)	26.40	7.61 (Si)
PASG.E	8.34	0.34 (Al); 2.15 (Si)	27.20	1.36 (Al); 3.42 (Si)
PASGN.E	7.57	2.40 (Na); 0.27 (Al); 2.30 (Si)	25.23	7.25 (Na); 1.26 (Al); 3.15 (Si)
PG.N	9.71	0.15 (Na)	28.57	—
PNG.N	9.21	2.72 (Na)	26.40	7.61 (Na)
PASG.N	8.78	0.34 (Al); 2.41 (Si); 0.12 (Na)	27.20	1.36 (Al); 3.42 (Si)
PASGN.N	8.54	2.62 (Na); 0.29 (Al); 1.83 (Si)	25.23	7.25 (Na); 1.26 (Al); 3.15 (Si)

reducing agent on the electrooxidation of ethanol. Moreover, the results obtained are also consistent with previous conclusions: catalysts modified by the Al-Si system owned a superior activity in comparison with Pd/rGO catalysts and catalysts reduced by NaBH₄, whose activities are much higher than those reduced by EG.

Besides, the poisoning resistance capacity of these catalysts in the electrochemical ethanol oxidation in alkaline mediums estimated by chronoamperometry (CA) (see Figure 3(b)) provided the same results. After 4000 s of working, the PASGN.N catalytic current density reached 680 mA·mg⁻¹_{Pd} ($I_F^{4000} \sim 32.27\%$ compared with the value of CA- I_F^0 at the beginning), 2.36 times higher than non-Na-doped PASG.N catalyst ($I_F^{4000} \sim 17.85\% \cdot I_F^0$), and 6.1 times higher than Na-doped PASNG.E reduced by EG ($I_F^{4000} \sim 15.64\% \cdot I_F^0$). Consequently, Na presence may assist the Pd-base catalysts in enhancing the resistance against poisoning of intermediate compounds in ethanol electrooxidation in alkaline media.

Figure 4 presents Raman spectra of GO and PASG.N catalyst. The peak intensities of the G band (I_G) at ~ 1600 cm⁻¹ corresponding to the sp²-hybrid carbon state in the hexagonal lattice of graphite and the D band (I_D) at 1350 cm⁻¹ being characteristic for the vibration of sp³-hybrid C in the disorder structure of graphene sheets are clearly presented in [22]. The Raman spectra of catalysts were also similar to those of GO, but the intensity of I_D/I_G ratio of catalyst increased in the following order: GO (0.92) < PASG.N (1.02) < PASGN.N (1.10) < PASG.E (1.98). In addition, $I_D > I_G$ due to the presence of defects as well as the presence of Pd cluster, of metal or metal oxides on the graphene support [20, 30, 31]. This confirmed that the catalyst synthesis using chemical reduction process removes effectively the functional groups containing oxygen on the GO surface to form rGO.

FT-IR spectra of catalysts are shown in Figure 5. In the infrared spectra of graphene oxide, there are some

characteristic vibration bands containing oxygen groups such as O-H near 3500 cm⁻¹ and around 1400 cm⁻¹, C=O at 1760 cm⁻¹, and C-O around 1100 cm⁻¹, respectively. However, in that of PASGN.N catalyst, intensity of these peaks was reduced clearly. Moreover, the presence of C=C bond near 1600 cm⁻¹ was found out in the catalyst. Consequently, the reduction from GO to rGO was successful.

TEM images of the catalysts are introduced in Figure 6. The average particles size d_n was calculated from particle size distribution using the following equation [32]:

$$d_n = \frac{\sum n_k d_k}{\sum n_k}, \quad (1)$$

where n_k is the frequency of occurrence of particles with size d_k from the TEM images.

The result showed that a less uniform and sparse dispersion of metallic nanoparticles are described for the catalysts. In addition, the PASG catalysts reduced by both EG and NaBH₄ have a quite homogenous dispersion of active phase (dark spherical particles on rGO surface), but their sizes are different. For example, the PASG.N and PASGN.N catalysts (reduced by NaBH₄) have their activity particle size from 7 nm to 14 nm, while that of PASG.E catalyst (reduced by ethylene glycol) was three times larger, about 20 nm to 36 nm. It means that reducing agent NaBH₄ is improving the size of the catalytic active phase particle. Furthermore, TEM images of the PASGN.N (Na-doped) (see Figure 6(c)) and PASG.N (non-Na-doped) (see Figure 6(b)) catalyst introduced that Na-doped significantly enhanced the dispersion of metallic nanoparticles on graphene support surface. The metal nanoparticles of PASGN.N catalysts expanded with higher density than those of PASG.N catalyst, which explained the increase in the number of active sites on the surface of graphene support, considerably enhancing the catalytic activity of electrooxidation of ethanol. Moreover, the metal

FIGURE 2: XPS spectrum (a), Pd 3d spectrum (b), and C 1s spectrum of the PASG.N catalyst (c).

