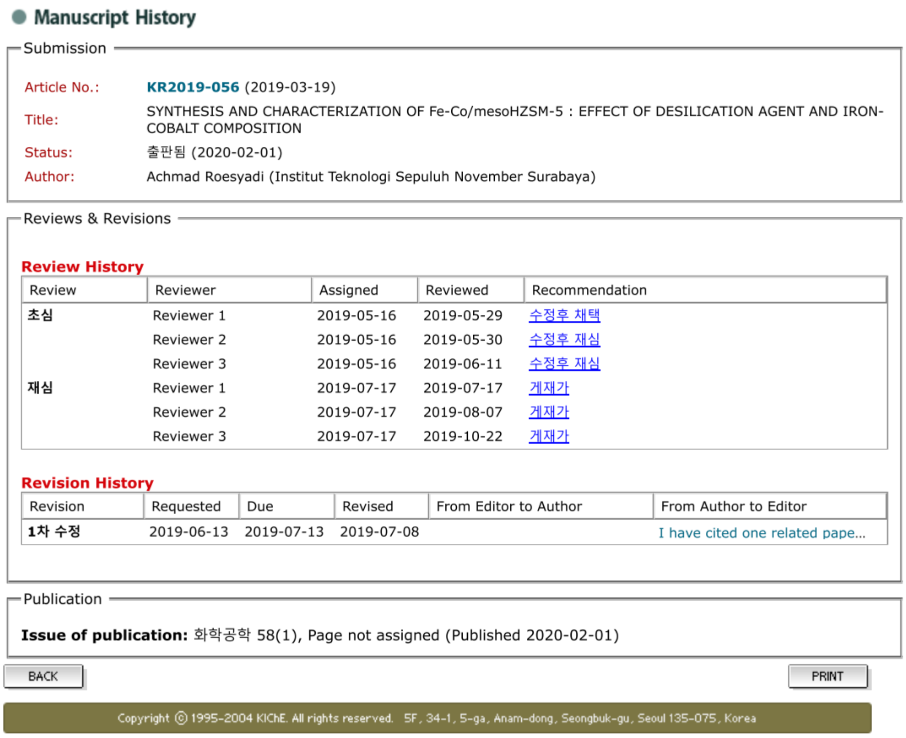

Manuscript History

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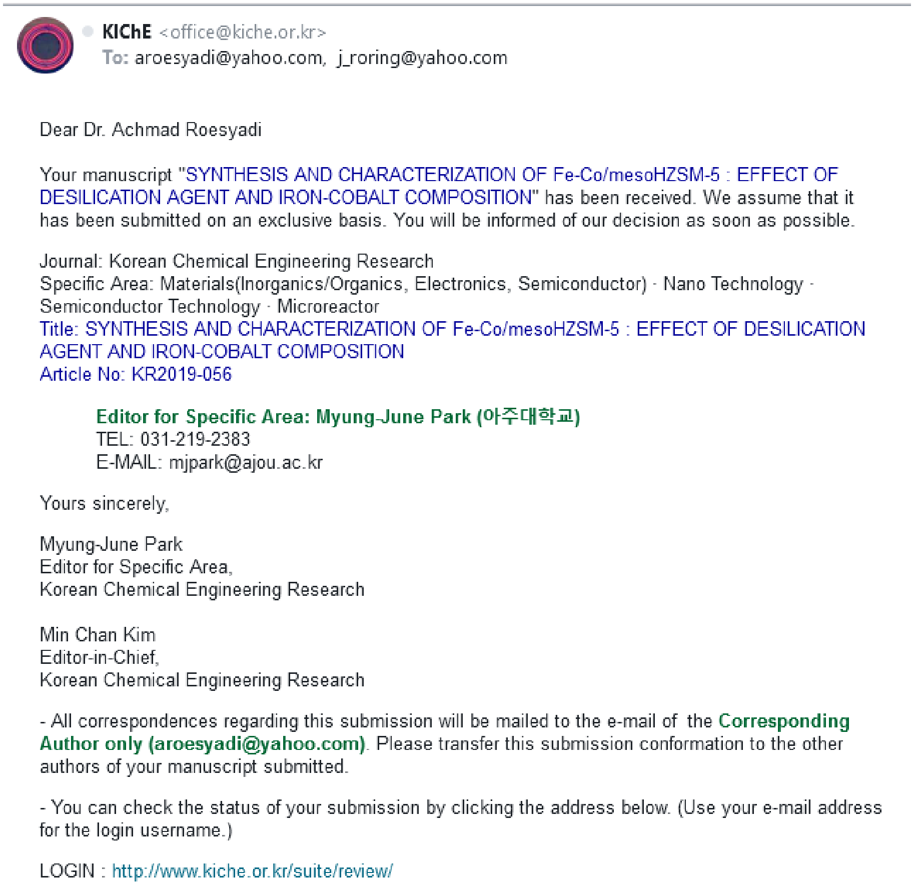

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To: aroesyadi@yahoo.com, j_roring@yahoo.com

Dear Dr. Achmad Roesyadi

Your manuscript "SYNTHESIS AND CHARACTERIZATION OF Fe-Co/mesoHZSM-5 : EFFECT OF DESILICATION AGENT AND IRON-COBALT COMPOSITION" has been received. We assume that it has been submitted on an exclusive basis. You will be informed of our decision as soon as possible.

Journal: Korean Chemical Engineering Research
Specific Area: Materials(Inorganics/Organics, Electronics, Semiconductor) · Nano Technology · Semiconductor Technology · Microreactor
Title: SYNTHESIS AND CHARACTERIZATION OF Fe-Co/mesoHZSM-5 : EFFECT OF DESILICATION AGENT AND IRON-COBALT COMPOSITION
Article No: KR2019-056

Editor for Specific Area: Myung-June Park (아주대학교)
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Yours sincerely,

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Dear Dr. Achmad Roesyadi

Your manuscript entitled "SYNTHESIS AND CHARACTERIZATION OF Fe-Co/mesoHZSM-5 : EFFECT OF DESILICATION AGENT AND IRON-COBALT COMPOSITION", which was submitted to Korean Chemical Engineering Research, has been reviewed by reviewers. You can access to the comments through the journal's website (see the instructions below). I would like to ask you to revise your manuscript very carefully based on the reviewer's comments. Please use red-colored letters for corrections so that editors and reviewers can easily recognize the corrected parts. Then, please submit the list of point-by-point response (answers and corrections) to all the comments along with your revised manuscript.

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SYNTHESIS AND CHARACTERIZATION OF Fe-Co/mesoHZSM-5 : EFFECT OF DESILICATION AGENT AND IRON-COBALT COMPOSITION

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ABSTRACT

The effect of sodium hydroxide (NaOH) and potassium hydroxide (KOH) as desilication agent and impregnated composition of iron and cobalt on characterization (???) of Fe-Co/meso-HZSM-5 catalyst has been studied.
→ This sentence is too long, and simply aimless
Synthesis of Fe-Co/meso-HZSM5 catalyst, intended to be applied in FT reaction has been investigated. The study emphasized on studying the effect of desilication agents: NaOH and KOH, on the catalyst materials properties. Additionally, impregnation composition of active metal (Fe and Co) was also examined.

Ammonium ZSM-5 was converted to HZSM-5 through calcination process. HZSM-5 was desilicated with NaOH and KOH, then impregnated with 10% metal loading and 10-50% Fe content in Fe-Co.

→ *How about*:
HZSM-5, converted from ammonium ZSM-5 through calcination, was treated with NaOH and KOH for desilication, followed by impregnation with 10% metal loading.

Fe composition in the initial mixture of Fe-Co was varied at 10-50%.

→ This is another vague statement, why should it be based on Fe-Co? Why don't we just say Fe , for example 2 % from total composition?

This materials were reduced continuously by hydrogen at 400^{0}C for 10 hours.
→ *After impregantion, reduction was applied by flowing hydrogen gas at 400^{o}C for 10 hours.*

Desilication of HZSM-5 with NaOH and KOH solutions lead to catalyst mesoporosity enlargement (increase???)

Although, KOH solutions induced greater mesoporous volumes, but it destroyed the crystal structure of HZSM-5. NaOH solutions lead to increased mesopore surface area (about 100%) from 266.28 m^2/g (for HZSM-5) to 526.03 m^2/g (for NaOH-desilicated HZSM-5). It also increased pore volume from 0.14 cc/g to 0.486 cc/g.

The use of KOH solution induced greater mesoporous volumes. However, it imposed detrimental effect on zeolite crystal structure. NaOH solutions, on the other hand, increased mesopore area as high as 100%, indicated from surface area increase from 266.28 m2/g of HZSM-5, to 526.03 m2/g of NaOH-desilicated HZSM-5. In addition, the application of NaOH solution has increased pore volume from 0.14 cc/g to 0.486 cc/g.

Reduced materials at 400^{0}C for 10 hours leads to more Fe-Co alloy and less oxide form of Fe_2O_3 dan Co_3O_4.

→ *Further, more Fe-Co alloy(s) (???) and less oxide of iron (Fe_2O_3) as well cobalt (Co_3O_4) had been commonly observed in the produced catalysts*

Keywords: HZSM-5, mesopore, impregnation, Fe-Co, desilication

I suggest you to take any short course or workshop to improve your writing skill.
It will give lots of benefits for your career as an academic.

INTRODUCTION

Zeolites are aluminosilicate crystals with unique pore structures. Zeolites are widely used in the adsorption, separation and catalytic processes (i.e. cracking and other hydrotreating process) due to their unique properties: homogeneous micropores, high thermal stability, acidity, and unique metallic species stability [1]. Microporous HZSM-5 has been inapplicable in catalyzing large molecules, because of diffusion limitations in micropore channels and carbon deposition in the pore system. Construction of HZSM-5 materials with larger pore sizes can improve reaction efficiency and minimize channel closure. The pore size of the material can be classified into micropores (pore diameter smaller than 2 nm), mesopores (pore diameter 2-50 nm) and macropores (pore diameter greater than 50 nm). The mesoporous structure provides greater space for metal catalysts to occupy more support pores. The micropore structure can be converted to mesopore using desilication process. Desilication is a process used to form mesopores through decreasing silicon content in zeolites. Alkaline solutions, concentration, temperature, process duration dan Si/Al ratio affect the desilicated mesopore material. Commonly, Tetrapropylammonium hydroxide (TPAOH) or NaOH solution are used as desilication agents. TPAOH treatment provides larger mesoporous area than NaOH, but NaOH solution gives a larger pore volume [2]. TPAOH is more expensive and difficult to obtain, so that the use of NaOH has been more attractive. The use of other bases such as KOH solution is still possible in this desilication process. Nitric acid solution was used to transform the mesoporous HZSM-5 into amorphous structure. The formation of the amorphous phase could improve the adhesion of the metal catalyst on the mesoporous HZSM-5 support [3, 4].

Metallic iron and cobalt were used as polimerization catalyst at Fischer-Tropsch synthesis. The impregnated iron and cobalt into HZSM-5 could be used as bifunction catalyst which combined polimerizing synthesis gas and cracking long chain hydrocarbon for making biofuel [5–8]. Cobalt catalyst has some advantages compared to iron catalyst and it is preferable to use in Fischer-Tropsch synthesis. But cobalt catalyst has some disadvantages (ADD the disadvantage) . Iron catalyst was added in little amount to improve the cobalt catalyst performance (improve olefin sensitivity, reduce methane selectivity, reduce temperature and pressure sensitivity to product distribution and reduce the catalyst price). The comparison of both catalyst can be seen as follows [9] . In this research, the catalyst has been made by less iron content to improve major cobalt catalyst. The incipient wetness impregnation has been selected as a method for metallic impregnation into mesoporous HZSM-5 support. The reduction would convert oxide form to their free metallic form of Fe and Co [8, 10, 11].

Commented [O1]: Such as???

This research investigated the effect of NaOH and KOH as desilication agent for HZSM-5 pore enlargement and other characteristics. The effect of impregnated composition of iron and cobalt on characterics of Fe-Co/meso-HZSM-5 was also investigated.

This characterization will be used to make Fischer-Tropsch reaction decision in the next steps.

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How about:
The data obtained from this study will be used to develop zeolites based catalyst for Fischer-Tropsch reaction???

METHODS

Materials used in this experiment were zeolite ZSM-5 in ammonium form (CBV 8014, Amberlyst International), $Fe(NO_3)_3.9H_2O$ (Merck), $Co(NO_3)_2.6H_2O$ (Merck), NaOH p.a. (Merck), KOH p.a. (Merck), nitric acid p.a. (Merck), Hydrogen and Nitrogen gas (PT. Samator Gas Industry, Surabaya, Indonesia), aquadest. The equipment used were the calcination reactor (Figure 1), quartz furnace crussible, hotplate magnetic stirrer, vacuum filter, air compressor, hot air oven, syringe, digital scales and standard glasswares.

