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Abstract. The combination of bimetallic Fe-Co (as polymerization catalyst) and HZSM-5 (as cracking catalyst) could convert synthesis gas to biofuel in one-step Fischer-Tropsch synthesis. Mesoporous HZSM-5 gave better conversion, because it increased reactants and products diffusivity. The effect of impregnated ratio of iron and cobalt on characterization of Fe-Co/meso-HZSM-5 catalyst had been studied. HZSM-5 was made from ammonium ZSM-5 through calcination process, then it was desilicated with NaOH and impregnated with 10% metal loading and 0-100% Fe content in Fe-Co (%w). The material results were reduced continuously by hydrogen at 400℃ for 10 hours. Treatment of HZSM-5 in various ratio of iron and cobalt leads to mesoporosity development. The iron and cobalt impregnation decreased the total surface area from 350.859 m^2/g (on HZSM-5) to 231.852-329.606 m^2/g (on Fe-Co/HZSM-5). Increasing cobalt content in Fe-Co impregnation on HZSM-5 decreased total surface area and increased average pore diameter. Impregnation process lowered the crystallinity but still maintained the material crystal structure. 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 30Fe-70Co/HZSM-5. Iron and cobalt impregnation occupied the active sites formed from alcohol groups function that was indicated with decreasing alcohol groups area in FTIR spectra.

1. Introduction

Zeolites are extensively used in the adsorption, separation and catalytic processes due to their homogeneous micropores, high thermal stability, acidity, and unique ability in stabilizing metallic species [1]. Microporous HZSM-5 failed 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 mesoporous structure (pore diameter 2-50 nm) provides greater space for metal catalysts to occupy more support pores. Mesoporous zeolites are known as hierarchycal zeolite due to micropore and mesopore content in its structure. Desilication (decreasing silicon in zeolite) process was most effective methods and commonly used to convert micropore to mesopore. The number of silicon atoms in the skeleton that can be released without damaging the structure is regulated using characteristics inherent in zeolites (Si/Al ratio and skeletal topology) and using alkali treatment conditions (type and concentration of desilication agents). Desilication agents not only create mesopores but also affect the acidity of zeolite hierarchies, modify the number of acid sites, the nature

and ease of access. NaOH solution were used as desilication agents due to larger desilicated pore volume [2]. Concentration, distribution, strength and stability of hydrothermal acid sites were also the decision factors for the application of desilicated zeolite catalysts. Complete information on the acidity of zeolite from the alkali treatment can be obtained from the analysis of the vibrational region the hydroxyl streching of the IR spectrum (FTIR). Amorphous phase formation will increase the adhesion of metal catalyst to mesoporous HZSM-5 support. Nitric acid solution was used to transform the mesoporous HZSM-5 into amorphous structure [3, 4]. The formation of the amorphous phase could improve the adhesion of the metal catalyst on the mesoporous HZSM-5 support.

Combined metallic catalyst and HZSM-5 could be used as catalyst of Fischer-Tropsch synthesis. Incipient wetness impregnation method is more suitable to be used for mesoporous HZSM-5 zeolite support. The HZSM-5 support used is in the form of powder so that the mixed salt solution containing the catalyst metal can be distributed homogeneously when sprayed on the support. The impregnated iron and cobalt on HZSM-5 could be used to combine polimerizing synthesis gas and cracking long chain hydrocarbon for making biofuel in one reactor [5–8]. Mesoporosity and acidity affected to product selectivity. High acidity of zeolite increased paraffin C_2-C_4 content duo to higher molecules overcracking. Ionic sodium adding to zeolite decreased acidity and produced higher paraffin [7, 9]. Metallic oxide was reduced in hot flowing hydrogen to form free metallic Fe and Co. This research investigated the effect of impregnated ratio of iron and cobalt on Fe-Co/HZSM-5's characteristic and performance.

