CHAPTER 3

RESULTS AND DISCUSSIONS

This results fromplatinum-based ternary catalysts were divided into three groups which were PtCoCr, PtCoM (M=Cu,Cr,Fe and Ni) and PtCuNi groups.

The first group provided theresults ofPtCoCr as a catalysts supported on treated and untreated carbon(Vulcan XC-72)by microwave and $NaBH_4$ reductionmethods. The catalysts were selected by the overview study which thatplatinum-basedternary catalystin the form of PtCoCr/C was the highest performance among ternary catalysts[31,46,70,71]. This research focused on the catalysts formation between two methods, particle size, size distribution and particle dispersion on treated and untreated carbon supporters.

In the second group,PtCoMtype (M=Cu,Cr,Fe and Ni) was synthesized as a catalyst supported on treated carbon N115 by reflux method. This group of catalyst used the PtCo catalyst as a base catalyst because the overview binary catalysts found that the PtCo was the highest performance[37,72,73]. The PtCo catalyst was added one metal to formternary catalysts. The metals were added in this catalyst such as copper, chromium, iron and nickel.

For the final group, PtCuNitype was synthesized as a catalyst supported on treated carbons by microwave, reflux, and $NaBH_4$ reductionmethod. The research focused on this catalyst because the standard reduction potentials of platinum and copper were positive (E°_{Pt}=1.18, E°_{Cu}=0.37). However, standard reduction potentials of nickel was - 0.257, so it was difficult to be reduced to metal. In order to prove that nickel ion could be reduced to nickel metal, the experiment was performed by

dissolving nickel nitrate in ethylene glycol. The $NaBH_4$ was added for a reduction process and the reaction was allowed to stir overnight. The final product was filtered, washed with methanol and dried in oven for overnight. The product was annealed at 600 ˚C for 4hours under N_2 gas. The XRD patterns showed in Figure 3.1indicate that no signal of nickel phase was observed from the pristine sample. However, the signal of nickel was found from the annealedsample at 2θ = 44.52, 51.92 and 76.40 with corresponding to (111), (200) and (220) plane of Ni (JCPDS No. 00-004-0850). The results confirmthat nickel ion was able to be reduced to nickel metalby $NaBH_4$. The absence of nickel signal primitive sample might be because of amorphous nickel phase containing in the sample[74-75]. Fromthe evidence, PtCuNi catalystwas feasibly synthesizedinthis study.

The results were explained in two parts. In the first part, the result of treated carbon was explained. Whereas, the results of catalysts on supported carbon prepared by technique was explained in the second part.

3.1 Treated and untreated carbons analyses

The functional groupmodificationon carbon surface was applied to two types of carbon which were carbon Vulcan XC-72 and carbon N115. The physical properties of both carbons were shown in Table 3.1 and shapes of both carbons were shown in Figure 3.2 by TEM technique. The shape and particle size of both carbons were similar. The particle size from carbonVulcan XC-72 and carbon N115 were 32.85±5.54 and 32.99±7.94 nm, respectively. The particle size histograms from carbon were shown in Figure 3.3.For other reason, carbon N115 was made in Thailand (Thai Carbon Black Public Co. LTD).

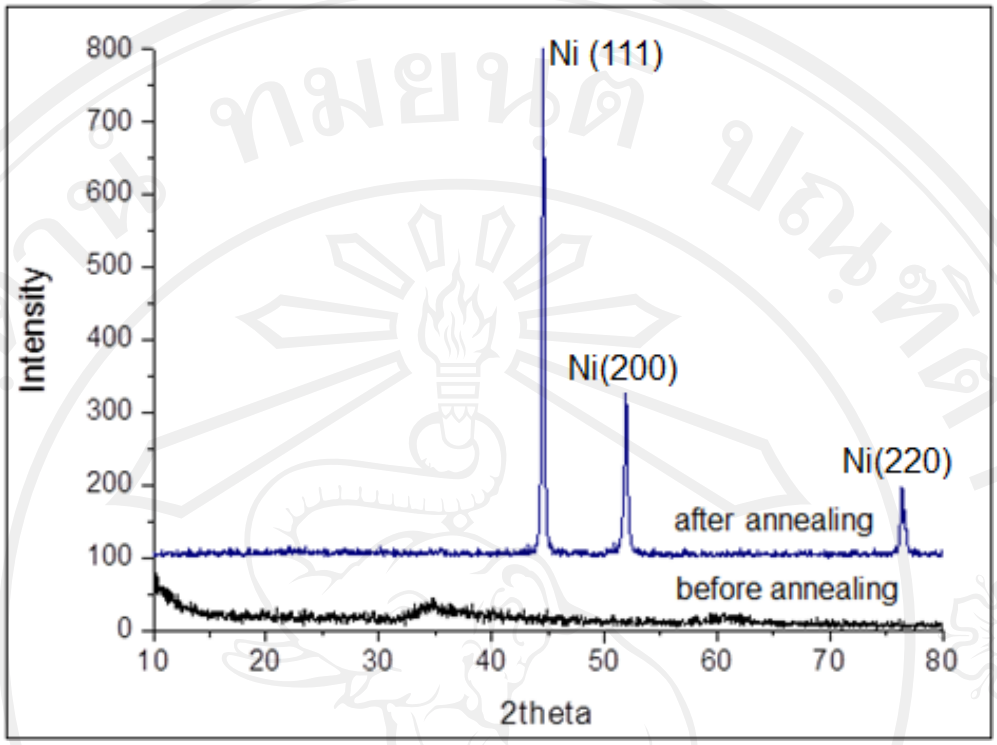


Figure 3.1 Powder XRD patterns of nickel prepared by $NaBH_4$ reduction method for before (below) and after (upper) annealing samples.

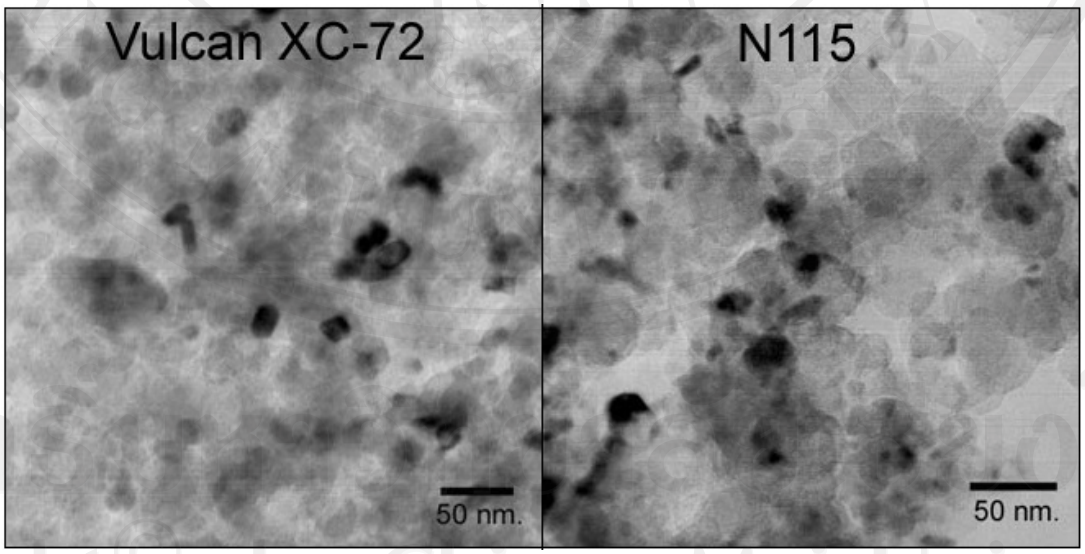


Figure 3.2 TEM images of carbon Vulcan XC-72 and carbon N115

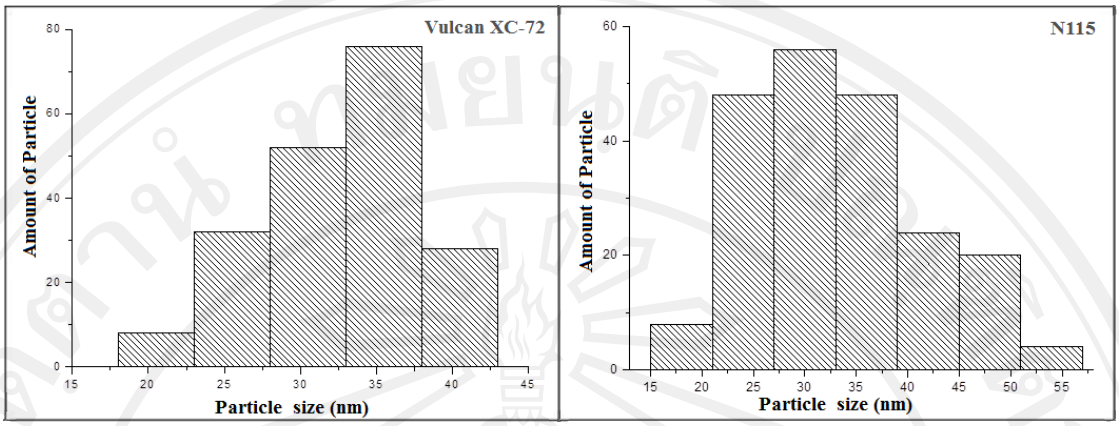


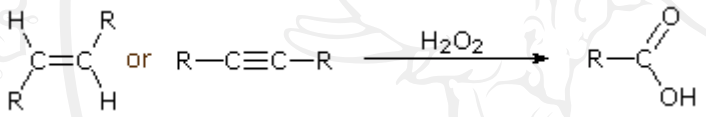
Figure 3.3Particle sizehistograms of carbon Vulcan XC-72 and carbon N115

Table 3.1 Thephysical propertiesof carbon Vulcan XC-72 and carbon N115

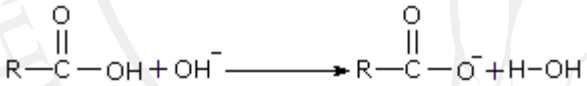
Carbon	Vulcan XC-72	N115
Specific surface area (m^2/g)	254[76]	146.4[77]
Conductivity (s/cm)	4.0[76]	$7.99x10^{-7}$[78]
Particle size (nm)	32.85±5.54	32.99±7.94
DBP ($cm^3/100$ g)	175[79]	94.0[77]
Pour density (kg/m^3)	264[80]	345[81]
Porous area (m^2/g)	76[80]	137[81]

In comparison, both treated and untreated carbons were characterized by FTIR technique as shown in Figure3.4. It can be seen that the untreated carbon's bands at 2357, 2015 and 1591cm^{-1}were corresponded to the vibration of –C≡C–, –C=C=C– and –C=C–, respectively. Whereas, the carbon treated by hydrogen peroxidewere detected the bandsat 2362, 2038 and 1647$cm^{-1}$and were corresponded to the vibration of –C≡ C–, –C=C=C– and –C=C–, respectively, which were similar to the untreated carbon. However, a small band at 1693cm^{-1} and 1518 cm^{-1}were additionally detected

which was identified as –C=O of carboxylic group and (–C(=O)–O–), respectively. The appearance of this functional group was due to hydrogen peroxide which acted as a strong oxidizing agent[82]andcan oxidize the carbon–carbon bond on carbon surface to carboxylic group[83,84]. The mechanism for this reaction was shown in Eq 3.1Thecarboxylic group, witha negatively charged functional group in solution is shown in Eq 3.2.This functional group can improve the formation of Pt-based ternary catalysts on carbon due to electrostatic interaction between metal ion, which is a positive charge, and carboxylic group (negative charge).



(3.1)[84]



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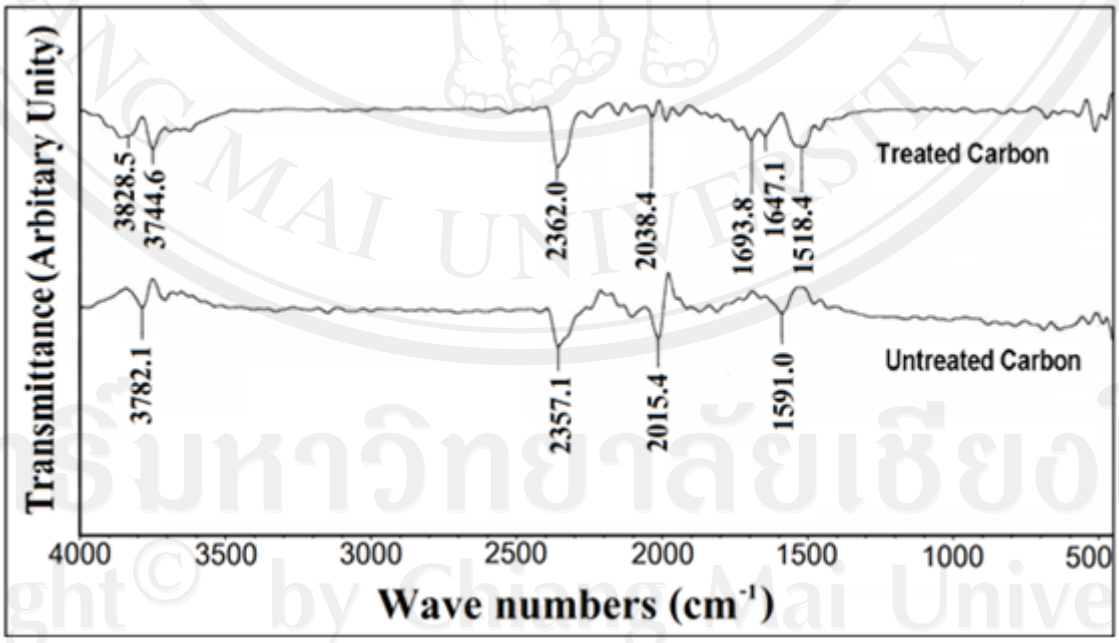

Figure 3.4 FTIR spectrums from treated carbon and untreated carbon

3.2 The Characterization

The catalysts were firstly characterized the physical propertiesby XRD, SEM, EDS, TEM and XAStechnique. Second, the electrochemical properties were investigated by CV and single cell testing. XRD technique was used to identify the sample phases. SEM technique was used toobserve metals dispersion on carbon supporter. Elemental composition and quantity was analyzed by EDStechnique. While particle size and size distributions of metalswere observed byTEM technique. The XAS technique was used to indicate the oxidation number and local structure of metals. CV technique was included in this studyin order to test the electro-catalytic activity of prepared sample. Moreover, single cell testing provides plot of polarization curvewhich was performed to investigate cell performance.

3.2.1 Powder X-ray diffraction (XRD)

All catalysts were characterized by XRDtechnique. InFigure 3.5 – 3.8, broad peak at $2\theta \approx 25.34^{o}$was observed corresponded to (002) plane of carbon (JCPDS No. 00-041-1487). For the catalysts in the first group, metal phasescontaining in catalysts from microwave and $NaBH_4$ reduction method were compared (Figure 3.5). For the catalysts from microwave method, only platinum peak at $2\theta = 39.80$ was found which corresponded to (111) plane of platinum (JCPDS No. 00-004-0802). While other diffracted planes of platinum was not obviously observedbecause there was a small amount of platinum containing in the sample (it was which confirmed by EDS). The absence of other diffracted planes of platinum was assured by the intensities on plane (200) and (220) as 53 and 31 which was lower than baseline. The metals such as cobalt, chromium or metal oxide were also not clearly observed as they appeared in

the area of platinum broad peak or their small amount in samples. The catalysts from $NaBH_4$ reductionmethod were unclearly observed in those XRD patterns. Peak broadening was possibly influenced small particle size where the unclear metals peaks might be because of small particles size effect and small amount of metals. Therefore, the SAD and XAS were then applied to identify the occurrence of these metals.

