



The Investigation of Active Sites on Nickel Oxide Based Catalysts towards the *In-situ* Reactions of Methanation and Desulfurization

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The research is financed by Universiti Teknologi Malaysia and Ministry of Science, Technology and Innovation, Malaysia through IRPA Vot 79252

Abstract

Supported nickel oxide based catalysts of Fe/ Co/ Ni (10: 30: 60)-Al₂O₃ and Pr/ Co/ Ni (5: 35: 60)-Al₂O₃ that were prepared by wetness impregnation method showed potential catalysts for the in-situ reactions of H₂S desulfurization and CO₂ methanation from ambient temperature up to 300 °C. X-ray Photoelectron Spectroscopy revealed Ni₂O₃ and Fe₃O₄ as the surface active components on the Fe/ Co/ Ni (10: 30: 60)-Al₂O₃ catalyst, while Ni₂O₃ and Co₃O₄ on the Pr/ Co/ Ni (5: 35: 60)-Al₂O₃ catalyst. Energy Dispersive X-ray analysis indicated the presence of 2.7 % and 0.9 % of sulfur on the spent Fe/ Co/ Ni (10: 30: 60)-Al₂O₃ and Pr/ Co/ Ni (5: 35: 60)-Al₂O₃ catalysts, respectively. N₂ adsorption-desorption analysis showed reduction of 5.5 % on the surface area of the spent Fe/ Co/ Ni (10: 30: 60)-Al₂O₃ catalyst. However, the surface area of the spent Pr/ Co/ Ni (5: 35: 60)-Al₂O₃ catalyst increased by 8.6 %.

Keywords: Active site, Methanation, Desulfurization, Nickel oxide, Catalyst

1. Introduction

Sour crude natural gas is usually contaminated by the presence of carbon dioxide (CO₂) and hydrogen sulfide (H₂S). Catalysts for the CO₂ methanation have been extensively studied because of their application in the conversion of CO₂ gas in the presence of hydrogen to produce methane, which is the major component in natural gas. However, in real natural gas, there is also presence of H₂S which in the invention of methanation catalyst, its presence should be considered, since it could cause poisoning of the nickel catalyst.

The essential requirement for the correct selection of the oxide system is its ability to accept and to activate CO₂ and H₂S. The acidic nature of CO₂ and H₂S necessitates the employment of a catalytic system with Lewis basic properties such as Group VIII metals. According to Miao et al. (1997), the activity and selectivity of the catalysts are most probably related to the changeable valence of M⁰/ M²⁺. The major reasons for the much slower development of the catalysts science of mixed metal oxide is its significantly complexity compared with metal based catalysts e.g. possible presence of multiple oxidation states, variable local coordination, coexisting bulk and surface phases as well as different surface termination functionalities such as M-OH, M=O or M-O-M [Wachs et al., 2005].

According to Inui et al. (1979), the CO₂ methanation activity of the nickel based composite catalyst from the substrates of iron group metals following this order: Ni > Co > Fe. Nickel based catalysts are generally considered as reference methanation catalysts and proven to eliminate H₂S by desulfurization process. Song et al. (1998), who studied on the amorphous Ni-Zr alloys for methanation activity, detected Ni₂O₃ as the major Ni-containing species on the oxidized Ni₃₆Zr₆₄ surface at 250 °C. Wojcieszak et al. (2004), who worked on the mesoporous molecular sieves supported nickel catalyst for the hydrogenation of benzene, also found out the dominant nickel form on the surface of Ni impregnated AIMCM-41 catalyst was Ni₂O₃. El-Shobaky et al. (2003) observed a significant increment in the catalytic activity of NiO/ MgO system due to treatment with small amount of CoO. Souma et al. (1995) investigated that methanation seems to be accelerated by the absorption of H₂ on metallic Ni or Co. Methane formation from carbon was easier on Co (001) than on Fe (110).

In addition, it had been found by Curtis et al. (1999) that sulfur at levels above 2000 ppm would bring about poisoning effect for the supported cobalt Fischer-Tropsch catalyst. Medina et al. (2000) concluded that carbon dioxide hydrogenation on Fe has the advantage of no catalyst deactivation. Based on the mechanism of the Fischer-Tropsch synthesis involving unreduced iron catalyst [Blanchard et al., 1982], it is attractive to consider the oxidized state of iron

as the active phase in Fischer-Tropsch synthesis. It is of interest to note that the partially pre-reduced catalyst containing Fe_3O_4 as a major phase was more active than the catalyst pre-reduced to $\alpha\text{-Fe}^{2+}$. Previous research showed that Pr_6O_{11} is the most active oxide among rare earth metals because praseodymium possesses stable multiple oxidation state [Wang et al., 2002]. The addition of increasing amounts of Pr_6O_{11} caused the conversion rate of side product to decrease with an apparent minimum.