2. 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), nitric acid p.a. (Merck), Hydrogen and Nitrogen gas (PT. Samator Gas Industry, Surabaya), 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.
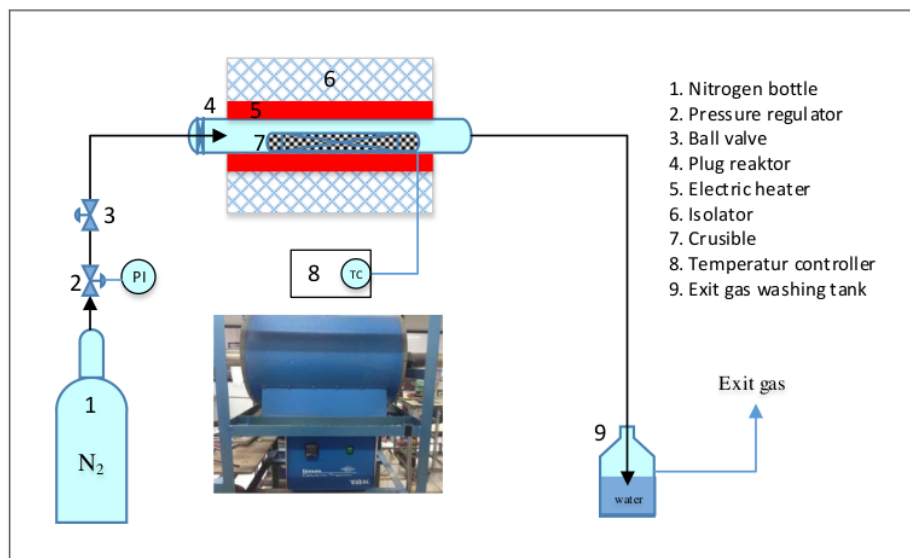
Figure 1. Tube furnace reactor (Linn Elektro Therm) for calcination process

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 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°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 [10, 11]. 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 mesoHZSM-5. Loading metal catalyst was 10% and Fe content in Fe-Co was varied of 0-100%. 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. The impregnated materials were reduced in continuous flow of H_2 gas at 400°C for 10 hours. This catalyst was used on Fischer-Tropsch reaction at 200-250°C, 20 bar, 25 mL/min in continuous fixed bed reactor for 120 hours.

Brunauer–Emmett–Teller (BET), X-ray Diffraction (XRD) and Energy Dispersive X-ray spectroscopy (EDX) analysis were used for materials characterization.

3. Result and Discussion

Impregnation ratio gave different change of total surface area (S_{total}), mesopore volume (V_{meso}) and average pore diameter ($d_{average}$) as shown in Table 1. Desilicated HZSM-5 provided total surface area 350.859 m^2/g and decreased after impregnation with Fe and Co. Higher cobalt content decreased total surface area. Cobalt occupied more micropore in HZSM-5 than iron, that caused decreasing of micropore volume. This phenomena was also indicated by increasing average pore diameter, due to cobalt also occupied the surface area outside of the pore. It would give the greater mesopore volume read from BET analysis. All catalyst was still classified as mesopore material (pore diameter 2-50 nm) except 0Fe-100Co/HZSM-5 catalyst that had pore diameter larger than 50 nm. It also had least surface area among other catalyst.

Table 1. Comparison of surface characteristics (BET analysis) for meso-HZSM-5 and impregnated Fe-Co/meso-HZSM-5 in various Fe and Co ratio.

| Sampel	S_{total} m^2/g	V_{total} cc/g	V_{mikro} cc/g	V_{meso} cc/g	$d_{average}$ nm
HZSM-5	350.859	0.6203	0.139	0.4813	35.3585
0Fe-100Co/HZSM-5	231.852	0.8197	0.015	0.8047	70.7084
10Fe-90Co/HZSM-5	284.901	0.6990	0.120	0.579	49.0692
20Fe-80Co/HZSM-5	278.700	0.6950	0.116	0.579	49.8736
30Fe-70Co/HZSM-5	296.921	0.4990	0.123	0.376	33.6089
100Fe-0Co/HZSM-5	329.606	0.6090			36.9510

Iron and cobalt composition used in impregnation were 0, 10, 20, 30 and 100% Fe content in Fe-Co with 10% metallic loading. The characteristic of result composition and loading after impregnation can be seen in Table 2. The average total loading was 10.83%. The result composition of Fe and Co showed similar as initial composition due to good affinity between metal precursor and meso-HZSM-5. The impregnated Fe and Co were not distributed homogeneously, then the EDX analysis might show more or less loading and composition reading.