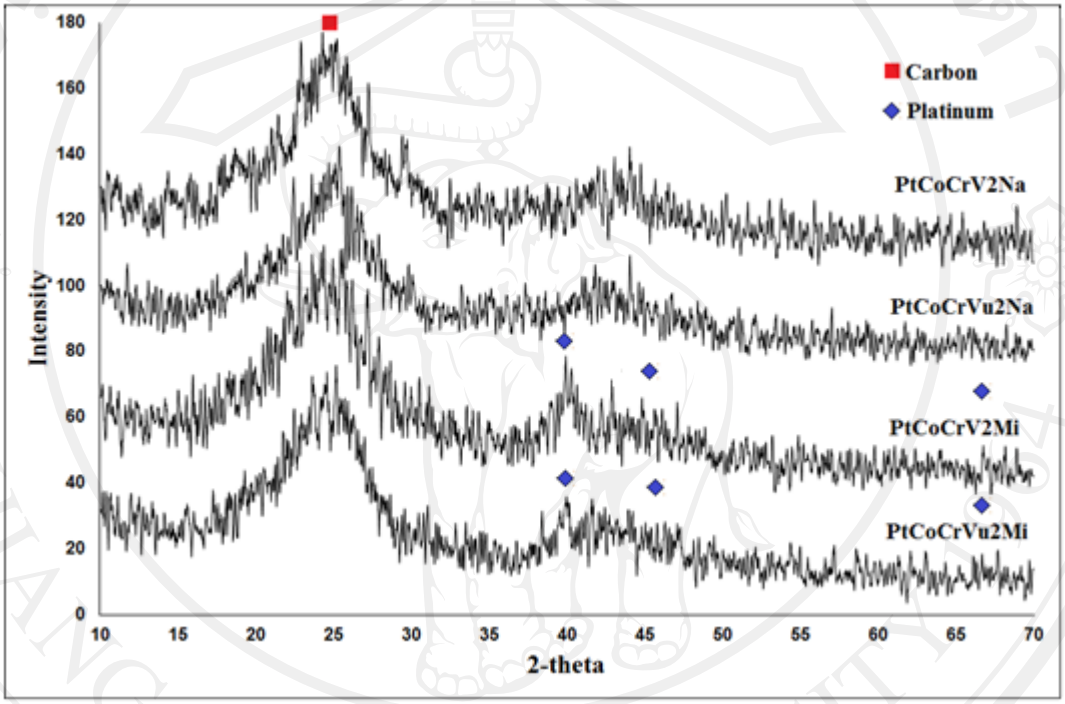

Figure 3.5Powder XRD patterns of platinum-cobalt-chromium catalysts supported on treated or untreated carbon by microwave and $NaBH_4$ reductionmethods

The XRD patterns of second group catalysts shown in Figure 3.6.In this group, other transition metals (Cu,Cr,Ni, and Fe) was changed when the binary catalyst was fixed as PtCo alloy. The result for this group was separated into two parts. First part was PtCoCu catalyst and second part was other catalysts. The PtCoCu catalyst in the first part showedthe diffracted peak at 2θ = 40.93, 47.23 and 69.37 which corresponded to (111), (200) and (220) planes of PtCoCu alloy (Simulated unit cell by

CaRIne V3.1 from Patent No. 5,178,971 was shown in Figure 3.9). For other catalysts in the second part, (PtCoNi, PtCoFe and PtCoCr) showedthe peaks at 2θ = 39.63, 46.29 and 67.25 which corresponded to (111), (200) and (220) planes of platinum. However, the other metal (Co,Cr,Ni, and Fe) or metal oxides were unclearly observed because of the smallest particle size or lowest amount of metals support on carbon.Therefore, the electron diffraction was further used to identify them.

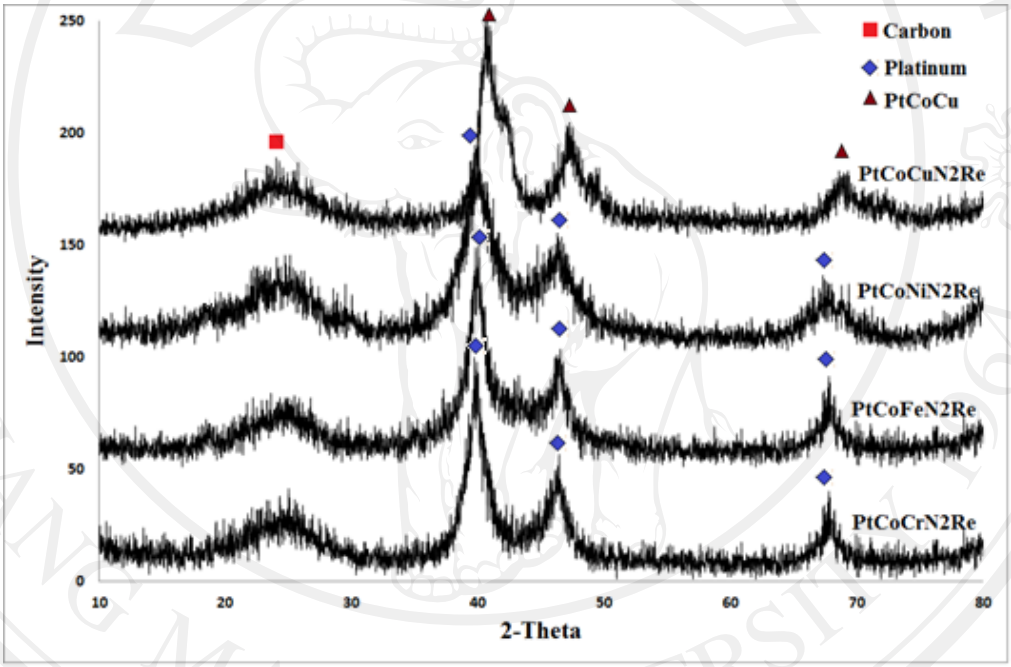

Figure 3.6Powder XRD patterns of platinum-cobalt-metal catalysts supported on treated carbon by reflux method.

The XRD patterns of third group catalyst were shown in Figure 3.7-3.8.The catalysts in this group were prepared by three methods (microwave, reflux, and $NaBH_4$ reductionmethod) on two types of carbon (VulcanXC-72 and N115) with two weight ratio (2:1:1 and 6:1:1). The catalysts supported on carbon N115 with the ratio 2:1:1 and ratio 6:1:1 were shown in Figure 3.7. In contrast, the catalysts supported on

carbon Vulcan XC-72 with the ratio of 2:1:1 and 6:1:1 were shown in Figure 3.8. The resultsof all catalysts in this group were separated into two parts. First part, the catalysts were prepared by microwave method and in the next part, the catalysts were prepared by reflux and $NaBH_4$ reductionmethods. Catalysts which synthesized by microwave at ratio of 2:1:1 and 6:1:1 showed peak at 2θ = 39.80, 46.16 and 67.44 with corresponding to (111), (200) and (220) plane of platinum. The XRD patterns form this part showed only platinum peak while the other metals (Cu and Ni) or metal oxide were unclearly observed because of the small amount of metals supported on carbon. Next part, catalysts showed board peaks at 2θ = 41.12, 47.85 and 69.99 with corresponded to (111), (200) and (220) plane of PtCuNi alloy (Simulated unit cell by CaRIne V3.1 from Patent No.5,178,971 was shown in Figure 3.10). The XRD patterns for all samples showed board peaks for metal alloy because small particle size effect.

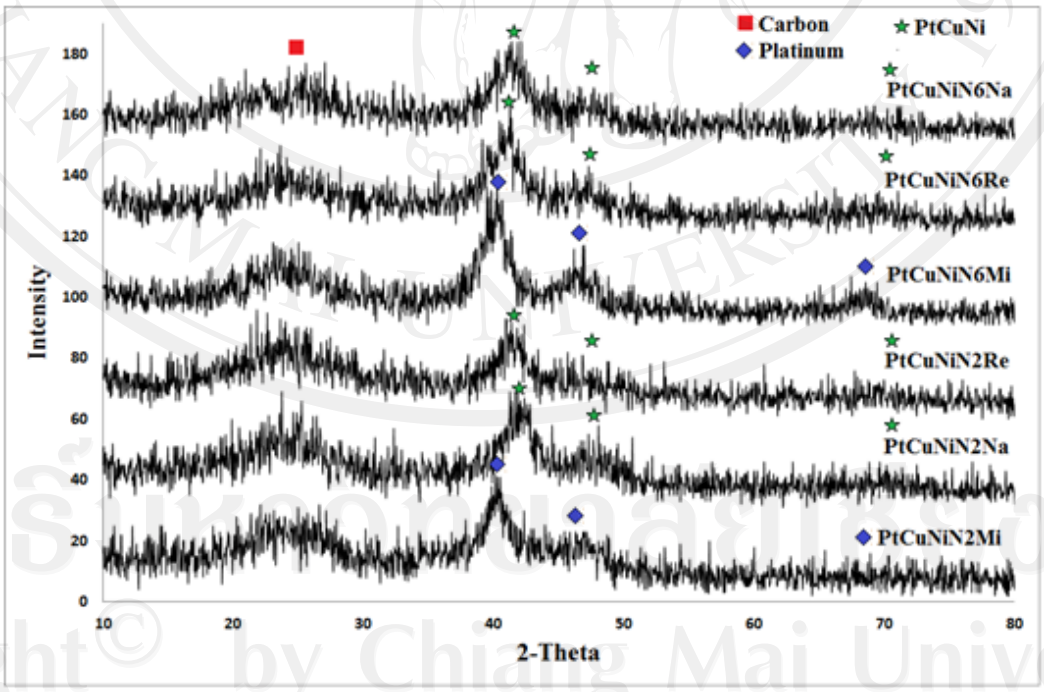

Figure 3.7 Powder XRD patterns of platinum-copper-nickel catalysts supported on treated carbon N115 by microwave, reflux and $NaBH_4$ reductionmethods.

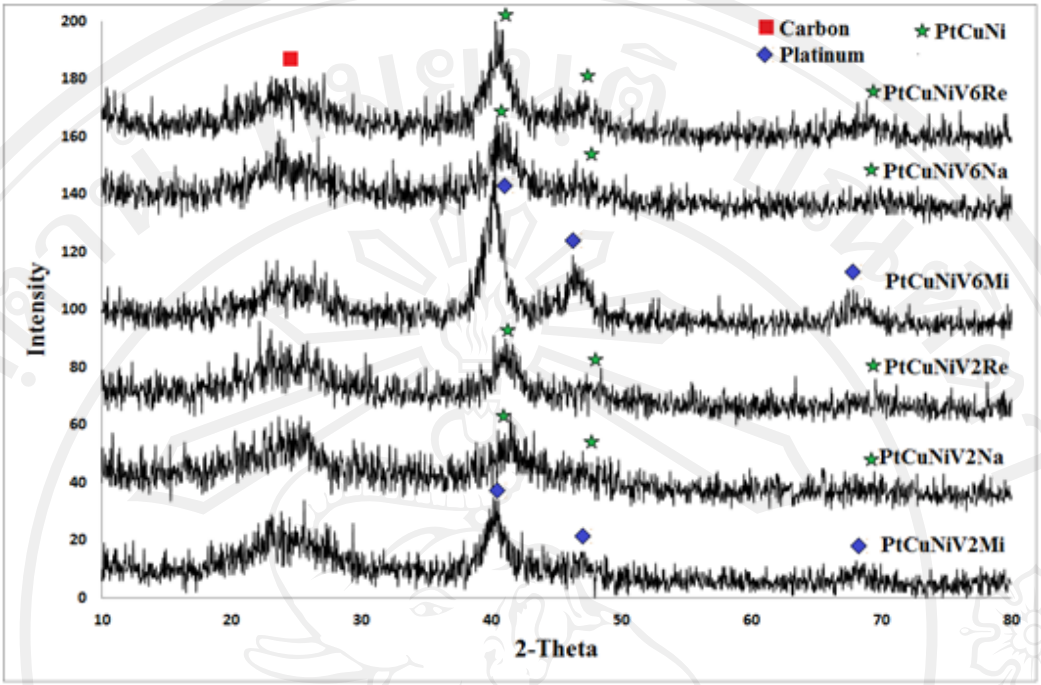

Figure 3.8 Powder XRD patterns of platinum-copper-nickel catalysts supported on treated carbon VulcanXC-72 by microwave, reflux and $NaBH_4$ reductionmethods.

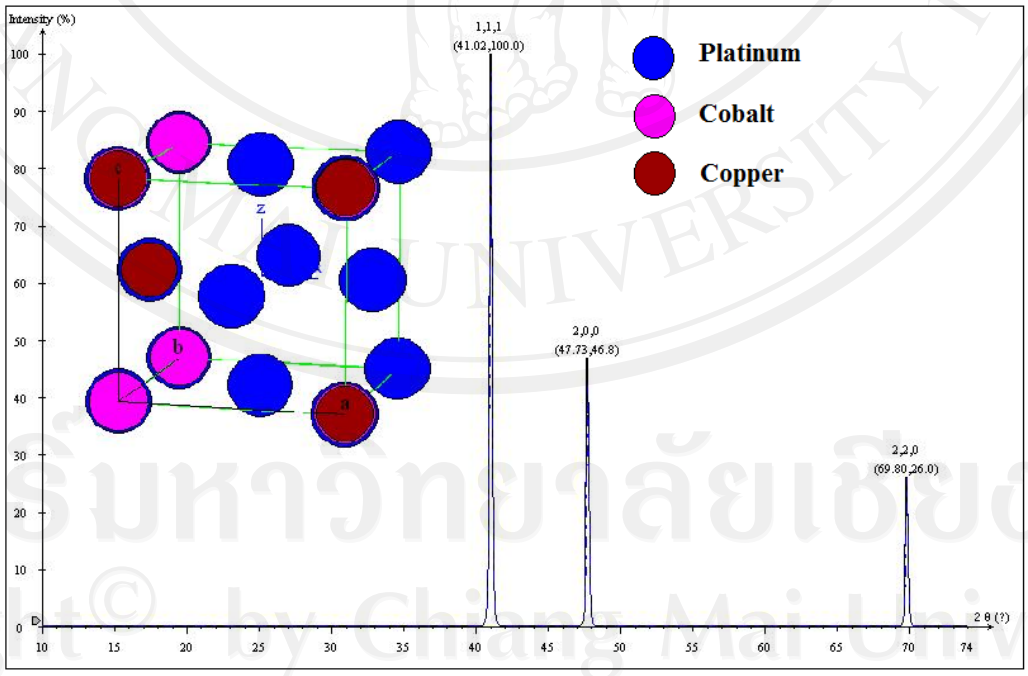

Figure 3.9 Simulated platinum-cobalt-copper unit cell by CaRIne V3.1 from Patent data No. 5,178,971 and XRD pattern.

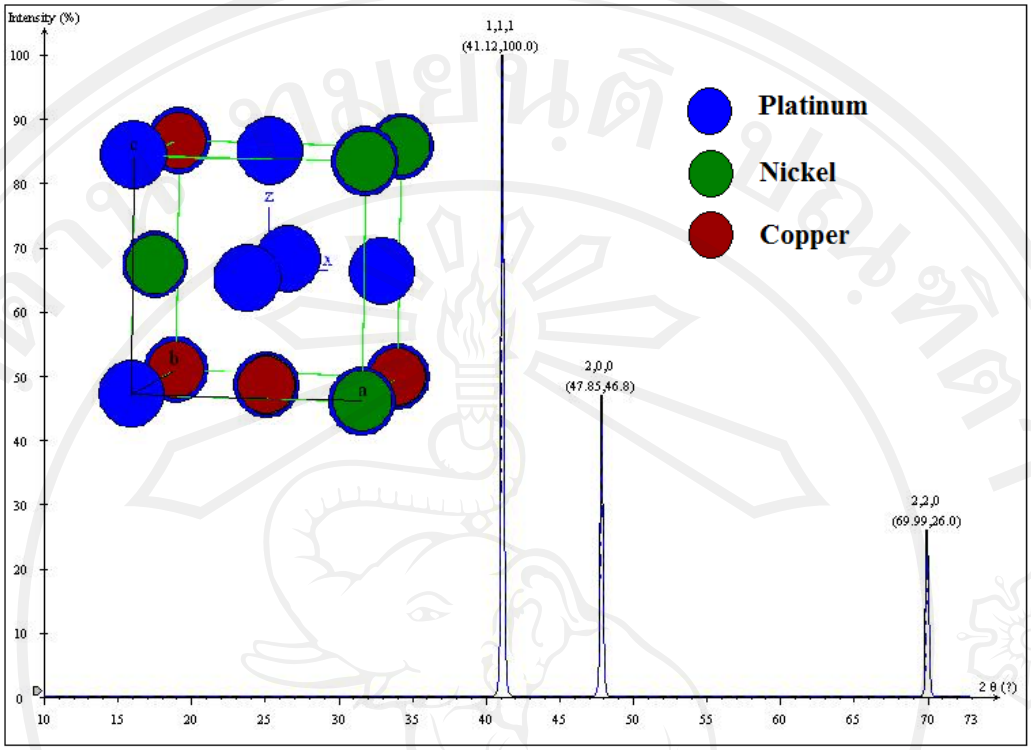

Figure 3.10 Simulated platinum-cobalt-nickel unit cell by CaRIne V3.1 from Patent data No. 5,178,971 and XRD pattern.