The ammonium salt of ZSM-5 was calcined at 550^0C for 5 hours to obtain microporous HZSM-5. HZSM-5 was desilicated by 1 M KOH and 1 M NaOH solution with stirring at 70^0C for 1 h. The suspension was cooled down in an ice bath, separated from the zeolite crystals by dispersion in deionized water and filtered until neutral pH, stated for 24 hours at 50^0C, dried at 120^0C for 12 hours and finally calcined at 550^0C for 5 hours. The mesoporous HZSM-5 product was treated using 1 M HNO_3 solution at 70^0C for 2 h and stirred to form an amorphous phase. Subsequently, the sample was washed with deionized water, dried and calcined by the same procedure after the desilication above [12, 13]. Iron and cobalt from $Co(NO_3)_2.6H_2O$ and/or $Fe(NO_3)_3.9H_2O$ solutions, were impregnated using incipient wetness impregnation (IWI) process on amorphous meso-HZSM-5. Loading metal catalyst was 10% and Fe content in Fe-Co was varied of 10-50%. The impregnated HZSM-5 was kept in desiccator at room temperature for 24 hours, dried in oven at 120^0C for 12 hours and then calcined at 550^0C for 2 hours. The impregnated materials were reduced in continuous flow of H_2 gas at 400^0C for 10 hours.

Brunauer–Emmett–Teller (BET), X-ray Diffraction (XRD) and Scanning electron microscopy (SEM) with Energy Dispersive X-ray spectroscopy (EDX) analysis were used for materials characterization. The BET model was used to analyze the volume and surface area of micropore and mesopore (deriving from t-plot data) [14], the pore size distribution (deriving from BJH model) [15]. The XRD analysis was used to determine the crystal structure and the form of the impregnated iron and cobalt. The SEM was used to analyze the structure image for material. The Si and Al concentration in the solid materials before and after alkali treatment were analyzed with EDX.

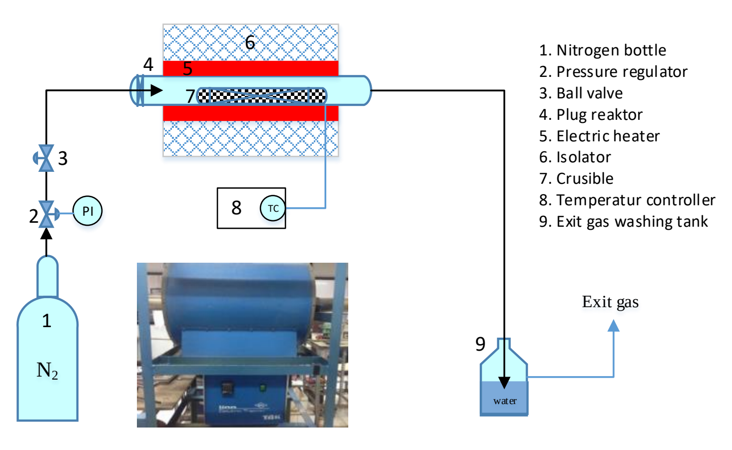

Figure 1. Tube furnace reactor (Linn Elektro Therm) for calcination process

RESULT AND DISCUSSION

Effect of desilication agent for mesopore development

Ammonium ZSM-5 (Si/Al = 40) was converted to microporous HZSM-5 through calcination process. The formation of mesoporous structures was obtained through the desilication process in which silicon was removed from zeolite framework. Generally, silicon and aluminum in the zeolite framework are removed with the use strong bases such as NaOH and KOH. But silicon is more soluble in NaOH and KOH solution in form $Si(OH)_4^-$ than of aluminium. Aluminum has been less soluble in strong base solutions because the negative charge on the aluminum tetrahedral limits the interaction of Al and the strong base. The desilication process decreased the Si/Al ratio in HZSM-5 [16]. BET (Branauer-Emmett-Teller) analysis was used to determine surface area, pore volume and pore size (Table 1). Pore size distribution in untreated HZSM-5 and desilicated HZSM-5 had been analyzed by N_2 adsorption isotherm (Figure 1).

The analysis confirmed that mesopore structure enlargement could be achieved, pore diameter in range of 2-50 nm was observed. In Fogure 2, The N_2 adsorption and desorption isotherms profile showed a small and constantly adsorptive volume at various pressures [17], which has been a confirmation of micropore presence without significant mesopore in HZSM-5. The NaOH treated ZSM5 shows very unusual N_2 physisorption pattern. This is an adsorption hysteresis. According to IUPAC isotherm classification standard by Sing et al [17]: “Hysteresis appearing in the multilayer range of physisorption isotherms is usually associated with capillary condensation in mesopore structure”, N_2 physisorption pattern in Figure 2 respects to Type H4 in this classification, that is often associated with narrow slit-like pores. This phenomena has been indicated by decrease of mesopore (0.3496 cc/g) and micropore (0.137cc/g) ratio. (Table 1). The BET model confirmed that micropore volume (0.124 cc/g) was more dominant than mesopore volume (0.0161 cc/g). Both NaOH and KOH desilicated HZSM-5 enhanced nitrogen uptake at higher pressure, which indicated the presence of more mesopore in the hierarchycal pore system (micropore and mesopore mixture) as shown in Figure 3.

The NaOH desilicated HZSM-5 increased mesoporous diameter from 3.4-12.4 nm to 6.1-29.9 nm. The mesoporous volume also increased about 20.7 times from 0.0161 to 0.3496 cc/g. The surface area of the pore increased about 98% from 266.288 to 526.035 cc/g.

The KOH desilicated HZSM-5 increased mesoporous diameter from 3.4-12.4 nm to 2.1-48.0 nm. The mesoporous volume also increased about 54 times from 0.0161 to 0.3496 cc/g. The surface area of the pore showed similar value (266.288 to 258.470 cc/g). KOH desilicated HZSM-5 gave similar nitrogen uptake with untreated HZSM-5 at lower to intemediate pressure and rise significantly at higher pressure (Figure 2). The increasing of pore diameter and volume but stagnant surface area was interesting phenomena for KOH treatment. The KOH treatment destroyed crystalline structure of HZSM-5 (Figure 4) that caused decreasing surface area that might increased before.

Mesoporous formation as indicated by increasing in mesoporous area and volume was due to the OH-alkali ions which were selectively bound to the silicon framework [16]. The Si/Al ratio decreased from 40 (for initial feedstock ZSM-5 ammonium) to 27.9832 (untreated HZSM-5), subsequently further decreased to 22.1059 in the desilication of NaOH and to 16.3032 at KOH desilication as shown in Table 1. The strength of the KOH base ($pK_b = 0.5$) is greater than NaOH ($pK_b = 0.2$), so that the KOH solution was stronger in removing Si in the zeolite structure of HZSM-5 than NaOH solution. The larger the pK_b, the more OH-ions were released and the more Si could be removed from the HZSM-5 zeolite framework, enlarging the pore volume. This result supported the HZSM-5 crystalline destroying during KOH treatment.

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Biased due to previous author is avoided as far as possible.
➔Better to paraphrase:
The NaOH treated ZSM5 shows very unusual N_2 physisorption pattern. This is an adsorption hysteresis, which according to IUPAC isotherm classification standard, has been associated with capillary condensation inside pore structure [17]. The N_2 physisorption pattern in observed in Figure 2 refers to Type H4 of the classification, which is ususally associated with narrow slit-like pores

Table 1. Comparison for HZSM-5, desilicated HZSM-5 (NaOH) and desilicated HZSM-5 (KOH) in pore characteristics (BET) and Si/Al ratio (EDX)

Sampel	**S_{total}** m^2/g	**V_{total}** cc/g	**V_{mikro}** cc/g	**V_{meso}** cc/g	**d_{meso}** nm	**Si/Al**
HZSM-5	266.288	0.1401	0.124	0.0161	3.4-12.4	27.9832
Desilicated HZSM-5 (NaOH)	526.035	0.4866	0.137	0.3496	6.1-147.6	22.1059
Desilicated HZSM-5 (KOH)	258.47	0.9737	0.085	0.8887	1.7-99.8	16.3032

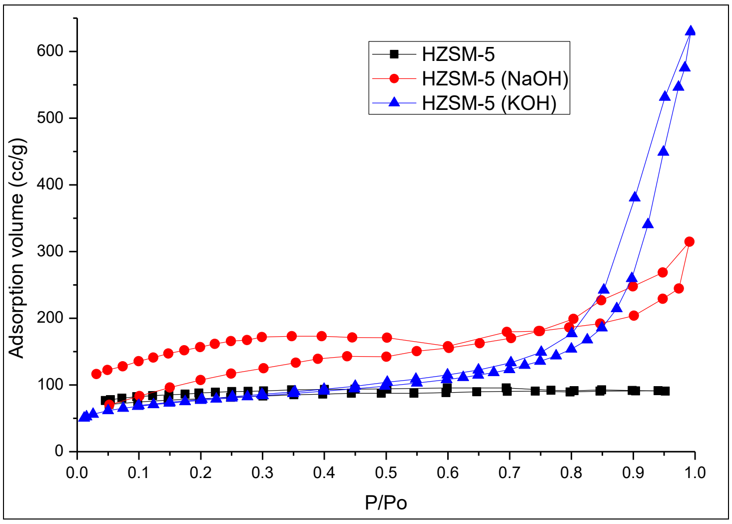

Figure 2. N_2 adsorption and desorption isotherms profile at 77 K for untreated HZSM-5 dan desilicated HZSM-5 with NaOH and KOH solution.

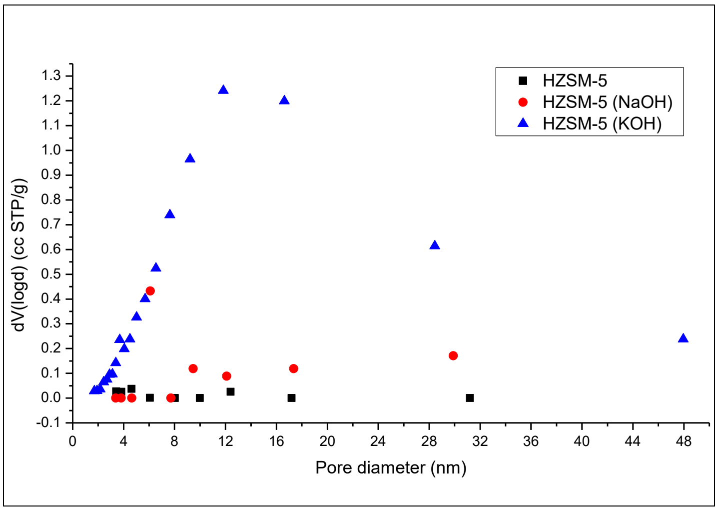

Figure 3. Pores size distribution profile BJH adsorption for untreated HZSM-5 dan desilicated HZSM-5 with NaOH dan KOH solution.

The crystallinity and type of component were analyzed by XRD according to diffraction angle (2θ) on the X-ray diffraction spectra. XRD analysis was performed on microporous HZSM-5, mesoporous HZSM-5 (NaOH and KOH desilication), impregnated and reduced Fe-Co/HZSM-5. Comparison of crystallinity of microporous HZSM-5, mesoporous HZSM-5 (NaOH and KOH desilication) can be seen in Figure 4. The crystallinity of the microporous HZSM-5 and the mesoporous HZSM-5 (NaOH desilication) showed identical spectral patterns with sharp peaks formed at 2θ angle of 7.89^0, 8.08^0, 23^0, 23.27^0 and 23.91^0. These both results were identical with ZSM-5 and HZSM-5 spectra that were shown in Figure 4 (inset), with peaks were at $7\text{-}8^0$ and $23\text{-}24^0$ which was the characteristic peak of HZSM-5 [18]. Garcia-Martinez and Li [19] explained that "*As compared with the isotherms of nitrogen sorption, the micropore volumes calculated from the isotherms and the crystallinity determined by X-ray diffraction (XRD) patterns of the samples did not change by the alkali treatment*". The parent HZSM-5 and NaOH treated HZSM-5's XRD pattern had identical pattern but they gave different peak intensity. Desilication just reduced Si content from zeolite framework and it need to maintain the crystallinity and characteristic for catalyst support. These results indicated that HZSM-5 desilication using 1 M NaOH solution maintained the original crystal structure. Different phenomena showed in desilication using 1 M KOH solution. Although the spectral peaks had the same 2θ position as the previous spectra, but the intensity was much smaller. I indicated that the crystallinity of the HZSM-5 which was dissolved with the KOH solution

Commented [O4]: paraphrase

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decreased significantly because of the considerable Si adsorption shown by the decrease of Si/Al ratio from 40 to 16.3032 (EDX analysis). The previous studies about KOH desilication could not be found. According to similar characteristic of NaOH and KOH, this research investigated the possibility of KOH desilication. Unfortunately, it was found that KOH destroyed the crystallinity of desilicated HZSM-5 zeolites. NaOH desilicated HZSM-5 was further investigated with various composition metal (iron and cobalt) impregnation.

