

CoMo/USY Catalysts Prepared by Precipitation Methods: Effect of pH Treatment

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Abstract. The Effect of pH treatment in the CoMo/USY catalysts prepared by precipitation was investigated. The pH of the precursor solution was controlled at pH 2, 7, and 8. Catalysts were characterized by XRF, XRD, N₂ adsorption, and IR spectroscopy. It was established that pH treatment in the catalysts significantly influences on the metal loading. Catalysts at pH 7 had maximal of amount total metals with particles type of CoO, MoO₃, Co, and Mo. Metal loading affects the decreasing of surface area, pore volume, and average pore radius. In addition, the number of hydroxyl group in the catalyst was less than USY followed by shifting of its wavenumber.

1. Introduction

Hydrotreatment is a hydrocarbon refining process producing clean fuels with better performance by using H₂ over a catalyst. The catalysts has an important role to providing active sites for the hydrotreatment reactions. The conventional catalysts such as CoMo/Al₂O₃ was the most commonly used catalysts in hydrotreatment studies. Although hydrotreatment reactions using these catalyst have a disadvantage, since the Al₂O₃ as supports was not contributed to the catalyst active sites. Therefore, zeolites may become a good choice as catalyst support, due to their important role to improve catalytic activity, selectivity, or stability by imparting shape selectivity [1,2]. In contrast to Al₂O₃, zeolite USY (ultra stable Y zeolite) as supports has acid site serving as active site for hydrogenation reactions. Therefore, the combination of CoMo active site with USY as supports will result in a multifunctional catalyst with better activity.

Catalyst properties and activity strongly depend on the preparation method. Catalysts which were obtained via precipitation method exhibited more high activity rather than via impregnation, due to high metal loading, high metal surface area, small metal particle sizes as well as a high number of acidic sites [3]. Variables of catalyst preparation such as types of precipitant, types of precursor, pH of precursor solution, aging time, and temperature have significant effects on the catalyst properties prepared by the precipitation method. According to Koo *et al.* [4], the pH of the precursor solution plays an important role in adjusting the loading amount and particle size of Ni metal and consequently has effects on the activity of catalyst. Salim *et al.* [5] prepared Ni/Celite catalyst by precipitation method for soybean oil hydrogenation and investigated effects of temperature of precipitation, aging temperature, and aging time on the textural properties of the prepared catalyst. The increases of aging time and aging temperature improve the interaction between the support and precursor of active metal to allow the preparation of catalyst with large surface area and high metal dispersion.



2. Experimental

2.1 Materials.

Commercial USY zeolite was obtained from Tosoh Japan Corporation in its NH_4^+ form. H-USY support was prepared by calcined at 550 °C for 1 h. The precursors of ammonium heptamolybdate tetrahydrate $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}]$ and Cobalt (II) nitrate hexahydrate $[\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}]$ were obtained from Merck in p.a grade. The solution of 25 % ammonia (NH_3) was used as precipitant agent in this investigation and it was obtained from Merck in p.a grade.

2.2 Preparation of catalysts.

CoMo/USY catalysts were prepared by precipitation method with some pH treatments. CoMo-USY-x catalysts where “x” is the pH treatment in the preparation process. H-USY (10 g) was added into a two neck flask with several distilled water. The pH was maintained by either (1) without treatment so the pH was at 2; (2) a solution of 25% ammonia was added hence the pH has changed into 7; And (3) pH at 8. Ammonium heptamolybdate tetrahydrate (0.981 g), cobalt (II) nitrate hexahydrate (0.777 g), and distilled water was added simultaneously hence the total volume has reached 50 mL. The slurry was kept stirred slowly and heated at temperature 60 °C for 2 h. The precipitate was filtered and dried at room temperature overnight. The prepared catalysts were dried by rotary evaporator, calcined in N_2 flow at 550 °C for 3 h, and then reduced in H_2 flow at 400 °C for 2 h. The atomic concentration of prepared catalysts were analyzed by energy dispersive X-ray fluorescence (Bruker S2 Ranger). The crystal structure of catalysts were analyzed by X-ray diffraction (XRD, Rigaku miniflex 600 benchtop, $\text{CuK}\alpha$ radiation). The particles type was estimated by Le Bail method using Rietica software. The textural characteristics was determined by SAA (quantachrome E 1600) through the nitrogen adsorption at -195.7 °C after the samples were pretreated at 280 °C for 3 h under vacuum. The specific surface area was calculated using the BET method at a relative partial pressure P/P_0 of 0.05 - 0.3. The total pore volume and average pore radius were determined using the BJH model. The function group was analyzed by infrared spectroscopy (FTIR Shimadzu 8201 PC, KBr powder) with a resolution of 2 cm^{-1} in the range at 400 - 4000 cm^{-1} .