FIGURE 3: CV (a) and CA (b) curves of (A) PASG.E, (B) PASGN.E, (C) PASG.N, and (D) PASGN.N catalysts in a (NaOH 0.5 M + $\text{C}_2\text{H}_5\text{OH}$ 1 M) solution at a scan rate of $50 \text{ mV} \cdot \text{s}^{-1}$.

FIGURE 4: Raman spectra of (a) GO, (b) PASG.N, (c) PASGN.N, and (d) PASG.E.

FIGURE 5: FTIR spectra of (a) GO and (b) PASGN.N.

FIGURE 6: Continued.

FIGURE 6: TEM images and particle size distributions of PASG.E (a), PASG.N (b), and PASGN.N (c) catalysts with different magnifications.

nanoparticles in the PASGN.N catalyst tend to aggregate from 2 to 3 particles to form larger ones at the edges of graphene sheets.

The EASA (electrochemical active surface area) of the Pd-based electrodes is determined by estimating the charge used in the reduction of palladium (II) oxide into palladium metal and using relation: $EASA = Q/S$, where Q is the Coulombic charge (in mC) and S is the proportionality constant which is taken $0.405 \text{ mC}\cdot\text{cm}^{-2}$ in the case of reduction of a monolayer of PdO [4]. Average particles size d_n and EASA are present in Table 3.

In fact, EASA of catalysts were in descending order as follows: PASG.E ($150.2 \text{ m}^2\cdot\text{g}^{-1}_{\text{Pd}}$) < PASG.N ($193.7 \text{ m}^2\cdot\text{g}^{-1}_{\text{Pd}}$) < PASGN.N ($207.6 \text{ m}^2\cdot\text{g}^{-1}_{\text{Pd}}$). This affection is similar to the TEM image described in Figure 6. The particles size is higher, the activity surface is lower [33].

On the other hand, the Na addition also improved stability of Pb-based catalyst in ethanol electrooxidation. In order to study the catalytic lifetime of PASGN.N and PASG.N catalyst in alkaline medium, 500 cycles of a successive sweep from -0.8 V to 0.5 V were carried out. The corresponding electrochemical activity results were noted in Table 4. The CV curve of the scanning cycles of PASGN.N catalyst was exhibited by the forward scanning peak current density in Figure 7. After the first 15 cycles to activate the catalysts, electrochemical activity of PASGN.N catalyst became stable. Therefore, the highest peak current density of the 15th cycle ($I_F 15^{\text{th}}$) was chosen as a reference. After 200 cycles, the electrochemical activity of the catalysts decreased quite slowly where $I_F 200^{\text{th}}$ was equal to 84% of the reference. The slow reactivity holds up to 500 cycles, where the forward current density value $I_F 500^{\text{th}}$ was equal to 68% of the reference. Similarly, the electrochemical activity of PASG.N also decreased as the number of sweep rounds increased. However, the rate of decreasing catalytic activity of PASG.N is faster than that of PASGN.N (see Table 4), where its 500th current density remained 27%.

Besides, the combination between active phase (Pd nanoparticles) and support, graphene can become more

TABLE 3: EASA result of catalyst.

Catalyst	Average particles size (nm)	EASA ($\text{m}^2\cdot\text{g}^{-1}_{\text{Pd}}$)
PASG.E	28.07	150.2
PASG.N	10.49	193.7
PASGN.N	9.97	207.6

sustainable under the presence of Al-Si-Na addition, which is observed on TEM images of the catalysts after 500 scanning cycles (see Figure 8). For instance, in case of PASGN.N, the metal particles tend to aggregate into clusters of very large size, from 60 nm to 130 nm, which dispersed in separate zones. The density of metallic nanoparticles on the graphene surface is also considerably reduced while that at the edges of graphene sheets tends to increase. However, in case of PASG.N catalyst, almost no metallic particles are presented on the surface of the graphene after 500 scanning cycles. This result is in accordance with the catalytic deactivation after 500 scanning cycles as described previously.