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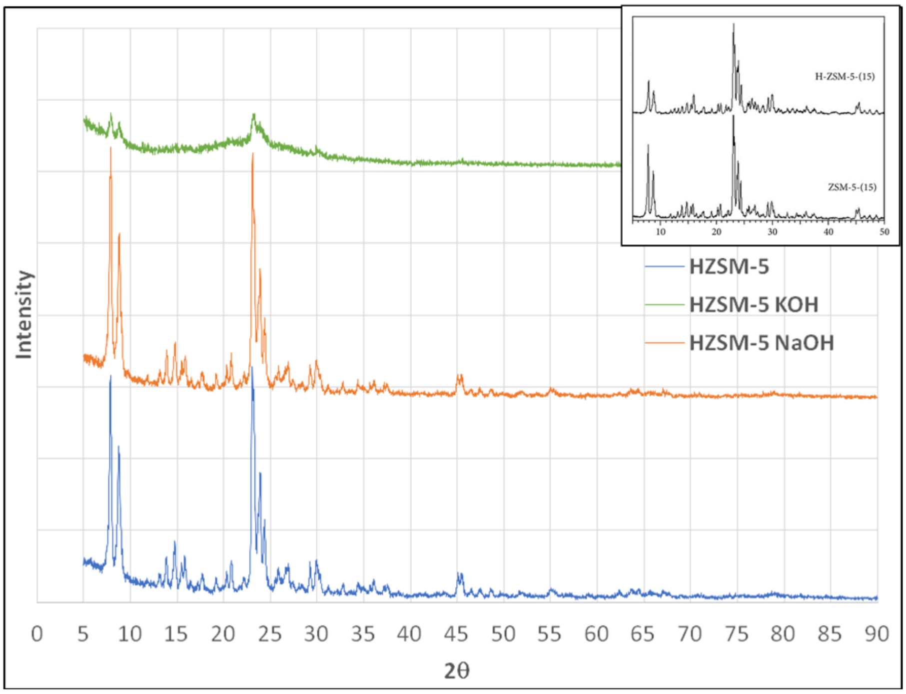

Figure 4. XRD spectra for HZSM-5, desilicated HZSM-5 (NaOH) and desilicated HZSM-5 (KOH). Inset : ZSM-5 and HZSM-5 Spectra [18]

Solution of 1 M HNO_3 was used to form amorphous phase formation of the mesoporous HZSM-5 that treated at 70^0C for 2 hours in the stirred tank. Subsequently, the sample was washed with deionized water, dried and calcined by the same procedure after the above desilication process. The formation of an amorphous phase was characterized by XRD spectra as shown in Figure 6. The noise of spectra showed the amorphous phase that were formed during process.

Observation of the morphological changes of HZSM-5 before and after desilication was carried out through Scanning Electron Microscope (SEM) at 15,000 times magnification can be seen in Figure 5. Desilicated HZSM-5 (NaOH) showed the rigid particles structure, the similar structure with original HZSM-5. It indicated crystallinity structure in the zeolite HZSM-5. Desilicated HZSM-5 (KOH) showed larger pore and less rigid comparing with original HZSM-5 and desilicated HZSM-5 (NaOH). It indicated the crystalline degradation in KOH desilication treatment.

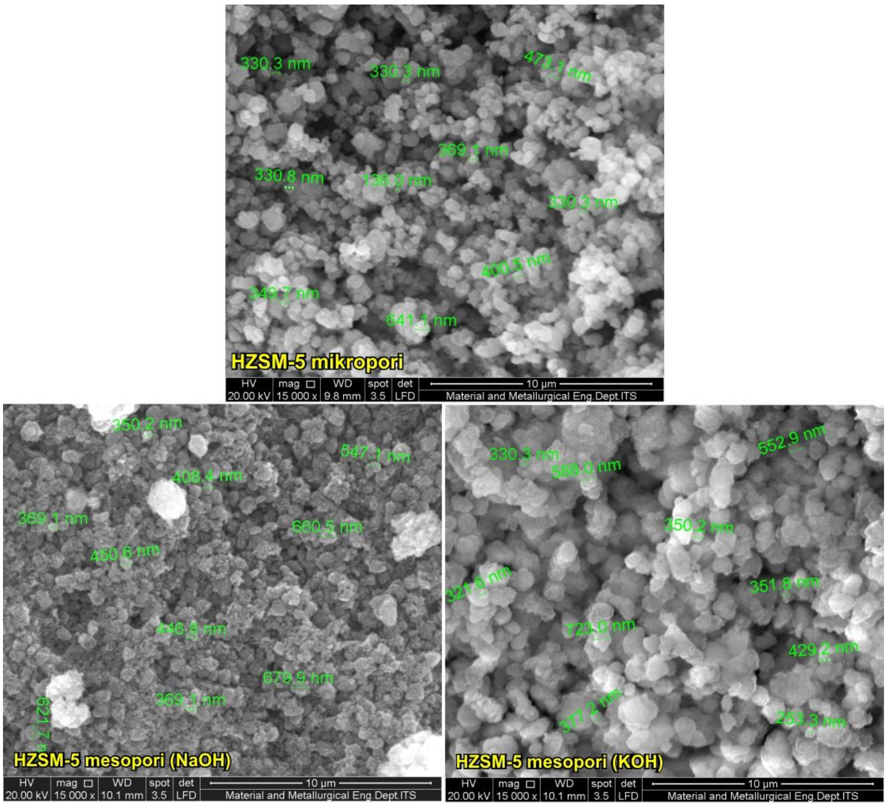

Figure 5. SEM image for HZSM-5, desilicated HZSM-5 mesopore (NaOH) dan desilicated HZSM-5 mesopore (KOH)

Effect of iron and cobalt composition in Fe-Co/HZSM-5 characteristics

The Fe and Co catalysts loading was 10% weight in mesoporous desilicated HZSM-5 (NaOH). The catalyst composition were 10Fe-90Co, 20Fe-80Co, 30Fe-70Co, 40Fe-60Co, 50Fe-50Co/HZM-5. Impregnated varied composition of Fe and Co into meso-HZSM-5 had been analyzed with XRF. Table 2 showed comparison of the prepared Fe content and impregnated Fe and Co into HZSM-5 from NaOH and KOH desilication. The real Fe and Co composition were at column 5 and 6 in Table 2. The metal composition still was in tolerance limit from designed composition (less than 5%). Column 3 and 4 were the overall composition in all of metal in catalyst (zeolite material and metal catalyst). The absorption of Fe-nitrate solution was less than the absorption of Co-nitrate in mesoporous HZSM-5 pore, so that the Fe content obtained was smaller than the prepared one. The absorption of Fe-nitrate and Co-nitrate into impregnated HZSM-5 (NaOH) was larger than impregnated HZSM-5 (KOH). It could be seen that iron and cobalt content (XRF reading) in desilicated NaOH was larger than KOH. Impregnated HZSM-5 (KOH) had better mesopore stucture, but less crystallinity that gave less affinity with Fe and Co precursor. Loading quantities could not be calculated from XRF results because Al metal and its compounds were not identified from this analysis. The loading of catalyst was calculated from EDX analyzing (Table 3). The average metal loading was 13.5%. The results indicated the nonhomogeneous distributed/impregnated metal on HZSM-5. EDX has some limitations. EDX analyze the narrow spot from sample surface (required stable, flat, homogeneous and void free speciments), then non-homogeneous metal distribution in this study might lead to different content of value.

Table 2. Impregnated iron and cobalt composition according to XRF analysis

Desilication Agent	**Catalyst**	**Iron and Cobalt Content (XRF Reading)**		**Iron and Cobalt Composition**	
		Fe	**Co**	**Impregnated Fe**	**Impregnated Co**
NaOH	10Fe-90Co/HZSM-5	4.150%	26.800%	13.41%	86.59%
NaOH	20Fe-80Co/HZSM-5	11.000%	51.430%	17.62%	82.38%
NaOH	30Fe-70Co/HZSM-5	15.800%	45.230%	25.89%	74.11%
NaOH	40Fe-60Co/HZSM-5	21.400%	40.000%	34.85%	65.15%
NaOH	50Fe-50Co/HZSM-5	27.100%	33.300%	44.87%	55.13%
KOH	10Fe-90Co/HZSM-5	1.805%	16.198%	10.03%	89.97%
KOH	20Fe-80Co/HZSM-5	3.219%	14.149%	18.53%	81.47%
KOH	30Fe-70Co/HZSM-5	4.818%	12.146%	28.40%	71.60%
KOH	40Fe-60Co/HZSM-5	6.512%	10.897%	37.40%	62.60%
KOH	50Fe-50Co/HZSM-5	8.841%	9.365%	48.56%	51.44%

Table 3. Fe and Co impregnated into HZSM-5 (NaOH) according to EDX analysis

Catalyst	**Synthesized Composition**	**Resulted Composition (EDX)**

	Fe (%w)	Co (%w)	Loading (%w)	Fe (%w)	Co (%w)	Loading (%w)
10Fe-90Co/HZSM-5	10	90	10	10.1909	89.8091	16.11
30Fe-70Co/HZSM-5	30	70	10	20.6542	79.3458	13.22
50Fe-50Co/HZSM-5	50	50	10	38.4509	61.5491	11.71

The impregnated mesoporous HZSM-5 was reduced to obtain a metal catalyst on the active surface. The reduction was done in the furnace using excess hydrogen stream at 400^0C for 8 hours. XRD analysis was used to observe the reduction results. The diffraction angle position of the metal peaks refers to the spectral database of Tavasoli et al [20]. Figure 7 showed the spectra of Fe. Co and Fe-Co alloys formed. There was still Fe_2O_3 and Co_3O_4 oxides presented in the catalyst. which indicated an imperfect reduction process. The reduction results of 30, 40 and 50% Fe content in Fe-Co showed Fe-Co alloys was formed much more than Fe_2O_3 and Co_3O_4 oxides. Fe and Co were not appeared on the spectra as they may occur around the diffraction angle of 45^0 which is very close to the Fe-Co diffraction angle. The opposite result is obtained on the results of the composition of 10% and 20% Fe in Fe-Co. The presence of Co_3O_4 oxide was more dominant than the Fe-Co alloy formed. When viewed thoroughly. only Co_3O_4 oxides was likely to form. This suggested that the reduction conditions used was more suitable for Fe reduction than Co.