Table 2. Iron and cobalt loading and composition in impregnated Fe-Co/meso-HZSM-5 (EDX analysis) in various impregnation ratio.

Catalyst	Initial Composition		Initial Loading			Loading (EDX analysis)			Composition (EDX analysis)	
	Fe (%)	Co (%)	Total (%)	Fe (%)	Co (%)	Fe (%)	Co (%)	Total (%)	Fe (%)	Co (%)
0Fe-100Co/HZSM-5	0	100	10	0	10	0.00	12.84	12.84	0.00	100.00
10Fe-90Co/HZSM-5	10	90	10	1	9	1.49	7.21	8.70	17.13	82.87
20Fe-80Co/HZSM-5	20	80	10	2	8	0.99	5.34	6.33	15.64	84.36
30Fe-70Co/HZSM-5	30	70	10	3	7	5.77	7.21	12.98	44.45	55.55
100Fe-0Co/HZSM-5	100	0	10	10	0	13.31	0.00	13.31	100.00	0.00

The X-ray diffraction (XRD) showed the crystallinity and type of component according to diffraction angle (2θ) on spectra. The XRD analysis was performed on ZSM-5, microporous HZSM-5, mesoporous HZSM-5 (desilicated HZSM-5) and impregnated Fe-Co/HZSM-5 in various composition of Fe and Co as shown in Figure 2. The proscedure from ZSM-5 to impregnated Fe-Co/HSZM-5 kept the material crystallinity with 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 (unique characteristic of zeolite HZSM-5) [12]. But the intensity of impregnated Fe-Co/HZSM-5 was lower than unimpregnated materials. Impregnation process lowered the crystallinity but still maintained the material crystal structure. The iron and cobalt precursors impregnated on mesoporous HZSM-5 was reduced to obtain free metal catalyst on the active sites