3. Result and Discussion

3.1 Physical properties of CoMo/USY catalysts.

The atomic concentration, specific surface area, total pore volume, and average pore radius of the CoMo/USY catalysts upon pH variation in the precursor solution are summarized in the Table 1. The atomic concentration of cobalt and molybdenum were influenced by the pH of precursor solution, due the pH treatment has changed precursor salts into hydroxides or other salts [4,6,7]. The metal atoms may attach to the pore surface of support, hence the metal concentration may affect the surface area, pore volume, and pore size of the catalysts [8].

Table 1. Physical properties of CoMo/USY catalysts

Sample	Atomic concentration (%)				Specific surface area (m^2/g)	Total Pore Volume (cm^3/g)*	Average pore radius (\AA)
	Co	Mo	Si	Al			
CoMo/USY-2	1.96	4.99	22.42	5.88	497.90	0.31	13.36
CoMo/USY-7	3.98	3.39	20.72	5.45	476.15	0.34	15.21
CoMo/USY-8	4.35	0.04	34.64	7.47	500.34	0.38	16.22

*Pores with radius less than 1079.74 \AA

The Co concentration was increased, whereas Mo concentration reduced with an increase in pH. The increase in pH has changed Co salts into hydroxides, consequently Co was easier to precipitate on the support surface. Molybdenum salts may change into hydroxide at pH 3 – 6, whereas at pH 7 molybdenum start to be dissolved and form MoO_4^{2-} ions. Therefore, when catalysts were filtered, the soluble Mo containing species was washed out, which would lead to the decrease in Mo concentration in the catalysts under pH 7 and 8. Both Co and Mo were showed high concentration in the CoMo/USY-7 catalysts, due to formation of hydroxides during the preparation process. However, Co and Mo hasn't changed into hydroxides at pH 2, but they were obtained in the catalysts CoMo/USY-2. It was indicated that Co and Mo were trapped in USY pores by other supporting method, such as impregnation under pH 2 [9,10].

Specific surface area, total pore volume, and average pore radius were reduced with an increase in metal concentration (Co and Mo). Metal atoms has entered and attached into USY pores during the preparation process of the catalyst, thus lead to the decrease of pore size and surface area. However, different phenomena occurred at CoMo/USY-2, which has higher specific surface area rather than CoMo/USY-7, whereas total pore volume and average pore radius were smallest rather than others. Typically, physical properties such as metal concentration and pore volume have a significant effect on catalytic performance [11]. Therefore, the CoMo/USY-7 catalysts is expected to have good catalytic activity due to the high metal concentration and pore volume.

3.2 Particles type of CoMo/USY catalysts.

Figure 1 illustrates the XRD pattern of the USY supports and CoMo/USY catalysts prepared by precipitation method. According to Figure 1, the XRD pattern of catalysts CoMo/USY under pH 2, 7, and 8 were similar to USY supports. That was indicated that metal loading was not changed the crystal structure of USY, significantly. The XRD pattern of both Co and Mo were not observed since its crystallite size or intensity were extremely small.

