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Characteristic of ZSM-5 catalyst supported by nickel and molybdenum

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Abstract. Ni and Mo doped on the ZSM-5 catalyst has been prepared. In this study the effect of metal concentration on the character of the catalyst was determined by varying the concentration of Ni and Mo by 1 to 5% (wt) against the ZSM-5 using impregnation method. The characterization results show that the catalyst contains Ni by 4%, while Mo was 5%, on the other hand, Mo was more dispersed in ZSM-5 particles compared to Ni. The total acidity for Mo-ZSM-5 catalysts was higher than Ni-ZSM-5. The surface area of ZSM-5 after loading by Ni and Mo decreased significantly, but the pore size increased slightly. Meanwhile the pore volume for the Ni-ZSM-5 was relatively the same as the pore volume of the ZSM-5 but the Mo-ZSM-5 was reduced by about 20%.
Keywords: ZSM-5, catalyst characters, Ni, Mo

1. Introduction

Currently, the type of catalyst used in the process of converting vegetable oils into biofuels is metal which is loaded on supporting materials such as zeolite. Zeolites or zeolite-like materials generally have high porosity, surface area and thermal stability so zeolite has many applications including adsorbents [1-3], catalysts [4], photocatalyst [5], cation exchanger [6], fertilizers [7] and various other things. In addition, the acid-base properties in zeolites are also easily controlled. Therefore, zeolite is very promising as a catalyst support [8, 9].

Until now, there have been many investigations to modify zeolites to metal-zeolite by loading metals in supporting materials, in this case zeolite. This is done to increase catalytic activity. As a result the properties will change, such as the distribution and size of the active phase, thermal stability and reducibility [10]. Metal catalyst (M)-ZSM-5 can be made through several methods such as impregnation, solid ion exchange, liquid ion exchange and in situ synthesis. The synthesis of Fe-ZSM-5 or Cu-ZSM-5 catalyst with SSIE method (solid ion exchange) was carried out by Jouini *et al*. [11]. On the other hand, Cu, La and Zn have also been loaded on the HZSM-5 using the impregnation method [12]. The most commonly used method is impregnation because of its ease of implementation, although it has weaknesses in the form of non-uniform metal distribution and low thermal stability [13-15].

Loading of various metals in supporting materials and their applications has been widely exploited such as Ni loaders in various types of Ni-SAPO-34 zeolites, Ni-MCM-41, Ni-HY, Ni-SAPO-11 and Ni-H-beta [16].. In its application, metal-zeolite catalysts are widely used in various reactions, including for thermo-catalytic pyrolysis [17].

Meanwhile, loading Cu in the ZSM-5 and its application as a catalyst has been carried out for NO_x with NH_3 [18]. Other studies, Zn, Ga, Ni, Co, Mg, and Cu have also been loaded on the ZSM-5 and have been used as catalysts in bio-oil production. The results showed that Ni-based catalysts clearly could increase the selectivity of benzene production, aromatic hydrocarbons and polycyclic C10. Meanwhile Zn-ZSM-5 was the most effective catalyst for the production of aromatic hydrocarbons [19]. In addition, the ZSM-5 modified with Co, Ni and Zn metals were capable of increasing selectivity in bio-oil production [20].

Because of the important role of catalysts in biofuel synthesis, it is necessary to determine the character of the catalyst after being modified with metal. In this paper, commercial ZSM-5 with Si/Al ratio about 70 with homogeneous particle shape and size used as the support. Ni/ZSM-5 and Mo/ZSM-5 prepared by wet impregnation method. The influence of concentration and type of metal of Ni or Mo/ZSM-5 was assessed for the surface area, distribution and acidity of the catalyst.