The morphology characteristic of PASGN.N catalyst before and after 500 scanning cycles were observed more clearly on the SEM image (see Figure 9). The result showed that the catalyst looked as a homogeneous “block;” however, it was broken to pieces after the reaction. Moreover, Figure 9(b) also shows the number of particles with columnar shape. It seems that the active phase Pd may be separated from support and may agglomerate after hundreds of cycles. As a result, catalytic activity was reduced.

Figure 10 presented XRD patterns of PASGN.N catalyst before and after 500 cycles of the reaction. The peak at 2θ value of 40.1° corresponding to the planes Pd (111) [34, 35] was shown in the pattern of catalyst before the reaction (see Figure 10(a)) while two peaks of planes PdO (110) and PdO (103) [35] were introduced in the catalyst after the reaction. Consequently, PdO crystal is forming during the reaction. This may be a cause of reduction of the catalytic activity.

TABLE 4: Forward current density of PASGN.N and PASG.N catalysts after 500 scanning cycles in a (NaOH 0.5 M + C₂H₅OH 1 M) solution at a scan rate of 50 mV·s⁻¹.

Catalyst	Forward current density I_F (mA·mg ⁻¹ _{Pd})						
	I_F 15 th	I_F 100 th	I_F 100 th / I_F 15 th	I_F 200 th	I_F 300 th	I_F 400 th	I_F 500 th
PASGN.N	16138	14175	0.88	13816	12751	12342	10864
PASG.N	10705	9100	0.85	8565	6884	4956	2884

FIGURE 7: CV curves of catalytic PASGN.N after 500 scanning cycles in a (NaOH 0.5 M + C₂H₅OH 1 M) solution at a scan rate of 50 mV·s⁻¹.

FIGURE 8: TEM images of PASGN.N and PASG.N catalysts before (a, b) and after 500 scanning cycles (c, d) in a (NaOH 0.5 M + C₂H₅OH 1 M) solution at a scan rate of 50 mV·s⁻¹.

4. Conclusion

In conclusion, electrooxidation of ethanol was carried out on several Pd-based bimetallic or multimetallic catalysts

supported on graphene. For all catalysts investigated, the role of promoting agents was confirmed when catalytic activity was enhanced in the presence of Al, Si, Al-Si, and Al-Si-Na. In addition, in comparison with the reducing

FIGURE 9: SEM images of PASGN.N catalysts before (a) and after (b) 500 scanning cycles in a (NaOH 0.5 M + C₂H₅OH 1 M) solution at a scan rate of 50 mV·s⁻¹.

FIGURE 10: XRD patterns of PASGN.N catalysts before (a) and after (b) 500 scanning cycles in a (NaOH 0.5 M + C₂H₅OH 1 M) solution at a scan rate of 50 mV·s⁻¹.

agent EG during synthesis, NaBH₄ significantly not only improved the dispersion of metal nanoparticles on the support surface but also reduced crystalline size. As a result, catalytic electrochemical activity was increased. Specifically, PASGN.N catalysts presented the superior activity in electrooxidation of ethanol in the alkaline medium when the current density was more than 16000 mA·mg⁻¹_{Pd}, which is the best results reported in this study. This value is higher than activity of Pd-based catalyst with different promoter [20, 36] or activity of Pt-base catalyst [37] with the same promoter. Another result in this particle is that the electrochemical stability of PASGN.N catalyst was relatively good: after 500 scanning cycles, the current density diminished 32% compared with the highest peak current density of the 15th cycle. In conclusion, the obtained results have opened a new studying direction about synergistic effects of Al-Si-Na addition which both enhances activity and improves stability of Pd-based catalysts in ethanol electrooxidation in alkaline medium. In the same way, the content of noble metal is also reduced.

