

Preparation of Co-Mo Catalyst using Activated Carbon Produced from Egg Shell and SiO₂ as Support.

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ABSTRACT

The preparation of a series of Cobalt-Molybdenum (Co-Mo) catalyst supported with SiO₂ and carbonized egg shells was investigated using standard procedures the catalyst were further calcined at a temperature of 500°C generate the internally consistent set, the metal atoms content were varied in a regular manner. The ratio 1:4 (Co²⁺: Mo⁶⁺) by weight was employed for the various catalysts prepared. The carbonized egg shells were divided into two parts; the first part was leached with HNO₃ while the other part was not leached.

Activity tests were run using these catalysts containing leached and unleached carbon for the hydrogenation of methyl orange. A change in absorbance with respect to the unhydrogenated methyl orange at a wave length of 460nm was observed to be 0.07 and 0.067 when the catalyst containing the leached carbonized egg shell (catalyst A) and the catalyst containing the unleached (catalyst B) activated carbon were used for the hydrogenation reaction, respectively. This confirms that catalyst A is more efficient in hydrogenating methyl orange than catalyst B.

(Keywords: methyl orange, hydrogenation, Cobalt-Molybdenum catalyst)

INTRODUCTION

Production of active hydrogenation and hydrodesulphurization (HDS) catalysts is one of the most urgent subjects issue in the petroleum industry. Industrial applications of hydrodesulphurization catalyst are generally solid consisting of metals, metal oxides and some salts [1].

These catalysts may be classified in accordance with their customary use. Vigorous catalysts

suitable for the hydrogenation of alkyne and alkene linkages, aldehydes, and ketones include nickel, cobalt, molybdenum, and tungsten oxides and sulphides. Mild catalysts useful for stepwise hydrogenation include oxides of copper, zinc, chromium, metallic platinum, and palladium. Hydrogen is absorbed on the metal surface [2].

Activated carbon has been utilized as an efficient sorbent for odor removal, solvent recovery, decolonization, dechlorination, ozone annihilation, H₂S/CS₂ removal, gold recovery, filtration, condensed deviling, fuel gas cleaning, industrial wastewater treatment, drinking water conditioning, etc. Activated carbons can be prepared from a variety of materials. The most commonly used raw materials for the preparation of activated carbons in commercial practice are peat, coal, lignite, wood, and agricultural by-products. Production of activated carbon from agricultural by-products serves a double purpose by converting unwanted, surplus agricultural waste to useful, valuable material and provides an efficient adsorbent material for the removal of organic pollutants from water/waste water.

Activated carbons have a large adsorption capacity for a variety of organic pollutants but are expensive due to difficult regeneration and higher disposal cost [3–9]. In view of the high cost and tedious procedure for the preparation and regeneration of activated carbon, there is continuing search for the development of adsorbents using cheaper raw materials. Many researchers have studied the feasibility of less expensive activated carbons prepared from spent oil shake [5,6], bagasse fly ash [4], tamarind nut [8], soyabean hulls [7], *Salvinia molta* Mitchell [9], and coconut husk [3] for the removal of phenolic compounds.

Solids such as carbon [10], silica [11], and titanium [14] have been reported as active carriers of hydrodesulphurization and hydrogenation

catalyst. Co–Mo or Ni–Mo(W)-based catalysts have been extensively used in industry for HDS reactions [19, 20]. Topsøe and co-workers [19, 21-22], proposed a so-called CoMoS model, in which Co decorates the edge sites of highly dispersed MoS₂ crystallites, has attracted increasing attention as catalytically active sites in Co–Mo sulfide catalysts.

It is considered that understanding the active sites of the catalysts are extensively promoted by their selective preparations. It has been found [23-26] that the addition of a chelating agent, such as nitrilotriacetic acid (NTA), in an impregnation solution provides a method to prepare selectively a Co(Ni)MoS phase, excluding the formation of separate Co(Ni) sulfide phases. Numerous studies [27-30] on the catalyst systems, accordingly, have been carried out to understand the mechanism of synergy generation between Co and Mo, the structure of catalytically active sites, the reaction mechanisms of HDS and hydrogenation, support effects, and so on.