2. Experimental

2.1. Materials

ZSM-5 synthetic Zibo Linxi Chemical Co., Ltd. China, nickel chloride hexahydrate ($NiCl_2.6H_2O$) Merck, ammonium heptamolybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}.4H_2O$) Merck, distilled water, double-distilled water, ammonia sol 30% (merck)

2.2. Preparation catalyst

Preparation of Metal/ZSM-5 catalysts were carried out by conventional wet impregnation. A certain amounts of ZSM-5 added with nickel chloride hexahydrate ($NiCl_2.6H_2O$) at various concentrations from 0.5% -5% wt based on ZSM-5 weight as described by table 1. The suspension was dissolved by adding distilled water then stirred for 2 hours at room temperature. Furthermore, evaporation of the solvent to obtain crude was conducted. Next step was to dry of the crude using oven until a constant weight was obtained. Finally, heating of Ni/ZSM-5 powders for calcination for 5 hours at 550°C under nitrogen gas flow, oxygen and hydrogen. Preparation of Mo/ZSM-5 were done by impregnated ammonium heptamolybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}.4H_2O$) into ZSM-5. The concentration of Mo used in the suspension were 0.5-5 wt% too.

Table 1. The sample code

Sample	Code
ZSM-5	ZSM-5
ZSM-5 impregnated with Ni 0.5%	Ni 1
ZSM-5 impregnated with Ni 1%	Ni 2
ZSM-5 impregnated with Ni 2%	Ni 3
ZSM-5 impregnated with Ni 4%	Ni 4
ZSM-5 impregnated with Ni 5%	Ni 5
ZSM-5 impregnated with Mo 0.5%	Mo 1
ZSM-5 impregnated with Mo 1%	Mo 2
ZSM-5 impregnated with Mo 2%	Mo 3
ZSM-5 impregnated with Mo 4%	Mo 4
ZSM-5 impregnated with Mo 5%	Mo 5

2.3. Catalyst characterization

2.3.1. Total Acidity. Total acidity was determined by gravimetric method. Porcelain crucible being heated at 110°C for 1 hour then weighed (as W_1). Amount of 0.1-gram catalyst put into the porcelain crucible and heated at the same temperature for 1 hour, then weighed (as W_2). Next step sample is then put into desiccator and divorced. Ammonia gas is flowed to the desiccator until saturated by the gas (until visible fog). The desiccator faucet is closed and the desiccator is left for 24 hours. After that samples were weighed as W_3. Total acidity is calculated by the following equation.

$$\text{Total acidity} = \frac{(W3-w2)}{(W2-W1)M}$$

Where *M:* Molecular weight of NH_3

2.3.2. FTIR. Analysis of functional group of Ni/ZSM-5 and Mo/ZSM-5 catalysts by FT-IR were carried out in wavenumber 400 cm^{-1} to 4000 cm^{-1} using the Transmittance method.

2.3.3. Morphology of surface catalyst. The morphology of the Ni/ZSM-5 and Mo/ZSM-5 catalysts were characterized by SEM (JEOL JED 2300). The voltage of maximum acceleration was set at 20 kV.

2.3.4. Element analysis. Analysis of elemental content in the catalyst using energy-dispersive X-ray Fluorescence (hereafter ED-XRF). Time of analysis was set to 60 s, maximum current of 366 μA and voltage was set at 20 kV.

3. Results and Discussion

Total acidity is defined as the number of acid sites both Brønsted and Lewis acids found on ZSM-5 catalysts. The acidity of the catalyst plays an important role for cracking catalysts. Catalysts that have high acidity can affect product formation. The Brønsted acid site and the Lewis acid site of the catalyst play a role in the process of hydrogenation and the formation of reactive carbocation [21]. Determination of the total acidity of ZSM-5 was carried out using the gravimetric method with ammonia as an adsorbate base. The total acidity of ZSM-5 before and after loading with Ni and Mo metals is shown in Fig. 1.