The objective of this research is to assign the active sites of the nickel oxide based catalysts. The nickel oxide based catalysts should be capable to achieve both low temperature and high conversion of sour gases to be applicable in gas industry. At low temperature, application of the novel catalyst in gas industry is more likely. It is a challenge to propose the active sites for in-situ reactions of methanation and desulfurization to facilitate future studies.

2. Materials and Methods

2.1 Preparation of Catalysts

$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ produced by GCE Laboratory Chemicals was dissolved with minimum amount of distilled water. Mixed catalysts solution was prepared by mixing appropriate amount of metal nitrate salts. Wet impregnation method was used to prepare Al_2O_3 supported catalyst by impregnating the catalyst solution on Al_2O_3 beads (MERCK Eurolab) support for 15 minutes. It was then dried at 80°C for 24 hours and calcined in air at 400°C for 5 hours.

2.2 Characterization of catalysts

XPS analysis was done by using Kratos instrument XSAM HS surface analysis spectrometer with Mg $K\alpha$ X-ray source (1253.6 eV). Sample was introduced into the spectrometer in flowing argon atmosphere, and evaporated at least 6×10^9 Torr before spectrum was recorded. The spectrum was taken at 10 mA and 14 kV energy source at 2 sweeps. For EDX analysis, sample was scanned using Zeiss Supra 35 VP FESEM operating of 15 kV couple with EDX analyzer. The catalyst sample was bombarded by electron gun with tungsten filament under 25 kV resolution. N_2 adsorption-desorption isotherms for the catalysts were measured by Micromeritics ASAP 2010. All samples were evacuated at 120°C prior to the measurement.

3. Results and Discussion

3.1 Characterization of Catalysts

3.1.1 X-ray Photoelectron Spectroscopy (XPS)

XPS is a unique surface sensitive technique for chemical analysis. Figure 1 shows the XPS spectra resulted from wide scan in the region of 0-1100 eV, while Figure 2 reveals high resolution XPS spectra obtained over fresh and spent Pr/Co/Ni (5: 35: 60)- Al_2O_3 catalysts. Table 1 depicts the parameters obtained by deconvolution of XPS spectra for these two catalysts.

1.57 % of Ni was detected in the surface composition of fresh Pr/Co/Ni (5: 35: 60)- Al_2O_3 catalyst. The binding energies of Ni ($2p$) were characteristic of NiO at the E_b of 854.21 eV ($2p_{3/2}$) and 871.72 eV ($2p_{1/2}$), similar assignment of NiO to the data obtained made by Lorenz et al. (1979) who studied XPS on NiO/ SiO_2 and NiO- Al_2O_3 / SiO_2 catalysts; and Nefedov et al. (1975) who investigated on some coordination compounds. E_b value of 529.41 eV resulted from the deconvolution of O ($1s$) also confirmed the existence of NiO. However, the existence of Ni ($2p$) peak at E_b of 856.83 eV ($2p_{3/2}$) and 874.30 eV ($2p_{1/2}$) is attributed to the existence of Ni^{3+} in Ni_2O_3 . According to Nascente who worked on Ni/ Pd thin metallic film, E_b of 856 eV was corresponding to Ni_2O_3 . Alumina supported nickel oxide calcined at 350°C also revealed the characteristic peak corresponding to Ni^{3+} at $E_b = 856.9$ eV [Salagre et al., 1996]. The most intense peak at E_b of 531.52 eV resulted from deconvolution of O ($1s$) over the fresh catalyst also referred to the existence of Ni_2O_3 and Al_2O_3 . Ni^{3+} showing a higher binding energy because the E_b of the metal increases when the covalency decreases [Vederine et al., 1978]. In other words, as the ionic radius of $\text{Ni}^{2+} > \text{Ni}^{3+}$ and furthermore the covalency of Ni^{3+} decreases compare to Ni^{2+} . Ni^{3+} is known to be more reactive than Ni^{2+} due to its higher metallic property. Ni_2O_3 is suggested to be responsible as active site for this catalyst. By observing $2p_{3/2}$ peak area, the existence of NiO was observed as 31 % more than Ni_2O_3 . When NiO was more dominant on the fresh Pr/Co/Ni (5: 35: 60)- Al_2O_3 catalyst, low catalytic activity was observed. It is presumed that the lower H_2S desulfurization activity over Pr/Co/Ni (5: 35: 60)- Al_2O_3 catalyst at reaction temperature below 200°C was due to lack of Ni_2O_3 , which is an oxygen rich compound. Ni_2O_3 structure is believed to play an important role in the nickel cation reduction and the oxygen release process [Yoon et al., 2006]. This suggestion is further supported when the dominant nickel form on the surface of Ni impregnated AlMCM-41 catalyst was found out to be Ni_2O_3 [Wojcieszak et al., 2004]. This oxidized phase served as a matrix which decreased the Ni atoms agglomeration.