Papadopoulou and co-worker [31] prepared a series of CoMo/γ-Al₂O₃ catalysts using various methodologies. One of them was prepared by depositing the Mo species on the support via the equilibrium deposition filtration (EDF) technique and then the Co species by dry impregnation. Another (co-EDF) catalyst was prepared by depositing the Co and Mo species simultaneously via EDF. A third catalyst (co-WET) was prepared by depositing Mo and Co species simultaneously using the wet impregnation method. The fourth catalyst(s-DRY) was prepared by depositing the Mo species through wet impregnation and then the Co species by dry impregnation, then fifth catalyst (WET) was prepared by mounting the Mo species through successive dry impregnations and then the Co species by dry impregnation. Their catalytic activity for the hydrodesulfurization of thiophene was determined. The trend observed was given as (EDF>co-EDF>co-WET>s-DRY>WET). The EDF and co-EDF catalysts were reported to exhibited relatively low hydrogenating activity.

The catalytic performance of Co–Mo sulfide catalysts depends strongly on preparation variables and additives [19]. The preparation method may modify the edge dispersion and stacking degree of MoS₂ particles and the efficiency of transformation of Co to CoMoS phases.

In this present study we prepared Co-Mo/ SiO₂ - activated carbon catalysts for leached and unleached activated carbons with varying amount of Co and Mo content. The catalytic activities of the catalysts produced were compared for the hydrogenation of methyl orange.

EXPERIMENTAL PROCEDURE

Materials and Methods

All reagents and chemicals used in the study were of AR grade. Ammonium Heptamolybdate (AHM), Cobalt Chloride (CoCl₂.6H₂O), and SiO₂. Egg shells, cellulose filter muffle furnace (Uniscope SM9080), UNISPEC SM7504UV spectrophotometer

Preparation of Activated Carbon

The raw material (i.e., egg shells) was collected. The collected material was thoroughly washed with double distilled water to remove any extraneous material and then dried at room temperature. 250g of the dried egg shell was carbonized for about 4 hours to remove the non-carbonaceous components. The carbonized egg shell was collected, grounded and sieved with a 90µm mesh.

Two types of activated carbon were prepared, namely leached and unleached activated carbon. The leached carbon was prepared by carefully pouring 50g of carbonized egg shell into a beaker containing 40ml of concentrated HNO₃. After allowing the mixture to settle for a while a litmus paper was used to check the level of acidity of the mixture's filtrate. Continuous washing of the mixture was carried out with double distilled water until the filtrate was acid free.

The acid free leached carbonized egg shell was dried at 130–150°C for 24 hours and then subjected to thermal activation at different temperatures at 600 and 800°C for 1 hour in a muffle furnace.

The unleached activated carbon those not undergo the addition of HNO₃, undergoes the other procedures outlined above.

Activation is carried out under closely controlled process parameters to get optimum properties. Finally, the product is adequately cooled before it

is exposed to the atmosphere. The temperature and time were optimized by observing the surface properties of the activated products obtained.

Preparation of Co-Mo Catalyst and Characterization

The technique used for the preparation of catalyst below is the impregnation technique which involves the procedure stated below:

1. Evaluation of the porous support.
2. Contracting the support with a solution containing a soluble salt of the component being added.
3. Drying the component.
4. Calcination and activated of the component.

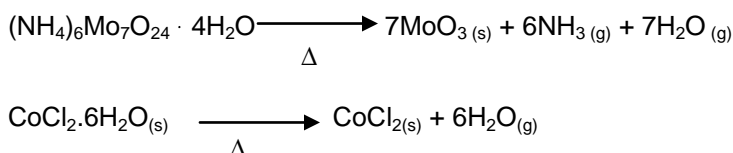
A weighed amount of ammonium heptamolybdate AHM (aqueous mixture) was put into a beaker and impregnated drop wise onto a known weight of leached and unleached activated carbon/SiO₂ in the crucible.

The solution was stirred and well soaked. The solution was then kept in the muffle furnace at a temperature of 120-130°C to dry for 6 hours. After the 6 hours duration the furnace was reset to 500°C for calcinations of the MoO₃-Activated carbon which took 4 hours.

A weighed freshly prepared cobalt chloride of weighed amount was impregnated in drop wise into the crucible containing MoO₃/SiO₂-Activated carbon. The solution was stirred and well soaked, the other crucibles containing MoO₃-Activated carbon was also impregnated with various amount of CoCl₂. Drying and calcination were also carried out at 120°C for 6 hours and 500°C for 4 hours, respectively. This method was used for both leached and unleached activated carbon.

The ratio of Co²⁺ (CoCl₂): Mo⁶⁺ (MoO₃) used for the various catalysts prepared is 1:4. The formulae below was used for preparation of the catalyst, shown in the table below is the comparison between the expected theoretical weight and experimental weight.