Symbols

d_k :	Particle size
d_n :	Average particle size

EASA:	Electrochemical active surface area
FT-IR:	Fourier transform infrared
ICP-OES:	Inductively coupled plasma-optical emission spectrometry
I_D :	Peak intensity of the D band in Raman spectra/cm ⁻¹
I_F :	Forward scanning peak current density in cyclic voltammetry curves/mA·mg ⁻¹ _{Pd}
I_F 15 th :	Highest peak current density of the 15 th cycle in cyclic voltammetry curves/mA·mg ⁻¹ _{Pd}
I_F 200 th :	Peak current density of the 200 th cycle in cyclic voltammetry curves/mA·mg ⁻¹ _{Pd}
I_F 500 th :	Peak current density of the 500 th cycle in cyclic voltammetry curves/mA·mg ⁻¹ _{Pd}
I_F^0 :	Catalytic current density at the beginning in chronoamperometry curves/mA·mg ⁻¹ _{Pd}
I_F^{4000s} :	Catalytic current density in chronoamperometry curves/mA·mg ⁻¹ _{Pd}
I_G :	Peak intensity of the G band in Raman spectra/cm ⁻¹
I_R :	Reverse scanning peak current density in cyclic voltammetry curves/mA·mg ⁻¹ _{Pd}
n_k :	Frequency of occurrence of particles
Q :	Coulombic charge used in the reduction of palladium (II) oxide into palladium metal/mC
S :	Proportionality constant in the case of reduction of a monolayer of PdO/mC·cm ⁻²
SEM:	Scanning electron microscope
TEM:	Transmission electron microscope
XPS:	X-ray photoelectron spectroscopy
XRD:	X-ray diffraction.

Data Availability

The data used in the study are available from the corresponding authors upon request.

Additional Points

Highlights. Nanocatalysts based on Pd/rGO were synthesized for the electro-oxidation of ethanol in alkaline medium. The random presence of Na was found out when reduced agent NaBH₄ was used instead of EG. Al-Si-Na addition enhances the

activity of Pd-base catalyst and improves its electrochemical stability after 500 scanning cycles. Al-Si-Na addition improves dispersion and combination of the active phase Pd on reduced graphene oxide surface. NaBH_4 -reducing PdAlSiNa/rGO has the highest electrocatalytic activity, $16138 \text{ mA} \cdot \text{mg}_{\text{Pd}}^{-1}$.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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References