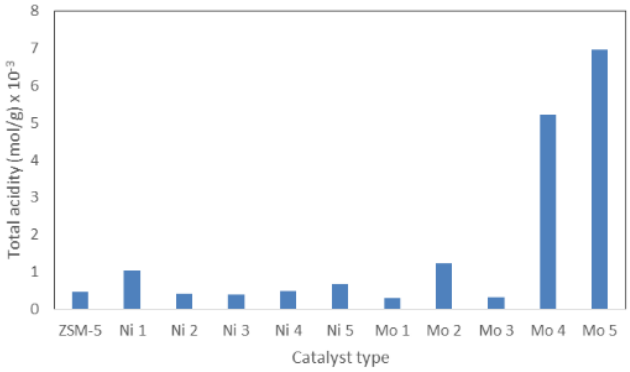

Figure 1. Total acidity of catalyst ZSM-5 after impregnation by Ni and Mo.

In the process of loading metals, Ni and Mo in ZSM-5 were calcined at high temperatures by H_2 gas flow. This treatment caused metal ions from the precursor solution to turn into metals with valence = 0. The metal was not charged because it was reduced by H_2 gas. The reduced state allowed the metal to adsorb ammonia better. Therefore, Ni-ZSM-5 and Mo-ZSM-5 are abler to absorb ammonia. Fig. 1 shows that in the impregnation of ZSM-5 with Ni there were no significant changes, although at 0.5% Ni-ZSM5 gave almost twice the acidity compared to ZSM5. At Ni concentrations of more than 0.5% acidity

tends to decrease. This may occur because Ni covered most of the ZSM-5 cavities and pores, so that Lewis acid sites in these cavities and pores could not absorb ammonia base. Hence acidity was only measured by Brønsted acid sites on the surface. It should be remembered that when the Lewis acid site in the ZSM-5 was lost due to the closure of ZSM-5 layer by metal, the metal could also increase the number of Brønsted acid sites through the formation of Al-OH-M which is the hydroxy bridge. However, the number of Brønsted acid sites is less than the number of Lewis acid sites [22, 23].

Unlike Ni, Mo's impregnation of ZSM-5 shows that the more amount of Mo loaded, the total acidity increases except for Mo3. A decrease in total acidity in Mo3 may be caused by blocking the ZSM5 cavities or pores as a result of uneven metal distribution. Meanwhile, the increase in total acidity with increasing Mo concentration on the ZSM-5, may be due to the number of acidic locations and even distribution. This is supported by SEM data which shows that Mo-ZSM-5 particles are more evenly distributed. Determination of the number of acid sites provides information that the number of acid sites contained in the catalyst is directly proportional to the active site of the catalyst which determines the catalyst activity and bond interactions that occur between the catalyst and reactants. Therefore, Mo4 and Mo5 are expected to have high reactivity and activity in catalytic reactions.

To determine the ammonia adsorption on the surface of Ni-ZSM-5 and Mo-ZSM-5 catalysts, FT-IR was analysed. The spectra for Ni-ZSM-5 and Mo-ZSM-5 after ammonia adsorption are shown in Fig. 2.

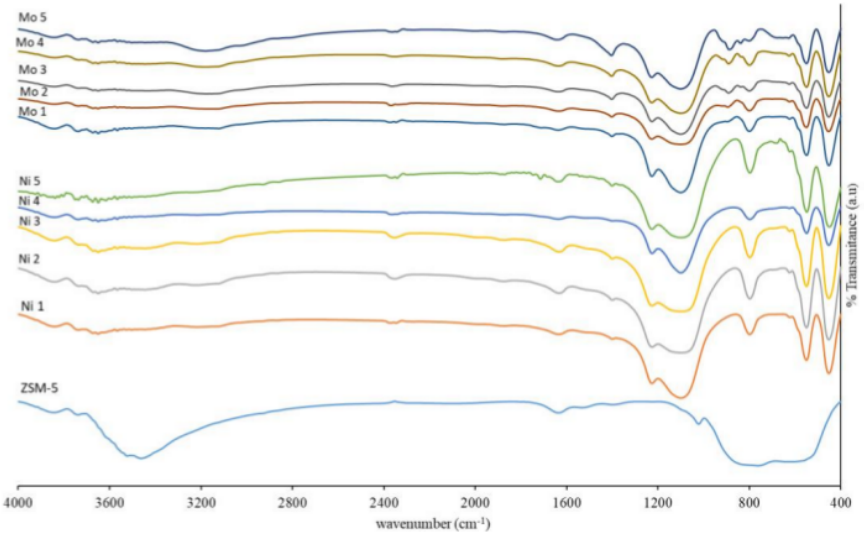

Figure 2. Spectra FTIR of ZSM-5, Ni/ZSM-5 and Mo/ZSM-5.