The equation for the reaction is:



$$\text{Weight of the catalyst} = \frac{(\text{Weight of Mo}^{6+} + \text{Weight of Co}^{2+})}{25} \times 100$$

$$\text{Weight of the support} = \text{weight of catalyst} - (\text{Weight of Mo}^{6+} + \text{Weight of Co}^{2+})$$

Table 1: Leached and Unleached Activated Carbon Catalyst.

(a) Theoretical Results for Both Catalysts (Leached and Unleached).

Sample	Wt. of AHM(g)	Wt. of CC(g)	Wt. of support(g)	Wt. of Mo ⁶⁺ (g)	Wt. of Co ²⁺ (g)	Wt. of catalyst(g)
1	2.431	0.908	7.437	1.983	0.496	9.916
2	4.650	1.736	14.220	3.792	0.948	18.960
3	6.500	2.427	19.875	5.300	1.325	26.50

CC= Calcium Chloride, support = Activated carbon/ SiO₂.

(b) Experimental Results for the Leached Activated Carbon (Catalyst A).

Sample	Wt. of AHM(g)	Wt. of CC(g)	Wt. of support(g)	Wt. of catalyst(g)
1	2.431	0.908	7.437	8.312
2	4.650	1.736	14.220	17.901
3	6.500	2.427	19.875	25.0

CC= Calcium Chloride, support= Activated carbon/ SiO₂.

(c) Experimental Results for the Unleached Activated Carbon (Catalyst B).

Sample	Wt. of AHM(g)	Wt. of CC(g)	Wt. of support(g)	Wt. of catalyst(g)
1	2.431	0.787	7.437	8.435
2	4.650	1.504	14.220	18.430
3	6.500	2.102	19.875	25.701

CC= Calcium Chloride, support = Activated carbon/ SiO₂.

HYDROGENATION/REDUCTION OF METHYL ORANGE

The hydrogenation system was setup. A conical flask with an outlet was setup and connected to another conical flask by rubber tube and glass tube.

The first conical flask (A) served as the hydrogen generation while the second flask (B) serves as the hydrogenation flask.

0.5g of the catalyst was weighed and added into the hydrogenation flask containing 150ml of 6.5mg/L of methyl orange. Hydrogen gas was generated from the first flask (A) through a reaction between zinc dust and Hydrochloric acid

of known concentration. The sand bath was used as a source of heat on which the hydrogenation flask was placed. The tap of the burette was opened to purge the system and to also allow for the activation of the catalyst.

The hydrogenation system was maintained at a temperature of about 230°F (110°C) for 3hours. The system was allowed to cool and then filtered with 0.5µm cellulose nitrate filter. The reaction product was measured spectrophotometrically using a UNISPEC SM7504UV spectrophotometer. The concentration change was calculated from the linear calibration plot of the non-hydrogenated methyl orange at a wavelength of 465 nm.

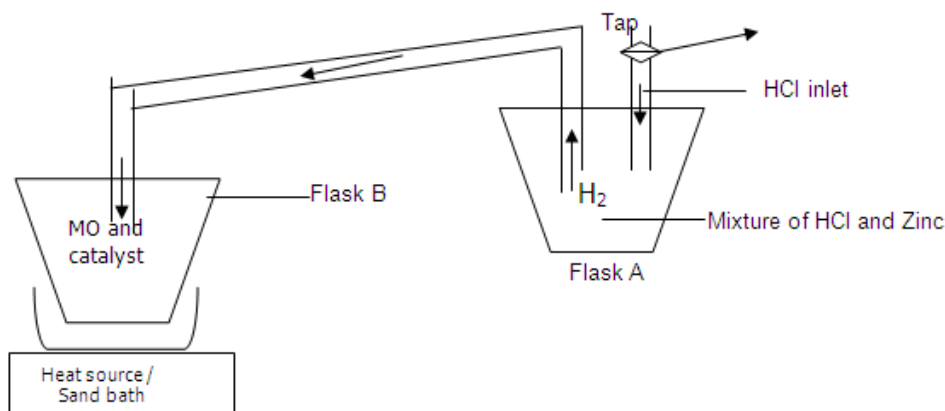


Figure 1: Setup for the Hydrogenation of the Methyl-Orange.

RESULTS AND DISCUSSION

The spectral plot of the various catalyst in distilled water were carried out after subjecting the various catalyst to the same temperature at which the hydrogenation reaction took place (110°C) for 3 hours in the absence of methyl orange, this reaction was carried out in order to check the influence of filtration and color change produced by the catalyst after the reaction. The spectra graphs of the various catalyst where given in Figure 2 below.