After exposure towards the catalytic testing environment, the surface composition of Ni^{3+} was increased to 2.28 %. The existing peaks were attributed to Ni^{3+} in Ni_2O_3 species at the E_b value of 856.80 eV ($2p_{3/2}$) and 874.32 eV ($2p_{1/2}$). NiO was disappeared in the spent catalyst. This was also supported by 59 % reduction of peak area on the O ($1s$) peak at 529.73 eV. It is believed that NiO was transformed into Ni_2O_3 during prolong catalytic testing process. Similar

phenomenon was also reported by Djaidja et al., (2000) where NiO phase was disappeared in their used Ni/ Sm₂O₃ and Ni/ La₂O₃ catalysts. They suggested that Ni₂O₃ phase is necessary in the oxidative transformation of methane reaction course. Dong et al., (1998) had also observed the growth of Ni₂O₃ layers on the surface of Ni particles after exposure in a mixture of H₂ and Ar gas atmosphere of 760 Torr. No NiO phase was detected by them. The absence of NiO is presumably responsible for the increasing of the catalytic performance over this catalyst at maximum study temperature of 300 °C.

There was 0.49 % of Co revealed in the surface composition of fresh Pr/ Co/ Ni (5: 35: 60)-Al₂O₃ catalyst. Binding energies of 779.79 eV (*2p*_{3/2}) and 793.96 eV (*2p*_{1/2}) suggesting the presence of spinel compound, Co₃O₄, on the surface of the catalyst. This is in good agreement with Kim (1975) who studied the electronic structure of cobalt oxides and Zeng et al. (1995) who worked on the effect of ZrO₂ matrix on surface Co₃O₄-CO position. The presence of Co₃O₄ is supported by the O (1s) peak at *E*_b value of 529.41 eV, which was also suggested by Natile and Glisenti (2003) who studied on NiO/ Co₃O₄ nanocomposite catalyst. NO₂ formed during the decomposition of Co(NO₃)₂•6H₂O during preparation could oxidize Co²⁺ to Co³⁺ even at low calcination temperature. Once oxidized, the Co ions have a high tendency to form Co₃O₄ [Arnoldy and Moulijn et al., 1985]. The existence of the spinel compound in the catalyst is presumed to be good for the catalytic efficiency as it provides more active sites for the reaction and also it could be easily changed forms according to the environment; whether it is more to Co²⁺ or Co³⁺. After catalytic testing, the Co (*2p*) peaks shifted to a higher *E*_b of 781.70 eV (*2p*_{3/2}) and 796.11 eV (*2p*_{1/2}), but indicating no changes of Co oxidation state on the surface of the catalyst. The O (1s) peak remained in the same region, at *E*_b of 529.73 eV, with 59 % reduction of peak area. This peak is attributed to the existence of Co₃O₄ only. This reduction on peak area was due to the disappearance of NiO. 0.48 % of Co was still observed on the spent catalyst surface. In this stage, an optimum amount of Co spinel compound is presumed to be the reason for the increasing of the catalytic activity [Zhang et al., 2002].

There are two Al (*2p*) peaks obtained from the fresh Pr/ Co/ Ni (5: 35: 60)-Al₂O₃ catalyst, indicating the existence of Al in two different environments. At *E*_b value of 74.70 eV, it is attributed to Al₂O₃. The O (1s) peak at 531.52 eV also referred to the existence of Al₂O₃. When Al atom is on the outermost surface, the influence of the surrounding chemical environment on Al *2p* spectrum is significant. On the outer surface, alumina is in contact with atmosphere and absorbed water. Therefore, the surrounding chemical environment of alumina on the outer surface is different from that in inner layer [Zheng et al., 2008]. This contributed to the formation of Al³⁺-OH which was shown at *E*_b of 76.63 eV. As the binding energy increases, so does the ionic character of the bonding. Wojcieszak et al. (2004) also observed similar XPS result from their AIMCM-41 support. Al₂O₃ (*E*_b 75 eV) was assigned to framework aluminium species and to extra framework Al³⁺ (*E*_b 77.5 eV). The extra framework Al³⁺ species is easily affected by the surrounding environment. Adsorbed water on the catalyst surface or Al³⁺ with the surface hydroxyl was observed at the O (1s) *E*_b value of 533.19 eV. However, only one peak was detected at *E*_b value of 74.11 eV on the spent catalyst. It is attributed to the existence of Al₂O₃. The detected weight percentage of Al also decreased in the spent catalyst compared to the fresh catalyst; in agreement with the only peak existed in the spent catalyst. After exposure to the catalytic testing environment, the increment of O (1s) peak area at 533.62 eV is due to the adsorbed water on the surface, one of the products from methanation reaction.