The XRD patterns for this research were separated into three groups which were 1). pattern without metal peak, 2). pattern with only platinum peak,and 3). pattern withternary metal alloy peak.

First group, catalysts such as PtCoCrV2Na and PtCoCrVu2Na were counted as the metalphase unidentificationbecause of low amount of metal and small particle size of metals. However, these catalysts were confirmed the existence of Pt-CoO-Cr_2O_3 from SAD pattern of TEM and from XAS techniques.The reason for the formation of CoO andCr_2O_3 phase instead of cobalt and chromium metals was the cobalt ion (+2) and chromium ion (+3) were the most oxidation stateunder air atmosphere[85,86]

although the standard reduction potentials of both species were higher than$NaBH_4$(E^0_{Co}= - 0.28, E^0_{Cr}= - 0.74and E^0_{NaBH4}= - 1.65)[87,63].

Second group, the catalysts PtCoCrV2Mi, PtCoCrVu2Mi, PtCoCrN2Re, PtCoFeN2Re, PtCoNiN2Re, PtCuNiN2Mi, PtCuNiN6Mi, PtCuNiV2Mi, and PtCuNiV6Mi were identifiedand observed platinum as a major phase. For the sample PtCoCrV2Mi and PtCoCrVu2Mi catalysts, the absence of cobalt metal formation could be explained by the insufficient of microwave energy to support the reduction of Co^{2+} ion to cobalt metal while the absence of chromium metal Cr_2O_3 (identify by XAS) was that because the chromium ion (Cr^{+3}) is the most stable oxidation state[58]. It has a negative standard reduction potential and hence a high possibility to occur as an oxide[85,86].For the samples from reflux method which were PtCoCrN2Re, PtCoFeN2Re, and PtCoNiN2Re catalysts, only platinum phase was found.Other metals which held negative standard reduction potentials (E^0_{Co}= - 0.28, E^0_{Cr}= - 0.74, E^0_{Fe}= - 0.04, and E^0_{Ni}= - 0.257)[87],werestable in oxide formula. Finally, the samplePtCuNiN2Mi, PtCuNiN6Mi, PtCuNiV2Mi, and PtCuNiV6Mi catalysts, contained only platinum phase because alloy phase was unable to synthesize by microwave method where copper and nickel ionswere favorable CuO[88,89] and NiO[90,91] phase by this method. The microwave which used in this study was low irradiation to reduce the metal ion to metal in air atmosphere.

Third group, the catalysts PtCoCuN2Re, PtCuNiN2Re, PtCuNiN6Re, PtCuNiN2Na, PtCuNiN6Na, PtCuNiV2Re, PtCuNiV6Re, PtCuNiV2Na, and PtCuNiV6Na were identified as platinum-based ternary catalysts. The unit cell from these catalysts was cubic and space group was Fm3m. The 2θ position of (111) plane of sample was compared with platinum ternary alloy from Patent No. 5,178,971 and

platinum metal shown in Table 3.2. From PtCoCuN2Re,the position of (111) plane was closer to platinum alloy's than platinum metal's because the unit cell from platinum alloy was smaller than platinum metal. This alloy was counted assubstitutional alloy; metal was replaced by other metals at the same position. In this sample, cobalt and copper with the smaller atomic radius than platinum had replaced the platinum position. After the metals were mixed to form alloy, the acquired alloy phase provided the different unit cell parameters from the metal. In case of the atomic distance, the distance between the same atomic types appeared further than the distance from heteroatom by the effect of the atomic force.For the same reason, the position of (111) plane of PtCuNi alloy and PtCoCu alloy catalysts also appeared closer to platinum alloy's than platinum metal's.

The platinum-based ternary catalysts were the formation of platinum, copper and cobalt or nickel. These catalysts were prepared by reflux and $NaBH_4$ reductionmethods.The reducing agent using inreflux method wasethylene glycol and $NaBH_4$ reductionmethod was $NaBH_4$. The reducing agent in these two methods had electrons that can donate to the metal ion. The alloy formation was explained in Figure 3.11. When metal ions approached near the carbon surface, the reducing agents gave the electron to metal ion which later grew on the carbon supporter.

For the sample contained platinum and copper had positivestandard reduction potentials,so it was simple to be reduced.Nickel and cobalt, which held the negative standard reduction potentials as -0.257 and -0.28, respectively, were difficult to be reduced to metal. For PtCoCuN2Re catalyst formed as alloy because of standard reduction potentials from platinum and copper were positive whichsimpleto be

reduced by reducing agent. Solution contained metal ion (Pt, Cu and Co) as the positive change near the carbon surface which was negative change. When ethylene glycol was heated by reflux method, it reduced metal ion near the carbon surface to metal-alloy. The platinum and copper ions were easier to be reduced than other metalwhen all metal ions were close to the carbon surface. The ethylene glycol at 170 °C can reduce platinum, copper and cobalt ions to formPtCoCu alloy.Thesample PtCuNiN2Re, PtCuNiN6Re, PtCuNiV2Re, and PtCuNiV6Rewere prepared by reflux methodwhile the sample PtCuNiN2Na, PtCuNiN6Na, PtCuNiV2Na, and PtCuNiV6Na were prepared by$NaBH_4$ reductionmethod.The results from these catalysts appeared similarly as the result from sample PtCoCuN2Re catalysts which the alloy phase was found except the sample from $NaBH_4$ reductionmethodwhich used $NaBH_4$ as a reducing agent.

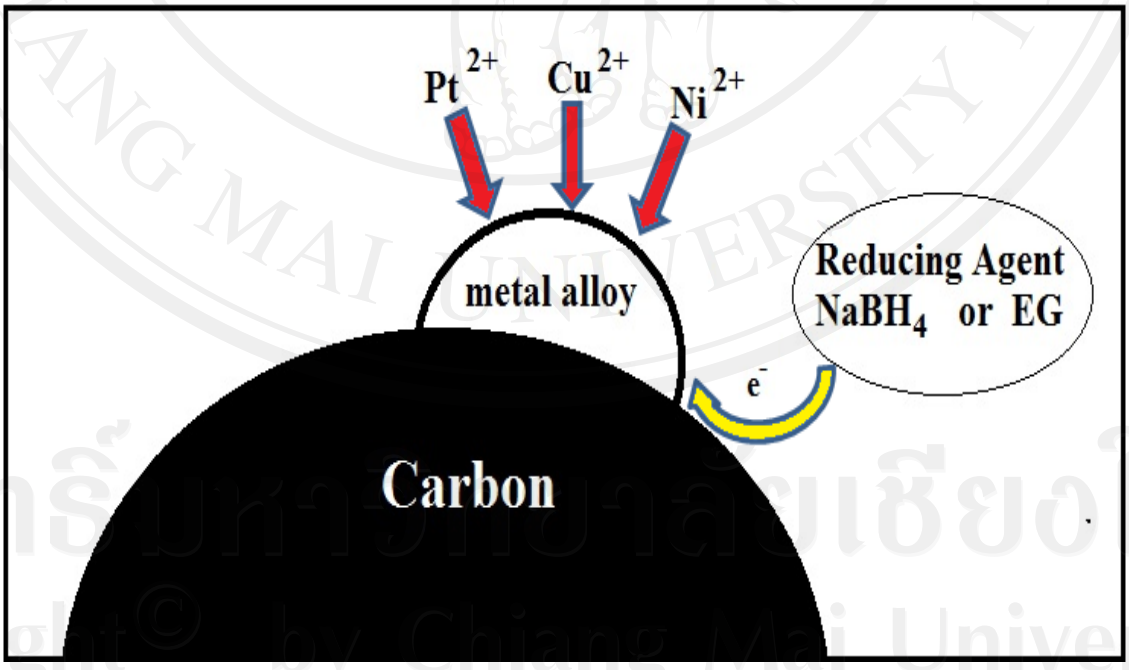

Figure 3.11Theformation of platinum alloy by reducing agent

Table 3.2 Compared peak position of (111) between standard and sample with unit cell parameters. (* from JCPDS No. 00-004-0802, ** from Patent No. 5,178,971)

Sample	2θ (111)	a(Å)
Pt STD*	39.76	3.920
PtCoCu STD**	41.02	3.808
PtCuNi STD**	41.12	3.799
PtCuNiN2Na	41.64	3.752
PtCuNiN6Na	41.24	3.787
PtCuNiV2Na	41.40	3.773
PtCuNiV6Na	40.88	3.819
PtCoCuN2Re	40.93	3.810
PtCuNiN2Re	41.00	3.808
PtCuNiN6Re	41.16	3.794
PtCuNiV2Re	41.04	3.805
PtCuNiV6Re	40.76	3.830

3.2.2 Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS)

The catalysts for all groupcharacterized by SEM technique was shown in Figure 3.12-3.14. The Figure 3.12 showed catalyst in the first group which only carbon surface of carbon Vulcan XC-72 was observed because the supported metals had very fine particle which was beyond the detection limit of this technique.Their

particle size distribution and morphologies were further investigated by TEM. For Figure 3.12- 3.14, the catalysts in second and third groups were presented, respectively.The results were similar to the catalysts in the first group that only the surfaces of carbon Vulcan XC-72 and carbon N115 were observed.

The qualitative and quantitative analyses of elements for all samples were conducted by EDStechnique as shown in Table 3.3- 3.5. The intensities of EDS peaks of carbon, oxygen and all metals on carbon were presented.The observed oxygen from this technique was majorlycome from carboxylic group on treated carbon surface. The comparison of metal amount on treated carbon and untreated carbon was demonstrated in Table 3.3 where all metals (Pt, Co and Cr) were found on both carbon supporters. However,there was no evidence of cobalt metal occurrence on both carbon supporters from microwave method. The reason for the absence of cobalt metal can be explained by the insufficient of microwave energy to support the reduction of Co^{2+} ion to Co metal. It was noted that the intensities of EDS spectrums, which corresponded to higher amount of all metals on treated carbon were higher than the metals on untreated carbon. The quantitative analysis from EDS spectrum showed that the metals on treated carbon were relatively higher than on untreated carbon. For Table 3.4-3.5, the elemental amounts contained in each catalyst from second and third groups, were presented, respectively. All metals supported on carbon, however, the amount of the observed metals was less than theoreticalmetals ratio.

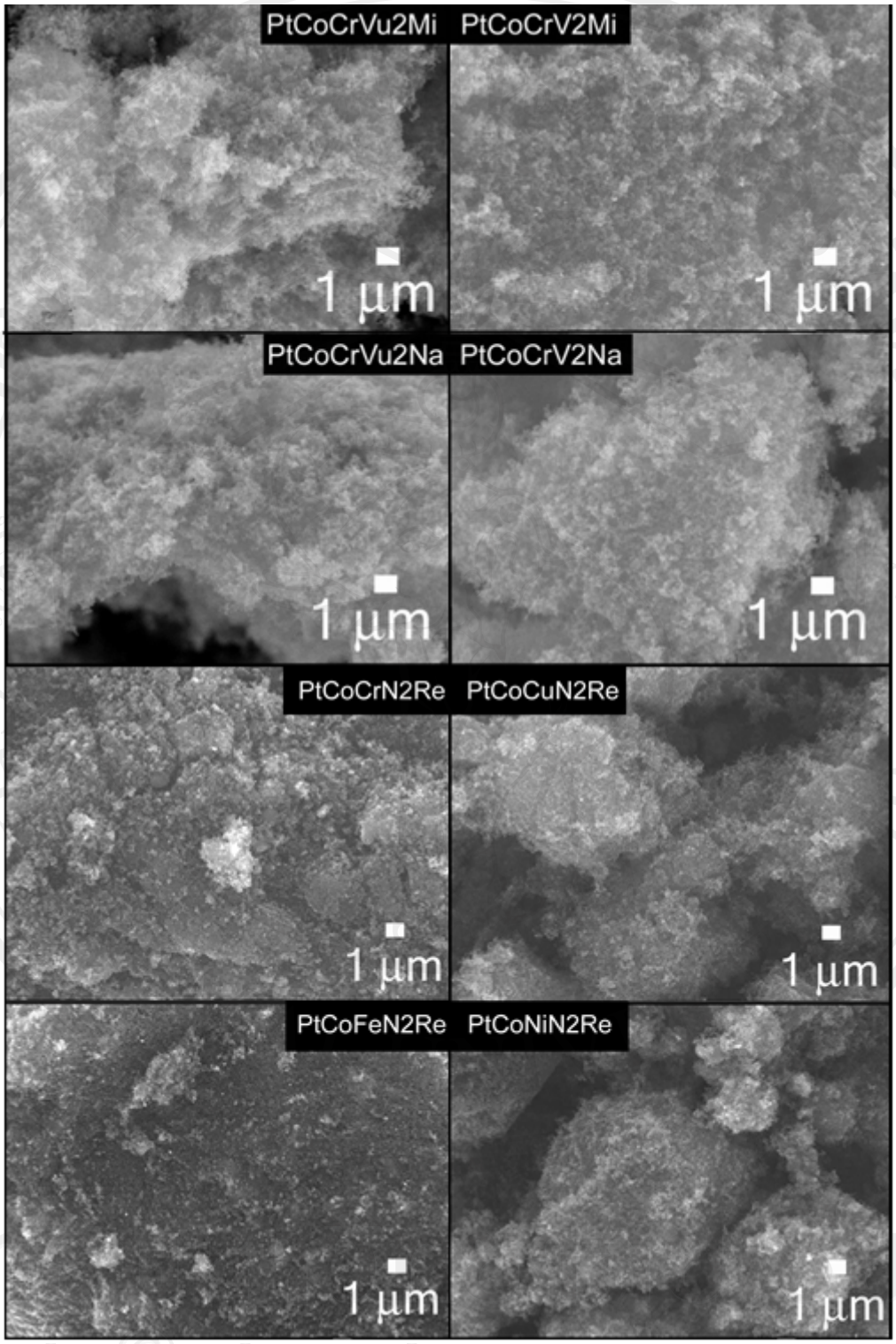

Figure 3.12 SEM pictures of platinum-cobalt-chromium catalysts supported on treated or untreated carbons by microwave and $NaBH_4$ reductionmethod and platinum-cobalt-metal catalysts supported on treated carbon by reflux method.

Table 3.3 Percent weights of platinum, cobalt, chromium, oxygen and carbon of platinum-based ternarycatalysts from EDS.

