Research Article

Novel Nano- $\text{Fe}_2\text{O}_3\text{-Co}_3\text{O}_4$ Modified Dolomite and Its Use as Highly Efficient Catalyst in the Ozonation of Ammonium Solution

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Catalytic ozonation is a new method used for removal of NH_4OH solution. Therefore, high catalytic performance (activity and selectivity) should be achieved. In this work, we report the synthesis and catalytic performance of $\text{Fe}_2\text{O}_3\text{-Co}_3\text{O}_4$ modified dolomite in the catalytic ozonation of NH_4OH solution. Dolomite was successfully activated and modified with Fe_2O_3 and Co_3O_4 . Firstly, dolomite was activated by heating at 800°C for 3 h and followed by KOH treatment. Activated dolomite was modified with Fe_2O_3 by the atomic implantation method using FeCl_3 as Fe source. Fe_2O_3 modified dolomite was further modified with Co_3O_4 by precipitation method. The obtained catalysts were characterized by X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), energy-dispersive X-ray spectroscopy (EDS), scanning electron microscopy (SEM), N_2 adsorption-desorption (BET), and temperature-programmed reduction ($\text{H}_2\text{-TPR}$). From SEM image, it was revealed that nano- Fe_2O_3 and Co_3O_4 particles with the size of 80–120 nm. Catalytic performance of activated dolomite, Fe_2O_3 modified dolomite, and $\text{Fe}_2\text{O}_3\text{-Co}_3\text{O}_4$ modified dolomite in catalytic ozonation of NH_4^+ solution was investigated and evaluated. Among 3 tested catalysts, $\text{Fe}_2\text{O}_3\text{-Co}_3\text{O}_4$ modified dolomite has the highest NH_4^+ conversion (96%) and N_2 selectivity (77.82%). Selectivity toward N_2 over the catalyst was explained on the basis of bond strength M-O in oxides through the standard enthalpy ΔH_f° of oxide. Catalyst with lower ΔH_f° value has higher N_2 selectivity and the order is the following: Co_3O_4 (ΔH_f° of 60 kcal (mole O)) $>$ Fe_2O_3 (ΔH_f° of 70 kcal (mole O)) $>$ MgO (ΔH_f° of 170 kcal (mole O)). Moreover, high reduction ability of $\text{Fe}_2\text{O}_3\text{-Co}_3\text{O}_4$ modified dolomite could improve the N_2 selectivity by the reduction of NO_3^- to N_2 gas.

1. Introduction

Agricultural and industrial effluents containing ammonia ($\text{NH}_4^+\text{-N}$) discharged from production operation, dairy processor, and fertilizer plants could reduce water quality and cause a danger to human health [1]. Methods for removal of NH_4OH solution such as biological nitrification processes, ion exchange, membrane separation, chlorination, and catalytic degradation have often been used [2–6]. However, ion exchange and membrane separation methods require expen-

sive operating costs and can cause secondary pollution, while biological methods require a long treatment time and strict operation control [3–5]. An alternative approach is the catalytic ozonation. Liu et al. investigated the employing of MgO as an effective catalyst for the catalytic ozonation of NH_4^+ solution. This MgO catalyst exhibited high NH_4OH conversion (95%) but the N_2 selectivity was very low; nitrites and nitrates were the main products [6]. Ichikawa et al. have examined a series of metal oxides such as MgO , Co_3O_4 , Fe_2O_3 , and CuO for catalytic ozonation of NH_4^+ ion to

nitrogen gas (N_2O , N_2) and found that Co_3O_4 exhibited the highest N_2 selectivity as compared to that of MgO , CuO , and Fe_2O_3 [4]. Liu et al. demonstrated that the $\text{SrO-Al}_2\text{O}_3$ composite was an effective catalyst for ultrasound-assisted ozonation of NH_4^+ solution. NH_4^+ conversion of 83.2% and gaseous nitrogen selectivity of 51.8% were achieved [7]. Chen et al. 2018 reported the synthesis of $\text{MgO-Co}_3\text{O}_4$ (molar ratio 8:2) and claimed that an ammonia nitrogen removal and gaseous nitrogen selectivity reached to the value of 85.2% and 44.8%, respectively [8].

