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# Preparation of Co-Mo catalyst using activated carbon produced from egg shell and SiO<sub>2</sub> as support – A hydrogenation study

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**ABSTRACT:** The preparation of a series of cobalt-molybdenum (Co-Mo) catalysts supported on SiO<sub>2</sub> and carbonized egg shells were investigated using standard procedures; the catalysts were further calcined at the 500 °C temperature to generate the internally consistent set, and the metal atoms content were varied in a regular manner. The ratio 1:4 (Co<sup>2+</sup>: Mo<sup>6+</sup>) by weight was employed for the various catalysts prepared. The carbonized egg shells were divided into two parts: the first part was leached with HNO<sub>3</sub>, as the other one was not leached. Activity tests were run using these catalysts containing leached and unleached carbon for the hydrogenation of methyl orange; the changes in absorbance regarding the unhydrogenated methyl orange at a wavelength of 460 nm were respectively 0.07 and 0.067 when the catalyst containing the leached carbonized egg shell (catalyst A) and the catalyst containing the unleached activated carbon (catalyst B) were used for the hydrogenation reaction. This confirms that catalyst A is more efficient in hydrogenating methyl orange than catalyst B.

Keywords: methyl orange; hydrogenation; cobalt-molybdenum catalyst

# Introduction

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

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

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Vigorous catalysts suitable to the hydrogenation of alkyne and alkene linkages, aldehydes and ketones include nickel, cobalt, molybdenum, and tungsten oxides, as well as sulphides. Catalysts working under mild conditions 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 used as an efficient sorbent to odor removal, solvent recovery, decolorization, dechlorination, ozone annihilation, H<sub>2</sub>S/CS<sub>2</sub> 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. The production of activated carbon from agricultural by-products serves a double purpose of converting unwanted, surplus agricultural waste into useful, valuable material and provides an efficient adsorbent material for the removal of organic pollutants from 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 a continued 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], soybean hulls [7], salvinea molta Mitchell [9], and coconut husk [3] for the removal of phenolic compounds.

Solids such as carbon [10], silica [11] and titania [14] have been reported as active carriers of hydrodesulphurization and hydrogenation catalysts. Co-Mo or Ni-Mo (W)-based catalysts have been extensively used in industry for HDS reactions [19, 20]. The so-called CoMoS model proposed by Topsøe et al. [19, 21, 22] has attracted attention. It is considered that understandings of 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 selectively prepare 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 investigate 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 et al. [31] prepared a series of  $CoMo/\gamma-Al_2O_3$  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 catalyst (co-EDF) 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 the 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 exhibit 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  $MoS_2$  particles and the efficacy of transforming Co into CoMoS.

In this study we prepared  $Co-Mo/SiO_2$ -activated carbon catalysts for leached and unleached activated carbons with a varying amount of Co and Mo content. The catalytic activities of the catalysts produced were compared for the hydrogenation of methyl orange.

# **Material and Methods**

#### Materials and methods used

All reagents and chemicals used in the study were of analytical reagent grade. Ammonium Heptamolybdate (AHM), Colbalt Chloride (CoCl<sub>2</sub>.6H<sub>2</sub>O) and SiO<sub>2</sub>. Egg shells, cellulose filter muffle furnace (Uniscope SM9080), UNISPEC SM7504-UV spectrophotometer.

#### Preparation of activated carbon

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

Two types of activated carbon were prepared, namely leached and unleached activated carbon.

The leached carbon was prepared by carefully pouring 50 g of carbonized egg shell into a beaker containing 40 mL of concentrated  $HNO_3$ . 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 between 600 and 800 °C for 1 hour in a muffle furnace.

The unleached activated carbon was prepared by subjecting the carbonized egg shell to thermal activation at different temperatures between 600 and 800  $^{\circ}$ C for 1 hour in a muffle furnace.

Activation was carried out under closely controlled process parameters to get optimum properties. Finally, the product was adequately cooled before it was 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 preparing the catalyst below is the impregnation which involves the following procedure:

- 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 activation of the component.

A weighed amount of ammonium heptamolybdate AHM (aqueous mixture) was dispensed into a beaker and impregnated dropwise onto a known weight of leached and unleached activated carbon/SiO<sub>2</sub> in the crucible. The solution was stirred and well soaked. The solution was dried in a muffle at the 120-130 °C temperature for 6 hours. After this time the temperature of the furnace was adjusted to 500 °C for calcinations of the MoO<sub>3</sub>-activated carbon, which took 4 hours.

A weighed freshly prepared Cobalt Chloride of weighed amount was impregnated in dropwise into the crucible containing  $MoO_3/SiO_2$ -activated carbon. The solution was stirred and well soaked; the other crucibles containing  $MoO_3$ -activated carbon were also impregnated with various amounts of  $CoCl_2$ . 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  $Co^{2+}$  (CoCl<sub>2</sub>): Mo<sup>6+</sup> (MoO<sub>3</sub>) used for the various catalysts prepared is 1:4. The equations below were used for preparing the catalyst; tables 1-3 present the

comparison between the expected theoretical weight and the experimental weight observed.