Sample	Element (Wt %)				
	C	O	Pt	Co	Cr
PtCoCrVu2Mi	87.35	7.99	3.51	0.04	1.11
PtCoCrVu2Na	86.60	5.51	5.28	1.73	0.88
PtCoCrV2Mi	85.98	6.17	5.63	0.00	2.22
PtCoCrV2Na	82.71	5.18	6.65	3.38	2.08

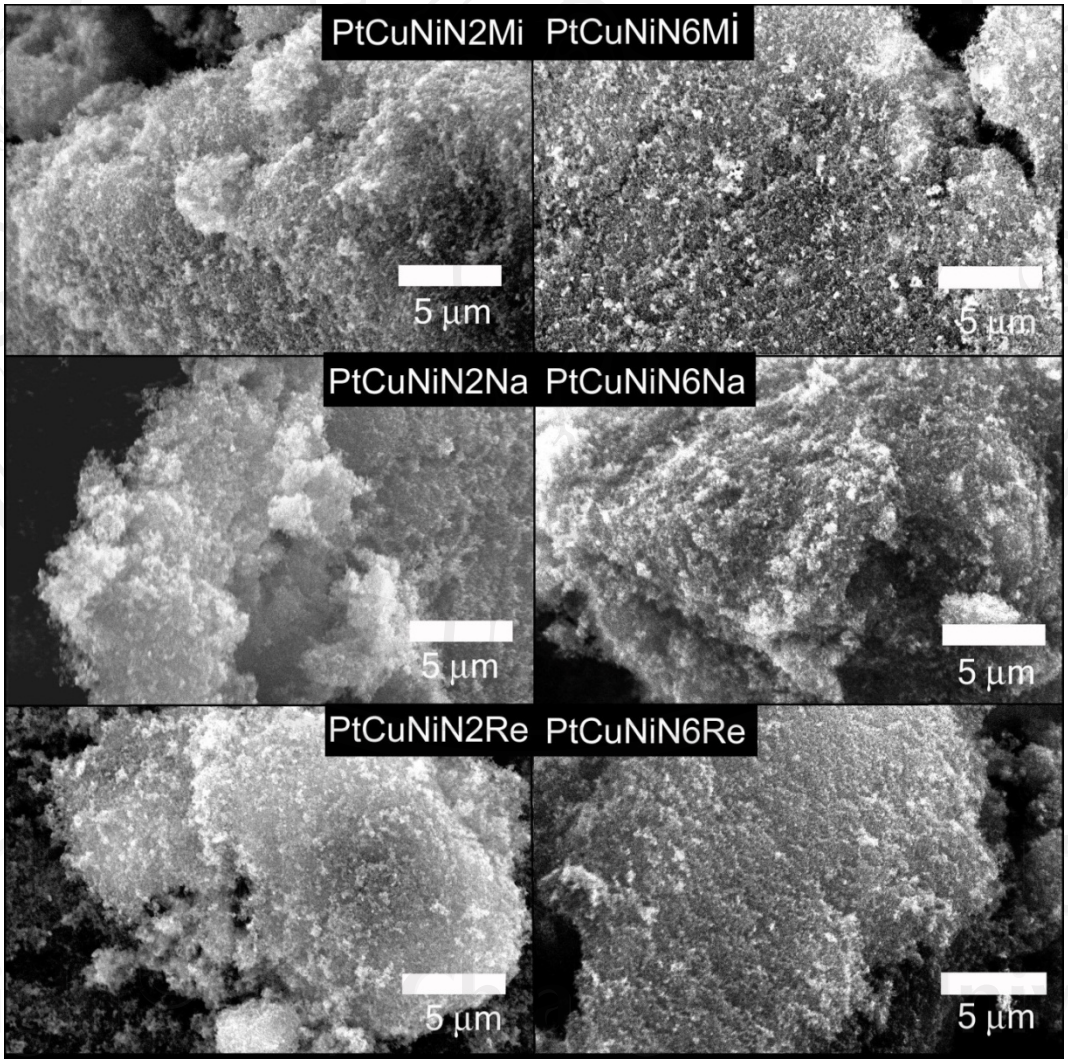

Figure 3.13SEM pictures of platinum-copper-nickel catalysts supported on treated carbon N115 by microwave, reflux and $NaBH_4$ reductionmethods.

Table 3.4 Percent weights of platinum, cobalt, metals(chromium, copper, nickel, and iron), oxygen and carbon of platinum-based ternarycatalyst from EDS.

Sample	Element (Wt %)				
	C	O	Pt	Co	M
PtCoCrN2Re	74.52	11.68	10.06	1.29	2.46
PtCoCuN2Re	78.17	6.08	10.28	0.17	5.30
PtCoFeN2Re	76.20	9.59	11.38	1.22	1.30
PtCoNiN2Re	73.55	11.21	8.50	1.17	5.57

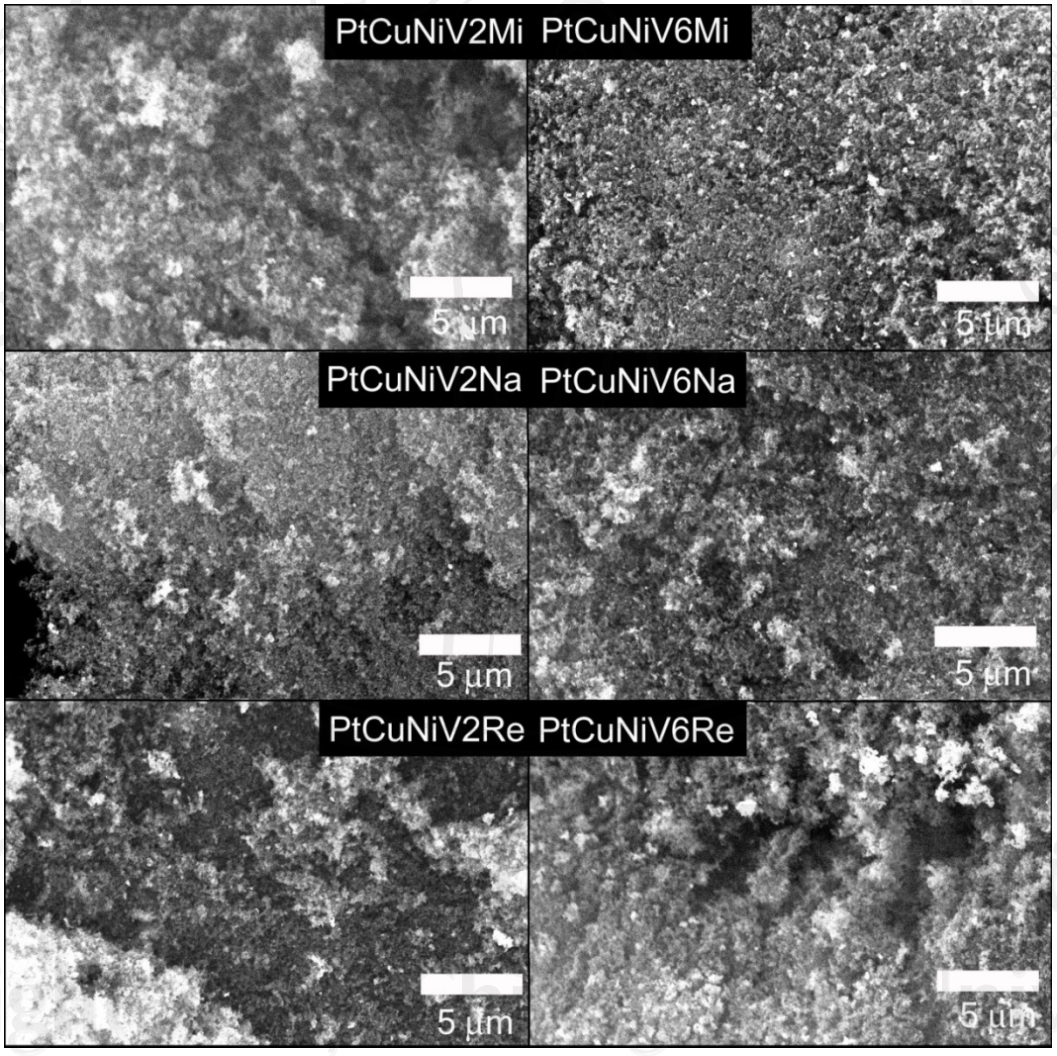

Figure 3.14SEM pictures of platinum-copper-nickel catalysts supported on treated carbon VulcanXC-72 by microwave, reflux and $NaBH_4$ reductionmethods.

Table 3.5 Percent weights of platinum, copper, nickel, oxygen and carbon of platinum-based ternarycatalyst from EDS.

Sample	Element (Wt %)				
	C	O	Pt	Cu	Ni
PtCuNiN2Mi	74.07	10.87	7.35	5.52	2.19
PtCuNiN2Na	75.07	12.79	5.32	4.46	2.16
PtCuNiN2Re	74.42	9.46	8.40	4.81	2.92
PtCuNiN6Mi	78.64	9.52	10.17	1.55	0.27
PtCuNiN6Na	74.65	9.52	10.17	1.55	0.27
PtCuNiN6Re	75.72	6.93	12.34	2.45	2.56
PtCuNiV2Mi	82.27	9.02	7.18	1.47	0.22
PtCuNiV2Na	80.11	7.08	7.39	5.05	0.56
PtCuNiV2Re	79.31	3.74	12.79	3.71	0.42
PtCuNiV6Mi	83.37	4.48	10.57	1.51	0.28
PtCuNiV6Na	81.35	5.55	9.37	2.72	1.02
PtCuNiV6Re	77.66	9.74	10.32	2.18	0.29

3.2.3 Transmission electron microscopy (TEM)

The TEM images of catalyst on untreated and treated carbons for microwave and $NaBH_4$ reductionmethods were shown in Figure 3.15.It was found that the catalysts were nanoparticles with a good dispersion on carbon surface. The average particle size was shown in Table 3.6 and Figure 3.16. The particle size histograms wereshown in Figure 3.17. The results showed that particle size of catalysts on treated carbon was smaller than the catalyst particles on untreated carbon for both methods.The smaller particle size was possibly influenced by the carboxylic groupson carbon surface which had negative change. Therefore, they absorbed metal ions to near carbon surface and diffused metal ion to all surface. In general, the catalyst with a good uniform by

distribution of nanoscales particles will improve the fuel cell performance due to high surface area. The selected area electron diffraction (SAD) patterns for the catalysts in this group were inserted in TEM images. From $NaBH_4$ reduction method,the diffracted ring patterns of (002), (101) and (102) planes of carbon and (111), (200) and (220) planes of platinum were identified. For microwave method, the ring patternscontained (002), (101) and (102) planes for both carbons were obtained. In addition, spot pattern of platinum,which corresponded to (1-11), (-111) and (002) planes,was found for the catalyst on untreated carbon while only (1-11) plane of platinum was observed for the catalyst with treated carbon. It was confirmed that the catalysts in this group had platinum as the major phase. Other metals (cobalt and chromium) were not appeared in SAD patterns in this technique.

Table 3.6Average particle size of all catalysts in this research

Sample	Particle size (nm)	Sample	Particle size (nm)
PtCoCrVu2Mi	2.72±0.41	PtCoCrN2Re	3.55±0.90
PtCoCrV2Mi	2.43±0.34	PtCoCuN2Re	4.09±0.69
PtCuNiN2Mi	3.14±0.52	PtCoFeN2Re	3.22±0.60
PtCuNiN6Mi	3.26±0.65	PtCoNiN2Re	3.28±0.47
PtCuNiV2Mi	3.17±0.66	PtCuNiN2Re	3.16±0.55
PtCuNiV6Mi	4.41±0.74	PtCuNiN6Re	3.46±0.88
PtCoCrVu2Na	2.97±0.63	PtCuNiV2Re	3.51±0.58
PtCoCrV2Na	1.93±0.35	PtCuNiV6Re	3.96±0.67
PtCuNiN2Na	2.81±0.52	PtCuNiV2Na	2.78±0.70
PtCuNiN6Na	2.75±0.56	PtCuNiV6Na	2.73±0.55

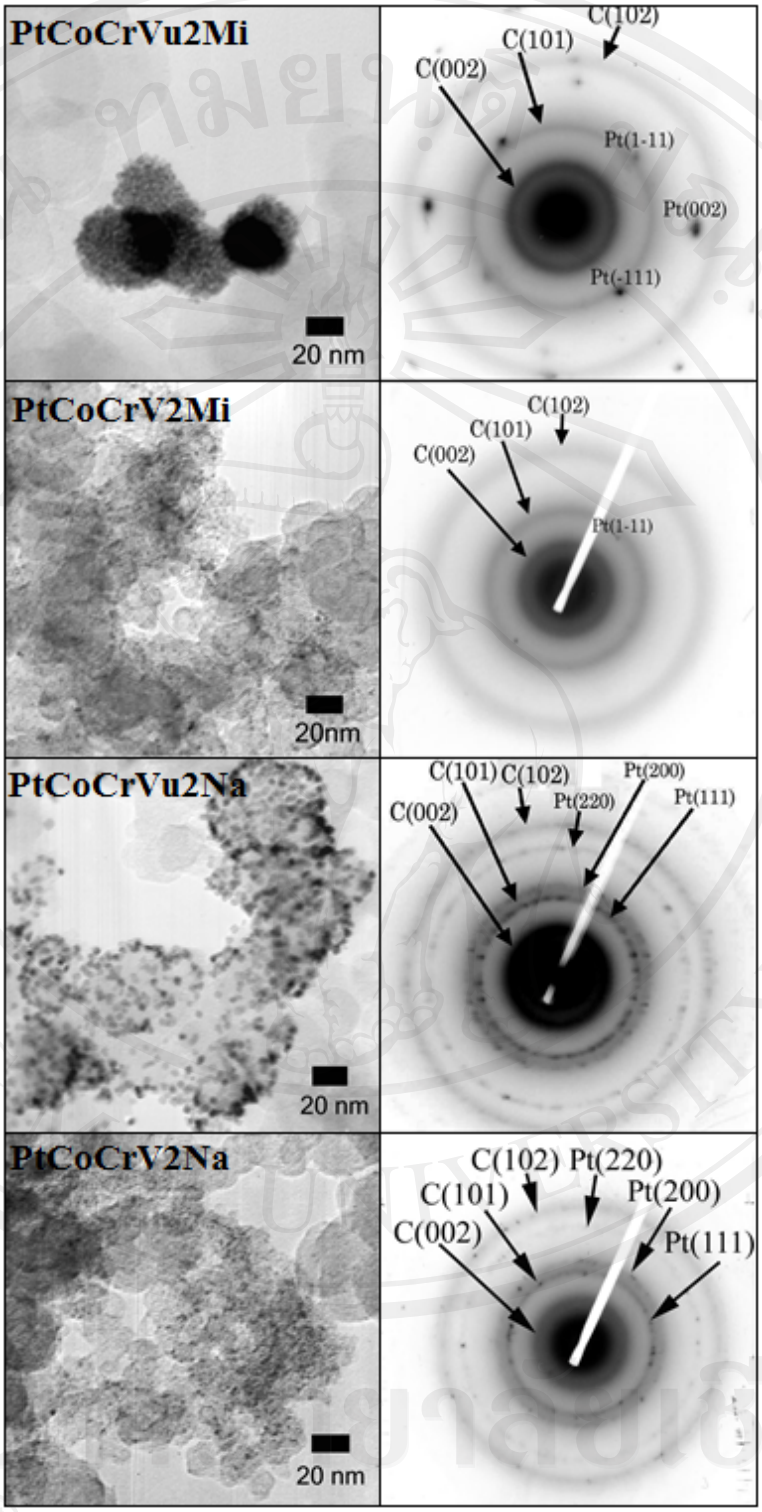

Figure 3.15TEM images with the corresponding SAD patterns of platinum-cobalt-chromium catalysts supported on treated or untreated carbon by microwave and$NaBH_4$ reductionmethods.

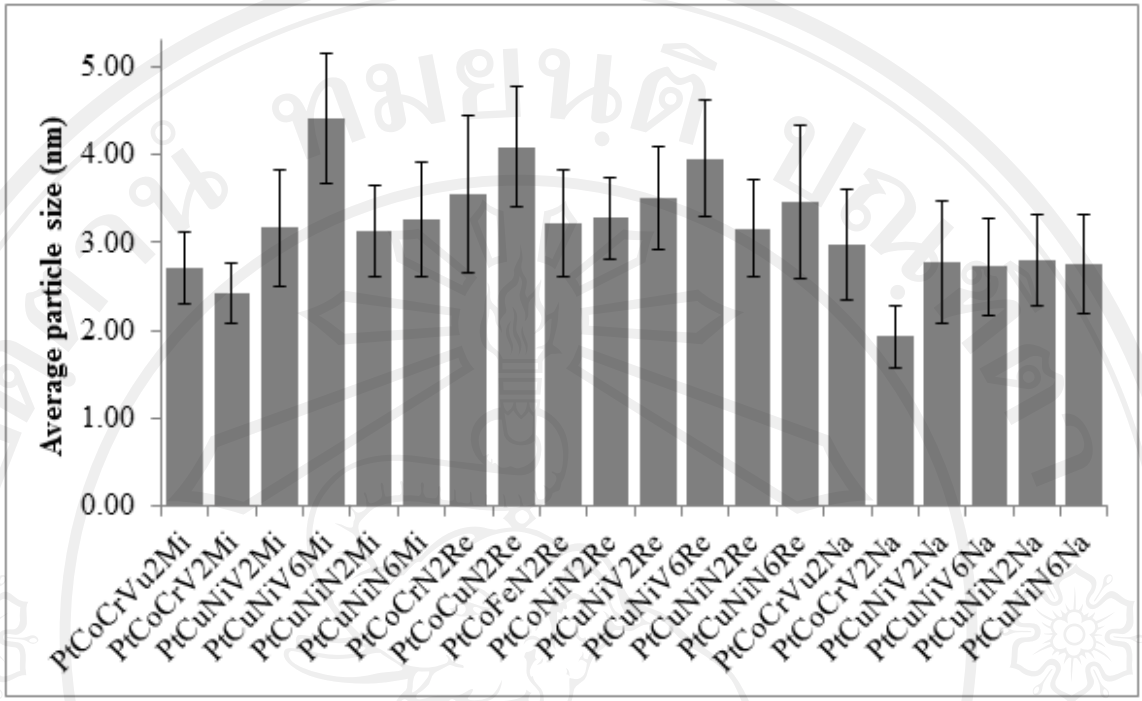

Figure 3.16Average particle size of all catalysts in this research

Figure 3.18-3.22 shows the TEM images with the corresponding SAD patterns ofcatalysts on treated carbon supporter from second and third groups.It was found that the catalysts were nanoparticles with a good dispersion on carbon surface. The average particle size was shown in Table3.6 and Figure 3.16. The particle size histograms wereshown in Figure 3.23-3.25. The catalysts prepared by $NaBH_4$ reductionmethod had smaller size than the catalysts from microwave and reflux methods.