Dolomite is a mineral clay composed of calcium magnesium carbonate $\text{CaMg}(\text{CO}_3)_2$ [9]. However, raw dolomite cannot be used as adsorbent and catalyst due to its low surface and high impurities. Therefore, the activation or modification of dolomite is necessary to expand its application. Chaudhary and Prasad reported that thermally activated dolomite could enhance its surface area, pore size distribution, and pore volume, consequently increasing fluoride removal from aqueous solution [10]. Modified dolomite can be used as an efficient adsorbent for removal of arsenic and heavy metals and dyes from aqueous solution [11]. Thermally activated dolomite can be used as an efficient catalyst for biodiesel production and decomposition of pentachlorophenol [12, 13]. To our best knowledge, $\text{Fe}_2\text{O}_3\text{-Co}_3\text{O}_4$ modified dolomite used as an efficient catalyst in catalytic ozonation of NH_4^+ solution has not yet been reported in the literature.

In this work, we report the activation and Fe_2O_3 and $\text{Fe}_2\text{O}_3\text{-Co}_3\text{O}_4$ modification of dolomite. Activated and Fe_2O_3 and $\text{Fe}_2\text{O}_3\text{-Co}_3\text{O}_4$ modified dolomites were tested in the catalytic ozonation of NH_4OH solution, and catalytic ozonation performances of activated and modified dolomites were evaluated and rationalized.

2. Materials and Methods

2.1. Materials. The natural dolomite was provided by Ninh Binh mineral company Vietnam. Iron(III) chloride hexahydrate ($\text{FeCl}_3\cdot 6\text{H}_2\text{O}$, 98%), cobalt(II) chloride hexahydrate ($\text{CoCl}_2\cdot 6\text{H}_2\text{O}$, 98%), ammonium chloride (NH_4Cl , 99%), cetyltrimethylammonium bromide (CTAB, $\geq 98\%$), and natri hydroxit (NaOH , 97%) were provided by Sigma Corporation.

2.2. Materials

2.2.1. Activation of Raw Dolomite. Firstly, 10 g of dolomite was activated by heating at 800°C for 3 h in a furnace with a heating rate of $10^\circ\text{C}/\text{min}$. After calcination, $\text{CaMg}(\text{CO}_3)_2$ was converted into CaCO_3 , $\text{Ca}(\text{OH})_2$, and MgCO_3 as the following reactions:

Activated dolomite was treated with a solution of 10 M KOH for 24 h at 80°C . The solid product was separated from the mixture by centrifuge and then was washed several times

with distilled water until a pH of 7 and dried overnight at 80°C in a furnace.

2.2.2. Modification of Activated Dolomite with Fe_2O_3 . The incorporation of Fe ions into activated dolomite framework (denoted as $\text{Fe}_2\text{O}_3/\text{dolomite}$) was carried out by using an “atomic implantation” method. Atomic implantation has occurred in a tubular quartz reactor with two compartments, separated by a membrane of quartz fibers. 0.483 g of $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$ and 0.9 g of activated dolomite are introduced into each compartment. Tubular quartz reactor is placed in a tubular furnace and heated up at 500°C with a heating rate of $20^\circ\text{C}/\text{min}$. At this temperature, FeCl_3 is evaporated and with N_2 flow (60 mL/min) went through the membrane to the compartment containing the activated dolomite (Scheme 1). At this stage, FeCl_3 is dissociated into Fe^{3+} , Cl^- , and Fe^{3+} ions incorporated into an activated dolomite matrix. After one hour of heating at 500°C , the reactor is cooled down to the room temperature. The scheme of modifying dolomite by the atomic implantation method is illustrated as below.

2.2.3. Modification of $\text{Fe}_2\text{O}_3/\text{Dolomite}$ with Co_3O_4 (Denoted as $\text{Fe}_2\text{O}_3\text{-Co}_3\text{O}_4/\text{Dolomite}$) Was Performed by Precipitation Method. 0.8 g of $\text{Fe}_2\text{O}_3/\text{dolomite}$ was put into a glass reactor that contained 50 mL of H_2O (solution 1). After that, 0.8068 g of $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$ was added into 50 mL of H_2O and ultrasonic treatment for 60 minutes (solution 2). 2.4708 g of CTAB was put into 20 mL of H_2O , and then, the mixture was stirred to form a clear solution (solution 3). Solution 2 was dropwise added to solution 1, and then, solution 3 was dropwise added to the above mixture solution 1 + 2 and adjusted pH of 10 by adding 2 M NaOH solution. The mixture is further stirred and aged at 80°C for 24 h. The solid product is separated by centrifuge filtration and washed with distilled water until pH of 7. The product is dried at 90°C and calcined at 450°C for 3 h and then cooled down to room temperature.

