

Synthesis of the supported catalysts by co-impregnation and sequential impregnation methods

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Abstract. The non-sulfide catalysts Co-Mo/USY were prepared with three different methods, i.e. co-impregnation and two sequential impregnation procedures. The phases of the synthesized materials and their composition were characterized with X-ray diffraction. Furthermore, the X-ray diffraction patterns were analyzed using Le Bail methods with Rietica software. Finally, an overview of the substitution effect of cobalt and molybdenum on the metal content and acidity of the catalyst were also investigated.

1. Introduction

Transition metals are an important family of inorganic materials which have been a subject of intensive research due to their many applications, such as catalysts in a large variety of industrial processes that involve hydrogen evaluation reaction, and the activation or conversion of hydrocarbons [1–3]. For example, nickel oxide and molybdate based on alumina are important components of industrial catalysts for hydrodesulphurization [2,4]. Reference [4] investigates NiMo bimetal catalyst supported on a variety of zeolite types for HDS of thiophene. They discovered that the effect of the supported catalyst on HDS performance of thiophene over NiMo catalyst was great, and the HDS activity of NiMo could be improved by changing the supported catalyst. Their resulted research showed that USY is the best supported agent. On the other hand, the resulted of research [1] showed that a CoMo-based catalyst had good thermal stability in comparison with NiMo samples. In the other reference it was shown that CoMo-based catalysts are important components of the industrial catalysts used for hydrodeoxygenation of lignin [1].

Studies on catalysts to remove impurities from hetero_atom to allow its use in biofuel conversion are still popular. Previous researchers reported that the CoMo-based catalyst has the best catalytic performance. [5] Reported that despite its complex preparation, the best catalytic performance was shown by the sulfide catalysts of CoMo/Al₂O₃ as compared to Mo/Al₂O₃ and Pt/USY. In the HDO catalytic reaction, [6–8] also reported the same performance.

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According to [5,9], sulfidation processes can be ignored to simplify the overall preparation processes. Yet, an alternative for sulfidation processes is sought. Referring to [10], calcination, oxidation and reduction processes can be alternated with the sulfidation processes to simplify the preparation processes of CoMo-based catalysts. Seeking for supports then becomes the next priority.

Supports like zeolite, provide the catalytic functions, where the cracking reaction takes place on the zeolite's strong acid sites. The most important function of support is maintenance of a high surface area for the active component and acidity for hydrocracking reactions. A support material is chosen for a given application on the basis of several important characteristics including its inertness to undesired side reactions, appropriate mechanical properties (attrition resistance, strength, etc), stability under reaction conditions, a surface area and pore size distribution appropriate for the desired reaction, and its cost [11]. Zeolites are widely used for catalyst support and play an important function in the hydrocracking process because they improve the activity, selectivity, and stability of catalysts. Zeolites are defined as crystalline alumina silicates, and have been investigated and extensively used in industry. Zeolites have been successful because of their crystalline properties, high surface area, adsorption capacity, and uniform size distribution which enable shape selectivity [12].

The hydro treatment catalyst is a typical example of a bifunctional catalyst, in which both the hydrogenation/dehydrogenation and the cracking function play crucial roles. The hydrogenation/dehydrogenation functions come from the metal side, while cracking comes from support materials such as USY.

However, the preparation of bifunctional catalyst with high performance is very important, and is related to its application for future industrial use. Molybdenum oxide and cobalt oxide precursors on zeolite are prepared by a variety of techniques, solid state reaction [13], Chemical Vapour Deposition (CVD) [14], and impregnation methods [9,10,15]. The last method is the simplest one. Therefore, in this study, we prepared bimetal catalyst CoMo/USY with varied impregnated methods. The catalyst precursors were prepared by the same procedure described in our work in a previous publication [16].