SADpatterns of all samples from second and third groups were appeared as ring patterns which contained (002), (101) and (102) planes of carbon. The PtCoCrN2Re, PtCoFeN2Re, PtCoNiN2Re, PtCuNiN2Mi, PtCuNiN6Mi, PtCuNiV2Mi, and PtCuNiV6Mi contained (111), (200) and (220) planes of platinum. However, these catalysts contained all metals on carbon observed by EDS technique.The PtCoCuN2Re show the ring pattern contained (111), (200) and (220)

planes of platinum-cobalt-copper alloy. The PtCuNiN2Re, PtCuNiN6Re, PtCuNiN2Na, PtCuNiN6Na PtCuNiV2Re, PtCuNiV6Re, PtCuNiV2Na, and PtCuNiV6Na show the ring pattern contained (111), (200) and (220) planes of platinum-copper-nickel alloy. The SAD result was consistence with the results from XRD technique.

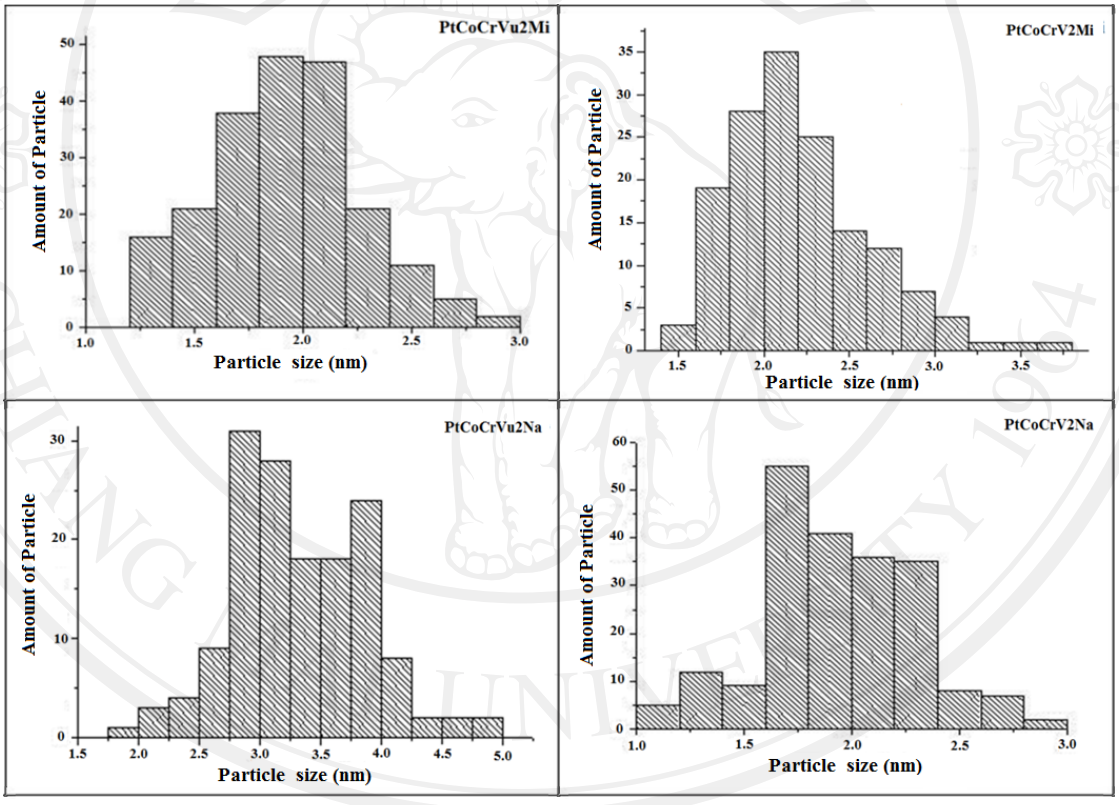

Figure 3.17Particle size histogramsofplatinum-cobalt-chromium catalysts supported on treated or untreated carbon by microwave and $NaBH_4$ reductionmethods.

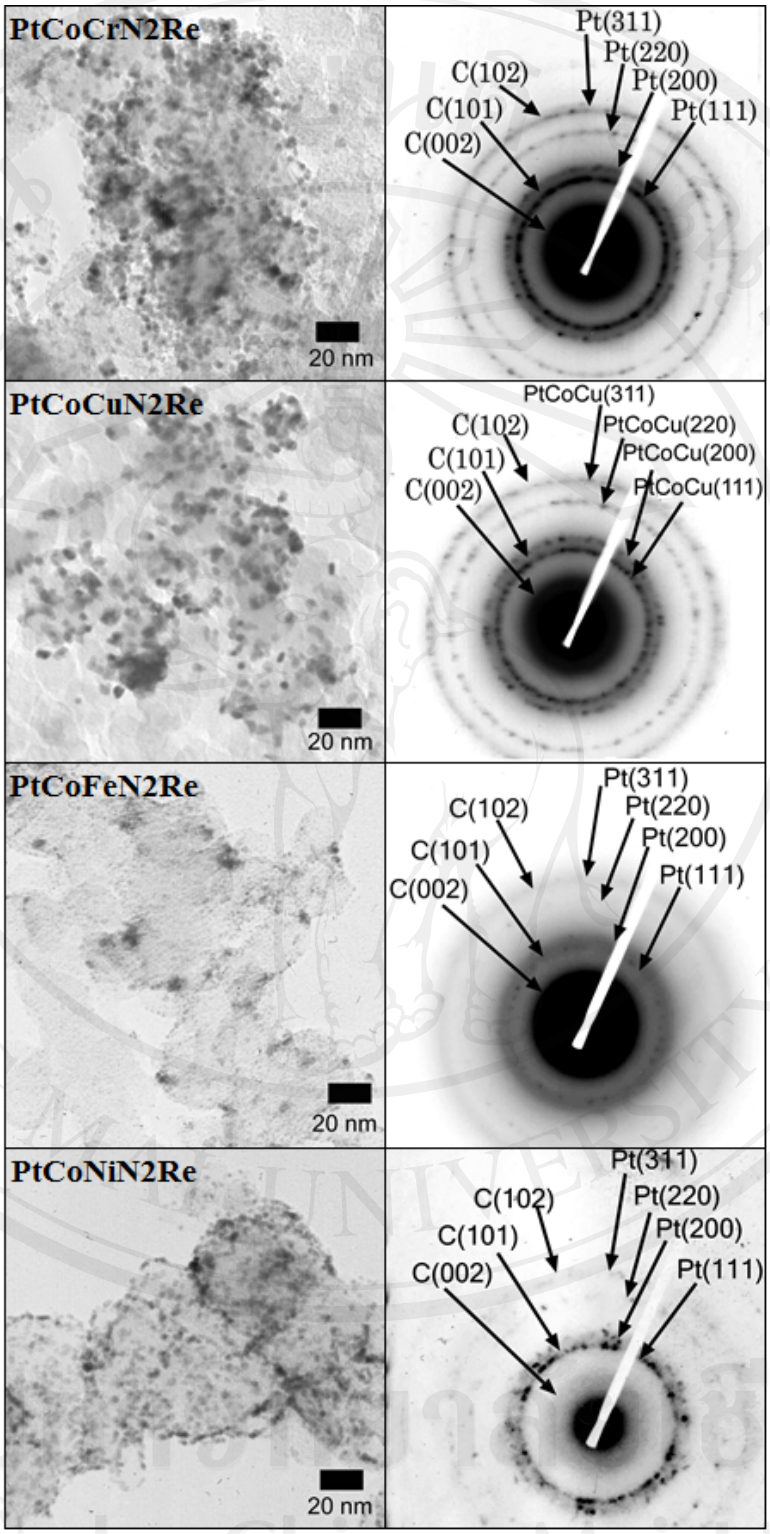

Figure 3.18TEM images with the corresponding SAD patterns of platinum-cobalt-metal (metal = chromium, copper, iron, and nickel) catalysts supported on treated carbon by reflux method.

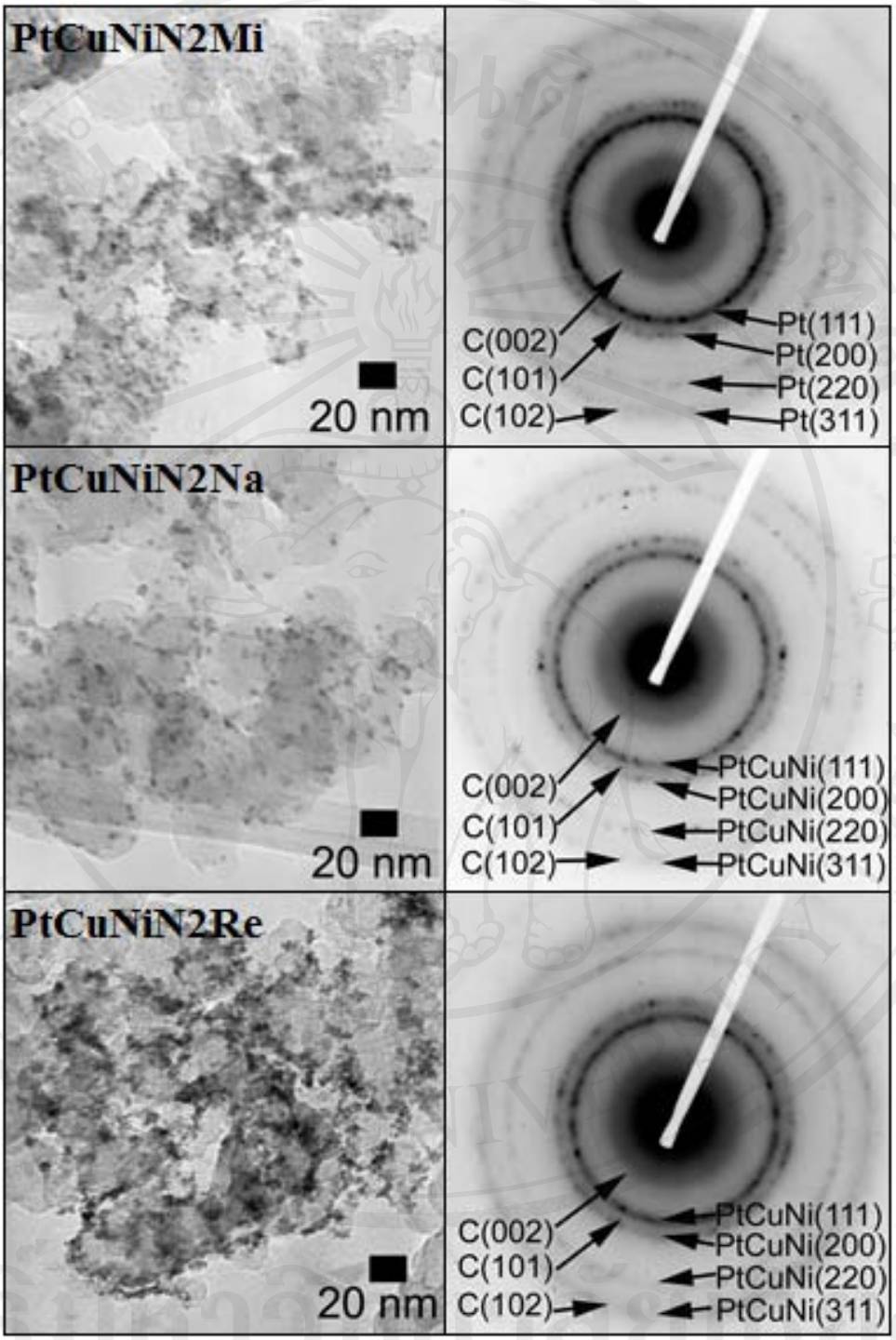

Figure 3.19TEM images with the corresponding SAD patterns of platinum-copper-nickel catalysts ratio 2:1:1 supported on treated carbon N115 by microwave, reflux and $NaBH_4$ reductionmethod.

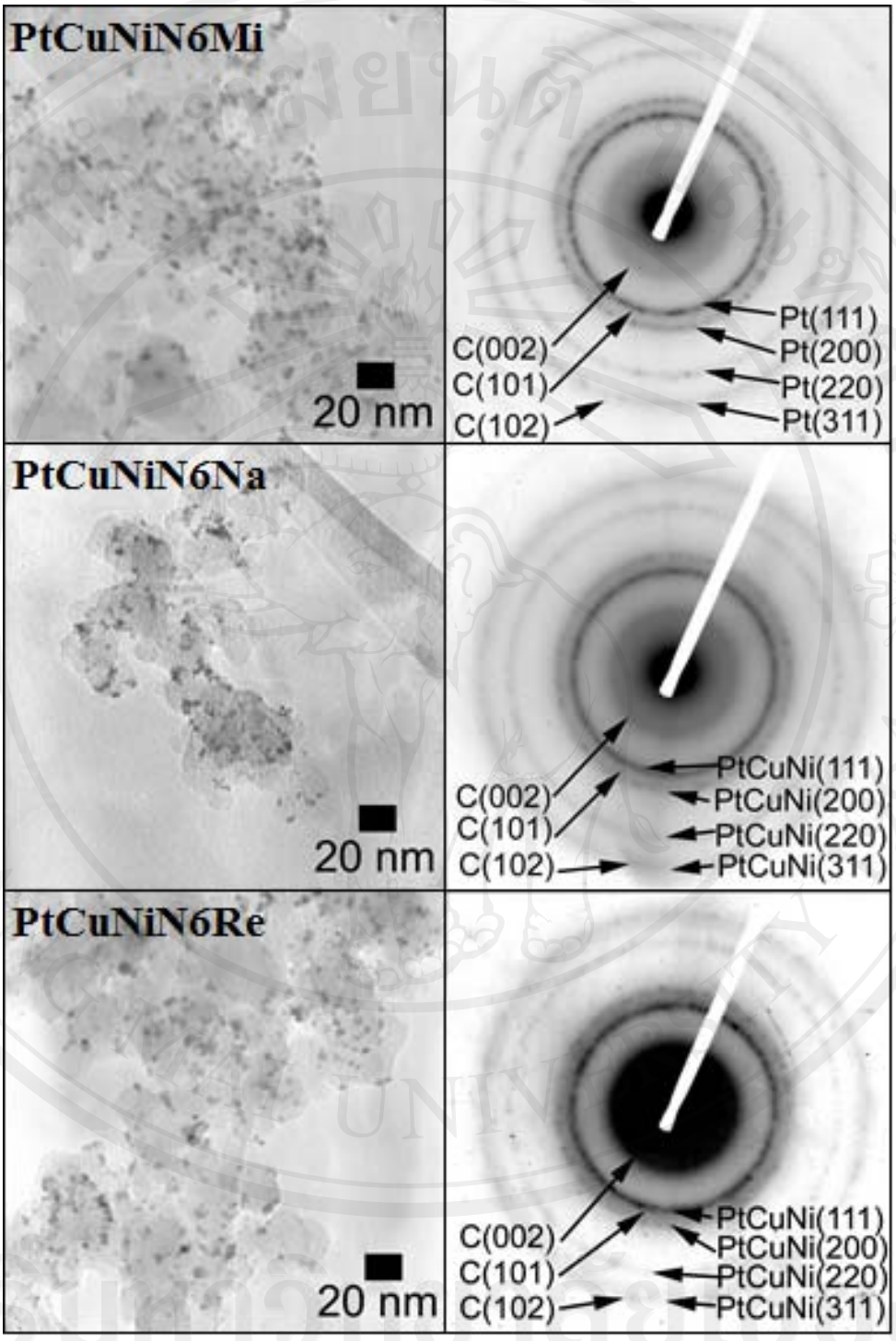

Figure 3.20TEM images with the corresponding SAD patterns of platinum-copper-nickel catalysts ratio 6:1:1 supported on treated carbon N115 by microwave, reflux and $NaBH_4$ reductionmethod.