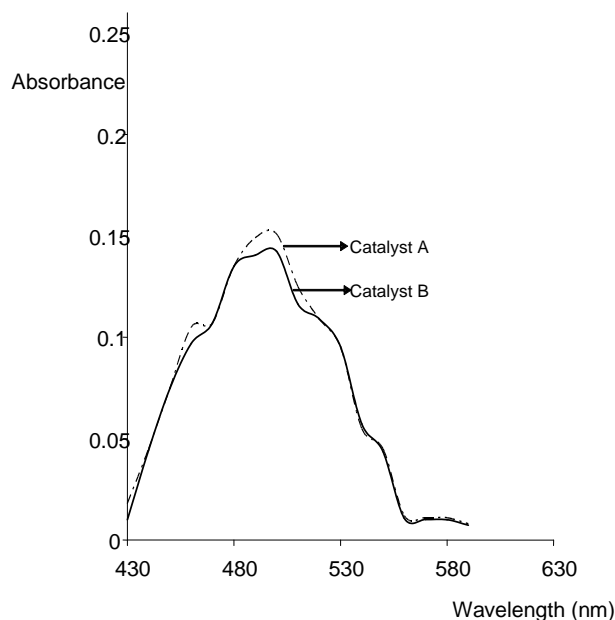


Figure 2: Spectra Plot of Solution Containing Catalyst A and B after Hydrogenation in the absence of Methyl Orange (MO); Catalyst A: Leached Activated Carbon from Egg Shell; Catalyst B: Unleached Activated Carbon from Egg Shell.

From the plots of the two catalysts, it can be reported that the catalyst prepared with leached activated carbon from egg shell (catalyst A) has a maximum absorbance of 0.151 at a wavelength of 500nm, while the catalyst prepared with unleached activated carbon from egg shell (catalyst B) has an absorbance of 0.142 at the same wavelength, which is around the wavelength of Co (II).

From Figure 3 above the concentration changes for the hydrogenated methyl orange were calculated at a wavelength of 460nm [31] with

reference to the unhydrogenated methyl orange. Changes in absorbance were observed to be 0.07 and 0.067 for the leached and unleached activated carbon, respectively.

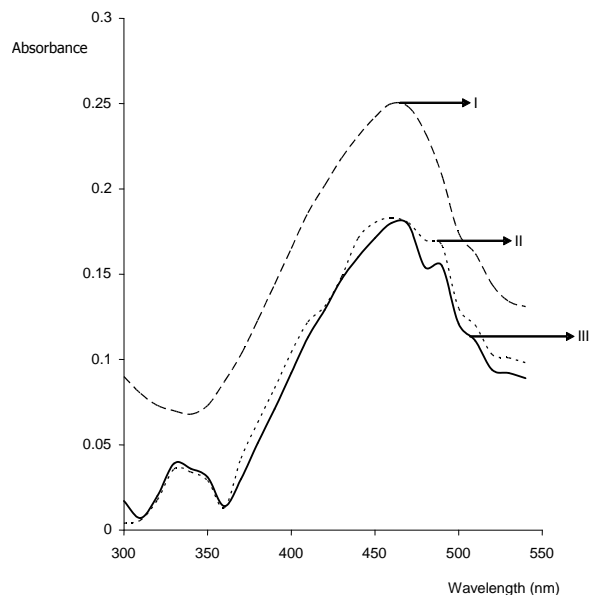


Figure 3: UV-Visible Spectra of Methyl Orange (Mo) Solution (6.5 mg/dm³) and the Sample Obtained after the Hydrogenation Reaction Experiment.

I = UV-visible spectra of methyl orange (Mo) solution (6.5mg/dm³)

II = UV-visible spectra of hydrogenated methyl orange (Mo) solution (6.5mg/dm³) using catalyst B

III = UV-visible spectra of hydrogenated methyl orange (Mo) solution (6.5mg/dm³) using catalyst A

This little change in absorbance was attributed to the low temperature of 110°C used to carry out the hydrogenation reaction. Where high conditions such temperatures and pressures higher than 300°C and 10 bar would favor more hydrogenolysis [17, 18].

The experiment performed with the leached activated carbon supported and silica as a support gave the best result for the hydrogenation process this is due to the change in absorbance and a faint pink-yellowish color observed and also the change in absorbance observed.

CONCLUSION

Both the leached and unleached activated carbon has great effect on the hydrogenation process. The hydrogenation reaction was conducted at a low temperature (110°C) so as to prevent a high pressure build-up in the glass system. Due to this low temperature the hydrogenation process could not be very effective [17]. At a temperature of about 500-1000°C which would impose a very high pressure into the system would be more effective.

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