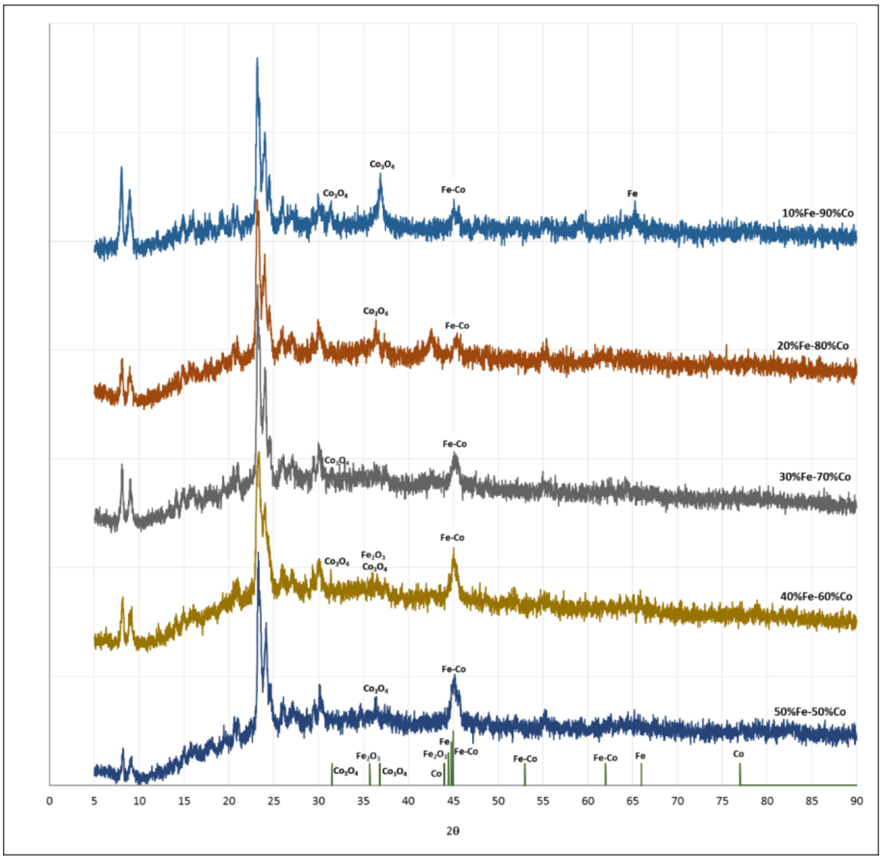

Figure 6. XRD Spectra for Fe-Co/HZSM-5 (NaOH) after reduction with varied composition of Fe and Co

CONCLUSION

The mesoporous volume of HZSM-5 increased from 0.0161 cc/g to 0.3496 cc/g (NaOH desilication) and to 0.8887 cc/g (KOH desilication). KOH give more mesopore structure in the HZSM-5, whilst KOH degraded the crystalline structure of HZSM-5. NaOH desilication gave a better result in increasing mesopore and maintaining crystalline structure. The absorption of Fe-nitrate and Co-nitrate into impregnated HZSM-5 (NaOH) was larger than impregnated HZSM-5 (KOH). The catalyst reduction produced Fe, Co, alloy Fe-Co and less oxides of Fe_2O_3 and Co_3O_4. The largest alloy Fe-Co could be found in 50Fe-50Co/HZSM-5.

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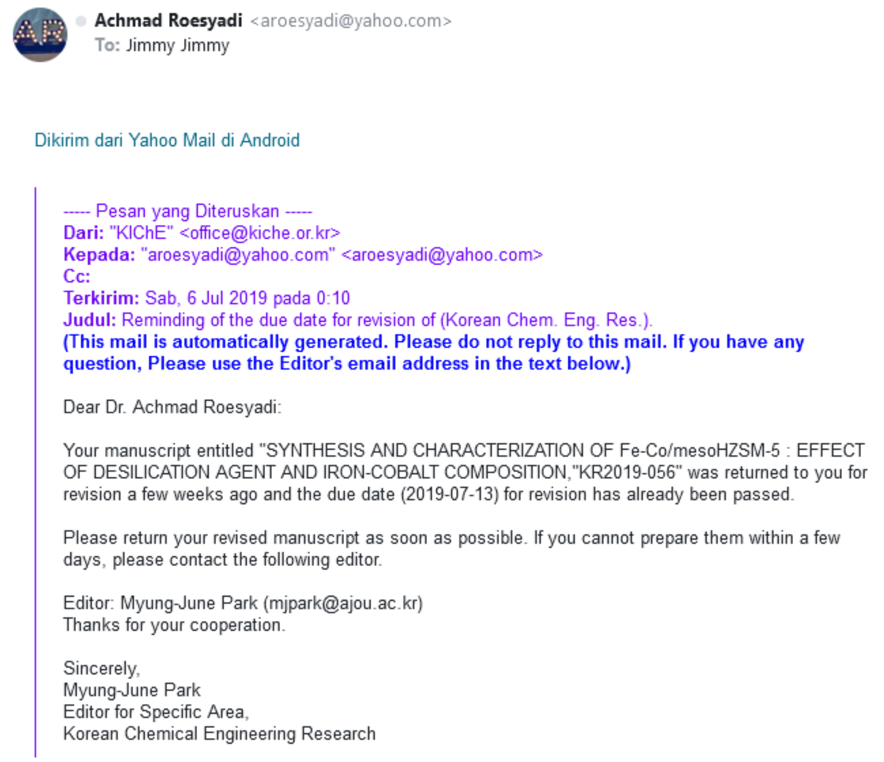
REVISI II



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> Dear Dr. Achmad Roesyadi:
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Reviewer 1

Overall Comments to Authors

The study is focused on the desilication of zeolite and effect of reduction on the nature of Fe-Co metallic nature. It seems tat the article contains some interesting results which may attract reader's attention and can be publishable in the journal after elucidating the raised issues:

1. The authors introduced Fe and Co on HZSM-5 by the incipient wetness method. This means that the metal loading content can be precisely controlled because exact volume of metal precursor solution as same as that of support is used without use of any solvent. However, the metal contents determined by XRD are largely different from those of actual ones. I think that ICP analysis is better to determined the metal content.
   Response:
   The results indicated the non-homogeneous distributed/impregnated metal on HZSM-5. We used EDX to determine the metal content (Table 3) because we

couldn't find other analyzing devices that more suitable (i.e. ICP). EDX analyze the narrow spot from sample surface, required stable, flat, homogeneous and void free speciments, then our non-homogeneous metal distribution in this study might lead to different content of value.
We have addressed this explains in page 10, paragraph 1, line 17-21.

2. Typo errors in the abstract as well as main body should be corrected.
   For example in the abstract
   0,14 cc/g to 0,486 cc/g, dan, etc.
   Response:
   We have addressed by typo error changing 0,14 [0.14]; 0,486 [0.486] in section abstract line 9; 526,035 [526.035] in page 5, paragraph 5, line 3; 258,470 [258.470] in page 5, paragraph 5, line 3; changing spektra [spectra] in Figure 4, line 2 and changing comparation [comparison] in page 10, paragraph 1, line 4.

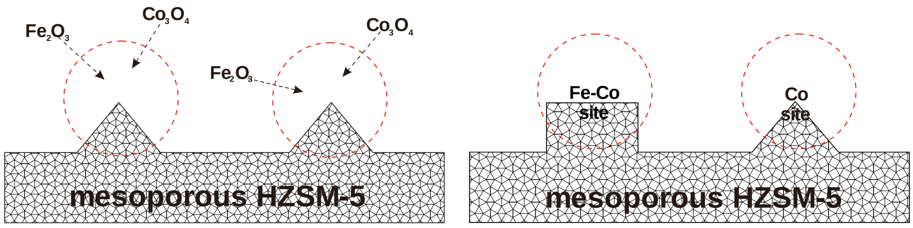
Reviewer 2

Overall Comments to Authors

The authors tried to address the effects of desilication and the metal impregnation on the surface characteristics of HZSM-5. NaOH and KOH were applied as desilication agents and significant porosity changes were seen in both cases, whilst using KOH resulted in destroying the crystalline nature of HZSM-5. Following the impregnation of various compositions of metal loads in Fe-Co, the study reported the dominant existence of Fe-Co alloy and less oxides of each metals. Current manuscript is not suitable for publication as is as there are some issues that need to be clarified. I would like to invite the authors to consider my comments as follows.

1. Additional descriptions on the value added by the study, the rationale behind using KOH as candidate whilst the result terminated its use (destroying the crystal structure of the zeolite though it enhanced the surface characteristics) and novelty of the work should be included to convince the reader that it is worthy enough to use the proposed catalyst in various applications. The basic theories and suggestions mentioned in the study shall be supported and referenced with previous studies. Moreover, elementary terminologies shall be removed.
   Response:
   The KOH desilication studies have not been found, then it may have not been investigated before. The possibility of KOH desilication was investigated here according to NaOH and KOH characteristics similarity. Unfotunately, we found that KOH destroyed the crystallinity of desilicated HZSM-5 zeolites. NaOH desilicated HZSM-5 was further investigated with various composition metal (iron and cobalt) impregnation. We hope that the surface characteristics of reduced materials could be the novelty of this paper.
   We have addressed this explains in page 8, paragraph 1, line 3-8.

2. Including schematic representations of elementary mechanisms with the catalyst components will be more valuable and upgrade the paper’s standard. The appearance of the characteristic graphs should be highly improved.
   Response:
   The schematic representations of elementary mechanisms for catalyst formation is added in Figure 7. It explains the transformation of iron and cobalt precursor to oxide form after impregnation and calcination, then becoming active metal catalyst Fe-Co alloys and Co on mesoporous HZSM-5.
   We have addressed this explains in page 11, paragraph 2, line 1-4 and Figure 7 in page 12.



(a) After Impregnation and Calcination (b) After Reduction

3. The effect of different parameters like temperature, method of reduction, concentrations of the desilicating agents should be added to further determine the catalyst performance over various conditions.
   Response:
   We have investigated the catalyst performance in continuous fixed-bed reactor for varied reaction temperature and time. This results are partly-finished, then we will publish them in our next paper.

4. There are lots of misused terms and poor verbal descriptions, thus the paper presentation needs more clarity in terms of grammar and spelling. It shall be re-written.
   Response:
   We have rewritten this paper, recheck the spelling and grammar carefully.

Reviewer 3

Overall Comments to Authors

The reviewer suggests the publication of this manuscript after the following issues are properly handled:

1. The introduction of Co/Fe to the desilicated ZSM-5 was made by IWI, which means that the loading amount would remain still after the IWI. The authors need to explain why the composition of Co/Fe varies in Table 2 and 3.
   Response:
   We analyzed metal composition with XRF. The real Fe and Co composition were at column 5 and 6 in Table 2. The metal composition still was in tolerance limit from designed composition (less than 5%). Column 3 and 4 were the overall composition in all of metal in catalyst (zeolite material and metal catalyst). May we omit the third and fourth column to avoid confusion?
   We used EDX to determine the metal content (Table 3) because we couldn’t find other analyzing devices that more suitable (i.e. ICP). EDX has some limitations. EDX analyze the narrow spot from sample surface (required stable, flat,

homogeneous and void free speciments), then our nonhomogeneous metal distribution gave the different content value.
We have addressed this explains in page 10, paragraph 1, line 17-21.

2. In Fig 2, the NaOH treated ZSM5 shows very unusual N2 physisorption pattern, which needs further explanation.
   Response:
   The NaOH treated HZSM-5 shows very unusual N2 physisorption pattern. This is an adsorption hysteresis, which according to IUPAC isotherm classification standard, has been associated with capillary condensation inside pore structure [Sing K el al, 1982]. The N2 physisorption pattern in observed in Figure 2 refers to Type H4 of the classification, which is ususally associated with narrow slit-like pores. This phenomena indicated by less mesopore (0.3496 cc/g) and micropore (0.137cc/g) ratio (Table 1).
   We have addressed this explains in page 4, paragraph 2, line 5-6 and in page 5, paragraph 1, line 1-4.

3. In Fig 4, even after the desilication, the XRD pattern of the NaOH treated ZSM5 presents almost the same crystallinity as the parent H-ZSM5. Again, this is not usual and needs further explanation.
   Response:
   Garcia-Martinez, J and Li, K (Mesoporous Zeolites : Preparation, Characterization and Apllications. Wiley-VCH Verlag GMbH & Co., Weinhmeim, Germany, 2015) in page 260 explain that "*As compared with the isotherms of nitrogen sorption, the micropore volumes calculated from the isotherms and the crystallinity determined by X-ray diffraction (XRD) patterns of the samples did not change by the alkali treatment*". In this response, we attach the supported data (original data and graph in excel file). The parent HZSM-5 and NaOH treated HZSM-5's XRD pattern had identical pattern but they gave different peak intensity. Desilication just reduced Si content from zeolite framework and it need to maintain the crystallinity and characteristic for catalyst support.
   We have addressed this explains in page 7, paragraph 1, line 11-15.

4. The authors claimed that "This suggested that the reduction conditions used was more suitable for Fe reduction than Co.", but this was the case for 10-50% Fe (90-50%Co) samples. The authors should examine the crystallinity for 10-50 % Co (90-50% Fe) samples.
   Response:
   Cobalt catalyst has some advantages compared to iron catalyst and it prefers to use in Fischer-Tropsch synthesis. The advantages are middle chain growth probability, very low water gas-shift activity and CO_2 selectivity, low reaction temperature. But cobalt catalyst has some disadvantages parameter that can be

reduced by iron catalyst added. Iron catalyst was added in little amount to improve the cobalt catalyst performance (improve olefin selectivity, reduce methane selectivity, reduce temperature and pressure sensitivity to product distribution and reduce the catalyst price) [Luo et al, 2006] . In this research, the catalyst was made by less iron content to improve cobalt performance as main catalyst.
We have addressed this explains in page 2, paragraph 2, line 4-11.