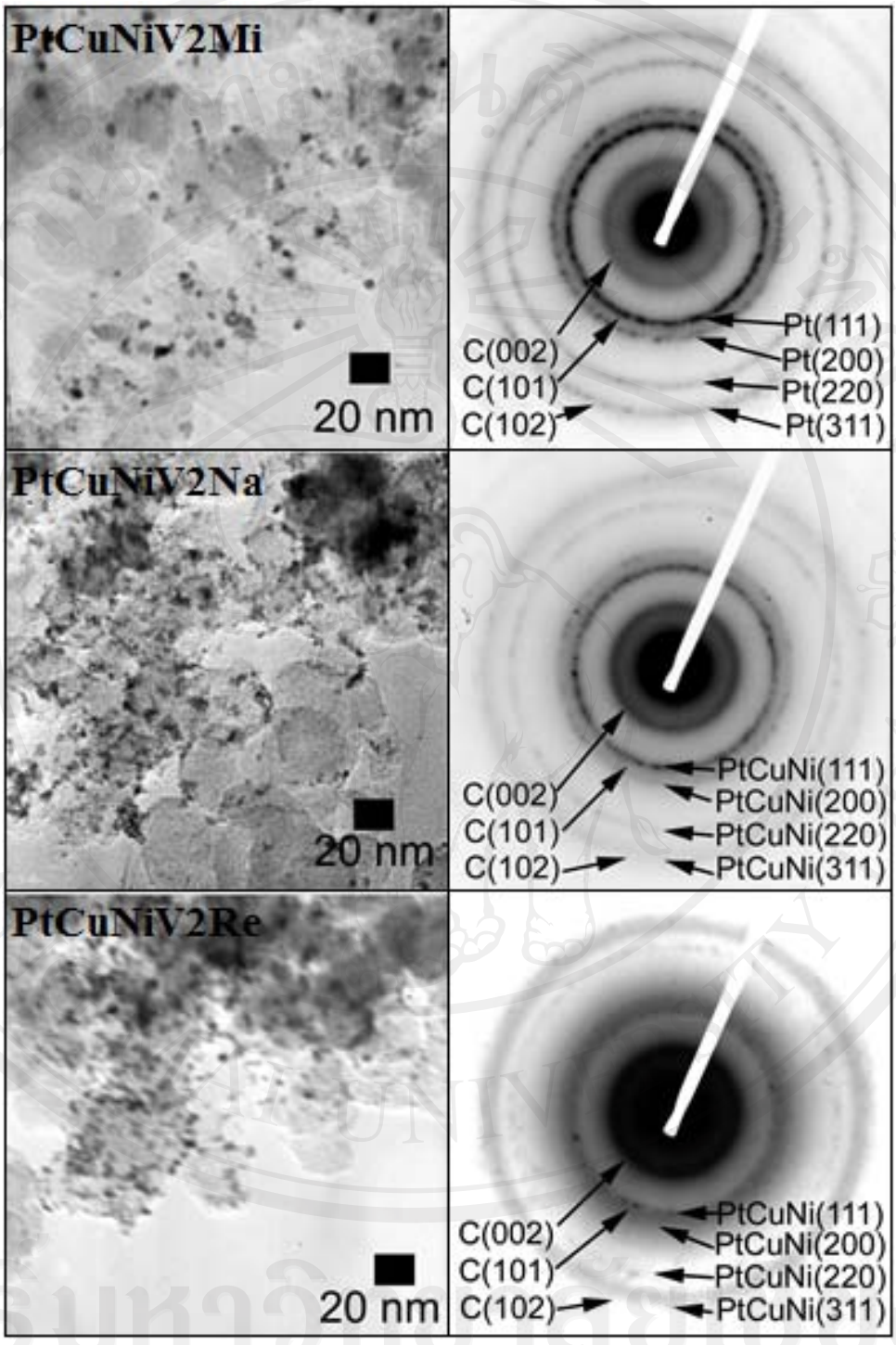

Figure 3.21TEM images with the corresponding SAD patterns of platinum-copper-nickel catalysts ratio 2:1:1 supported on treated carbon VulcanXC-72 by microwave, reflux and $NaBH_4$ reductionmethod.

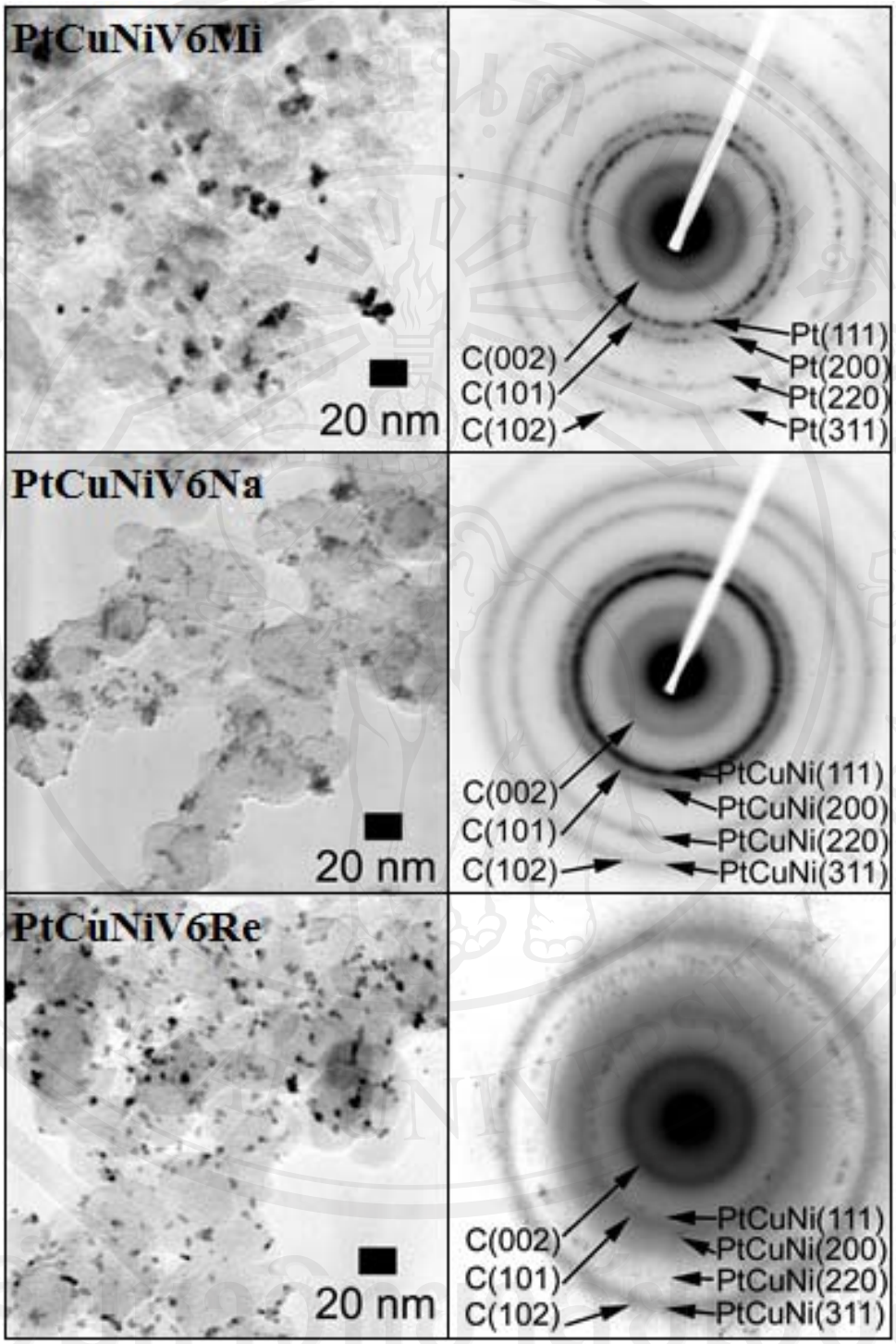

Figure 3.22TEM images with the corresponding SAD patterns of platinum-copper-nickel catalysts ratio 6:1:1 supported on treated carbon VulcanXC-72 by microwave, reflux and $NaBH_4$ reductionmethod.

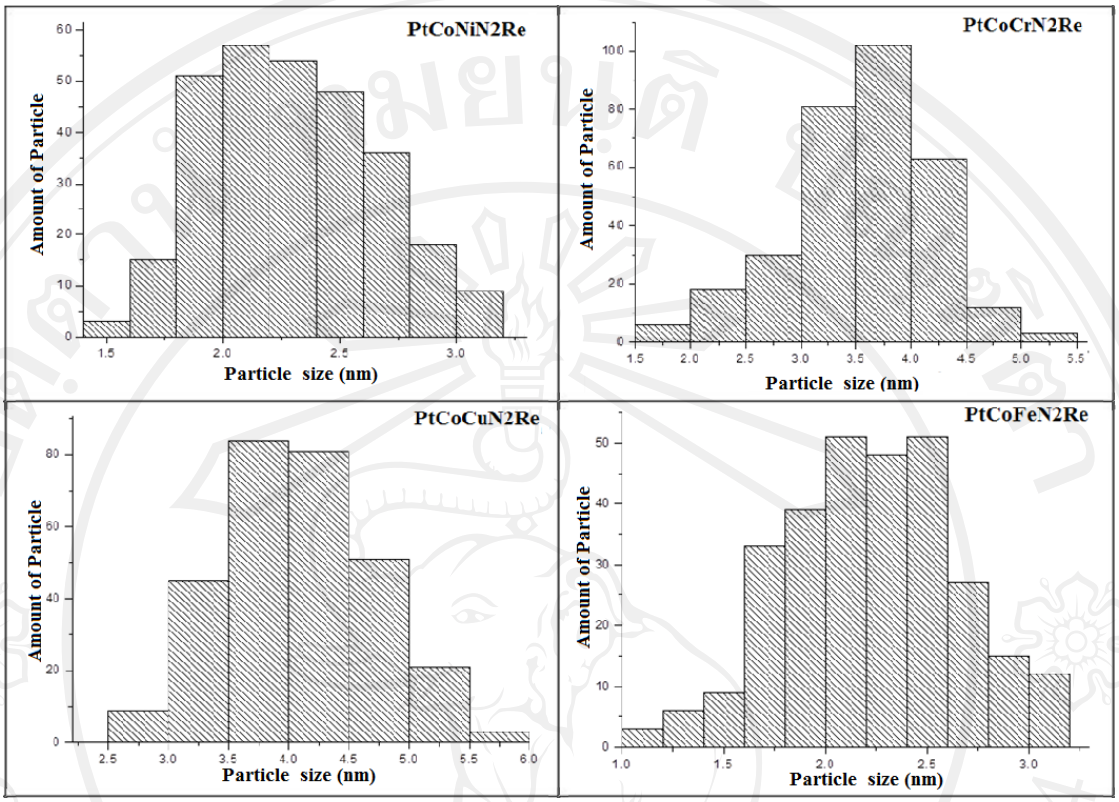

Figure 3.23 Particle size histogramsof platinum-cobalt-metal catalysts supported on treated carbon by reflux method.

3.2.4 X-ray absorption spectrometry (XAS)

The XAS technique was used to identify formative phasesof catalyst in the first group because the some metal phase could not be observed by XRD technique. This technique used Co, CoO and Co_3O_4 as cobalt standards and Cr and Cr_2O_3 as chromium standards to compare with samples. The XANES and EXAFS spectra for sample and cobalt standards were shown in fFigure 3.26. It confirmed that cobalt-contained phase in the samples obtained from$NaBH_4$ reduction method wasCoO compound because of the similarity of characteristic spectra ofCoO standard and sample.Conversely, there were no signals from cobalt-contained phase from samples which preparedby

microwave method.This result well agreed with the results from EDS and XRD technique.

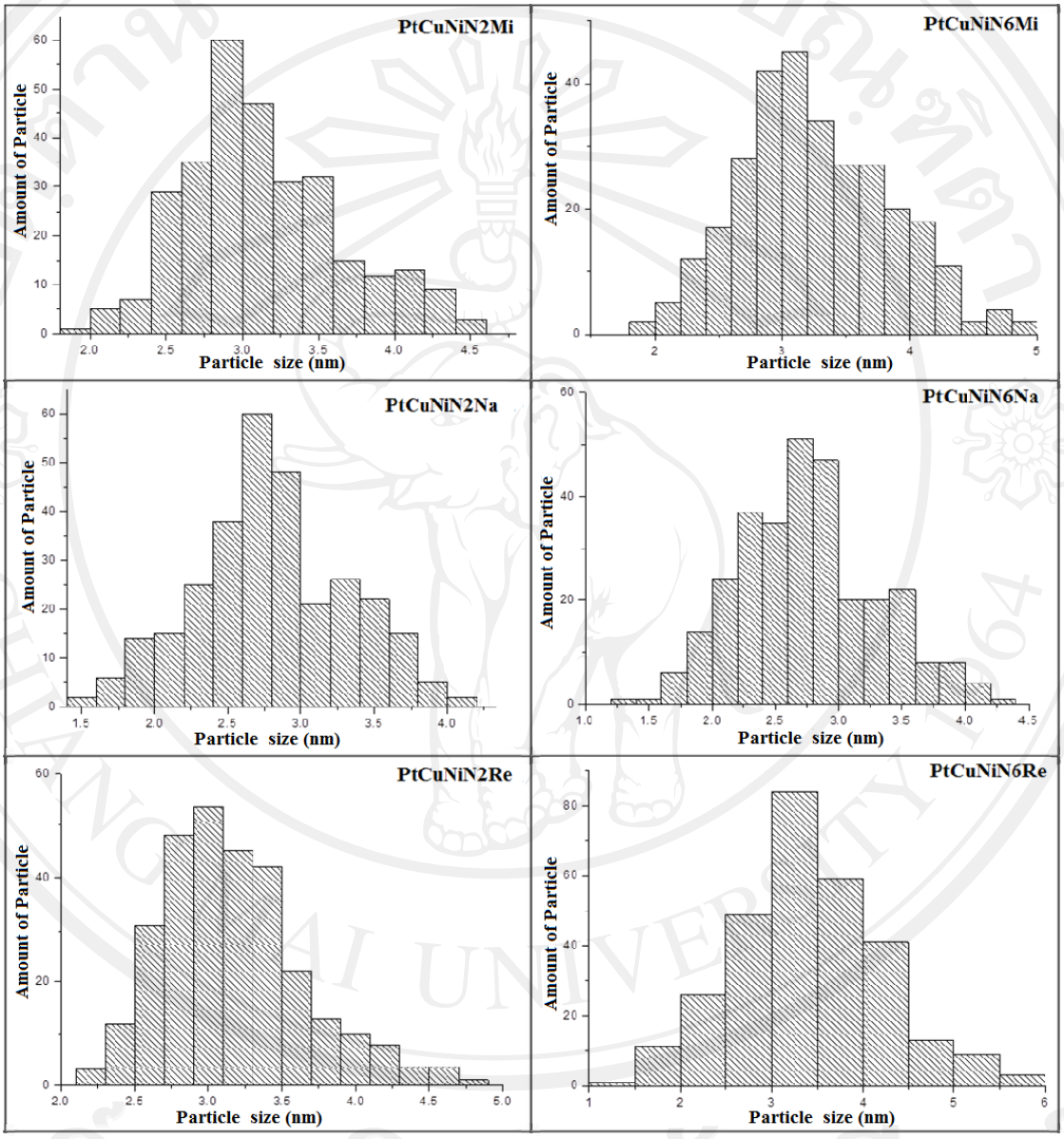

Figure 3.24Particle size histogramsof platinum-copper-nickel catalysts supported on treated carbon N115 by microwave, reflux and $NaBH_4$ reductionmethods.