area. The reduction was treated in the tube furnace using excess hydrogen stream at 400°C for 8 hours. The diffraction angle position of the iron, cobalt and their oxide peaks refers to the spectral database of Tavasoli et al [13]. Fe had spectrum on 44.8^0 and 66^0, Co had spectrum on 44^0, 77^0. Impregnated Fe and Co simultaneously formed Fe-Co alloy that had spectrum on 45^0, 53^0, 62^0. Oxide forms like Fe_2O_3 had spectrum 35.7^0, 44.5^0 and Co_3O_4 had spectrum on 31.5^0, 36.8^0. Figure 2 showed the spectra of Fe, Co and Fe-Co alloys and Fe/Co-oxide formed. 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 30Fe-70Co/HZSM-5. The impregnation ratio of iron and cobalt that approached to 1, gave more Fe-Co alloy. The Fe-oxide and Co-oxide were still existed in the catalyst, which indicated an imperfect reduction process. The diffraction angle of Fe-Co alloy (45^0) which was very close to the Fe and Co diffraction angle, thus the spectra of Fe and Co were not appeared as they may occur around.
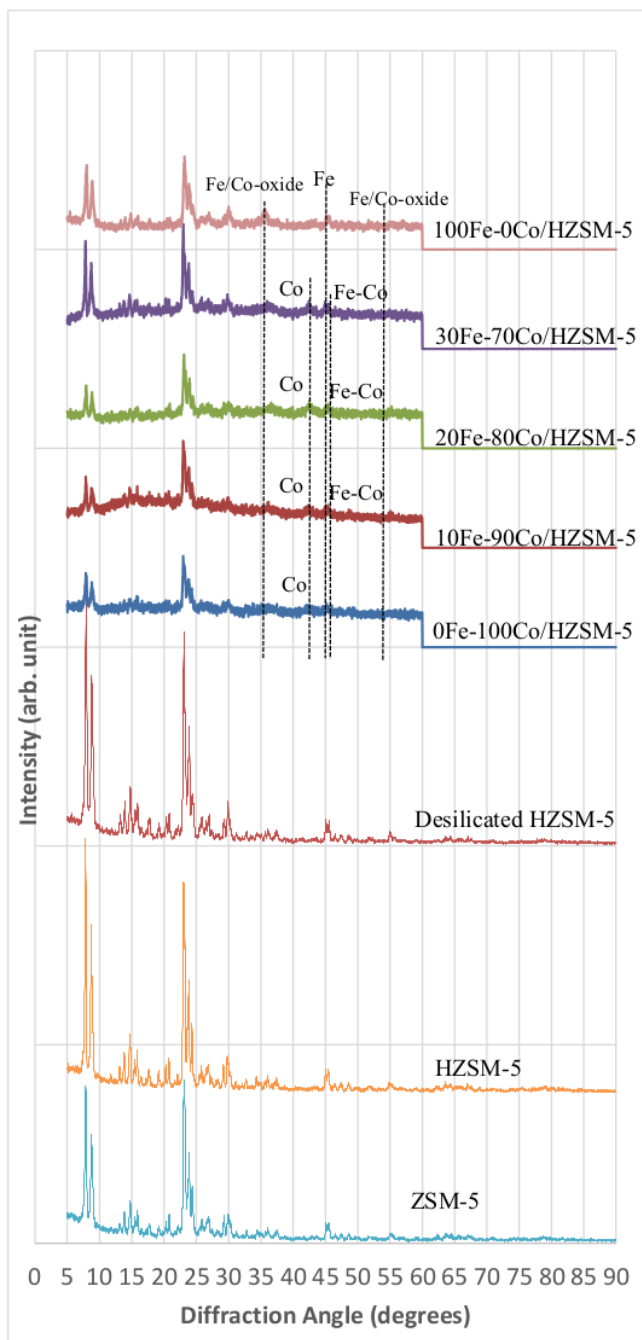
Figure 2. The XRD spectra for ZSM-5, HZSM-5, desilicated HZSM-5 and Fe-Co/HZSM-5 in various impregnation ratio after reduction by hydrogen at 400℃, 25 mL/min for 8 hours
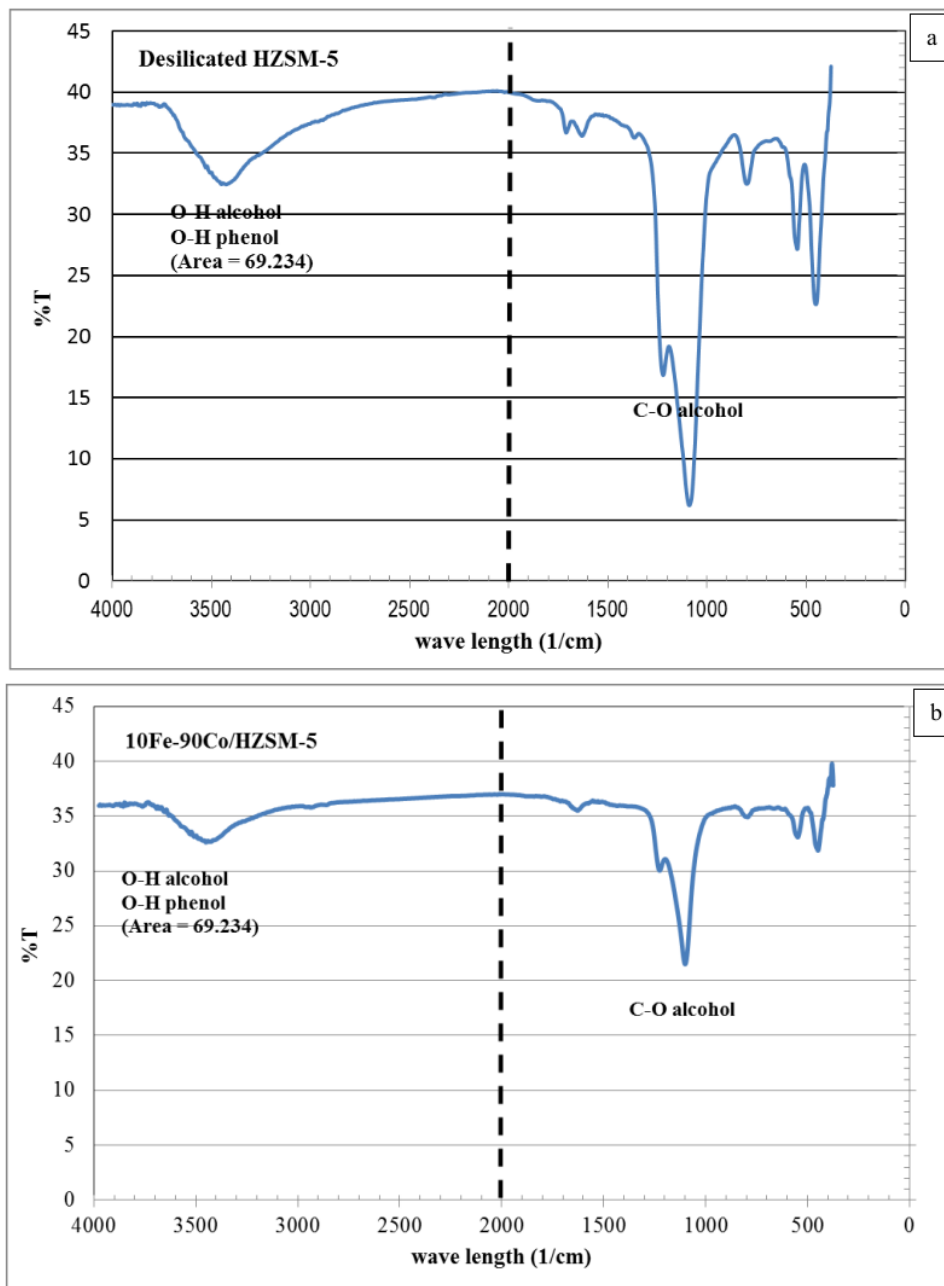
Figure 3. (a) Comparison of acidity and function groups of desilicated HZSM-5 and (b) impregnated catalyst material 10Fe-90Co/HZSM-5 (FTIR analysis)