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Synthesis and Characterization of Fe-Co/mesoHZSM-5 : Effect of Desilication Agent and Iron-cobalt Composition

Jimmy, Achmad Roesyadi†, Suprapto and Firman Kurniawansyah

Chemical Engineering Department, Institut Teknologi Sepuluh Nopember, ITS Sukolilo Campus, Surabaya, East Java, Indonesia-60111

(Received 24 October 2019; Received in revised form 20 May 2019; accepted 13 November 2019)

Abstract – Synthesis of Fe-Co/meso-HZSM5 catalyst, intended to be applied in Fischer-Tropsch (FT) reaction was investigated. The study emphasized the effect of desilication agents, NaOH and KOH, on the catalyst materials properties. Impregnation composition of active metal (Fe and Co) was also examined. HZSM-5, converted from ammonium ZSM-5 through calcination, was treated with NaOH and KOH for desilication, followed by impregnation with 10% metal loading. Fe composition in the initial mixture was varied at 10-50% from total composition. After impregnation, reduction was applied by flowing hydrogen gas at 400 °C for 10 hours. The use of KOH solution induced greater mesoporous volumes; however, it had a detrimental effect on zeolite crystal structure. NaOH solutions, on the other hand, increased mesopore area as high as 100%, indicated from surface area increase from 266.28 m^2/g of HZSM-5, to 526.03 m^2/g of NaOH-desilicated HZSM-5. In addition, the application of NaOH solution increased pore volume from 0.14 cc/g to 0.486 cc/g. Further, more Fe-Co alloys and less oxide of iron (Fe_2O_3) as well cobalt (Co_3O_4) had been commonly observed in the produced catalysts. The largest Fe-Co alloys could be found in 50Fe-50Co/HZSM-5.

Key words: HZSM-5, Mesopore, Impregnation, Fe-Co, Desilication

1. Introduction

Zeolites are aluminosilicate crystals with unique pore structures. They are widely used in the adsorption, separation and catalytic processes (cracking and other hydrotreating process) due to their unique properties. They have homogeneous micropores, high thermal stability, acidity, and unique ability to stabilize metallic species [1]. Microporous HZSM-5 has been inapplicable in catalyzing large molecules, because of the diffusion limitations in micropore channels and carbon deposition in the pore system. Construction of HZSM-5 materials with larger pore sizes can improve reaction efficiency and minimize channel closure. The pore size of the material can be classified into micropores (pore diameter smaller than 2 nm), mesopores (pore diameter 2-50 nm) and macropores (pore diameter greater than 50 nm). The mesoporous structure provides greater space for metal catalysts to occupy more support pores. The micropore structure can be converted to mesopore using desilication, which is a process used to form mesopores through decreasing of silicon content in zeolites. The type of alkaline, concentration, temperature, process duration and Si/Al ratio affect desilicated mesopore material resulting. Commonly, Tetrapropylammonium hydroxide (TPAOH) or NaOH solution are used as desilication agents. TPAOH treatment provides a larger mesoporous area than NaOH, but NaOH solution gives a larger pore volume [2]. TPAOH is more expensive and difficult to obtain, so the use of NaOH is more attractive. The use of other bases such as KOH solution is still possible in this desilication process. Nitric acid solution is used to transform the mesoporous HZSM-5 into amorphous structure. The formation of the amorphous phase can improve the adhesion of the metal catalyst on the mesoporous HZSM-5 support [3,4].

Metallic iron and cobalt are used as polymerization catalyst in Fischer-Tropsch synthesis. The impregnated iron and cobalt on HZSM-5 can be used as bifunction catalyst which combines polymerizing synthesis gas and cracking long chain hydrocarbon for making biofuel [5-9]. Cobalt catalyst has some advantages compared to iron catalyst and is preferred in Fischer-Tropsch synthesis. The advantages are middle chain growth probability, very low water gas-shift activity and CO_2 selectivity, and low reaction temperature. But cobalt catalyst has some disadvantages parameter that can be reduced by iron catalyst added. Iron catalyst is added in small amount to improve the cobalt catalyst performance (improve olefin selectivity, reduce methane selectivity, reduce temperature and pressure sensitivity to product distribution and reduce the catalyst price) [10,11]. In this research, the catalyst was made by less iron content to improve cobalt performance as main catalyst. Incipient wetness impregnation has been the considered method for metallic impregnation to mesoporous HZSM-5 support. The reduction would convert oxide form to their free metallic form of Fe and Co [8,12,13].

The study emphasized studying the effect of desilication agents, NaOH and KOH, on the catalyst materials properties. Additionally, impregnation composition of active metal (Fe and Co) was also

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examined. The data obtained from this study will be used to develop zeolites based catalyst for Fischer-Tropsch reaction.

2. Methods

Materials used in this experiment were zeolite ZSM-5 in ammonium form (CBV 8014, Amberlyst International), $Fe(NO_3)_3{\cdot}9H_2O$ (Merck), $Co(NO_3)_2.6H_2O$ (Merck), NaOH p.a. (Merck), KOH p.a. (Merck), nitric acid p.a. (Merck), Hydrogen and Nitrogen gas (PT. Samator Gas Industry, Surabaya, Indonesia), Aquadest. The equipment used was the calcination reactor (Fig. 1), quartz furnace crucible, hotplate magnetic stirrer, vacuum filter, air compressor, hot air oven, syringe, digital scales and standard glassware.

The ammonium salt of ZSM-5 was calcined at 550 °C for 5 hours to obtain microporous HZSM-5. HZSM-5 was desilicated by 1 M KOH and 1 M NaOH solution with stirring at 70 °C for 1 h. The suspension was cooled in an ice bath, separated from the zeolite crystals by dispersion in deionized water and filtered until neutral pH, stated for 24 hours at 50 °C, dried at 120 °C for 12 hours and finally calcined at 550 °C for 5 hours. The mesoporous HZSM-5 product was treated using 1 M HNO_3 solution at 70 °C for 2 h and stirred to form an amorphous phase. Subsequently, the sample was washed with deionized water, dried and calcined by the same procedure after the desilication above [14,15]. Iron and cobalt from $Co(NO_3)_2{\cdot}6H_2O$ and/or $Fe(NO_3)_3{\cdot}9H_2O$ solutions were impregnated using incipient wetness impregnation (IWI) process on amorphous meso-HZSM-5. Loading metal catalyst was 10% and Fe composition in the initial mixture was varied at 10-50% from total composition. The impregnated HZSM-5 was kept in desiccator at room temperature for 24 hours, dried in oven at 120 °C for 12 hours and then calcined at 550 °C for 2 hours. After impregnation, reduction was applied by flowing hydrogen gas at 400 °C for 10 hours.

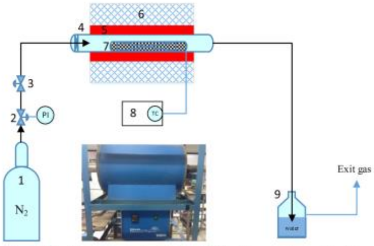


Fig. 1. Tube furnace reactor (Linn Elektro Therm) for calcination and reduction process.

1. Nitrogen bottle
2. Pressure regulator
3. Ball valve
4. Plug reaktor
5. Electric heater
6. Isolator
7. Crusible
8. Temperatur controller
9. Exit gas washing tank

Brunauer-Emmett-Teller (BET), X-ray diffraction (XRD) and scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDX) analysis were used for materials characterization. The BET model was used to analyze the volume and surface area of micropore and mesopore (deriving from t-plot data) [16], the pore size distribution (derived from BJH model) [17]. XRD analysis was used to determine the crystal structure and the form of the impregnated iron and cobalt. The SEM was used to analyze the structure image for material. The Si and Al concentration in the solid materials before and after alkali treatment were analyzed with EDX.

3. Result and Discussion

3-1. Effect of desilication agent for mesopore development

Ammonium ZSM-5 (Si/Al = 40) was converted to microporous HZSM-5 through calcination process in the tube furnace reactor (Fig. 1). The formation of mesoporous structures was obtained through the desilication process in which silicon was partly removed from zeolite framework. Generally, silicon and aluminum in the zeolite framework are removed with the use of strong bases such as NaOH and KOH. But silicon is more soluble in NaOH and KOH solution in form $Si(OH)_4^-$ than of aluminum. Aluminum is less soluble in strong base solutions because the negative charge on the aluminum tetrahedral limits the interaction of Al and the strong base. The desilication process decreased the Si/Al ratio in HZSM-5 [18]. BET (Brunauer-Emmett-Teller) analysis was used to determine surface area, pore volume and pore size (Table 1). Pore size distribution in untreated HZSM-5 and desilicated HZSM-5 was analyzed by N_2 adsorption isotherm (Fig. 2).

The analysis confirmed that mesopore structure enlargement could be achieved, pore diameter in range of 2-50 nm was observed. In Fig. 2, the N_2 adsorption and desorption isotherms profile showed a small and constantly adsorptive volume at various pressures [19], which was a confirmation of micropore presence without significant

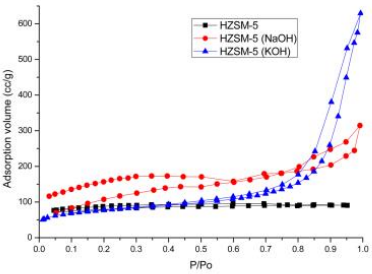


Fig. 2. N_2 adsorption and desorption isotherms profile at 77 K for untreated HZSM-5 and desilicated HZSM-5 with NaOH and KOH solution.

Table 1. Comparison for HZSM-5, desilicated HZSM-5 (NaOH) and desilicated HZSM-5 (KOH) in pore characteristics (BET) and Si/Al ratio (EDX)

Sample	S_{total}	V_{total}	V_{mikro}	V_{meso}	d_{meso}	Si/Al
	m^2/g	cc/g	cc/g	cc/g	nm	
HZSM-5	266.288	0.1401	0.124	0.0161	3.4-12.4	27.9832
Desilicated HZSM-5 (NaOH)	526.035	0.4866	0.137	0.3496	6.1-147.6	22.1059
Desilicated HZSM-5 (KOH)	258.470	0.9737	0.085	0.8887	1.7-99.8	16.3032

mesopore in HZSM-5. The NaOH treated HZSM-5 shows very unusual N_2 physisorption pattern. This is an adsorption hysteresis, which according to IUPAC isotherm classification standard, is associated with capillary condensation inside pore structure [17]. The N_2 physisorption pattern in observed in Fig. 2 refers to Type H4 of the classification, which is usually associated with narrow slit-like pores. This phenomenon is indicated by reducing mesopore (0.3496 cc/g) and micropore (0.137cc/g) ratio. (Table 1). The BET model confirmed that micropore volume (0.124 cc/g) was more dominant than mesopore volume (0.0161 cc/g). Both NaOH and KOH desilicated HZSM-5 enhanced nitrogen uptake at higher pressure, which indicated the presence of more mesopore in the hierarchycal pore system (micropore and mesopore mixture) as shown in Fig. 3.

The NaOH desilicated HZSM-5 increased mesoporous diameter from 3.4-12.4 nm to 6.1-29.9 nm. The mesoporous volume also increased about 20.7 times from 0.0161 to 0.3496 cc/g. The surface area of the pore increased about 98% from 266.288 to 526.035 cc/g.

The KOH desilicated HZSM-5 increased mesoporous diameter from 3.4-12.4 nm to 2.1-48.0 nm. The mesoporous volume also increased about 54-times from 0.0161 to 0.3496 cc/g. The surface area of the pore showed similar value (266.288 to 258.470 cc/g). KOH desilicated HZSM-5 gave similar nitrogen uptake with untreated HZSM-5 at lower to intemediate pressure and rise significantly at higher pressure (Fig. 2). The increasing of pore diameter and volume but stagnant surface area was an interesting phenomenon for KOH treatment. The KOH treatment destroyed the crystalline structure of HZSM-5 (Fig. 4) that caused decreasing surface area that might have before.

Mesoporous formation as indicated by increasing in mesoporous area and volume was due to the OH-alkali ions which were selectively bound to the silicon framework [18]. The Si/Al ratio decreased from 40 (for initial feedstock ZSM-5 ammonium) to 27.9832 (untreated HZSM-5), subsequently further decreased to 22.1059 in the desilication of NaOH and to 16.3032 at KOH desilication as shown in Table 1. The strength of the KOH base ($pK_b = 0.5$) is greater than NaOH ($pK_b = 0.2$), so that the KOH solution was stronger in removing Si in the zeolite structure of HZSM-5 than NaOH solution. The larger the pK_b, the more OH-ions were released and the more Si could be removed from the HZSM-5 zeolite framework, enlarging the pore volume. This result supported the HZSM-5 crystalline destroyed during KOH treatment.