Catalytic activity is determined by the chemical structure of the catalyst and its properties. In the hydrodesulphurization catalysts, the degree of acidity is one of the characteristics that determine the catalytic performance. The higher degree of acidity often results in higher catalytic activity [3]. As well as the degree of acidity, the catalytic activity is determined by many other characteristics e.g. the metal content and, the surface area. The metal content and surface area are simple and more accurate indicators of the degree of active site dispersion. That is why this research used those criteria to verify the catalysts obtained. In addition, the pattern of XRD from obtained catalyst, total pore volume and average pore radius are presented in order to complement the verification criteria of a good catalyst.

2. Experimental

2.1. Materials

The support material used in this research was NH₄-USY, which was purchased from Tosoh Inc (Japan). Other materials were ammonium heptamolybdate and cobalt nitrate hexahydrate purchased from Merck (Germany).

2.2. Methods

NH₄-USY was calcined at 550 °C for 1 hour to obtain USY. In order to address the above aforementioned research objectives, metal based-catalysts of Co and Mo supported on Ultra Stable Y-zeolite (USY) were prepared following some experimental treatments.

Three kinds of bimetal catalysts were prepared. The bimetal catalysts of (Co and Mo)/USY were prepared following the two main kind of impregnation methods - the co-impregnation method [4] and the sequential impregnation method [16]. First, in the co-impregnation method, an H-USY sample was mixed with a solution of (NH₄)₆Mo₇O₂₄·4H₂O, (Co (NO₃)₂·6H₂O, aquabidest and ammonia in a flask with a concentration of 8% w Mo metal and 2 % w Co. Then, the sample mixture was heated at a

temperature of 60 ° C for 2 h. The samples were dried with a vacuum evaporator at a temperature of 85 ° C for 16 hours at a pressure of 72 mbar. The resulting catalyst was called CoMo/USY.

The sequential impregnation method was carried out through two reversed mechanisms. The first was to support the precursor of Co, followed by ammonium heptamolybdate (Co_Mo/USY) and the second was conducted through the opposite sequence (Mo_Co/USY). The next important step in the process was activation. Here, all of the produced catalysts were activated through consecutive reactions namely calcination, oxidation and reduction. Calcination was conducted by leaving the produced catalyst at a high temperature in an atmosphere of nitrogen gas. Here the temperature was set to 500 °C whereas the flowrate of nitrogen was of 5 mL/min. The oxidation and reduction processes were conducted at a temperature of 400 °C at a gas flow rate of 5 mL/min.

2.3. Characterization of the Catalyst

All catalysts obtained were then verified according to several criteria. Phase characterization was carried out by X-ray diffraction (XRD) using an XRD Philips type X'Pert with CoK_α radiation. The data were collected in a step scan from 5 to 90° in 2θ with a step of 0.04°. All the structure refinements were carried out using Le bail methods with Rietica software. The chemical composition of the catalysts was determined using a Bruker S2 Ranger wavelength X-ray dispersive fluorescence spectrometer.

Using self-construction apparatus, the gravimetric analysis method was used to measure the total acidity. The method was carried out under standard pressure and temperature. At first, the porcelain crucible heated at 110 ° C for an hour. The crucible weight was labelled as W₁. Then 0.2 g of samples were placed into the porcelain crucible and heated at the same temperature for 1 hour. The weight of the porcelain crucible containing the sample was labeled as W₂. Then, the crucible containing the sample was inserted into the desiccators. In the next step, the ammonia gas was exposed to desiccators for 24 hours (before this treatment, the desiccators were made under vacuum conditions). The weight of the porcelain crucible was labeled as W₃.

$$\text{Total acidity} = \frac{(W_3 - W_2)}{(W_2 - W_1) \cdot M} \quad (1)$$

With M = molecular weight of NH₃ (gram/mol).

The IR spectra of samples were recorded using Shimadzu 8201 PC FTIR spectroscopy with KBr methods.

3. Results and Discussions

The characteristics of the catalyst support (USY) were reported in our previous publication. Now, a comparison of co-impregnation and sequential impregnation methods will be given.