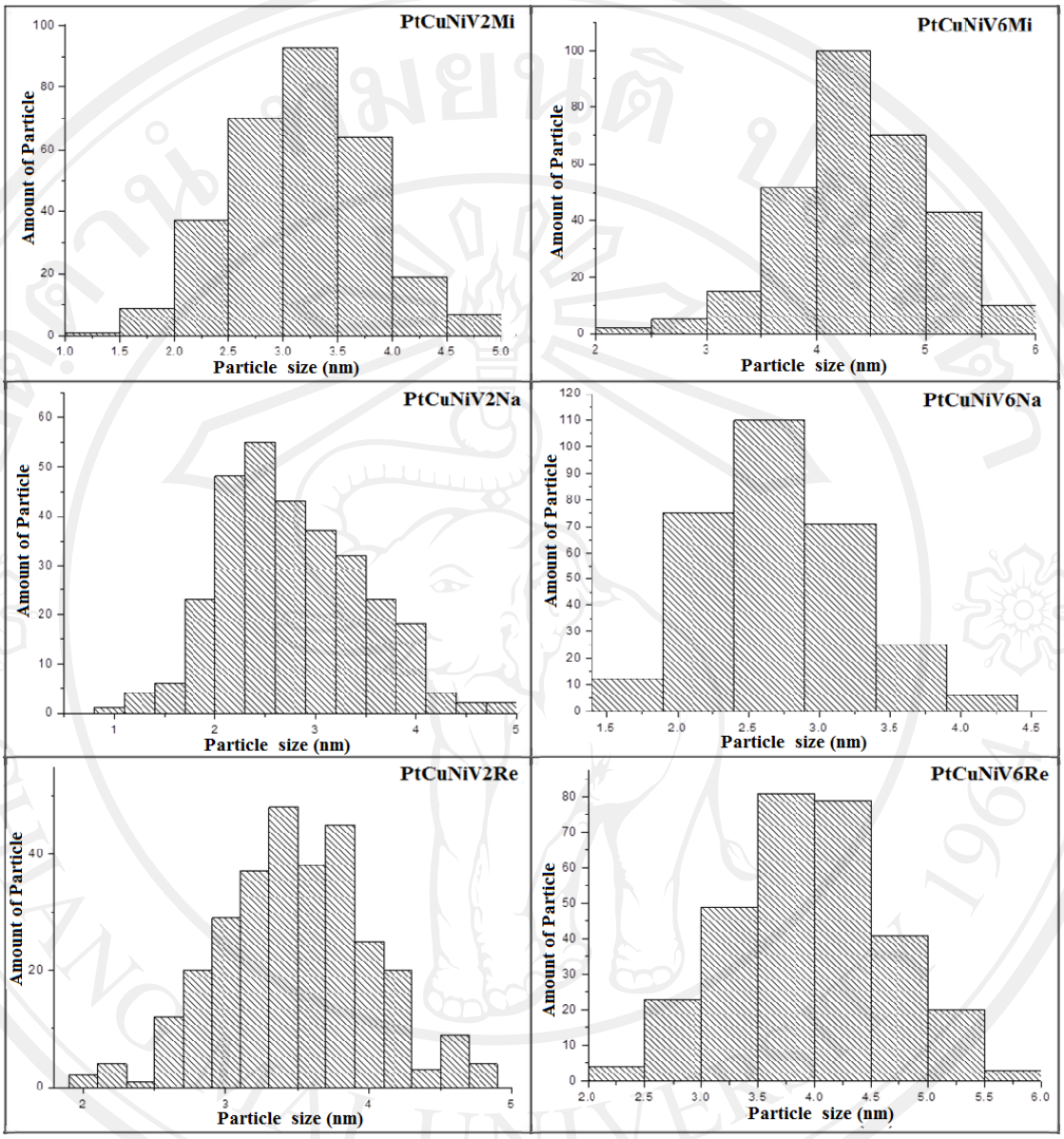

Figure 3.25Particle size histogramsof platinum-copper-nickel catalysts supported on treated carbon Vulcan XC-72 by microwave, reflux and $NaBH_4$ reductionmethods.

Figure 3.27 shows the XANES and EXAFS spectra of samples and chromium standards. All samples showed spectra which were similar to the spectrum of Cr_2O_3 standard. It can be concluded thatchromium-contained phase in the sample was Cr_2O_3 compound. The existence of oxide phase can be explained by the preferable

oxidation state as chromium ion (+3) and cobalt ion (+2)for the preparation process which conducted in air atmosphere.

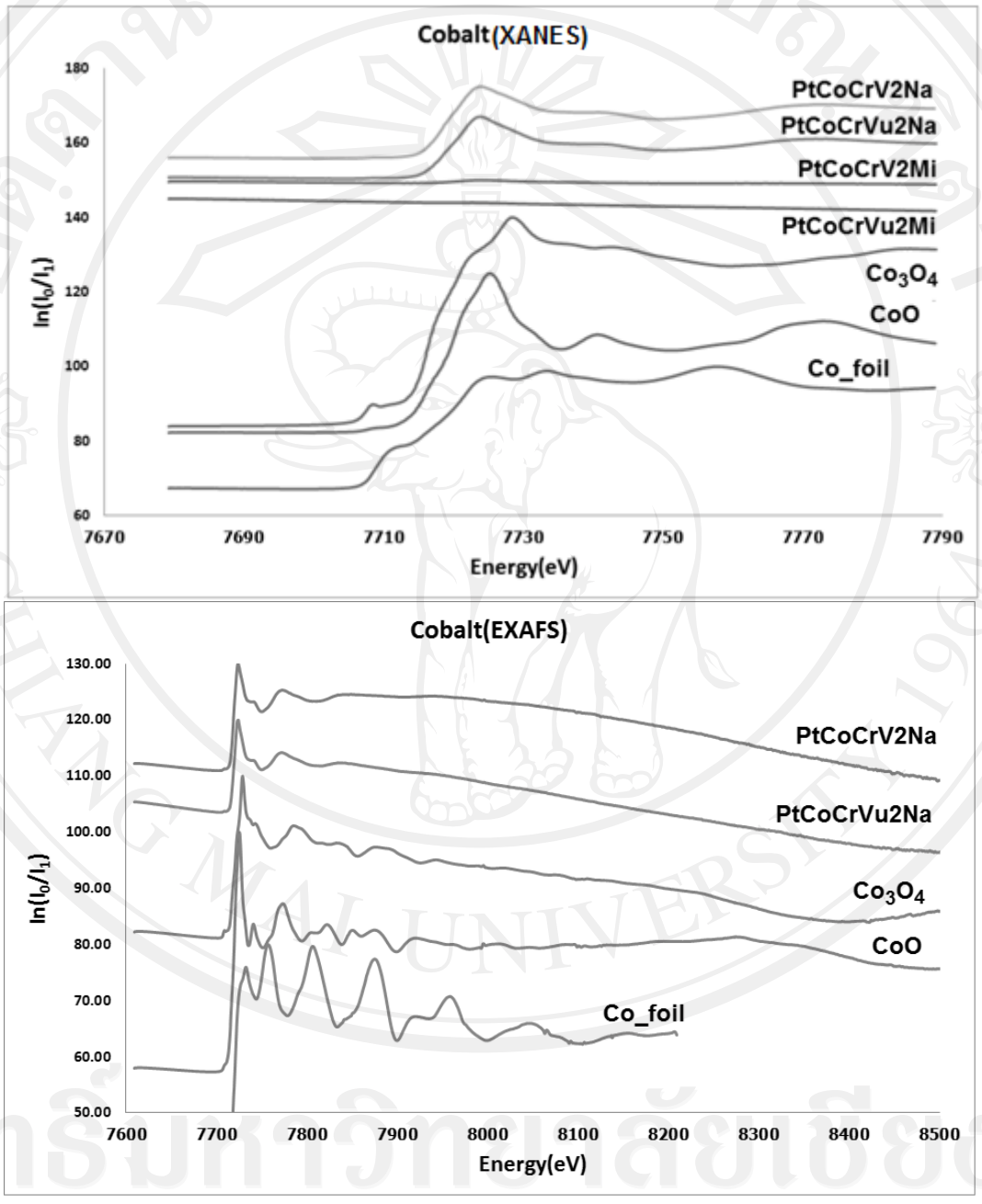

Figure 3.26 The XANES and EXAFS spectra of cobalt from catalysts supported on treated or untreated carbon by microwave and $NaBH_4$ reductionmethod compared with standard spectra of metal and metal oxides.

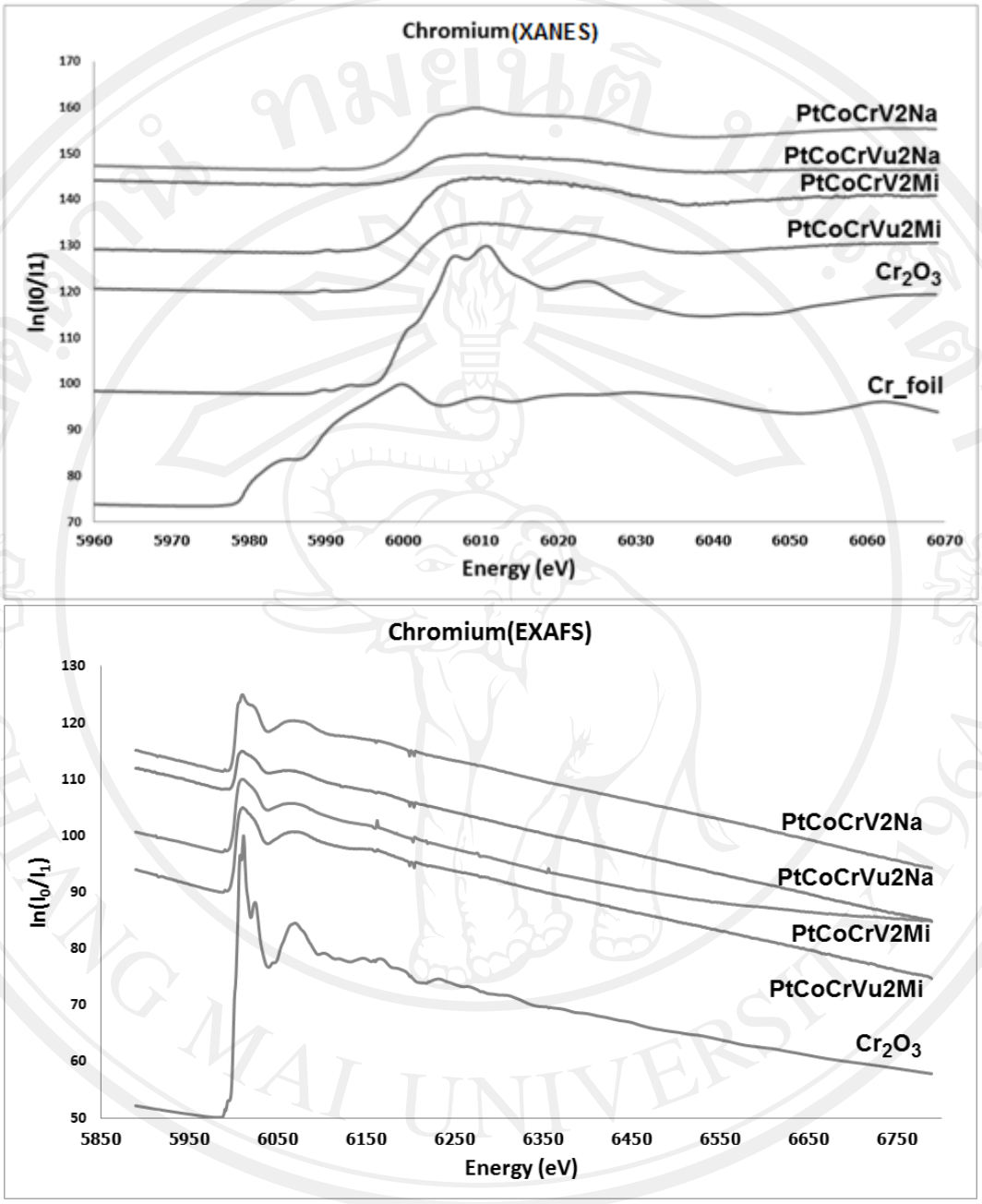

Figure 3.27 The XANES and EXAFS spectra of chromium from catalysts supported on treated or untreated carbon by microwave and $NaBH_4$ reductionmethod compared with standard spectra of metal and metal oxides.

3.2.5 Cyclic voltammetry (CV)

The electroactivities testing of the first group catalyst was investigated by CV. The comparison of voltammograms between the first group catalyst and commercial Pt/C catalystfrom Fuel Cells Scientific was performed. The CV spectrums are shown in Figure 3.28. The maximum potential, current from reduction reaction and % weight ratio were shown in Table 3.7. It can be seen thatall platinum-basedternary catalysts delivered higher current than commercial Pt/C when normalized by gram of platinum loading (weight calculation from EDS data). The PtCoCrV2Na showed highest current when comparedthe commercial Pt/C and PtCoCrV2Na, it wasfound that PtCoCrV2Nagave2 times higher currentthan commercial Pt/C. This catalyst shown highest performance because of the particle size for this catalyst was smaller than other catalysts in first group (shown in Table 3.6), particle from this catalyst was well dispersed on treated carbon surface than particle on untreated carbon(shown in Figure 3.15)and this catalyst appearedternary catalyst,Pt-CoO-Cr_2O_3(from XAS result).It can be concluded that the Pt-CoO-Cr_2O_3ternary catalyst supported on treated carbonprepared by$NaBH_4$ reduction method provided relatively higher potential than commercial catalyst. However,PtCoCrV2Na was confirmed by XAS to contain no platinum alloy catalyst. For this reason, this catalyst wasn't further tested the performanceby single cell testing.

Table 3.7Maximum potential and current from reduction reaction.

Sample	Potential (V)	Current (A/g_{Pt})	% Weight ratio (Pt:Co:Cr)
Pt/C (Fuel Cell)	0.394	14.30	20:0:0
PtCoCrVu2Mi	0.278	16.17	3.5:0:1
PtCoCrV2Mi	0.218	19.09	5.6:0:2.2
PtCoCrVu2Na	0.298	20.52	5.3:1.7:0.8
PtCoCrV2Na	0.304	28.83	6.6:3.3:2.1

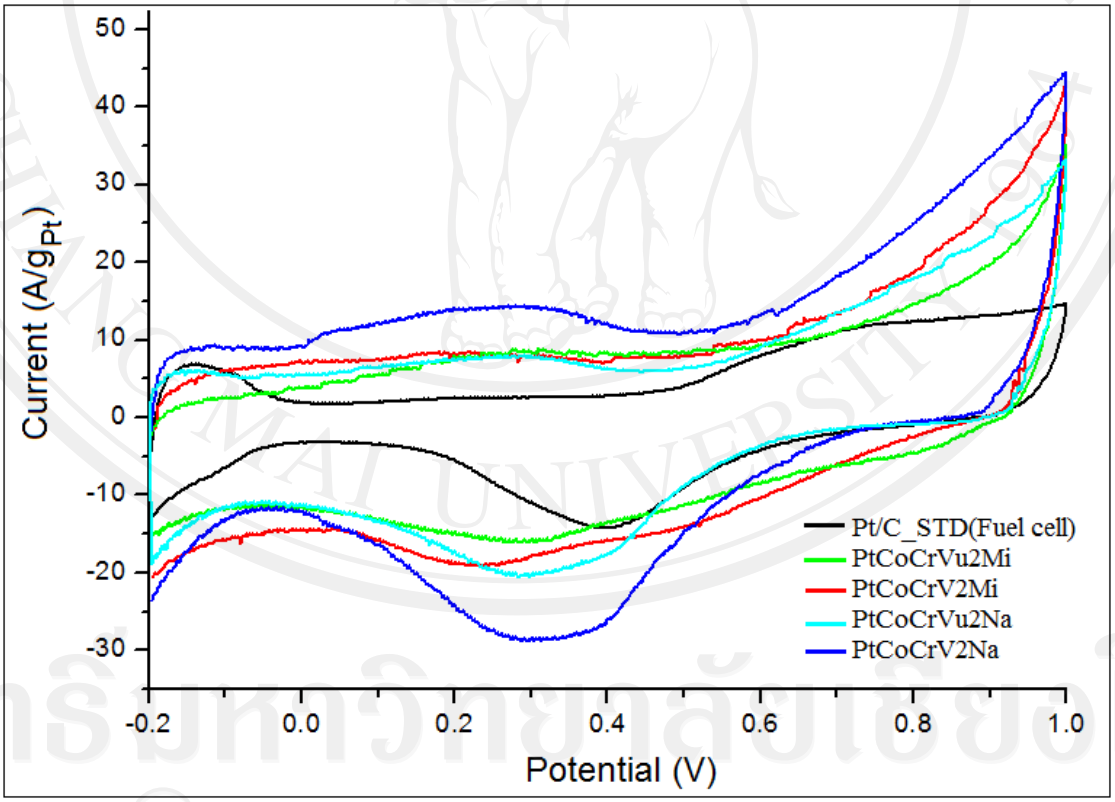

Figure 3.28 Cyclic voltammetry spectra the first group catalyst and commercial 20 % Pt/C catalyst standard from Fuel Cells Scientific.