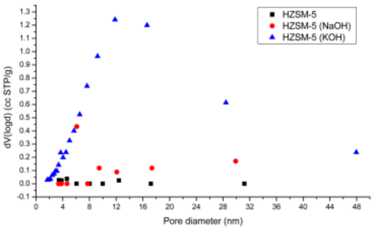


Fig. 3. Pores size distribution profile BJH adsorption for untreated HZSM-5 and desilicated HZSM-5 with NaOH dan KOH solution.

The crystallinity and type of component were analyzed by XRD according to diffraction angle (2θ) on the X-ray diffraction spectra. XRD analysis was performed on microporous HZSM-5, mesoporous HZSM-5 (NaOH and KOH desilication), impregnated and reduced Fe-Co/HZSM-5. Comparison of crystallinity of microporous HZSM-5, mesoporous HZSM-5 (NaOH and KOH desilication) can be seen in Fig. 4. The crystallinity of the microporous HZSM-5 and the mesoporous HZSM-5 (NaOH desilication) showed identical spectral patterns with sharp peaks formed at 2θ angle of 7.89°, 8.08°, 23°, 23.27° and 23.91°. These both results were identical with ZSM-5 and HZSM-5 spectra that are shown in Fig. 4 (inset), with peaks at 7-8° and 23-24° which was the characteristic peak of HZSM-5 [20]. Garcia-Martinez and Li [21] compared the micropore volumes calculated from the isotherms with the nitrogen sorption isotherms. Alkali treatment did not change the material crystallinity determined by X-ray diffraction (XRD). The parent HZSM-5 and NaOH treated HZSM-5's XRD pattern had identical pattern but they gave different peak intensity. Desilication just reduced Si content from zeolite framework and it was needed to maintain the crystallinity and characteristic for catalyst support. These results indicated that HZSM-5 desilication using 1 M NaOH solution maintained the original crystal structure. Different phenomenon showed in desilication using 1 M KOH solution. Although the spectral peaks had the same 2θ position as the previous spectra, but the intensity was much smaller. It indicated that the crystallinity of the HZSM-5 which was dissolved with the KOH solution decreased significantly because of the considerable Si adsorption shown by the decrease of Si/Al ratio from 40 to 16.3032 (EDX analysis). KOH desilication studies could not be found, so it may have not been investigated before. The possibility of KOH desilication was investigated here according to NaOH and KOH characteristics similarity. Unfortunately, it was found that KOH destroyed the crystallinity of desilicated HZSM-5 zeolites. NaOH desilicated HZSM-5 was further investigated with various composition metal

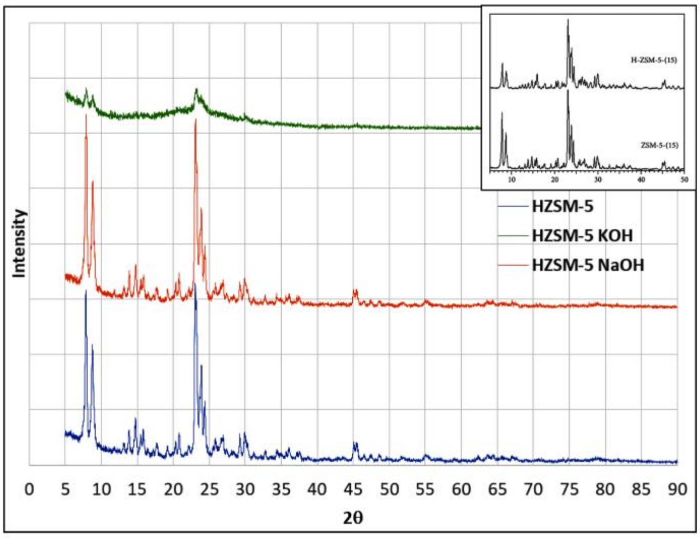


Fig. 4. XRD spectra for HZSM-5, desilicated HZSM-5 (NaOH) and desilicated HZSM-5 (KOH). Inset : ZSM-5 and HZSM-5 Spectra [20].

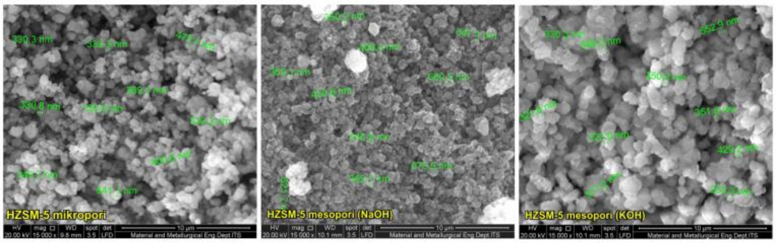


Fig. 5. SEM image for HZSM-5, desilicated HZSM-5 mesopore (NaOH) and desilicated HZSM-5 mesopore (KOH).

(iron and cobalt) impregnation.

Solution of 1 M HNO_3 was used to form amorphous phase formation of the mesoporous HZSM-5 that treated at 70 °C for 2 hours in the stirred tank. Subsequently, the sample was washed with deionized water, dried and calcined by the same procedure after the above desilication process. The formation of an amorphous phase was analyzed by XRD spectra as shown in Fig. 6. The noise of spectra showed the amorphous phase that was formed during the process.

The morphological changes of HZSM-5 before and after desilication were observed through scanning electron microscopy (SEM) at 15,000 times magnification (Fig. 5). Desilicated HZSM-5 (NaOH) showed the rigid particle structure, the similar structure with original HZSM-5. It indicated crystallinity structure in the zeolite HZSM-5. Desilicated HZSM-5 (KOH) showed larger pores and less rigidity compared with original HZSM-5 and desilicated HZSM-5 (NaOH). It indicated the crystalline degradation in KOH desilication treatment.

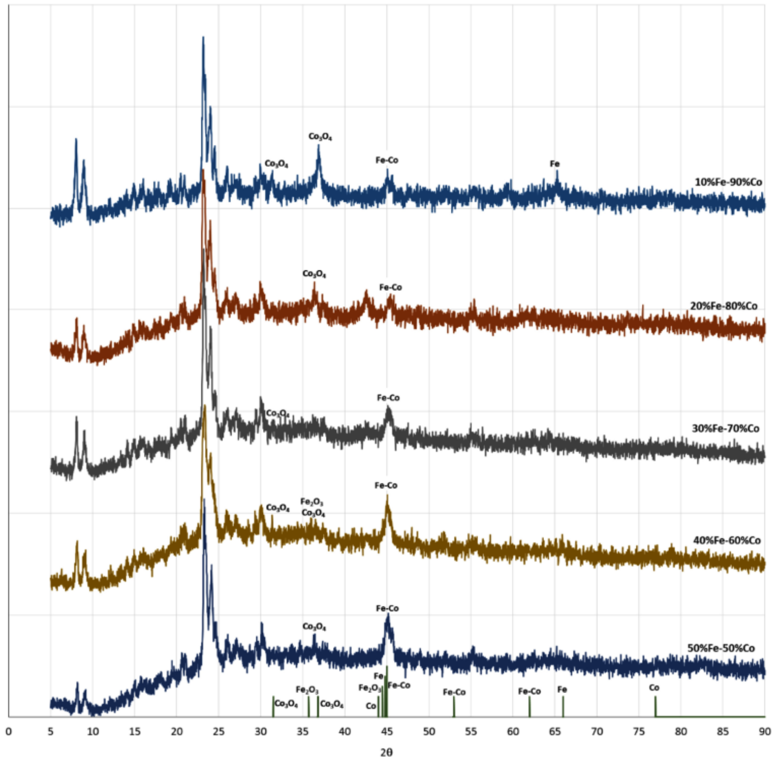
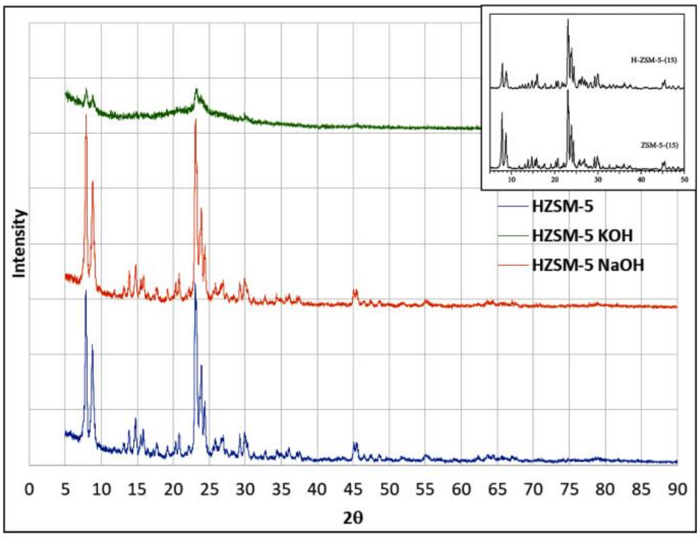


Fig. 6. XRD Spectra for Fe-Co/HZSM-5 (NaOH) after reduction with varied composition of Fe and Co.

3-2. Effect of iron and cobalt composition on Fe-Co/HZSM-5 characteristics

The Fe and Co catalysts loading was 10% weight in mesoporous desilicated HZSM-5 (NaOH). The catalyst compositions were 10Fe-90Co, 20Fe-80Co, 30Fe-70Co, 40Fe-60Co, 50Fe-50Co/HZM-5. Impregnated varied composition of Fe and Co into meso-HZSM-5 was analyzed with XRF. Table 2 shows a comparison of the prepared Fe content and impregnated Fe and Co into HZSM-5 from NaOH and KOH desilication. The real Fe and Co compositions were at column 5 and 6 in Table 2. The metal composition still was in tolerance limit from designed composition (less than 5%). Columns 3 and 4 were the overall composition in all of the metal in catalyst (zeolite material and metal catalyst). The absorption of Fe-nitrate solution was less than the absorption of Co-nitrate in mesoporous HZSM-5 pore, so the Fe content obtained was smaller than the prepared one. The absorption of Fe-nitrate and Co-nitrate into impregnated HZSM-5 (NaOH) was larger than impregnated HZSM-5 (KOH). It can be seen that iron and cobalt content (XRF reading) in NaOH desilicated HZSM-5 was larger than KOH. Impregnated HZSM-5 (KOH) had better mesopore structure, but less crystallinity that gave less affinity with Fe and Co precursor. Loading quantities could not be calculated from XRF results because Al metal and its compounds were not



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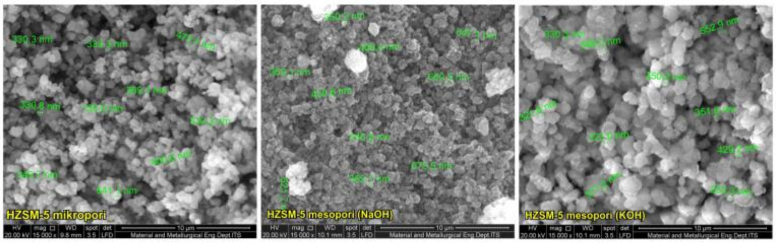

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Further, more Fe-Co alloys and less oxide of iron (Fe_2O_3) as well cobalt (Co_3O_4) were commonly observed in the produced catalysts. The largest Fe-Co alloys could be found in 50Fe-50Co/HZSM-5.

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Synthesis and Characterization of Fe-Co/mesoHZSM-5 : Effect of Desilication Agent and Iron-cobalt Composition

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Abstract – Synthesis of Fe-Co/meso-HZSM5 catalyst, intended to be applied in Fischer-Tropsch (FT) reaction was investigated. The study emphasized the effect of desilication agents, NaOH and KOH, on the catalyst materials properties. Impregnation composition of active metal (Fe and Co) was also examined. HZSM-5, converted from ammonium ZSM-5 through calcination, was treated with NaOH and KOH for desilication, followed by impregnation with 10% metal loading. Fe composition in the initial mixture was varied at 10-50% from total composition. After impregnation, reduction was applied by flowing hydrogen gas at 400 °C for 10 hours. The use of KOH solution induced greater mesoporous volumes; however, it had a detrimental effect on zeolite crystal structure. NaOH solutions, on the other hand, increased mesopore area as high as 100%, indicated from surface area increase from 266.28 m^2/g of HZSM-5, to 526.03 m^2/g of NaOH-desilicated HZSM-5. In addition, the application of NaOH solution increased pore volume from 0.14 cc/g to 0.486 cc/g. Further, more Fe-Co alloys and less oxide of iron (Fe_2O_3) as well cobalt (Co_3O_4) had been commonly observed in the produced catalysts. The largest Fe-Co alloys could be found in 50Fe-50Co/HZSM-5.