Fig. 2 shows the FTIR spectrum of ZSM-5, Ni-ZSM-5 and Mo-ZSM-5 at various metal concentrations contained in the range of wave numbers from 400 to 4000 cm^{-1}. According to Niu *et al.* [24] wide band at 3500 cm^{-1} in ZSM-5 shows a hydroxyl group derived from internal silanol. The absorbent band in the wave number region 3700-3800 cm^{-1} is silanol insulated on the outer surface and silanol contained in the ZSM-5 crystals. The band in the area of 3600 cm^{-1} is absorption from the Brønsted acid site. From Fig. 2 it can also be observed that the loading of Ni and Mo on the ZSM-5 causes absorption bands in the area of 3500 cm^{-1} to decrease dramatically and almost disappear. The presence of Ni and Mo metals interacts with these metals with OH groups and internal silanol groups, therefore $NiOH^+$ or $MoOH^+$ species are produced. Cations may interact with internal silanol groups. Ni-

O-Si is obtained from ZO-NiOH$^+$ + Si-OH → ZO-Ni-O-Si. Other information which can be obtained from Fig. 2 is a group of amines derived from ammonia which are absorbed by ZSM-5, Ni-ZSM-5 and Mo-ZSM-5. The absorption band in the wave number area around 2300 cm^{-1} shows the presence of an amine group in the sample that appears for all samples. This is in accordance with the reference indicated by ammonia adsorption occurring at wave number 2276-2500 cm^{-1}. In this study the lowest absorption intensity was in ZSM-5 before metal impregnation. The presence of ammonia is due to the presence of acid sites, both Brønsted acid and Lewis acid on ZSM-5. An increase in the total amount of acid correlates with an increase in absorption intensity in the area of the wave number around 2300 cm^{-1}. In addition, the amine group is also found in the area of the wave number 3300-3400 cm^{-1}.

Ni/ZSM-5 and Mo/ZSM-5 have a peak absorption at the wave number area 1300-1450 cm^{-1} which is the absorption peak characteristic N-H bonds and characteristic of the bond coordination of base with Lewis acid sites which is very strong. Around the wave number area also provides information about changes in the strength of the acid site Brønsted because of the addition of metal.