3.2.6The single cell testing

Single cell testing was applied to study the sample PtCoCuN2Re, PtCuNiN2Na, PtCuNiN2Re, PtCuNiN6Na, PtCuNiN6Re, PtCuNiV2Na, PtCuNiV2Re, PtCuNiV6Na, and PtCuNiN6Re. These samples were confirmed by XRD and SAD patternsthat the platinum alloy ternary catalysts on supported carbon was obtained. The results of PtCoCuN2Re and standard commercial catalysts tested by single cell testing were shown in Figure 3.29. Thepolarization curve was plotted between current density and voltage. The polarization curveof standard commercial Pt/C was similar to the curve fromPtCoCu/C. At voltage of 600 mV, current density of the standard commercial andPtCoCu/C were 0.14 A/cm^2 and 0.18 A/cm^2, respectively. However, the result from this graph wasincomplete because the platinum weight between standard catalysts and prepared catalysts were notequivalent. By calculatingplatinum weight in catalysts per mole by using platinum weight fromstandard commercial as 20 %wt. and platinum weight from sample by EDS technique. The newpolarization curve was shown in Figure 3.30. This graph showed the current density of that at 600 mVthe standard commercial and PtCoCu/C as 14.81 and22.57 kA/cm^2.mol$_{pt}$, respectively. It was found that PtCoCu on treated carbon N115 performed higher performance than standard catalysts withouthydrogen-peroxide generation (Eq 3.3, 3.4). Moreover, it has high kinetic parameters such as Tafel slope and exchanged current density values [46].

$$Pt\text{-}M + O_2 + e^- \rightarrow Pt\text{-}M\text{-}O\text{-}O^- + H^+ + e^- \rightarrow Pt\text{-}M\text{-}O\text{-}OH^- \quad (3.3)$$

$$Pt\text{-}M\text{-}O\text{-}OH^- + H^+ + e^- \rightarrow Pt\text{-}M\text{-}O^- + H_2O \quad (3.4)[31]$$

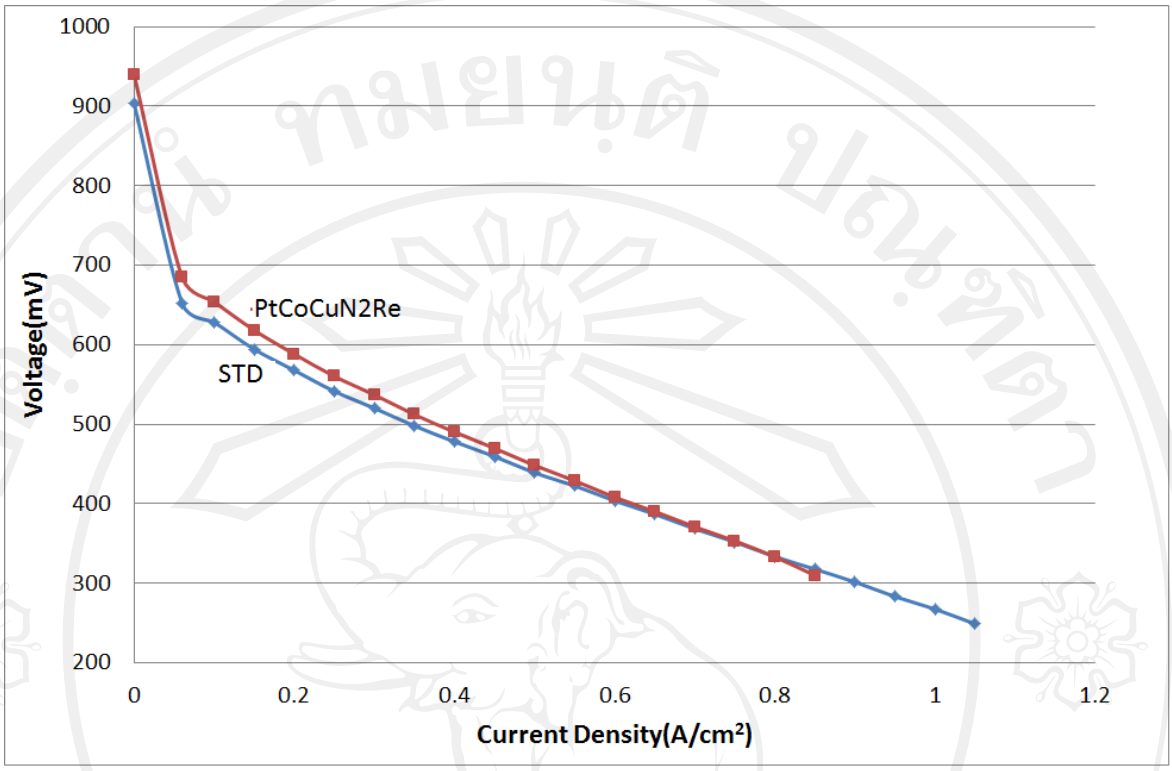

Figure 3.29Polarization curvesof standard commercial Pt/C and platinum-cobalt-copper catalysts supported on treated carbon by reflux method.

Figure 3.31showspolarization curvefrom single cell testing of standard commercial catalyst comparing with and PtCuNiN2Na, PtCuNiN2Re, PtCuNiN6Na, PtCuNiN6Re, PtCuNiV2Na, PtCuNiV2Re, PtCuNiV6Na, and PtCuNiN6Re catalysts. The current density at 600 mV, particle sizes and weight ratio (from EDS) for catalysts was shown in Table 3.8. It was found that the catalysts prepared by $NaBH_4$ reductionmethod shown higher performance than catalysts prepared by reflux method and standard commercial catalysts.The higher performance of catalysts prepared by $NaBH_4$ reductionmethod wasinfluenced by the smaller particle size than other catalysts(confirm by TEM). The fine particle catalysts performed better performance because active size was greater than large particle size catalysts [92]. The catalysts

prepared by $NaBH_4$ reductionmethod used $NaBH_4$ as a reducing agent. According to the reduction process of metal ion in Eq 1.9, if particle size of reducing agent was large, it would give more electrons to metal to grow [62]. The smaller size $NaBH_4$which dissolved in ethylene glycol, can reduce metal ion to metal and later form small size product. For reflux method which used ethylene glycol as a reducing agent, it had more electrons to donate to metal ion.

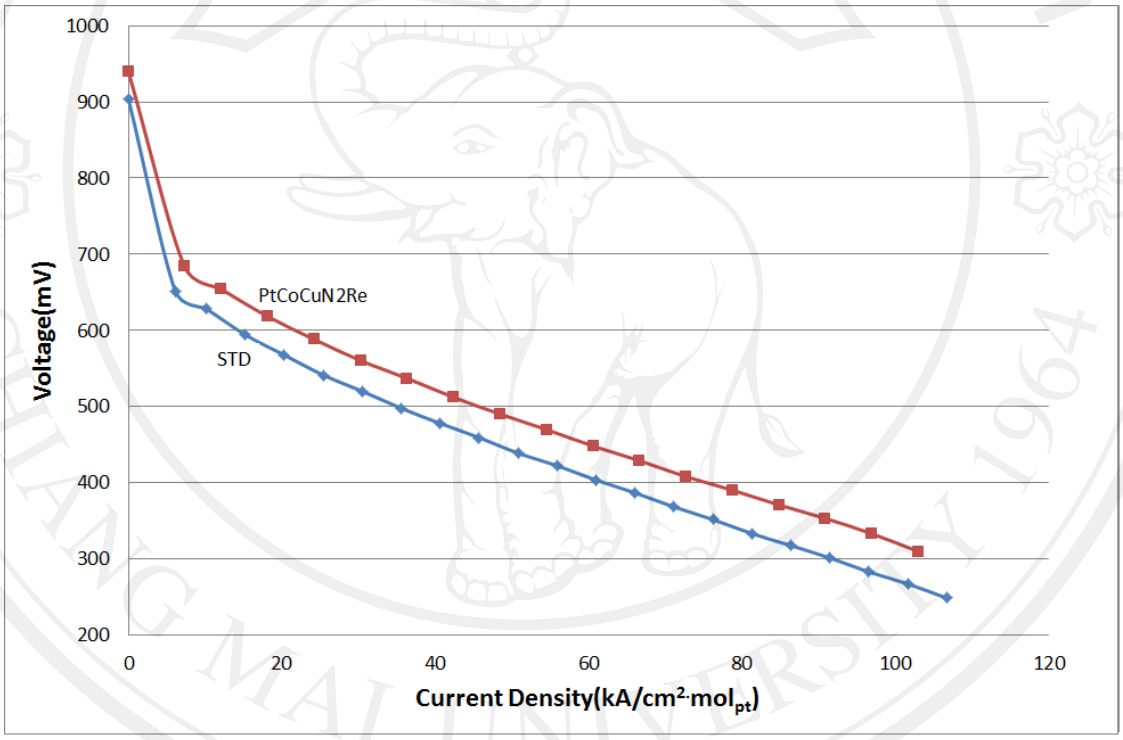

Figure 3.30Polarization curves of standard commercial Pt/C and platinum-cobalt-copper catalysts supported on treated carbon by reflux method calculated per mole platinum.

Table 3.8 Current density of catalysts at 600 mV

Sample	Current density ($kA/cm^2.mol_{pt}$)	Particle size (nm)	Weight ratio (Pt:M1:M2)
Pt/C STD	14.81	-	-
PtCoCuN2Re	22.57	4.09±0.69	10.28 : 0.17 : 5.30
PtCuNiN2Re	18.15	3.16±0.55	8.40 : 4.81 : 2.92
PtCuNiN6Re	14.81	3.46±0.88	12.34 : 2.45 : 2.56
PtCuNiV2Re	18.51	3.51±0.58	12.79 : 3.71 : 0.42
PtCuNiV6Re	24.44	3.96±0.67	10.32 : 2.18 : 0.29
PtCuNiN2Na	34.81	2.81±0.52	5.32 : 4.46 : 2.16
PtCuNiN6Na	42.96	2.75±0.56	10.17 : 1.55 : 0.27
PtCuNiV2Na	38.14	2.78±0.70	7.39 : 5.05 : 0.56
PtCuNiV6Na	54.07	2.73±0.55	9.37 : 2.72 : 1.02

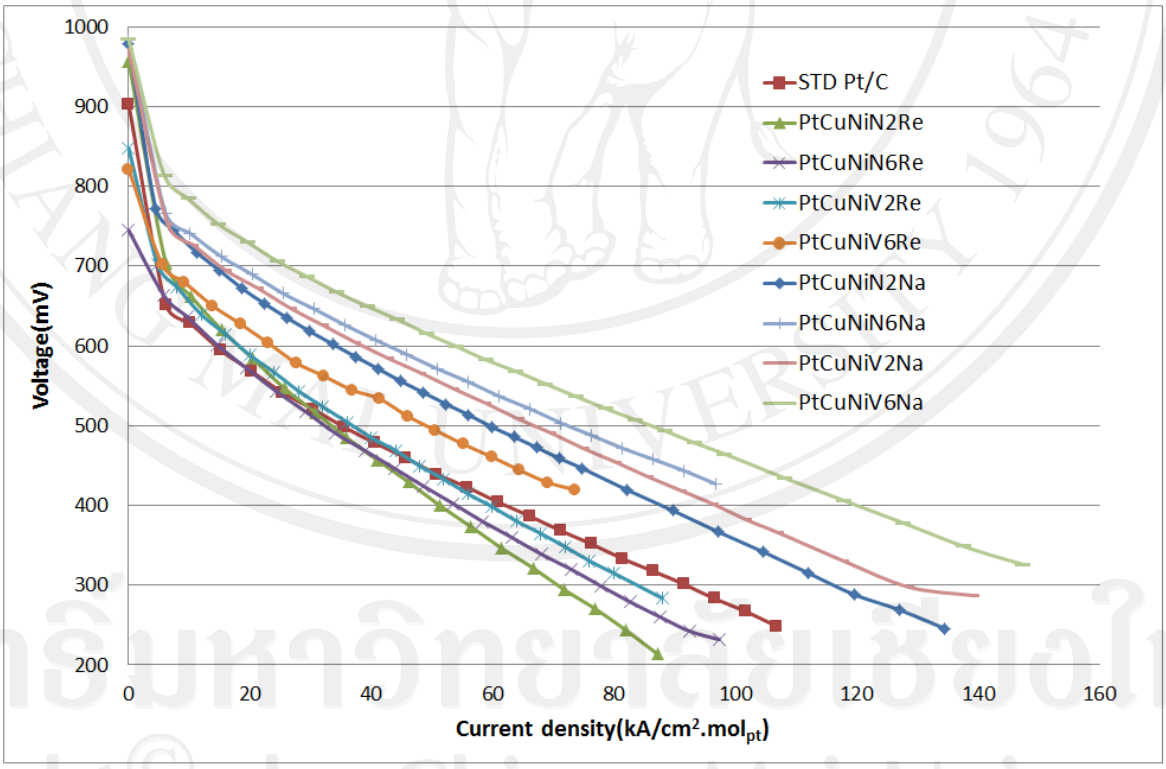

Figure 3.31Polarization curvesof standard commercial Pt/C and platinum-copper-nickel catalysts supported on treated carbons calculated permole platinum.

Considering on the platinum-copper-nickel catalysts on carbon with different composition as 6:1:1 and 2:1:1,the ratio of 6:1:1 showed higher performance because the larger amount of transition metal was considered as important factor for determining the catalyst performance. The alloy with larger transition metal has increases the catalytic activities. However, the excess of transition metal can feasibly decrease the catalytic activities [46]. In summary, the platinum-copper-nickelwith the ratio of 9:3:1 from EDS on carbon Vulcan XC-72 performed the highest performance among other catalysts in this part.

This research focused on the synthesis ofplatinum-based ternary catalysts for PEMFC cathode. The samples which were PtCoCuN2Re, PtCuNiN2Na, PtCuNiN2Re, PtCuNiN6Na, PtCuNiN6Re, PtCuNiV2Na, PtCuNiV2Re, PtCuNiV6Na, and PtCuNiN6Re,were confirmed by XRD and SAD patterns as metal alloy.The samples such as PtCoCrVu2Mi and PtCoCrV2Mi were confirmed phases as Pt-Cr_2O_3 and PtCoCrVu2Na and PtCoCrV2Nawere confirmed phases as Pt-CoO-$Cr_2O_3$by XAStechnique.These samples were not tested by single cell test station because it was not formed as metal alloy. The metals (such asPt, Co, Cr, Cu, Fe, and Ni) were found in all samples with EDStechnique. The TEM images indicated that the catalysts were well dispersed on treated carbon. The particle size of catalysts prepared by $NaBH_4$ reductionmethod was smaller than those prepared by reflux method. Comparing the catalysts fromthis research, it can be concluded that the PtCuNiV6Na catalysts with the ratio of 9:3:1 showed the highest performance at the current of54.07 $kA/cm^2.mol_{pt}$and the voltage of 600 mV. The reason is because of this catalyst was confirmed by XRD as theplatinum-based ternary alloy compaund. The composition

from this catalyst wasobserved to have appropriate ratio between platinum and other metals.