Key words: HZSM-5, Mesopore, Impregnation, Fe-Co, Desilication

1. Introduction

Zeolites are aluminosilicate crystals with unique pore structures. They are widely used in the adsorption, separation and catalytic processes (cracking and other hydrotreating process) due to their unique properties. They have homogeneous micropores, high thermal stability, acidity, and unique ability to stabilize metallic species [1]. Microporous HZSM-5 has been inapplicable in catalyzing large molecules, because of the diffusion limitations in micropore channels and carbon deposition in the pore system. Construction of HZSM-5 materials with larger pore sizes can improve reaction efficiency and minimize channel closure. The pore size of the material can be classified into micropores (pore diameter smaller than 2 nm), mesopores (pore diameter 2-50 nm) and macropores (pore diameter greater than 50 nm). The mesoporous structure provides greater space for metal catalysts to occupy more support pores. The micropore structure can be converted to mesopore using desilication, which is a process used to form mesopores through decreasing of silicon content in zeolites. The type of alkaline, concentration, temperature, process duration and Si/Al ratio affect desilicated mesopore material resulting. Commonly, Tetrapropylammonium hydroxide (TPAOH) or NaOH solution are used as desilication agents. TPAOH treatment provides a larger mesoporous area than NaOH, but NaOH solution gives a larger pore volume [2]. TPAOH is more expensive and difficult to obtain, so the use of NaOH is more attractive. The use of other bases such as KOH solution is still possible in this desilication process. Nitric acid solution is used to transform the mesoporous HZSM-5 into amorphous structure. The formation of the amorphous phase can improve the adhesion of the metal catalyst on the mesoporous HZSM-5 support [3,4].

Metallic iron and cobalt are used as polymerization catalyst in Fischer-Tropsch synthesis. The impregnated iron and cobalt on HZSM-5 can be used as bifunction catalyst which combines polymerizing synthesis gas and cracking long chain hydrocarbon for making biofuel [5-9]. Cobalt catalyst has some advantages compared to iron catalyst and is preferred in Fischer-Tropsch synthesis. The advantages are middle chain growth probability, very low water gas-shift activity and CO_2 selectivity, and low reaction temperature. But cobalt catalyst has some disadvantages parameter that can be reduced by iron catalyst added. Iron catalyst is added in small amount to improve the cobalt catalyst performance (improve olefin selectivity, reduce methane selectivity, reduce temperature and pressure sensitivity to product distribution and reduce the catalyst price) [10,11]. In this research, the catalyst was made by less iron content to improve cobalt performance as main catalyst. Incipient wetness impregnation has been the considered method for metallic impregnation to mesoporous HZSM-5 support. The reduction would convert oxide form to their free metallic form of Fe and Co [8,12,13].

The study emphasized studying the effect of desilication agents, NaOH and KOH, on the catalyst materials properties. Additionally, impregnation composition of active metal (Fe and Co) was also

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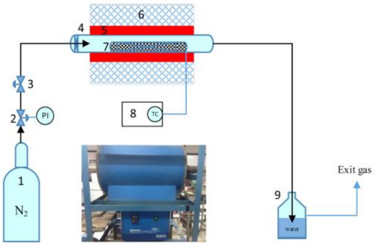
examined. The data obtained from this study will be used to develop zeolites based catalyst for Fischer-Tropsch reaction.

2. Methods

Materials used in this experiment were zeolite ZSM-5 in ammonium form (CBV 8014, Amberlyst International), $Fe(NO_3)_3 \cdot 9H_2O$ (Merck), $Co(NO_3)_2.6H_2O$ (Merck), NaOH p.a. (Merck), KOH p.a. (Merck), nitric acid p.a. (Merck), Hydrogen and Nitrogen gas (PT. Samator Gas Industry, Surabaya, Indonesia), Aquadest. The equipment used was the calcination reactor (Fig. 1), quartz furnace crucible, hotplate magnetic stirrer, vacuum filter, air compressor, hot air oven, syringe, digital scales and standard glassware.

The ammonium salt of ZSM-5 was calcined at 550 °C for 5 hours to obtain microporous HZSM-5. HZSM-5 was desilicated by 1 M KOH and 1 M NaOH solution with stirring at 70 °C for 1 h. The suspension was cooled in an ice bath, separated from the zeolite crystals by dispersion in deionized water and filtered until neutral pH, stated for 24 hours at 50 °C, dried at 120 °C for 12 hours and finally calcined at 550 °C for 5 hours. The mesoporous HZSM-5 product was treated using 1 M HNO_3 solution at 70 °C for 2 h and stirred to form an amorphous phase. Subsequently, the sample was washed with deionized water, dried and calcined by the same procedure after the desilication above [14,15]. Iron and cobalt from $Co(NO_3)_2 \cdot 6H_2O$ and/or $Fe(NO_3)_3 \cdot 9H_2O$ solutions were impregnated using incipient wetness impregnation (IWI) process on amorphous meso-HZSM-5. Loading metal catalyst was 10% and Fe composition in the initial mixture was varied at 10-50% from total composition. The impregnated HZSM-5 was kept in desiccator at room temperature for 24 hours, dried in oven at 120 °C for 12 hours and then calcined at 550 °C for 2 hours. After impregnation, reduction was applied by flowing hydrogen gas at 400 °C for 10 hours.



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8. Temperatur controller
9. Exit gas washing tank

Brunauer-Emmett-Teller (BET), X-ray diffraction (XRD) and scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDX) analysis were used for materials characterization. The BET model was used to analyze the volume and surface area of micropore and mesopore (deriving from t-plot data) [16], the pore size distribution (derived from BJH model) [17]. XRD analysis was used to determine the crystal structure and the form of the impregnated iron and cobalt. The SEM was used to analyze the structure image for material. The Si and Al concentration in the solid materials before and after alkali treatment were analyzed with EDX.

3. Result and Discussion

3-1. Effect of desilication agent for mesopore development

Ammonium ZSM-5 (Si/Al = 40) was converted to microporous HZSM-5 through calcination process in the tube furnace reactor (Fig. 1). The formation of mesoporous structures was obtained through the desilication process in which silicon was partly removed from zeolite framework. Generally, silicon and aluminum in the zeolite framework are removed with the use of strong bases such as NaOH and KOH. But silicon is more soluble in NaOH and KOH solution in form $Si(OH)_4^-$ than of aluminum. Aluminum is less soluble in strong base solutions because the negative charge on the aluminum tetrahedral limits the interaction of Al and the strong base. The desilication process decreased the Si/Al ratio in HZSM-5 [18]. BET (Brunauer-Emmett-Teller) analysis was used to determine surface area, pore volume and pore size (Table 1). Pore size distribution in untreated HZSM-5 and desilicated HZSM-5 was analyzed by N_2 adsorption isotherm (Fig. 2).

The analysis confirmed that mesopore structure enlargement could be achieved, pore diameter in range of 2-50 nm was observed. In Fig. 2, the N_2 adsorption and desorption isotherms profile showed a small and constantly adsorptive volume at various pressures [19], which was a confirmation of micropore presence without significant

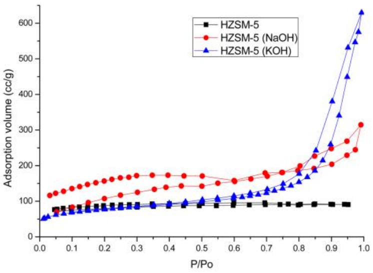


Fig. 2. N_2 adsorption and desorption isotherms profile at 77 K for untreated HZSM-5 and desilicated HZSM-5 with NaOH and KOH solution.

Table 1. Comparison for HZSM-5, desilicated HZSM-5 (NaOH) and desilicated HZSM-5 (KOH) in pore characteristics (BET) and Si/Al ratio (EDX)

Sample	S_{total}	V_{total}	V_{mikro}	V_{meso}	d_{meso}	Si/Al
	m^2/g	cc/g	cc/g	cc/g	nm	
HZSM-5	266.288	0.1401	0.124	0.0161	3.4-12.4	27.9832
Desilicated HZSM-5 (NaOH)	526.035	0.4866	0.137	0.3496	6.1-147.6	22.1059
Desilicated HZSM-5 (KOH)	258.470	0.9737	0.085	0.8887	1.7-99.8	16.3032

mesopore in HZSM-5. The NaOH treated HZSM-5 shows very unusual N_2 physisorption pattern. This is an adsorption hysteresis, which according to IUPAC isotherm classification standard, is associated with capillary condensation inside pore structure [17]. The N_2 physisorption pattern in observed in Fig. 2 refers to Type H4 of the classification, which is usually associated with narrow slit-like pores. This phenomenon is indicated by reducing mesopore (0.3496 cc/g) and micropore (0.137cc/g) ratio. (Table 1). The BET model confirmed that micropore volume (0.124 cc/g) was more dominant than mesopore volume (0.0161 cc/g). Both NaOH and KOH desilicated HZSM-5 enhanced nitrogen uptake at higher pressure, which indicated the presence of more mesopore in the hierarchycal pore system (micropore and mesopore mixture) as shown in Fig. 3.

The NaOH desilicated HZSM-5 increased mesoporous diameter from 3.4-12.4 nm to 6.1-29.9 nm. The mesoporous volume also increased about 20.7 times from 0.0161 to 0.3496 cc/g. The surface area of the pore increased about 98% from 266.288 to 526.035 cc/g.

The KOH desilicated HZSM-5 increased mesoporous diameter from 3.4-12.4 nm to 2.1-48.0 nm. The mesoporous volume also increased about 54-times from 0.0161 to 0.3496 cc/g. The surface area of the pore showed similar value (266.288 to 258.470 cc/g). KOH desilicated HZSM-5 gave similar nitrogen uptake with untreated HZSM-5 at lower to intermediate pressure and rise significantly at higher pressure (Fig. 2). The increasing of pore diameter and volume but stagnant surface area was an interesting phenomenon for KOH treatment. The KOH treatment destroyed the crystalline structure of HZSM-5 (Fig. 4) that caused decreasing surface area that might have before.

Mesoporous formation as indicated by increasing in mesoporous area and volume was due to the OH-alkali ions which were selectively bound to the silicon framework [18]. The Si/Al ratio decreased from 40 (for initial feedstock ZSM-5 ammonium) to 27.9832 (untreated HZSM-5), subsequently further decreased to 22.1059 in the desilication of NaOH and to 16.3032 at KOH desilication as shown in Table 1. The strength of the KOH base ($pK_b = 0.5$) is greater than NaOH ($pK_b = 0.2$), so that the KOH solution was stronger in removing Si in the zeolite structure of HZSM-5 than NaOH solution. The larger the pK_b, the more OH-ions were released and the more Si could be removed from the HZSM-5 zeolite framework, enlarging the pore volume. This result supported the HZSM-5 crystalline destroyed during KOH treatment.

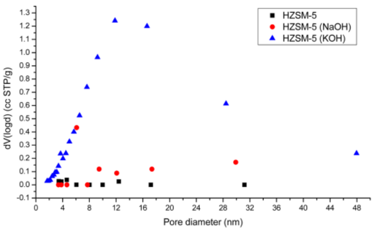


Fig. 3. Pores size distribution profile BJH adsorption for untreated HZSM-5 and desilicated HZSM-5 with NaOH dan KOH solution.