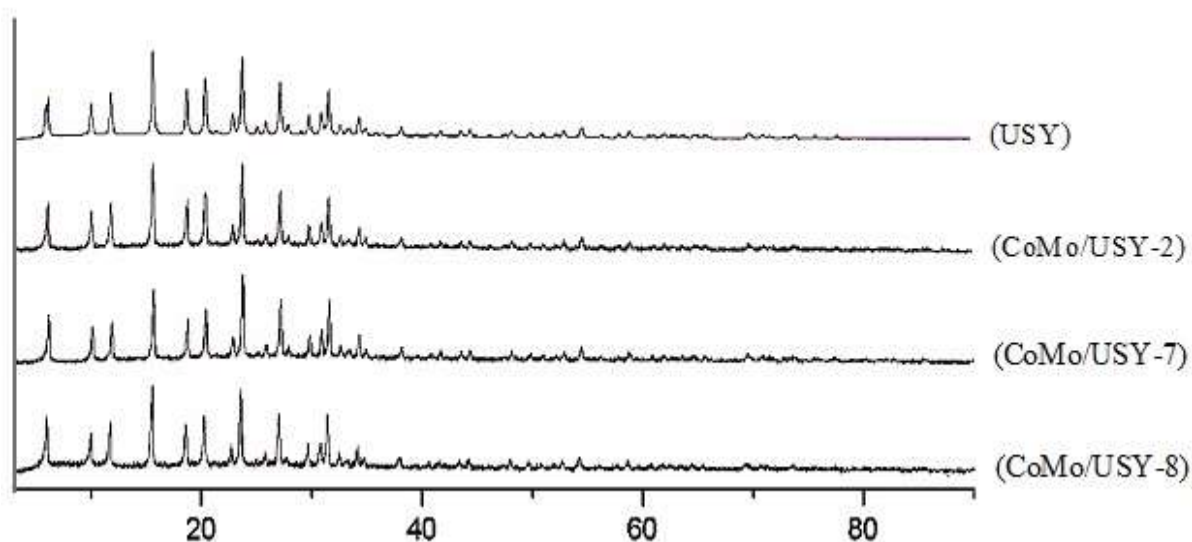


Figure 1. XRD pattern of USY and CoMo/USY catalysts

The particles type of the CoMo/USY catalysts upon pH variation in the precursor solution are summarized in the Table 2. The pH of precursor solution were not significantly influenced the particles type of catalysts, due the precursor salts and hydroxides were relatively easy to decomposed by calcination. According to Table 2, zeolite NaY and faujasite H particles type were dominant (more than 97 %) in the catalysts CoMo/USY, thus explained XRD pattern in Figure 1. In small number MoO_3 , Co, and Mo particles type were obtained on the catalysts based on refinement analysis of X-ray

diffraction. Molybdenum has interacted with more oxygen atoms, ammonia, and OH^- ions in the form of salts or hydroxides compared to cobalt. Therefore, some molybdenum were not clearly activated and obtained as MoO_3 particles type. CoO particles type was obtained only in the CoMo/USY-7 catalysts. It might be occurred due to the metal agglomeration at CoMo/USY-7 catalysts, which has higher metal concentration [8]. Particles type of metal have a significant effect on catalytic performance [12]. Augustine *et al.* [13] stated that the active metal on the cracking reaction was pure metal particles, therefore Co and Mo particles type estimated to be contribute as active metal which is increase catalytic activity.

Table 2. Particles type of CoMo/USY catalysts

Standard phase	Weight molar particles (%)		
	CoMo/USY-2	CoMo/USY-7	CoMo/USY-8
Zeolit Y ICSD #33599	✓	✓	✓
Zeolit Y ICSD #26920	✓	✓	✓
CoO ICSD #245320	-	✓	-
MoO_3 ICSD #644068	✓	✓	✓
CoMoO_4 ICSD #281235	-	-	-
Co ICSD #622439	✓	✓	✓
Mo ICSD #173127	✓	✓	✓
CoMo ICSD #624215	-	-	-