From the surface composition detected by XPS, 0.09 % of Pr was revealed on the surface of fresh Pr/ Co/ Ni (5: 35: 60)-Al₂O₃ catalyst. After catalytic activity measurement, the percentage of Pr was reduced to 0.02 %. This reduction would be either due to the deposition of sulfur, or agglomeration of other elements that forced the Pr element to move into the bulk of the catalyst.

Figure 3 depicts XPS spectra resulted from wide scan in the region of 0 - 1100 eV and the high resolution XPS spectra over fresh Fe/ Co/ Ni (10: 30: 60)-Al₂O₃ catalyst is shown in Figure 4. The atomic concentration of Ni detectable by XPS was low (0.93%), indicating the partial surface encapsulation of Ni in the alumina support [Salagre et al., 1996]. The Ni (*2p*_{3/2}) and Ni (*2p*_{1/2}) peaks at *E*_b = 856.67 eV and 874.37 eV are registered in the XPS spectra of Ni *2p* level of the fresh Fe/ Co/ Ni (10: 30: 60)-Al₂O₃ sample, respectively. This assignment is similarly as been suggested by Nascente (2005) and Salagre (1996). The O (1s) peak at *E*_b = 531.77 eV over fresh Fe/ Co/ Ni (10: 30: 60)-Al₂O₃ catalyst is attributed to the existence of O²⁻ in Ni₂O₃. Ni₂O₃ could act as an active site for oxidation reaction because its oxygen storage property is needed for the H₂S desulfurization reaction. It is known that the presence of Ni³⁺ may enhance the p-type character (oxygen rich) of the catalyst.

0.66 % of Fe was revealed in the surface composition. The oxides of α-Fe₂O₃, γ-Fe₂O₃ and Fe₃O₄ have almost identical core binding energies, but the absence of satellite peak had confirmed that the *E*_b at 711.45 eV (*2p*_{3/2}) and 725.09 eV (*2p*_{1/2}) is due to Fe₃O₄. This is also supported by the appearance of O 1s peak at *E*_b of 530.05 eV. This assignment is in good agreement with McIntyre and Zetaruk (1977), who studied iron oxides with XPS and Yamashita and Hayes (2007), who had analyzed XPS spectra of Fe²⁺ and Fe³⁺ ions in oxide materials. It is believed that spinel compound of Fe₃O₄ is good for the catalytic reaction as it able to provide more active sites. Based on the mechanism of the Fischer-Tropsch

synthesis involving unreduced iron catalyst [Blanchard., 1982], it is attractive to consider the oxidized state of iron as the active phase in Fischer-Tropsch synthesis. It is of interest to note that the partially pre-reduced catalyst containing Fe_3O_4 as a major phase was more active than the catalyst pre-reduced to $\alpha\text{-Fe}^{2+}$. According to Iyer et al. (2006), Fe_3O_4 was also reported as active phase in their enhanced hydrogen production integrated with CO_2 separation.

There are two peaks indicating Al^{3+} in Al_2O_3 ($E_b = 74.11$ eV) and $\text{Al}^{3+}\text{-OH}$ ($E_b = 76.30$ eV) on the fresh Fe/ Co/ Ni (10: 30: 60)- Al_2O_3 catalyst. When Al is on the outermost surface, it is in contact with atmosphere and absorbed water thus resulting in higher E_b .

Merely 0.08 % of cobalt was revealed in the surface composition compared to 0.66 % of iron. Similar condition was also detected by Kozhukharov et al. (2003), where the Co $2p$ partial contribution was not well expressed when there was presence of iron. It is believed that Co ions react with the substrates during the calcination and sintering process. Part of them being high chemical mobility and reactivity are incorporated into the bulk of the support. Furthermore, previous study suggested that the sorption affinity of cations depends not only on the valence of the cations but also on their radius. The ionic radii of Co^{2+} and Co^{3+} are 74 pm and 61 pm while Fe^{2+} and Fe^{3+} are 78 and 65 pm [Weast and Selby, 1966]. The smaller radii of the Co ions could disperse highly into the matrix and penetrate deeper into the support. Therefore, results in lower surface concentration of Co. The synthesis of highly dispersed Co catalysts requires the initial formation of very small CoO or Co_3O_4 crystallites. The formation of these small oxide clusters in turn requires strong interactions between the support and the Co precursor [Iglesia, 1997]. Because the mean free path of electrons in solids is very small, the detected electrons originate from only the top few atomic layers. While ionization occurs to a depth of a few micrometers, only those electrons that originate within tens of angstroms below the solid surface can leave the surface without energy loss [Moulder et al., 1992].