3.1. Phase composition of catalyst sample

Characterization of crystal structure and determination of the crystallographic parameters of metal oxide catalyst were performed by XRD. Figures 1a – 1d show the diffraction patterns of samples USY, CoMo/USY, Co_Mo/USY and Mo_Co/USY respectively. Then, the parameters are listed in Table 1. X-ray diffraction pattern for several catalyst samples (a) USY, (b) Mo_Co/USY, (c) Co_Mo/USY, and (d) CoMo/USY.

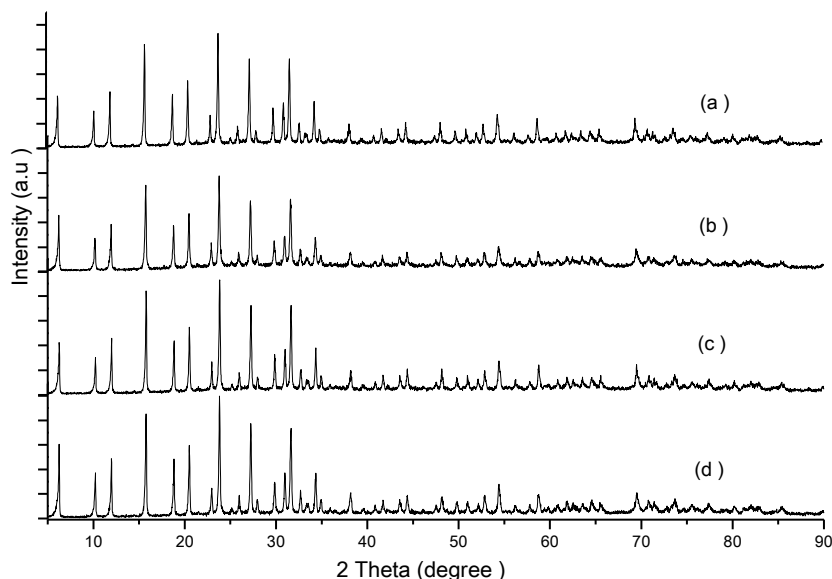


Figure 1. X-ray diffraction pattern for several catalyst samples. (a) USY, (b) Mo_Co/USY, (c) Co_Mo/USY, and (d) CoMo/USY.

Figure 1a-1d belonged to a typical diffraction pattern of the Y zeolite (Y) framework. Besides Y, we observed an extra crystalline phase. According to the ICSD #31542 data (see Figure 1a) the samples contained the type cubic Y (Fd-3mz space group, lattice parameter $a = b = c = 24.539 \text{ \AA}$) with chemical formula i.e. $\text{Na}_{0.36}\text{H}_{1.3}\text{Al}_{1.66}\text{Si}_{10.34}\text{O}_{24}$. However, we can determine the cell parameter and percentage-compounds of the samples based on the diffraction pattern data shown in Figures. 1a-1d which were refined using the Le bail method with RIETICA software (Table 1).

Figure 1 shows the three phases of metal oxide (ICSD #281235, #9865, and #3617). Although the catalysts have quite a similar character as regards the crystalline phase, they are slightly different in percentage-composition (Table 1).

Table 1. Percentage-composition of metal oxide.

Catalyst code	CoMoO4	CoO	MoO3
USY	na	na	Na
CoMo/USY	0.10	0.12	0.32
Co_Mo/USY	0.10	0.12	0.33
Mo_Co/USY	0.11	0.13	0.33

*na: not available

3.2. Metal Content

Indeed, high metal content is one of the criteria for a good catalyst. The metal content (based on the XRF data) for each impregnation method is presented in Figure 2.