3.3 Function group of CoMo/USY catalysts

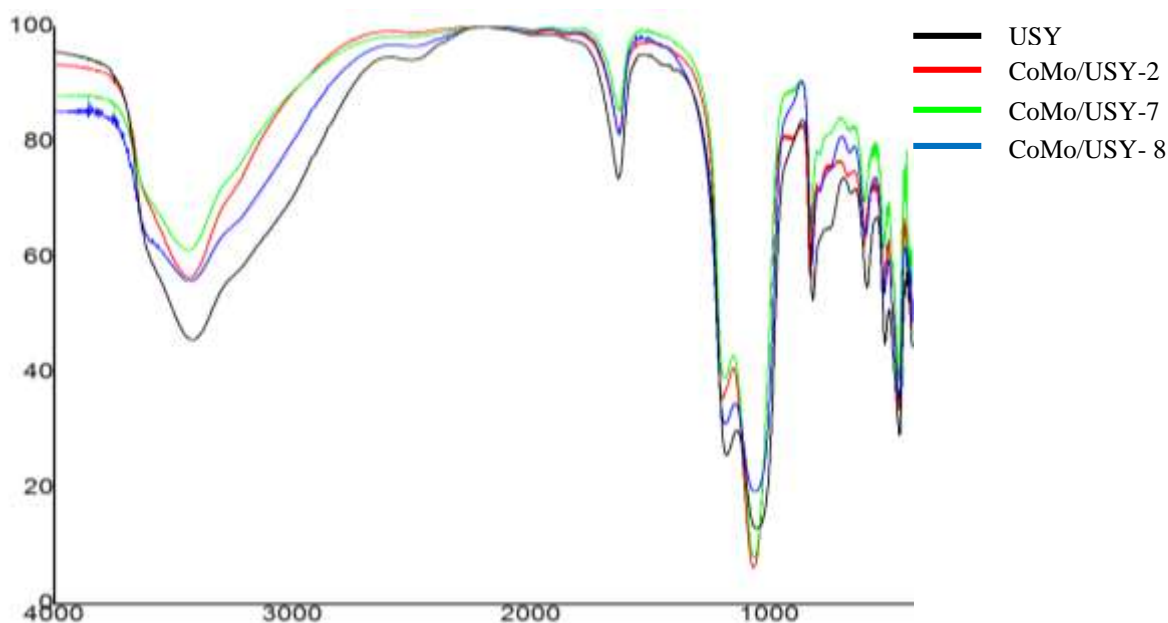


Figure 2. Infrared spectrum of USY and CoMo/USY catalysts

According to Figure 2, metal loading was not influenced the infrared spectrum of CoMo/USY catalysts, significantly compared to USY supports. It was indicated that metal loading was not changed the function group on the catalysts. The infrared spectrum of catalysts shows several bands attributed to hydroxyl group, internal tetrahedral structure, and external tetrahedral structure of USY, as presented in Table 3.

Cobalt and molybdenum loading was influenced OH stretch band at 3400 cm^{-1} , that attributed to Brönsted acid site on the catalysts. The transmittance of OH stretch band was increased with an increase of metal concentration on the catalysts. That was indicated that metal atoms was replaced H^+ ion, hence the number of Brönsted acid site were reduced on the catalysts. The transmittance of OH stretch band was highest in CoMo/USY-7, due to highest metal concentration. CoMo/USY-8 and CoMo/USY-2 has similar transmittance of OH stretch band, whereas CoMo/USY-8 has lower metal concentration. It was indicated that Brönsted acid sites were reduced significantly in the CoMo/USY-8 catalysts [14,15]. OH stretch band was slightly shifted to high wave number in an increase of metal concentration on the catalysts, which may confirm the proximity between metal atoms and OH groups [15]. That was indicated that metal loading may increase the OH group strength on the catalysts. The wavenumber of OH stretch was highest in CoMo/USY-7 catalysts, due to highest metal concentration. The amount and strength of OH group have a significant effect on catalysts acidity. Therefore, CoMo/USY-7 is expected to have a good catalytic performance in hydrogenation reaction.

Table 3. Infrared spectroscopy absorption of USY and CoMo/USY catalysts

Function group	Wave number (cm^{-1})			
	USY	CoMo/USY-2	CoMo/USY-7	CoMo/USY-8
O-H stretch	3396.79	3421.87	3426.69	3416.08
O-H bend	1634.74	1630.88	1626.06	1628.95
T-O-T asym stretch	1178.56	1195.92	1186.27	1184.34
T-O asym stretch	1051.25	1067.65	1062.82	1058.97
T-O-T sym stretch	816.89	828.46	826.53	822.68
T-O internal sym stretch	657.75	680.90	669.33	663.54
T-O internal bend	454.26	456.18	455.22	455.22

4. Conclusions

CoMo/USY catalysts were prepared by precipitation method with various pH treatment. Metal loading was strongly influenced by the pH of precursor solution. Both concentration of cobalt and molybdenum were highly obtained in the catalysts under pH 7. As the metal concentration increases, the specific surface area, total pore volume, and average pore radius were reduced on the catalysts. The pH of precursor solution were not significantly influenced the particles type of catalysts, since pure metal particles of Co and Mo were obtained on the catalysts for all pH treatments. Metal loading was influenced OH stretch band at 3400 cm^{-1} , that attributed to Brönsted acid site on the catalysts. The highest OH stretch wavenumber was occurred on the CoMo/USY-7 catalysts, indicating the strongest Brönsted acid site. Therefore, CoMo/USY-7 catalyst is considered a promising catalyst with good activity in hydrotreatment reaction.

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