3.1.2 Energy Dispersive X-ray Analysis (EDX)

As shown in Table 2, there was presence of 0.94 % of sulfur on the spent Pr/ Co/ Ni (5: 35: 60)- Al_2O_3 catalyst. Lower percentage of sulfur deposited on the catalyst demonstrated less deactivation effect over this catalyst compared to the Fe/ Co/ Ni (10: 30: 60)- Al_2O_3 catalyst. This also indicates that Pr/ Co/ Ni (5: 35: 60)- Al_2O_3 catalyst is more resistance to sulfur poisoning. Only 0.04 % of Pr was revealed on the fresh Pr/ Co/ Ni (5: 35: 60)- Al_2O_3 catalyst. After catalytic testing, the surface composition of Pr increased to 0.12 %. NiO was known to appear over the fresh catalyst from XPS analysis. At this stage, it is believed that NiO with larger ionic radii accommodated on the surface. Pr and Ni_2O_3 are presumed to be located in the deeper bulk structure. Therefore, the overall surface composition of Pr was revealed in small percentage. On the spent catalyst, depletion of Ni^{2+} to Ni^{3+} pushed the Ni migrated into the bulk structure. Hence, Pr could be revealed in larger surface composition when NiO was transformed into Ni_2O_3 . Although there is deposition of 0.94 % of sulfur, Pr still can be revealed as higher percentage. The catalytic activity over this catalyst is believed to be increased dramatically when NiO had been transformed into Ni_2O_3 .

EDX analysis shows that the composition of Fe on the fresh Fe/ Co/ Ni (10: 30: 60)- Al_2O_3 catalyst is 3.12 %, higher than Co that composed of 2.26 % only (Table 3). Theoretically, the surface composition of Co should be higher than Fe by referring to the loading of metal with ratio of Fe: Co: Ni = 10: 30: 60. This phenomenon was also observed from the XPS analysis. 0.66 % of Fe was revealed while only 0.08 % of Co was detected on the fresh Fe/ Co/ Ni (10: 30: 60)- Al_2O_3 catalyst by XPS. It is believed that Co ions with higher chemical mobility and reactivity were incorporated into the bulk of the support and Fe ions with higher atomic radii were stayed on the surface of the catalyst. Besides that, Co is presumed to be dispersed homogeneously into the bulk matrixes. From EDX analysis over the spent Fe/ Co/ Ni (10: 30: 60)- Al_2O_3 catalyst, 2.13 % reduction on the surface composition of Fe was revealed. It is believed that the deposition of 2.68 % of sulfur suppressed the agglomeration of Fe on the catalyst surface, as such forced Fe to migrate into the bulk matrixes. In addition, the surface composition of Ni and Co also shows reduction of 1.00 % and 0.45 %, respectively. Sulfur is known to poison the catalyst and lead to the deactivation effect. The catalytic activity over this catalyst gradually decreased after maximum conversion of 16 % of CO_2 at 120 °C. Al from the support dominated the surface area. This means that the catalyst was not distributed evenly on the surface or had been absorbed into the pores of the support due to the high surface area and porosity of Al_2O_3 support.

3.1.3 Nitrogen Adsorption Analysis

From Table 4, the surface area of the spent Pr/ Co/ Ni (5: 35: 60)- Al_2O_3 catalyst is 8.6 % higher than the surface area of its fresh catalyst. As such for this catalyst, it can be concluded that the increment of the surface area, did increase the catalytic activity of the Pr/ Co/ Ni (5: 35: 60)- Al_2O_3 catalyst at higher temperature (300 °C). By referring to the XPS analysis, it was known that Co ions with high mobility were incorporated into the bulk of the support when there was presence of Fe ions. For the Pr/ Co/ Ni (5: 35: 60)- Al_2O_3 catalyst, Co ions were detected as spinel compound of Co_3O_4 on the surface. Therefore, Co_3O_4 is presumed to give contribution on the increment of surface area over this catalyst. Besides that, NiO was present in the fresh Pr/ Co/ Ni (5: 35: 60)- Al_2O_3 catalyst but disappeared after catalytic testing. The transformation of NiO into Ni_2O_3 is believed to be able to generate new active sites for the in-situ reactions of methanation and desulfurization. Consequently, the surface area is increased when there is generation of new active

sites. The average pore diameter of Pr/ Co/ Ni (5: 35: 60)-Al₂O₃ catalyst, increases in accordance with the increased in surface area. The enlargement of pore diameter over the spent catalyst is believed to be resulted by from the collapsed of pores during the in-situ reactions of CO₂ methanation and H₂S desulfurization.