- [1] Y. Li, W. Gao, L. Ci, C. Wang, and P. M. Ajayan, "Catalytic performance of Pt nanoparticles on reduced graphene oxide for methanol electro-oxidation," *Carbon*, vol. 48, no. 4, pp. 1124–1130, 2010.
- [2] Q.-L. Zhang, J.-N. Zheng, T.-Q. Xu et al., "Simple one-pot preparation of Pd-on-Cu nanocrystals supported on reduced graphene oxide for enhanced ethanol electrooxidation," *Electrochimica Acta*, vol. 132, pp. 551–560, 2014.
- [3] L. Dong, R. R. S. Gari, Z. Li, M. M. Craig, and S. Hou, "Graphene-supported platinum and platinum-ruthenium nanoparticles with high electrocatalytic activity for methanol and ethanol oxidation," *Carbon*, vol. 48, no. 3, pp. 781–787, 2010.
- [4] R. Awasthi and R. N. Singh, "Graphene-supported Pd-Ru nanoparticles with superior methanol electrooxidation activity," *Carbon*, vol. 51, pp. 282–289, 2010.
- [5] Y. Wang, Y. Zhao, J. Yin, M. Liu, Q. Dong, and Y. Su, "Synthesis and electrocatalytic alcohol oxidation performance of Pd-Co bimetallic nanoparticles supported on graphene," *International Journal of Hydrogen Energy*, vol. 39, no. 3, pp. 1325–1335, 2014.
- [6] R. S. Amin, R. M. A. Hameed, and K. M. El-Khatib, "Microwave heated synthesis of carbon supported Pd, Ni and Pd-Ni nanoparticles for methanol oxidation in KOH solution," *Applied Catalysis B: Environmental*, vol. 148–149, pp. 557–567, 2014.
- [7] R. S. Amin, R. M. Abdel Hameed, K. M. El-Khatib, and M. Elsayed Youssef, "Electrocatalytic activity of nanostructured Ni and Pd-Ni on Vulcan XC-72R carbon black for methanol oxidation in alkaline medium," *International Journal of Hydrogen Energy*, vol. 39, no. 5, pp. 2026–2041, 2014.
- [8] C. A. L. Ricoa, J. G. Rosa, E. O. Ortega et al., "High performance of ethanol co-laminar flow fuel cells based on acrylic, paper and Pd-NiO as anodic catalyst," *Electrochimica Acta*, vol. 207, pp. 164–176, 2016.
- [9] S. Jongsomjit, P. Prapainainar, and K. Sombatmankhong, "Synthesis and characterisation of Pd-Ni-Sn electrocatalyst for use in direct ethanol fuel cells," *Solid State Ionics*, vol. 288, pp. 147–153, 2016.
- [10] K. Charoen, C. Warakulwit, C. Prapainainar, A. Seubsai, M. Chareonpanich, and P. Prapainainar, "Optimization of metal atomic ratio of Pd x Ru y Ni z on carbon support for ethanol oxidation," *Applied Surface Science*, vol. 421, pp. 2–17, 2017.
- [11] Q. Dong, Y. Zhao, X. Han, Y. Wang, M. Liu, and Y. Li, "Pd/Cu bimetallic nanoparticles supported on graphene nanosheets: facile synthesis and application as novel electrocatalyst for ethanol oxidation in alkaline media," *International Journal of Hydrogen Energy*, vol. 39, no. 27, pp. 14669–14679, 2014.
- [12] Z.-Z. Yang, L. Liu, A.-J. Wang et al., "Simple wet-chemical strategy for large-scaled synthesis of snowflake-like PdAu alloy nanostructures as effective electrocatalysts of ethanol and ethylene glycol oxidation," *International Journal of Hydrogen Energy*, vol. 42, no. 4, pp. 2034–2044, 2016.
- [13] Y.-G. Jo, S.-M. Kim, J.-W. Kim, and S.-Y. Lee, "Composition-tuned porous Pd-Ag bimetallic dendrites for the enhancement of ethanol oxidation reactions," *Journal of Alloys and Compounds*, vol. 688, pp. 447–453, 2016.
- [14] R. Jana, U. Subbarao, and S. C. Peter, "Ultrafast synthesis of flower-like ordered Pd3Pb nanocrystals with superior electrocatalytic activities towards oxidation of formic acid and ethanol," *Journal of Power Sources*, vol. 301, pp. 160–169, 2016.
- [15] F. Zhang, D. Zhou, and M. Zhou, "Ethanol electrooxidation on Pd/C nanoparticles in alkaline media," *Journal of Energy Chemistry*, vol. 25, no. 1, pp. 71–76, 2016.
- [16] C. Hu and X. Wang, "Highly dispersed palladium nanoparticles on commercial carbon black with significantly high electro-catalytic activity for methanol and ethanol oxidation," *International Journal of Hydrogen Energy*, vol. 40, no. 36, pp. 12382–12391, 2015.
- [17] G. Yang, Y. Zhou, H.-B. Pan et al., "Ultrasonic-assisted synthesis of Pd-Pt/carbon nanotubes nanocomposites for enhanced electro-oxidation of ethanol and methanol in alkaline medium," *Ultrasonics Sonochemistry*, vol. 28, pp. 192–198, 2016.
- [18] W. Chen, Y. Zhang, and X. Wei, "Catalytic performances of PdNi/MWCNT for electrooxidations of methanol and ethanol in alkaline media," *International Journal of Hydrogen Energy*, vol. 40, no. 2, pp. 1154–1162, 2015.
- [19] M. D. Stoller, S. Park, Y. Zhu, J. An, and R. S. Ruoff, "Graphene-based ultracapacitors," *Nano Letters*, vol. 8, no. 10, pp. 3498–3502, 2008.
- [20] J. L. Tan, A. M. De Jesus, S. L. Chua et al., "Preparation and characterization of palladium-nickel on graphene oxide support as anode catalyst for alkaline direct ethanol fuel cell," *Applied Catalysis A: General*, vol. 531, pp. 29–35, 2017.
- [21] Q. Liu, K. Jiang, J. Fan et al., "Manganese dioxide coated graphene nanoribbons supported palladium nanoparticles as an efficient catalyst for ethanol electrooxidation in alkaline media," *Electrochimica Acta*, vol. 203, pp. 91–98, 2016.
- [22] T. H. T. Vu, T. T. T. Tran, H. N. T. Le et al., "Pt-AlOOH-SiO₂/graphene hybrid nanomaterial with very high electrocatalytic performance for methanol oxidation," *Journal of Power Sources*, vol. 276, pp. 340–346, 2015.
- [23] W. S. Hummers and R. E. Offeman, "Preparation of graphitic oxide," *Journal of the American Chemical Society*, vol. 80, no. 6, 1339 pages, 1958.
- [24] H. Mao, T. Huang, and A. Yu, "Surface noble metal modified PdM/C (M = Ru, Pt, Au) as anode catalysts for direct ethanol fuel cells," *Journal of Alloys and Compounds*, vol. 676, pp. 390–396, 2016.
- [25] A. M. Hofstead-Duffy, D.-J. Chen, S.-G. Sun, and Y. J. Tong, "Origin of the current peak of negative scan in the cyclic