3.1. Morphology of catalyst

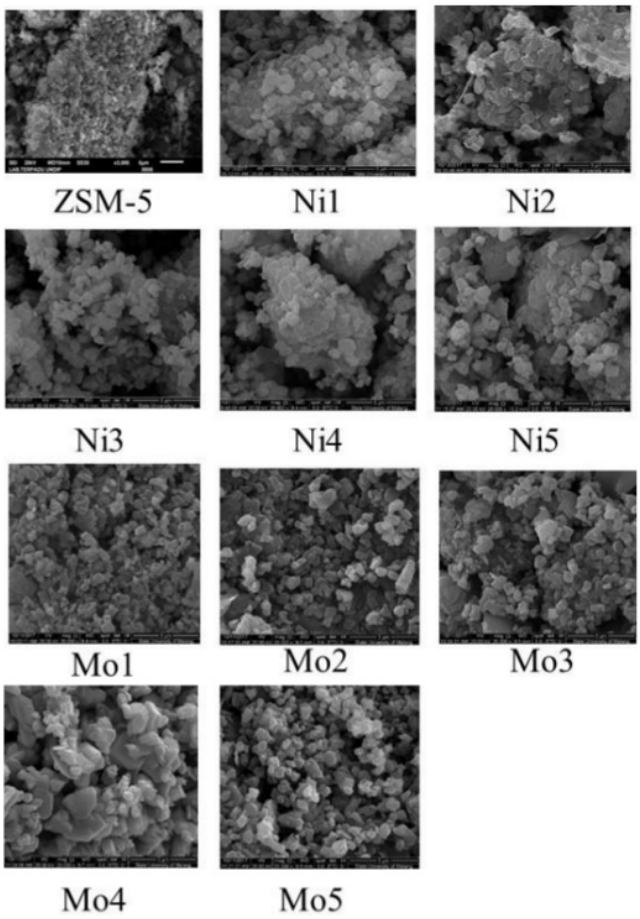

Figure 3. SEM images of ZSM-5, Ni/ZSM-5 and Mo/ZSM-5 at various concentration.

Surface morphology analysis aims to show differences in morphological uniformity both in size, shape and distribution the average crystal size. Fig. 3 shows that overall samples ZSM-5, Ni/ZSM-5 and Mo/ZSM-5 possessed average crystal size around 1-2 µm. Loading of metal Ni and Mo affects the ZSM-5 particles more dispersed. It appears that loading with Mo, the particles are more dispersed and not agglomerated, where this does not depend on the concentration. Mo seems to be a baffle so the particles don't accumulate, because $[Mo_7O_{24}]^{6-}$ the size is bigger and in the form of polyatomic anions the possibility of being dispersed evenly on the surface.

3.2. Element composition

Analysis using XRF (EDXRF) aims to determine the metals contained in ZSM-5. Analysis of the results of the content of Ni and Mo in Ni / ZSM-5 and Mo / ZSM-5 catalysts is presented in Table 2.

Table 2. Ni and Mo content in catalyst

Sample	ZSM5	Ni 1	Ni 2	Ni 3	Ni 4	Ni 5	Mo 1	Mo 2	Mo 3	Mo 4	Mo 5
% Ni	0.069	2.02	2.25	8.87	14.5	12.9	0.07	0.11	0.046	0.03	0.03
%Mo	ND	ND	ND	ND	ND	ND	ND	ND	27.4	26.1	33.8

From the results of the analysis it is known that Ni and Mo metals function as the promoter was successfully executed on ZSM-5. The higher the concentration, the greater the percentage of metal that is loaded. In Ni 5% metal loading, the developed percentage is even smaller, this is probably due to the saturation of the ZSM-5. While in the loading with Mo, at concentrations of 0.5% and 1% Mo it is not successfully carried out, it is likely that $(Mo_7O_{24})^{6-}$ is less dispersed on the catalyst.

Metal is an active catalytic site which plays an important role in providing product selectivity. On the other hand, the higher the metal content that is absorbed, the higher the acidity is expected. Therefore, acidity will increase its performance as a catalyst.

Measurement of surface area, total pore volume, and mean pore radius is carried out with using GSA the method Brunauer, Emmet, and Teller (BET). This method is based on the gas adsorption phenomenon on single layer that takes place at constant temperature. Results of surface area measurements, total pore volume, and average pore radius is presented in Table 3.

Table 3. Surface are, pore volume, pore radius of ZSM-5, Ni/ZSM-5 and Mo/ZSM-5

Parameter	ZSM-5	Ni/ZSM-5 5%	Mo/ZSM-5 5%
Surface area (m^2/g)	244.607	126.966	32.090
Pore volume (cc/g)	0.354	0.288	0.071
Pore radius (Å)	16.047	20.678	17.235

The table shows that the area surface and total volume of zeolite pore after impregnation with Ni and Mo experienced a very large decline, caused by Ni and Mo metals distributed on the surface and partially closed pores.

4. Conclusion

The characters ZSM-5 catalyst after loaded by Ni and Mo for the concentration 0.5%-5% wt showed that the largest metals loaded of Ni is metal precursor concentration of 4%, while at Mo at 5%. The particles of ZSM-5 which are embraced by Mo metal are more dispersed than Ni, as well as for the total acidity of the Mo/ZSM-5 catalyst higher than Ni/ZSM-5. Supported ZSM-5 by Ni and Mo decreased surface area significantly.

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