2.3. Characterization. The X-ray diffraction (XRD) measurements were performed on a D8 Advance diffractometer (Bruker, Germany) using CuK_α as radiation source, $\lambda = 0.15406$ nm, and a range of $2\theta = 10^\circ - 80^\circ$. The morphology of samples was examined by scanning electron microscopy on JEOL JSM 6500F. The FT-IR measurement was performed on a Jasco 4700 spectrometer. The surface area of samples was determined by BET measurements on Tristar-3000 instruments using nitrogen adsorbate. EDS of samples were measured on a JEOL JED-2300 spectrometer. Temperature-programmed reduction of hydrogen (H_2 -TPR) was performed on an Autochem II 29020 instrument (micromeritics) with a thermal conductor detector (TCD).

2.4. Evaluation of Catalytic Activity and Selectivity. Catalytic ozonation of NH_4^+ solution is carried out in a glass reactor equipped with heating and stirring systems. The reaction conditions are the following: reaction temperature of 50°C , NH_4^+ solution of 50 mg/L, catalyst dosage of 0.6 g/L, reaction time of 2 h, ozone flow of 30 mg/min, and NH_4Cl used as NH_4^+ source. NH_4^+ concentration was analyzed by the Nessler method. 1 mL of Nessler reagent is added to 25 mL of the

SCHEME 1: Scheme of modifying dolomite by “atomic implantation” method.

mixture of reaction product. NO_3^- and NO_2^- concentration was determined by using the spectrometric methods, which complies to ISO (ISO 7890-3:2006 and ISO 6777-1984). The solution was transferred to the cuvette of the spectrophotometer (UV-Vis Lambda 25, Germany) and measured under UV light at a wavelength of 425 nm [14–16].

The conversion and selectivity are calculated as follows:

$$\begin{aligned} \text{Conversion of } \text{NH}_4^+ &= \frac{\text{reacted } \text{NH}_4^+ (\text{mole})}{\text{initial } \text{NH}_4^+ (\text{mole})} \cdot 100\% \\ \text{Selectivity of } \text{NO}_3^- &= \frac{\text{NO}_3^- (\text{mole})}{\text{reacted } \text{NH}_4^+ (\text{mole})} \cdot 100\% \\ \text{Selectivity of } \text{N}_2 &= \frac{\text{N}_2 (\text{mole})}{\text{reacted } \text{NH}_4^+ (\text{mole})} \cdot 100\% \end{aligned} \quad (2)$$

3. Results and Discussion

3.1. X-Ray Diffraction. In X-ray diffraction pattern (XRD) of raw dolomite (Figure 1(a)) appeared the peaks at 30.9° , 41.1° , 44.9° , and 51.3° which are characteristic for $\text{CaMg}(\text{CO}_3)_2$. In addition, the appearance of peaks at 2θ of 23° , 29.6° , 36° , 39.6° , 43.2° , 47.6° , 48.5° , 57.3° , and 60.8° was assigned to CaCO_3 phase [17]. In the XRD pattern of activated dolomite (Figure 1(b)), specific peaks of $\text{CaMg}(\text{CO}_3)_2$ phase disappear. The new peaks at 2θ of 42.8° and 61.9° appear which is attributed to the reflecting plane (101) and (103) which are typical for the structure of MgO [18]. In the XRD pattern of Fe_2O_3 /dolomite (Figure 1(c)) appeared typical peaks of Fe_2O_3 phase at 2θ of 33.1° , 35° , 49.5° , and 54° which is attributed to the reflecting plane (104), (110), (024), and (116), respectively [19]. In the XRD pattern of $\text{Fe}_2\text{O}_3\text{-Co}_3\text{O}_4$ /dolomite (Figure 1(d)), beside the peaks of Fe_2O_3 phase, appear the peaks at 2θ of 37.9° , 44.8° , 55.6° , 59.3° , and 65.2° which are assigned to the reflecting plane (311), (400), (422), (511), and (440) of the Co_3O_4 phase, respectively [20].