The crystallinity and type of component were analyzed by XRD according to diffraction angle (2θ) on the X-ray diffraction spectra. XRD analysis was performed on microporous HZSM-5, mesoporous HZSM-5 (NaOH and KOH desilication), impregnated and reduced Fe-Co/HZSM-5. Comparison of crystallinity of microporous HZSM-5, mesoporous HZSM-5 (NaOH and KOH desilication) can be seen in Fig. 4. The crystallinity of the microporous HZSM-5 and the mesoporous HZSM-5 (NaOH desilication) showed identical spectral patterns with sharp peaks formed at 2θ angle of 7.89^{o}, 8.08^{o}, 23^{o}, 23.27^{o} and 23.91^{o}. These both results were identical with ZSM-5 and HZSM-5 spectra that are shown in Fig. 4 (inset), with peaks at $7\text{-}8^{o}$ and $23\text{-}24^{o}$ which was the characteristic peak of HZSM-5 [20]. Garcia-Martinez and Li [21] compared the micropore volumes calculated from the isotherms with the nitrogen sorption isotherms. Alkali treatment did not change the material crystallinity determined by X-ray diffraction (XRD). The parent HZSM-5 and NaOH treated HZSM-5's XRD pattern had identical pattern but they gave different peak intensity. Desilication just reduced Si content from zeolite framework and it was needed to maintain the crystallinity and characteristic for catalyst support. These results indicated that HZSM-5 desilication using 1 M NaOH solution maintained the original crystal structure. Different phenomenon showed in desilication using 1 M KOH solution. Although the spectral peaks had the same 2θ position as the previous spectra, but the intensity was much smaller. It indicated that the crystallinity of the HZSM-5 which was dissolved with the KOH solution decreased significantly because of the considerable Si adsorption shown by the decrease of Si/Al ratio from 40 to 16.3032 (EDX analysis). KOH desilication studies could not be found, so it may have not been investigated before. The possibility of KOH desilication was investigated here according to NaOH and KOH characteristics similarity. Unfortunately, it was found that KOH destroyed the crystallinity of desilicated HZSM-5 zeolites. NaOH desilicated HZSM-5 was further investigated with various composition metal

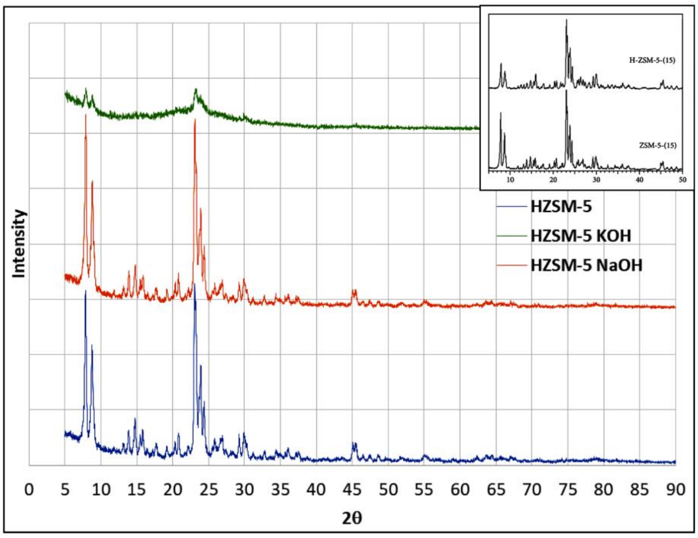


Fig. 4. XRD spectra for HZSM-5, desilicated HZSM-5 (NaOH) and desilicated HZSM-5 (KOH). Inset : ZSM-5 and HZSM-5 Spectra [20].

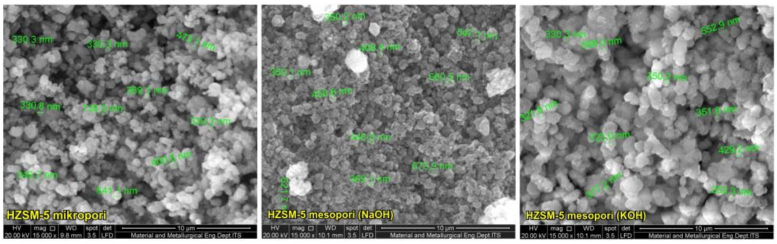


Fig. 5. SEM image for HZSM-5, desilicated HZSM-5 mesopore (NaOH) and desilicated HZSM-5 mesopore (KOH).

(iron and cobalt) impregnation.

Solution of 1 M HNO_3 was used to form amorphous phase formation of the mesoporous HZSM-5 that treated at 70 °C for 2 hours in the stirred tank. Subsequently, the sample was washed with deionized water, dried and calcined by the same procedure after the above desilication process. The formation of an amorphous phase was analyzed by XRD spectra as shown in Fig. 6. The noise of spectra showed the amorphous phase that was formed during the process.

The morphological changes of HZSM-5 before and after desilication were observed through scanning electron microscopy (SEM) at 15,000 times magnification (Fig. 5). Desilicated HZSM-5 (NaOH) showed the rigid particle structure, the similar structure with original HZSM-5. It indicated crystallinity structure in the zeolite HZSM-5. Desilicated HZSM-5 (KOH) showed larger pores and less rigidity compared with original HZSM-5 and desilicated HZSM-5 (NaOH). It indicated the crystalline degradation in KOH desilication treatment.

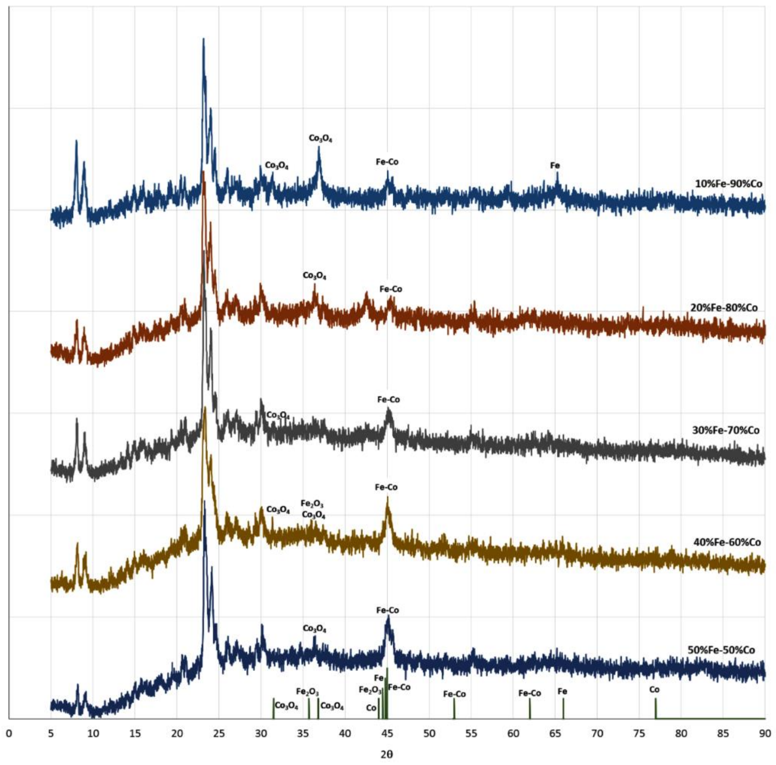


Fig. 6. XRD Spectra for Fe-Co/HZSM-5 (NaOH) after reduction with varied composition of Fe and Co.

3-2. Effect of iron and cobalt composition on Fe-Co/HZSM-5 characteristics

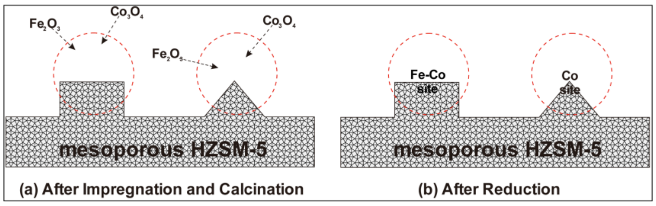
The Fe and Co catalysts loading was 10% weight in mesoporous desilicated HZSM-5 (NaOH). The catalyst compositions were 10Fe-90Co, 20Fe-80Co, 30Fe-70Co, 40Fe-60Co, 50Fe-50Co/HZM-5. Impregnated varied composition of Fe and Co into meso-HZSM-5 was analyzed with XRF. Table 2 shows a comparison of the prepared Fe content and impregnated Fe and Co into HZSM-5 from NaOH and KOH desilication. The real Fe and Co compositions were at column 5 and 6 in Table 2. The metal composition still was in tolerance limit from designed composition (less than 5%). Columns 3 and 4 were the overall composition in all of the metal in catalyst (zeolite material and metal catalyst). The absorption of Fe-nitrate solution was less than the absorption of Co-nitrate in mesoporous HZSM-5 pore, so the Fe content obtained was smaller than the prepared one. The absorption of Fe-nitrate and Co-nitrate into impregnated HZSM-5 (NaOH) was larger than impregnated HZSM-5 (KOH). It can be seen that iron and cobalt content (XRF reading) in NaOH desilicated HZSM-5 was larger than KOH. Impregnated HZSM-5 (KOH) had better mesopore structure, but less crystallinity that gave less affinity with Fe and Co precursor. Loading quantities could not be calculated from XRF results because Al metal and its compounds were not

Table 2. Impregnated iron and cobalt composition on Fe-Co/HZSM-5 catalyst according to XRF analysis

Desilication Agent	Catalyst	Iron and Cobalt Content (XRF Reading)		Iron and Cobalt Composition	
		Fe	Co	Impregnated Fe	Impregnated Co
NaOH	10Fe-90Co/HZSM-5	4.150%	26.800%	13.41%	86.59%
NaOH	20Fe-80Co/HZSM-5	11.000%	51.430%	17.62%	82.38%
NaOH	30Fe-70Co/HZSM-5	15.800%	45.230%	25.89%	74.11%
NaOH	40Fe-60Co/HZSM-5	21.400%	40.000%	34.85%	65.15%
NaOH	50Fe-50Co/HZSM-5	27.100%	33.300%	44.87%	55.13%
KOH	10Fe-90Co/HZSM-5	1.805%	16.198%	10.03%	89.97%
KOH	20Fe-80Co/HZSM-5	3.219%	14.149%	18.53%	81.47%
KOH	30Fe-70Co/HZSM-5	4.818%	12.146%	28.40%	71.60%
KOH	40Fe-60Co/HZSM-5	6.512%	10.897%	37.40%	62.60%
KOH	50Fe-50Co/HZSM-5	8.841%	9.365%	48.56%	51.44%

Table 3. Fe and Co impregnated into HZSM-5 (NaOH) according to EDX analysis

Catalyst	Synthesized Composition			Resulted Composition (EDX)		
	Fe (%w)	Co (%w)	Loading (%w)	Fe (%w)	Co (%w)	Loading (%w)
10Fe-90Co/HZSM-5	10	90	10	10.1909	89.8091	16.11
30Fe-70Co/HZSM-5	30	70	10	20.6542	79.3458	13.22
50Fe-50Co/HZSM-5	50	50	10	38.4509	61.5491	11.71



(a) After Impregnation and Calcination

(b) After Reduction

Fig. 7. Schematic representations of elementary mechanisms for catalyst transformation from iron and cobalt precursor to active metal catalyst Fe-Co alloys and Co on mesoporous HZSM-5.

identified from this analysis. The loading of catalyst was calculated from EDX analyzing (Table 3). The average metal loading was 13.5%. The results indicated the nonhomogeneous distributed/impregnated metal on HZSM-5. EDX has some limitations. EDX analyze the narrow spot from sample surface (required stable, flat, homogeneous and void-free specimens), then non-homogeneous metal distribution in this study might lead to different content of value.

The impregnated mesoporous HZSM-5 was reduced to obtain a metal catalyst on the active surface. The reduction was done in the furnace using excess hydrogen stream at 400 °C for 8 hours. XRD analysis was used to observe the reduction results. The diffraction angle position of the metal peaks refers to the spectral database of Tavasoli *et al*. [22]. Fig. 7 shows the spectra of Fe. Co and Fe-Co alloys formed. There were still Fe_2O_3 and Co_3O_4 oxides present in the catalyst. which indicated an imperfect reduction process. The reduction results of 30, 40 and 50% Fe content in Fe-Co showed Fe-Co alloys were formed much more than Fe_2O_3 and Co_3O_4 oxides. Fe and Co did not appear on the spectra as they may occur around the diffraction angle of 45° which is very close to the Fe-Co diffraction angle. The opposite result was obtained in the results of the composition of 10% and 20% Fe in Fe-Co. The presence of Co_3O_4 oxide was more dominant than the Fe-Co alloys formed. When viewed thoroughly, only Co_3O_4 oxides were likely to form. This suggested that the reduction conditions used were more suitable for Fe reduction than Co.

The schematic representations of elementary mechanisms for catalyst formation can be made according to these results. In Fig. 7, the transformation of iron and cobalt precursor to oxide occurred after impregnation and calcination. Reduction process produced active metal catalyst Fe-Co alloys and Co on mesoporous HZSM-5.

4. Conclusion

Although the use of KOH solution induced greater mesoporous volume, it had a detrimental effect on zeolite crystal structure. NaOH solutions, on the other hand, increased mesopore area as high as 100%, indicated from surface area increase from 266.28 m^2/g of HZSM-5, to 526.03 m^2/g of NaOH-desilicated HZSM-5. In addition, the application of NaOH solution increased pore volume from 0.14 cc/g to 0.486 cc/g.

Further, more Fe-Co alloys and less oxide of iron (Fe_2O_3) as well cobalt (Co_3O_4) were commonly observed in the produced catalysts. The largest Fe-Co alloys could be found in 50Fe-50Co/HZSM-5.

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