Characterization of acidity is necessary for understanding reactions catalysed by zeolites. Solid acids are composed of discrete active sites and, therefore, the concentration of acid sites must be determined separately from the catalytic activity of those sites. The acidity of materials could be investigated from groups function on the material surface. According to FTIR analysis showed on Figure 3, desilicated HZSM-5 had an alcohol groups function. Alcohols are weak acid and the hydroxyl group can act as a proton donor. The area indicated the quantity of this alcohol groups function and the presence of catalyst active sites on this material surface. Impregnated iron and cobalt was occupied this sites and reduced the amount of active sites. Impregnated metal catalyst of 10Fe-90Co occupied active sites on HZSM-5 and decreased the area (reducing area from 69.234 to 7.485).

4. Conclusion

The iron and cobalt impregnation decreased the total surface area from 350.859 m^2/g (on HZSM-5) to 231.852-329.606 m^2/g (on Fe-Co/HZSM-5). Higher cobalt content in Fe-Co impregnation on HZSM-5 decreased total surface area and increased average pore diameter. Impregnation process lowered the crystallinity but still maintained the material crystal structure. 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 30Fe-70Co/HZSM-5. Iron and cobalt impregnation occupied the active sites formed from alcohol groups function that was indicated with decreasing alcohol groups area in FTIR spectra.

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