3.1.1. Fourier-Transform Infrared Spectroscopy. As observed in Figure 2(a), in the FTIR spectrum of dolomite (raw ores) appeared the bands at 720 ; 873 ; 1429 ; 1797 ; 2516 ; and 2868 cm^{-1} which are assigned to the occurrence of fluctuations in dolomite structure [21, 22]. In the FTIR spectrum of activated dolomite (Figure 2(b)) appeared the band at 3448 cm^{-1} which was assigned to the vibration of OH groups [23]. In addition, the peak at 428 cm^{-1} is attributed to the stretching of Mg-O bonds [24]. In the FTIR spectrum of Fe_2O_3 /dolomite (Figure 2(c)) appeared the bands at 548 and 638 cm^{-1} which are characteristic for Fe-O bonding [25, 26]. In the FTIR spectrum of $\text{Fe}_2\text{O}_3\text{-Co}_3\text{O}_4$ /dolomite (Figure 2(d)) additionally appeared the band at 666 cm^{-1} , which assigned to the stretching of Co-O bond [27, 28].

3.1.2. Energy-Dispersive X-Ray Spectroscopy Analysis. From Figure 3 and Table 1, it was observed that the chemical composition of activated dolomite was slightly changed in O and Ca content between raw dolomite and activated dolomite. Thus, oxygen content decreases and calcium content increases. This is due to the decomposition of CaCO_3 to CaO and CO_2 . Comparing the chemical composition of activated, Fe_2O_3 /dolomite and $\text{Fe}_2\text{O}_3\text{-Co}_3\text{O}_4$ /dolomite, the redistribution of elements in these samples was observed. Oxygen and calcium content were reduced and replaced by Fe and Co content.

3.1.3. Scanning Electron Microscopy (SEM) Analysis. SEM images of raw dolomite, activated dolomite, Fe_2O_3 /dolomite, and $\text{Fe}_2\text{O}_3\text{-Co}_3\text{O}_4$ /dolomite samples were illustrated in Figure 4. SEM image of raw dolomite (Figure 4(a)) showed the rough surface with high disorder and particles size of about $2 \mu\text{m}$. Activated dolomite (Figure 4(b)) shows a smaller particle size of ca. $0.2\text{-}0.4 \mu\text{m}$ with uniform distribution. The strong reduction in size of dolomite can be explained by the fact that the thermal cracking of dolomite fragments and decomposition of carbonates to magnesium and calcium

FIGURE 1: XRD patterns of dolomite (raw ores) (a); activated treated dolomite (b); Fe_2O_3 /dolomite (c); $\text{Fe}_2\text{O}_3\text{-Co}_3\text{O}_4$ /dolomite (d).

FIGURE 2: FTIR spectra of dolomite (raw ores) (a); activated dolomite (b); Fe_2O_3 /dolomite (c); $\text{Fe}_2\text{O}_3\text{-Co}_3\text{O}_4$ /dolomite (d).

oxide and CO_2 . SEM image of Fe_2O_3 /dolomite (Figure 4(c)) presented crystals of sheet shape, with particle size of ca. 0.3 μm . SEM image of $\text{Fe}_2\text{O}_3\text{-Co}_3\text{O}_4$ /dolomite (Figure 4(d)) showed the nano- Co_3O_4 particles size of 80-120 nm, with aggregated form of 0.2-0.3 μm size.

3.1.4. N_2 Adsorption-Desorption Isotherm (BET) Analysis. N_2 adsorption-desorption isotherms of raw dolomite, activated

dolomite, Fe_2O_3 /dolomite, and $\text{Fe}_2\text{O}_3\text{-Co}_3\text{O}_4$ /dolomite samples are presented in Figure 5. N_2 adsorption-desorption isotherms of all dolomite samples look like a type IV according to the IUPAC classification [29]. However, the hysteresis loop on activated, Fe_2O_3 /dolomite, and $\text{Fe}_2\text{O}_3\text{-Co}_3\text{O}_4$ /dolomite samples was differentiated. This hysteresis loop is due to the capillary condensation of nitrogen which is often observed on mesoporous materials. Specific surface charge

FIGURE 3: EDS spectra of Fe₂O₃/dolomite (a) and Fe₂O₃-Co₃O₄/dolomite (b).