- voltammetry of methanol electro-oxidation on Pt-based electrocatalysts: a revisit to the current ratio criterion,” *Journal of Materials Chemistry*, vol. 22, no. 11, pp. 5205–5208, 2012.
- [26] D. Y. Chung, K.-J. Lee, and Y.-E. Sung, “Methanol electro-oxidation on the Pt surface: revisiting the cyclic voltammetry interpretation,” *Journal of Physical Chemistry C*, vol. 120, no. 17, pp. 9028–9035, 2016.
- [27] Y. Zhao, X. Li, J. M. Schechter, and Y. Yang, “Revisiting the oxidation peak in the cathodic scan of the cyclic voltammogram of alcohol oxidation on noble metal electrodes,” *RSC Advances*, vol. 6, no. 7, pp. 5384–5390, 2016.
- [28] R. Krishna, D. M. Fernandes, A. Marinho, J. Ventura, C. Freire, and E. Titus, “Facile synthesis of well dispersed Pd nanoparticles on reduced graphene oxide for electrocatalytic oxidation of formic acid,” *International Journal of Hydrogen Energy*, vol. 42, no. 37, pp. 23639–23646, 2017.
- [29] N. Seriani, “Sodium promoter inducing a phase change in a palladium catalyst,” *Journal of Physical Chemistry C*, vol. 116, no. 43, pp. 22974–22979, 2012.
- [30] S. Yang, J. Dong, Z. Yao et al., “One-Pot synthesis of graphene-supported monodisperse Pd nanoparticles as catalyst for formic acid electro-oxidation,” *Scientific Reports*, vol. 4, no. 1, article 4501, 2014.
- [31] A. H. Al-Marri, M. Khan, M. R. Shaik et al., “Green synthesis of Pd@graphene nanocomposite: catalyst for the selective oxidation of alcohols,” *Arabian Journal of Chemistry*, vol. 9, no. 6, pp. 835–845, 2016.
- [32] Y. Fan, Y. Zhao, D. Chen, X. Wang, X. Peng, and J. Tian, “Synthesis of Pd nanoparticles supported on PDDA functionalized graphene for ethanol electro-oxidation,” *International Journal of Hydrogen Energy*, vol. 40, no. 1, pp. 322–329, 2015.
- [33] J. Perez, V. A. Paganin, and E. Antolini, “Particle size effect for ethanol electro-oxidation on Pt/C catalysts in half-cell and in a single direct ethanol fuel cell,” *Journal of Electroanalytical Chemistry*, vol. 654, no. 1-2, pp. 108–115, 2011.
- [34] L. Wang, J.-J. Zhai, K. Jiang, J.-Q. Wang, and W.-B. Cai, “Pd–Cu/C electrocatalysts synthesized by one-pot polyol reduction toward formic acid oxidation: structural characterization and electrocatalytic performance,” *International Journal of Hydrogen Energy*, vol. 40, no. 4, pp. 1726–1734, 2015.
- [35] J. Lin, T. Mei, M. Lv, C. Zhang, Z. Zhao, and X. Wang, “Size-controlled PdO/graphene oxides and their reduction products with high catalytic activity,” *RSC Advances*, vol. 4, no. 56, pp. 29563–29570, 2014.
- [36] J. Ma, J. Wang, G. Zhang et al., “Deoxyribonucleic acid-directed growth of well dispersed nickel-palladium-platinum nanoclusters on graphene as an efficient catalyst for ethanol electrooxidation,” *Journal of Power Sources*, vol. 278, pp. 43–49, 2015.
- [37] L. T. Tran, Q. M. Nguyen, M. D. Nguyen, H. N. T. Le, T. T. Nguyen, and T. H. T. Vu, “Preparation and electrocatalytic characteristics of the Pt-based anode catalysts for ethanol oxidation in acid and alkaline media,” *International Journal of Hydrogen Energy*, vol. 43, no. 45, pp. 20563–20572, 2018.