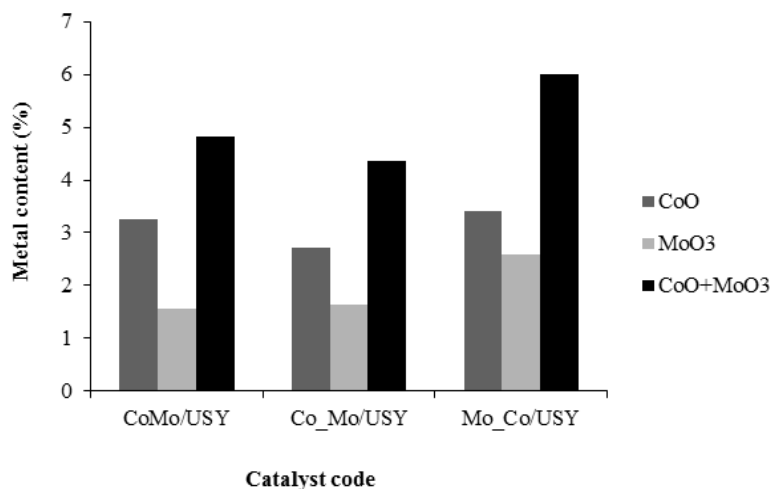


Figure 2. Totally impregnated metal for each impregnation methods.

According to Figure 2, use of the sequential impregnation method by adding Mo precursor followed by Co gives the best results as regards metal content. This method does not allow for competition between metals (Mo and Co) to adsorb into USY, but such competition between metals does exist in the co-impregnation method. A sequential impregnation method leads to greater metal content. This is because Co is smaller than Mo; hence, Co is easily impregnated upon the USY after Mo.

3.3. The acidity character

The acidity of catalysts plays an important role in the reaction behaviour of catalysts. A method often used to determine the acidity of catalysts is gravimetric and IR spectroscopy with adsorbed ammonia. The lone-pair electrons of nitrogen are involved in different types of interactions with the surface acid sites. The acidity for each applied method and each given impregnation method are presented in figure 3.

Figure 3 shows that the total acidity value is not always in line with the total metal content. There is a phenomenon of unequal distribution of the impregnated metal upon the surface of USY. The sintering phenomenon also occurs. This phenomenon causes the Co to become less capable of donating its acid sites. According to figure 4, use of the sequential impregnation method by adding Mo precursor followed by Co precursor gives the best result in terms of total acidity.

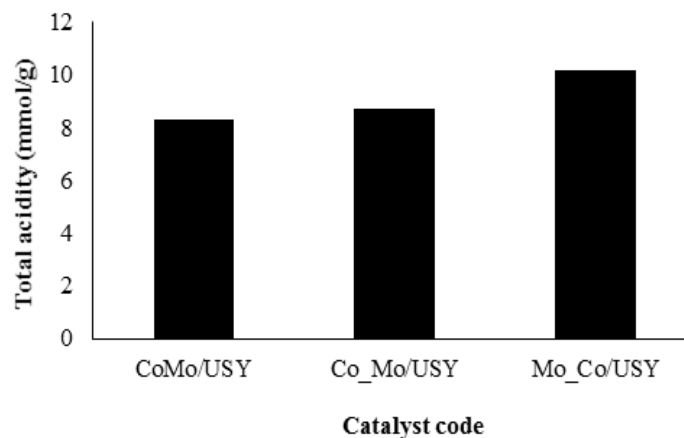


Figure 3. The total acidity for each given treatment.

Figure 4 displays the FTIR spectra of the catalyst products with various impregnation methods through careful analysis of the IR spectra. Ammonia sorption experiments, monitored with FTIR spectroscopy, were performed to determine the change in active (acid) sites with different impregnation methods. It is well known that ammonia is a useful probe molecule for Brønsted and Lewis acid sites and is characterized by the narrow and well-resolved bands in the region 1400-3750 cm^{-1} . Although the characteristic bands of the Brønsted and Lewis acid sites appear at a high wave number, all the spectra were recorded in the 400-4000 cm^{-1} range.

Three modes of adsorption have been observed: (a) proton transfer at Brønsted acidic surface sites (ammonium ions); (b) electron transfer at Lewis acidic surface sites (molecularly coordinated ammonia); and (c) hydrogen bonding to surface hydroxyl groups. All three modes of adsorption display IR spectra bands at different wave numbers and can be identified by their IR absorption bands.