TABLE 1: Element composition (wt%) of dolomite (raw ores), activated dolomite, Fe₂O₃/dolomite, and Fe₂O₃-Co₃O₄/dolomite samples.

Sample	Dolomite (raw ores) (% weight)	Activated dolomite (% weight)	Fe ₂ O ₃ /dolomite (% weight)	Fe ₂ O ₃ -Co ₃ O ₄ /dolomite	
				% weight	% atomic percentage
O	61.50	57.98	51.15	44.19	58.47
Mg	11.55	11.98	9.91	10.24	9.03
Ca	16.89	19.96	16.89	4.59	2.43
C	10.06	10.09	12.67	10.74	18.95
Cl	—	—	0.35	0.37	0.22
Fe	—	—	9.59	10.06	3.63
Co	—	—	—	20.27	7.27
Total	100	100	100	100	100

(S_{BET}), pore diameter (D_{BJH}), and pore volume (V_{pore}) are listed in Table 2.

As seen in Table 2, S_{BET} , V_{pore} , and D_{BJH} of activated dolomite were much higher than those of raw dolomite. This indicated the efficiency of activation, making dolomite structure more porous and consequently increasing the surface area, pore volume, and pore diameter. Modification of activated dolomite by Fe₂O₃ and Co₃O₄ led to

increase the surface area and pore volume (from 22 m²/g to 60 m²/g). This clearly indicated the formation of new mesoporous systems by the agglomeration of nano-Fe₂O₃ and Co₃O₄ particles. The decrease in pore diameter observed on Fe₂O₃/dolomite and Fe₂O₃-Co₃O₄/dolomite can be explained by the fact that nano-Fe₂O₃ and Co₃O₄ particles are located within the pores of activated dolomite, causing the narrowing pore diameter.

FIGURE 4: SEM images of raw dolomite (a); activated dolomite (b); Fe₂O₃/dolomite (c); Fe₂O₃-Co₃O₄/dolomite (d).

3.1.5. H₂-TPR Analysis. In the H₂-TPR profile of activated dolomite material (Figure 6(a)) appeared a peak at ca. 706°C which was assigned to the reduction of MgO to Mg [5]. In the H₂-TPR profile of Fe₂O₃/dolomite (Figure 6(b)) appeared peaks at 318°C, 408°C, 550°C, and 689°C which are characteristic for the reduction Fe₂O₃ to Fe₃O₄, reduction of Fe₃O₄ to FeO, and the reduction of MgO to Mg, respectively [5, 30]. H₂-TPR profile of Fe₂O₃-Co₃O₄ modified dolomite (Figure 6(c)) shows peaks at 328°C, 420°C, 548°C, and 688°C which is attributed to the reduction of Co³⁺ to Co²⁺, Co²⁺ to Co⁰, Fe₃O₄ to FeO, and MgO to Mg [30–32]. From the obtained results, it can be concluded that the Fe₂O₃ and Fe₂O₃-Co₃O₄ modified dolomite exhibits much higher reduction ability as compared to that of activated dolomite. Thus, much lower reduction temperature of modified dolomites (320–420°C) than that of activated dolomite (680–730°C) was noted. The Fe₂O₃-Co₃O₄/dolomite exhibited the highest peak intensity at 318–340°C, indicating a larger amount of H₂ reduction as compared to that of Fe₂O₃ modified dolomite. This lowest reduction temperature of Fe₂O₃-Co₃O₄ modified dolomite is due to the fact that M-O strength of this catalyst is weak. The high reduction ability of this catalyst played a decisive role in the improvement of N₂ selectivity, by enhancing the reduction of NO₃[−] to N₂.