However, the BET surface area over the spent Fe/ Co/ Ni (10: 30: 60)-Al₂O₃ catalyst shows 5.5 % reduction. This reduction is believed to be resulted from the deposition of sulfur on the catalyst surface or collapsed of the pores during prolong catalytic reaction. The smaller pore diameter shown by spent catalyst also proved the blockage of the pores by sulfur. Catalytic activity over this catalyst also decreased after reaching maximum 16.5 % conversion of CO₂ at 120 °C. The BET surface area is presumed to be reduced when there is no generation of new active sites. No transformation of active species occurred during the catalytic reaction as reported by XPS analysis.

4. Conclusion

XPS analysis, suggested that Ni₂O₃ and Co₃O₄ are the probable active sites on the Pr/ Co/ Ni (5: 35: 60)-Al₂O₃ catalyst. Meanwhile, Ni₂O₃ and Fe₃O₄ acted as the active phases on the Fe/ Co/ Ni (10: 30: 60)-Al₂O₃ catalyst. However, further investigation is still needed to support the present postulation of the active sites which are responsible to catalyze high CO₂ methanation rate at low temperature in the presence of H₂S, which is a deactivation source.

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Table 1. Parameters obtained by deconvolution of XPS spectra for fresh and spent Pr/ Co/ Ni (5: 35: 60)-Al₂O₃ catalysts.

Catalyst	Phase	Ni 2p _{3/2}	Ni 2p _{1/2}	Co 2p _{3/2}	Co 2p _{1/2}	Al 2p	O 1s
Pr/ Co/ Ni (5:35:60)-Al ₂ O ₃ (Fresh)	NiO	854.21	871.72				529.41
	Ni ₂ O ₃	856.83	874.30				531.52
	Co ₃ O ₄			779.79	793.96		529.41
	Al ₂ O ₃					74.70	531.52
	Al ³⁺ -OH					76.63	533.19
	Surface water						533.19
Pr/ Co/ Ni (5:35:60)-Al ₂ O ₃ Spent	Ni ₂ O ₃	856.80	874.32				531.78
	Co ₃ O ₄			781.70	796.11		529.73
	Al ₂ O ₃					74.11	531.78
	Surface water						533.62

Table 2. Comparison of elemental composition over the fresh and spent Pr/ Co/ Ni (5: 35: 60)-Al₂O₃ catalysts through EDX analysis.

Catalyst	Atomic ratio (%)					
	Pr	Co	Ni	Al	O	S
Pr/ Co/ Ni (5: 35: 60)-Al ₂ O ₃ (Fresh)	0.04	2.34	3.51	30.35	60.08	-
Pr/ Co/ Ni (5: 35: 60)-Al ₂ O ₃ (Spent)	0.12	2.36	3.15	27.31	62.84	0.94

Table 3. Comparison of elemental composition over the fresh and spent Fe/ Co/ Ni (10: 30: 60)-Al₂O₃ catalysts through EDX analysis.

Catalyst	Atomic ratio (%)					
	Fe	Co	Ni	Al	O	S
Fe/ Co/ Ni (10: 30: 60)-Al ₂ O ₃ (Fresh)	3.12	2.26	4.66	25.16	60.77	-
Fe/ Co/ Ni (10: 30: 60)-Al ₂ O ₃ (Spent)	0.99	1.81	3.66	24.74	64.01	2.68

Table 4. BET surface area and BJH desorption average pore diameter of the fresh and spent forms of Fe/ Co/ Ni (10: 30: 60)-Al₂O₃ and Pr/ Co/ Ni (5: 35: 60)-Al₂O₃ catalysts.

Catalyst	Condition	S _{BET} (m ² g ⁻¹)	d (nm)
Fe/ Co/ Ni (10: 30: 60)-Al ₂ O ₃	Fresh	175.01	9.24
Fe/ Co/ Ni (10: 30: 60)-Al ₂ O ₃	Spent	165.37	5.12
Pr/ Co/ Ni (5: 35: 60)-Al ₂ O ₃	Fresh	166.22	5.63
Pr/ Co/ Ni (5: 35: 60)-Al ₂ O ₃	Spent	180.45	5.88

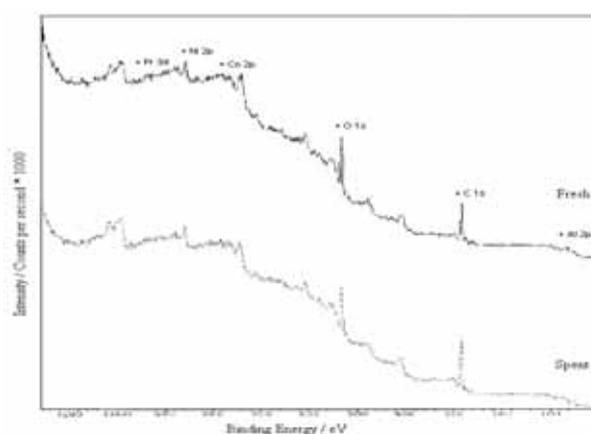


Figure 1. XPS spectra resulted from wide scan of fresh and spent Pr/ Co/ Ni (5: 35: 60)-Al₂O₃ catalysts.