Two bands at 3600 and 3500 cm^{-1} also indicated acid sites in the super cages (the high-frequency HF band) and in the sodalite cages (the low frequency LF band) of the USY, respectively [17]. The shift of the surface vibration mode of strained $\text{Al}(\text{Si})\text{--O--Al}(\text{Si})$ bridges to lower frequencies for Mo_Co/USY was attributed to an $\text{Al--O--M}(\text{metal})$ interaction (i.e. in the 3000-3750 cm^{-1} range). It was noticed that the slight red shift in the IR spectrum of the first type of sequential impregnation method's product (namely use of Mo_Co/USY catalyst) in comparison with the products of co impregnation and second type sequential impregnation methods (namely use of CoMo/USY catalyst and Co_Mo/USY catalyst), could also be caused by the stretching vibration frequency of aqua hydroxyl radicals. Therefore, hydrogen bonds were formed between the catalyst structures, resulting in the self-assembly of a 3D cage-like structure that improved the stability of the catalyst structure. The phenomenon is an indication that the Mo_Co / USY catalyst is more stable than other types.

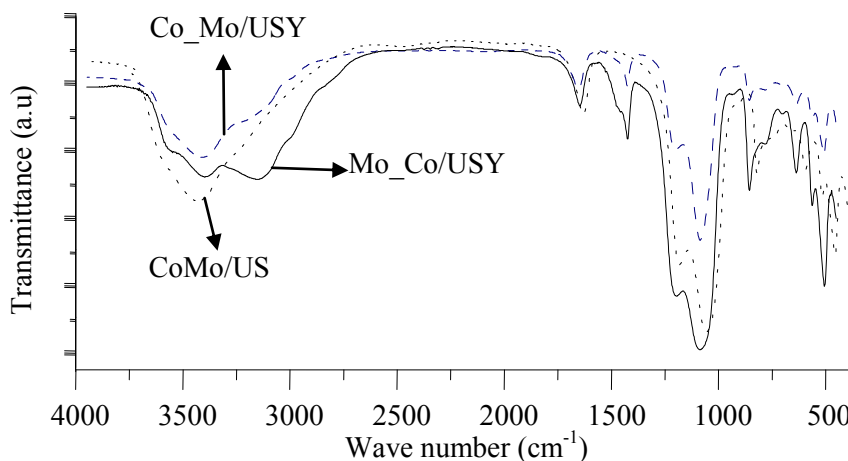


Figure 4. FTIR spectra of synthesized catalyst.

Ammonia, coordinated with the Lewis center, yields a band at *ca.* 1500 cm^{-1} , and the protonated ammonia on the Brønsted center, yields a band at *ca.* 1600 cm^{-1} . Both complexes also yield a peak at *ca.* 1500 cm^{-1} . The 1600 cm^{-1} band is generally assigned to hydrogen-bonded ammonia. In the FTIR spectra of synthesized catalyst, a small absorption band at *ca.* 1600 cm^{-1} , typical of the Brønsted acid site, was found for all samples. The presence of Lewis acid sites is indicated by a band at *ca.* 1500 cm^{-1} . The CoMo/USY catalyst did not exhibit any Lewis acidity as evidenced by the missing ammonia absorption band at around 1500 cm^{-1} , and we found that only a few Lewis acid sites could be observed for Co_Mo/USY . In CoMo/USY catalyst, the band in the 400 – 1100 cm^{-1} range was overlapped by the Mo_Co/USY catalyst.

The results of FTIR spectra analysis lead to the same conclusions as gravimetric methods. Both methods conclude that the catalyst which has the highest acidity is Mo₂Co/USY.

4. Conclusion

Based on all results, the best catalyst preparation is the sequential impregnation method, first adding first ammonium heptamolybdate followed by cobalt nitrate hexahydrate. CoMo and USY are expected to be used as bifunctional catalysts and for hydro-treatment.

Acknowledgment

This research is funded by The Ministry of Education and Culture through The Directorate of general of research and community service (DP2M DIKTI) under research competent Grant. Therefore, I would like to thank the Ministry of Education and Culture, especially DP2M DIKTI, for funding this research.

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