3.1.6. Catalytic Ozonation of NH₄⁺ Solution. NH₄⁺ conversion to NO₃[−] and N₂ overactivated and modified dolomites is presented in Figure 7. As seen in Figure 7, all samples exhibited high NH₄⁺ conversion (86–96%) and among these

catalysts, Fe₂O₃-Co₃O₄/dolomite has the highest activity (conversion of 96%). The N₂ selectivity is decreased in the order activated dolomite (45%) < Fe₂O₃/dolomite (65.13%) < Fe₂O₃-Co₃O₄/dolomite (77.68%) and NO₃[−] selectivity is increased in the order: activated dolomite (54.32%) > Fe₂O₃/dolomite (34.87%) > Fe₂O₃-Co₃O₄/dolomite (22.32%). Among the tested samples, Fe₂O₃-Co₃O₄/dolomite exhibited the highest N₂ selectivity of 77.68% and lowest NO₃[−] selectivity of 22.32%. The result obtained in this work is better than that reported in the literature. Thus, Chen et al. [8] have shown the N₂ selectivity of 44.8% over MgO-Co₃O₄ catalyst in the catalytic ozonation of ammonium solution. Liu et al. [7] have shown the conversion of 83.2% and gaseous nitrogen selectivity of 51.8% on SrO-Al₂O₃ catalyst in the catalytic ozonation of ammonium solution. The mechanism of catalytic ozonation of NH₄⁺ solution is involved with the following process. The ozonation reaction was conducted at pH of 9, and ammonium exists as NH₃ molecule, (Equation (3)). At pH of 9, the ozonation catalyzes the formation of HO₂[−] and OH radical, according to Equations (4) and (5) [8].

The decomposition of NH₃ in water through ozonation with a metal oxide catalyst is performed by hydroxyl radicals

FIGURE 5: (a) N₂ adsorption–desorption isotherms and (b) pore distribution of raw dolomite (A); activated dolomite (B); Fe₂O₃/dolomite (C); Fe₂O₃-Co₃O₄/dolomite (D).

TABLE 2: Textual characteristics of dolomite (raw ores), activated dolomite, Fe₂O₃/dolomite, and Fe₂O₃-Co₃O₄/dolomite samples.

Sample	S_{BET} (m ² /g)	V_{pore} (cm ³ /g)	D_{BJH} (nm)
Dolomite (raw ores)	2.0	0.008	18.35
Activated dolomite	22	0.159	32.31
Fe ₂ O ₃ /dolomite	39	0.206	21.87
Fe ₂ O ₃ -Co ₃ O ₄ /dolomite	60	0.262	16.65

(Equation (6)). In addition, the hydroxyl radical oxidizes NH₃ in the solution to intermediate product nitrite, which rapidly oxidizes to nitrate (Equation (7)) and (Equation (8)) [33]. NH₃ in solution can be oxidized to nitrate nitrogen by hydroxyl radical (Equation (9)).

In summary, the reactions occurring during ammonium decomposition by catalytic ozonation are as follows:

FIGURE 6: H₂-TPR profile of activated dolomite (a); Fe₂O₃/dolomite (b); Fe₂O₃-Co₃O₄/dolomite (c).

FIGURE 7: NH₄⁺ conversion and NO₃⁻ and N₂ selectivity of activated and modified dolomite. Initial ammonia concentration 50 mg/L, pH = 9, dosage of catalyst 1 g/L, flow rate of ozone 12 mg/min, reaction temperature 50°C, and reaction time: 60 min.

According to the mentioned reactions, in order to obtain high N₂ selectivity, reactions (11) and (12) should be suppressed. Ichikawa et al. studied the relationship between N₂ selectivity and standard enthalpy change of formation per mole of oxygen atom (ΔH_f°) of the metal oxides. Ichikawa

et al. found that the N₂ selectivity was high for the catalyst with a low value of ΔH_f° and N₂ selectivity was low for the catalyst with high value of ΔH_f° . For example, Co₃O₄ with ΔH_f° of 60 kcal (mole of O)⁻¹ has the highest N₂ selectivity of 90% and MgO with ΔH_f° of 140 kcal (mole O)⁻¹ has the

FIGURE 8: NH_4^+ conversion and N_2 and NO_3^- selectivity over $\text{Fe}_2\text{O}_3\text{-Co}_3\text{O}_4/\text{dolomite}$ after 3 cycles of reaction. Initial ammonia concentration 50 mg/L, pH = 9, dosage of catalyst 1 g/L, flow rate of ozone 12 mg/min., reaction temperature 50°C, and reaction time: 60 min.