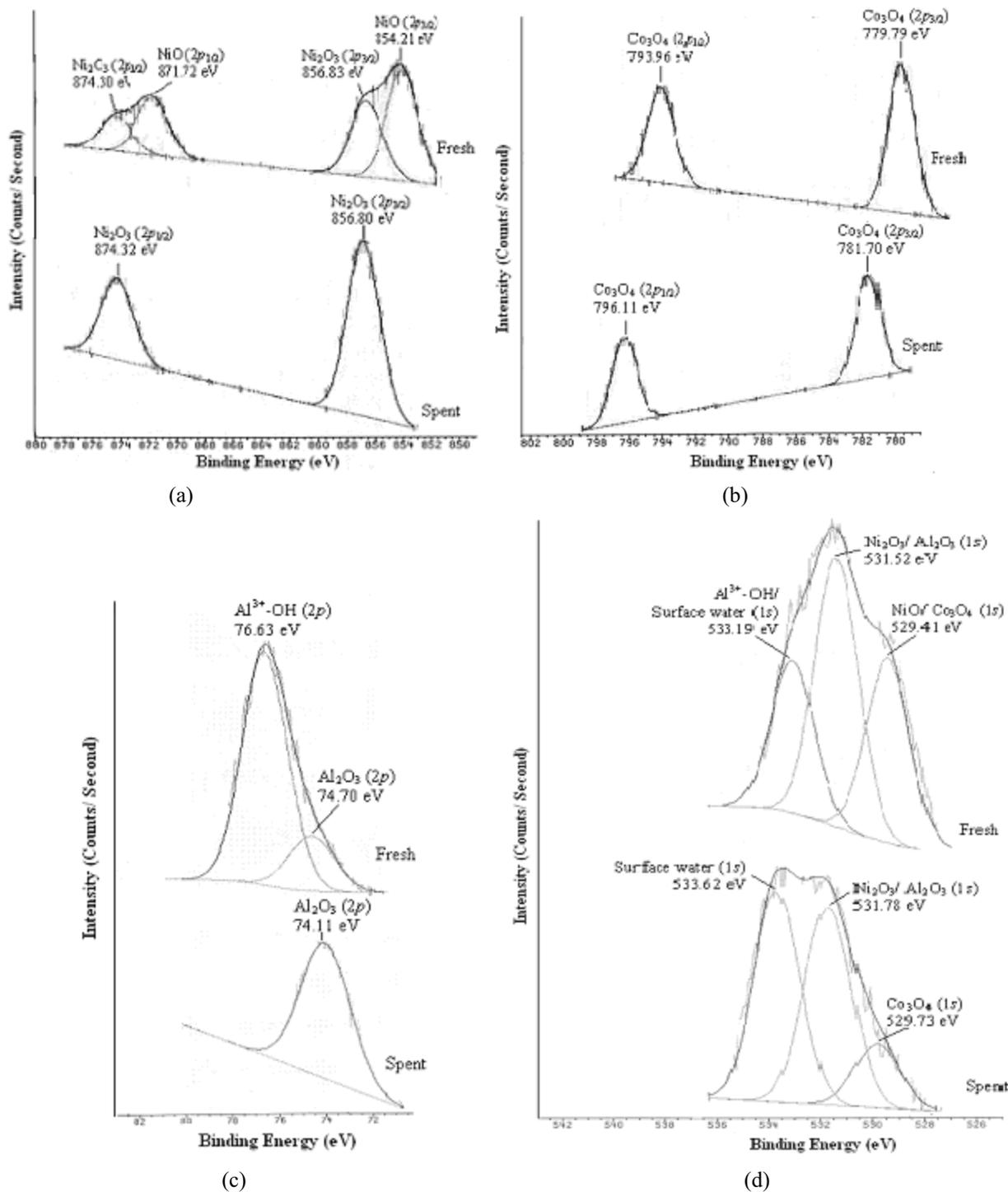


Figure 2. High resolution (a) Ni 2p; (b) Co 2p; (c) Al 2p; and (d) O 1s XPS spectra obtained from fresh and spent Pr/Co/Ni (5: 35: 60)-Al₂O₃ catalysts.