lowest N_2 selectivity of 20 kcal (mole O)⁻¹ [4]. They claimed that ΔH_f° indicates the bond strength between the metal cation (M) and lattice oxygen (M-O) in the metal oxides. Thus, the metal oxides with low ΔH_f° value have weak M-O bond strength. This means the weak bond strength between M on the surface and active oxygen (O^*) formed by the reaction of O_3 with the surface. O^* would be unstable, easy to participate in the NH_4^+ oxidation. Since NH_4Cl was used as a NH_4^+ source, Cl^- in solution could participate in the NH_4^+ oxidation. Cl^- anions could react with O_3 to form ClO^- which oxidized NH_4^+ ion to nitrogen [4, 7]. To investigate the stability of the catalysts, we carry out three cycles of catalytic ozonation of NH_4^+ solution over $\text{Fe}_2\text{O}_3\text{-Co}_3\text{O}_4/\text{dolomite}$, and the result is presented in Figure 8.

As observed in Figure 8, NH_4^+ conversion over $\text{Fe}_2\text{O}_3\text{-Co}_3\text{O}_4/\text{dolomite}$ after 3 cycles was slightly decreased, less than 5% as compared to that of the fresh catalyst. N_2 selectivity over $\text{Fe}_2\text{O}_3\text{-Co}_3\text{O}_4/\text{dolomite}$ after 3 cycles of reaction decreased only ca. 7-8% as compared to that of the fresh catalyst, while NO_3^- selectivity slightly increased (ca. 5%). From the obtained result, it could confirm that the $\text{Fe}_2\text{O}_3\text{-Co}_3\text{O}_4/\text{dolomite}$ has high activity stability and it can be reused.

To check the change of structure and morphology of the $\text{Fe}_2\text{O}_3\text{-Co}_3\text{O}_4/\text{dolomite}$ after 3 cycles of reaction, XRD pattern and SEM image of the spent catalyst were performed.

From XRD patterns (Figures 9(a) and 9(b)) and SEM images (Figures 9(c) and 9(d)), it can be seen that the structure and morphology of the spent catalyst were maintained; no change of metal oxide phase as well as agglomerating of metal oxide particles were noted. Based on the above results, the high catalytic activity and stability of the $\text{Fe}_2\text{O}_3\text{-Co}_3\text{O}_4/\text{dolomite}$ catalyst could be proved.

4. Conclusions

From the obtained results, some conclusions could be drawn.

It was successful to modify dolomite with Fe_2O_3 by using the “atomic implantation” method. By this method, nano- Fe_2O_3 particles with small size and high dispersion on dolomite surface were achieved.

It was also successful to modify $\text{Fe}_2\text{O}_3/\text{dolomite}$ with Co_3O_4 by the precipitation method. As seen in SEM images, nano- Fe_2O_3 , Co_3O_4 particles of 80-130 nm with high dispersion on dolomite surface were obtained.

Catalytic performance of activated dolomite, $\text{Fe}_2\text{O}_3/\text{dolomite}$, and $\text{Fe}_2\text{O}_3\text{-Co}_3\text{O}_4/\text{dolomite}$ in catalytic ozonation of NH_4^+ solution was investigated and evaluated. Among three catalysts, $\text{Fe}_2\text{O}_3\text{-Co}_3\text{O}_4/\text{dolomite}$ has the highest NH_4^+ conversion (96%) and N_2 selectivity (77.82%). Selectivity toward N_2 over the catalyst can be rationalized by bond strength M-O through the standard enthalpy ΔH_f° . The catalyst with low ΔH_f° value has higher N_2 selectivity. Moreover, the H_2 reduction ability also plays an important

FIGURE 9: XRD patterns of Fe_2O_3 - Co_3O_4 /dolomite before (a) and after (b) reaction 3rd cycle; SEM images of Fe_2O_3 - Co_3O_4 /dolomite before (c) and after (d) reaction 3rd cycle.

role in the improvement of N_2 selectivity by the reduction of NO_3^- to N_2 gas.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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