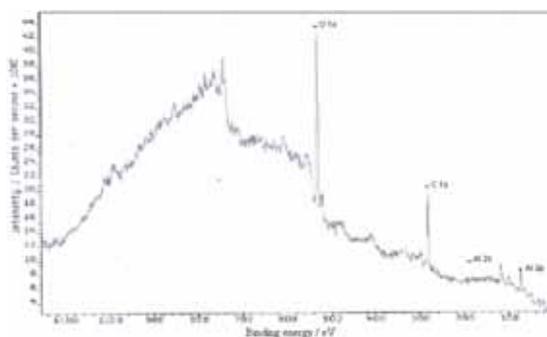


Figure 3. XPS spectra resulted from wide scan of fresh Fe/ Co/ Ni (10: 30: 60)-Al₂O₃ catalyst

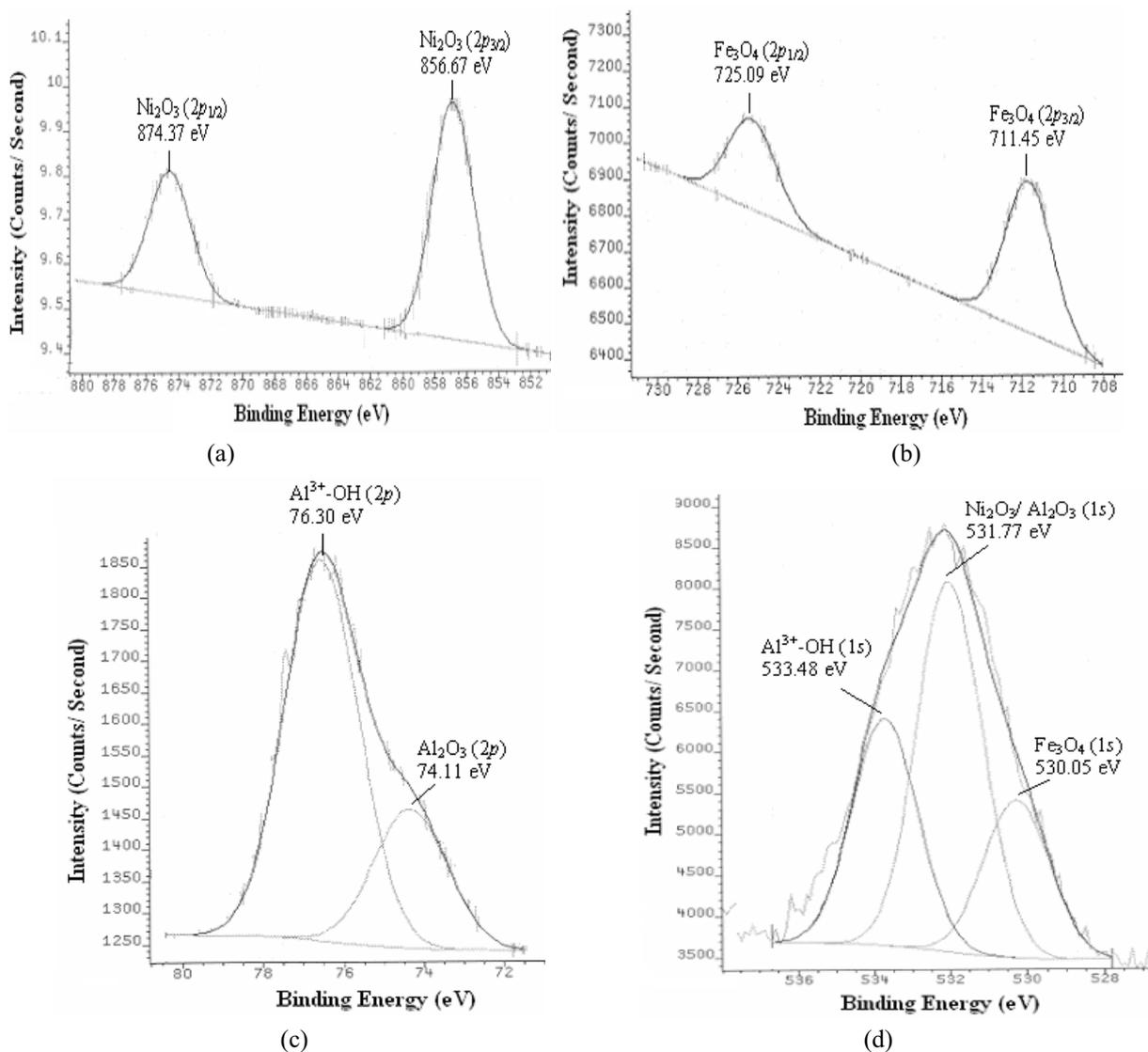


Figure 4. High resolution (a) Ni 2p; (b) Fe 2p; (c) Al 2p; and (d) O 1s XPS spectra obtained from fresh Fe/ Co/ Ni (10: 30: 60)-Al₂O₃ catalyst.