The equations for the reaction were:

Equation 1:  $(NH_4)_6 Mo_7 O_{24} \odot 4H_2 O \longrightarrow \Delta$ Equation 2:  $CoCl_2.6H_2 O_{(s)} \longrightarrow CoCl_{2(s)} + 6H_2 O_{(g)}$ 

Equation 3: Weight of the catalyst= (Weight of  $Mo^{6+}$  + Weight of  $Co^{2+}$ ) × 100 25

Equation 4: Weight of the support = weight of catalyst – (Weight of  $Mo^{6+}$  + Weight of  $Co^{2+}$ )

Table 1. Theoretical results for both catalysts (leached and unleached).

Sample	Wt. of AHM (g)	Wt. of CC <sup>ª</sup> (g)	Wt. of support <sup>b</sup>	Wt. of Mo <sup>6+</sup> (g)	Wt. of Co <sup>2+</sup> (g)	Wt. of catalyst (a)
1	2 /21	0 000	7 427	1 002	0.406	0.016
T	2.451	0.908	7.437	1.965	0.490	9.910
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
300 11						

<sup>a</sup>CC = calcium chloride. <sup>b</sup>Support = activated carbon/SiO<sub>2</sub>.

 Table 2. Experimental results for the leached activated carbon (catalyst A).

Sample	Wt. of AHM (g)	Wt. of CCª (g)	Wt. of support <sup>b</sup> (g)	Wt. of catalyst (g)
1	2.431	0.908	7.437	8.312
2	4.650	1.736	14.200	17.901
3	6.500	2.427	19.865	25.0
200				

<sup>a</sup>CC = calcium chloride. <sup>b</sup>Support = activated carbon/SiO<sub>2</sub>.

Table 3. Experimental results for the unleached activated carbon (catalyst B).

Sample	Wt. of AHM	Wt. of CC <sup>a</sup>	Wt. of	Wt. of
	(g)	(g)	support <sup>b</sup> (g)	catalyst (g)
1	2.431	0.787	7.434	8.435
2	4.650	1.504	14.210	18.430
3	6.500	2.102	19.843	25.701

<sup>a</sup>CC = calcium chloride. <sup>b</sup>Support = activated carbon/SiO<sub>2</sub>.

The tables 1-3 display the weight of the catalyst support and that of the catalyst prepared using the leached and unleached activated carbon. The slight difference in the reported theoretical weight compared to the experimental weight was due to the loss of some extraneous materials, such as impurities, during calcinations and activation of the catalyst and support.

#### Hydrogenation/reduction of methyl orange

The hydrogenation system setup was composed by a conical flask with an outlet

connected to another conical flask by a rubber tube and a glass tube. The first conical flask (A) served as the hydrogen generation, as the second flask (B) serves as the hydrogenation flask (Figure 1).



**Figure 1**. Setup for the hydrogenation of the methyl-orange.

0.5 g of the catalyst was weighed and added into the hydrogenation flask containing a solution of 150 mL methyl orange (0.0199 mM). Hydrogen gas was generated from the first flask (A) through a reaction between zinc dust (22 g) and hydrochloric acid (2 M). 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 also to allow the catalyst activation.

The hydrogenation system was maintained at a temperature of about 230 °F (110 °C) and pressure of  $2.64 \times 10^5$ Pa for 3 hours. The system was allowed to cool down and then filtered with 0.5 µm cellulose nitrate filter. The reaction product was spectrophotometrically measured using a UNISPEC SM7504UV spectrophotometer (Table 4). The concentration change was calculated from the linear calibration plot of the non-hydrogenated methyl orange at a wavelength of 465 nm.

absorbance	
Concentration (mol/dm <sup>3</sup> )	Absorbance
0.001	0.144
0.002	0.271
0.003	0.336
0.004	0.451
0.005	0.549
0.006	0.689
0.007	0.824
0.008	1.032
0.009	1.356

**Table 4**. Values of concentration (mol/dm<sup>3</sup>) of methyl orange and the corresponding absorbance.

Square correlation coefficient  $(R^2) = 0.9569$ .

The calibration plot of absorbance against concentration (mol/dm<sup>3</sup>) for methyl orange is shown in Figure 2.





### **Results and Discussion**

The spectral plot of the various catalyst in distilled water were carried out after subjecting the various catalysts to the same temperature at which the hydrogenation reaction took place (110 °C) for 3 hours in the absence of methyl orange; this blank experiment 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 catalysts are shown in Figure 3.

From the plots of the two catalysts, it may 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 500 nm, as the catalyst prepared with unleached activated carbon from egg shell (catalyst B) has an absorbance of 0.142 at the same wavelength, which is about the wavelength of Co (II).

Considering Figure 4, the concentration changes for the hydrogenated methyl orange were calculated at a wavelength of 460 nm [31] with reference to the unhydrogenated methyl orange. Changes in absorbance were observed to be 0.07 and 0.067, respectively, for the leached and unleached activated carbon.

With the catalyst used, it is possible to perform the hydrogenation of methyl orange at lower temperatures (a little above room temperature) and atmospheric pressure. Temperatures and pressures higher than 300  $^{\circ}$ C and 10 bars would favor the

hydrogenation of N=N [17, 18].



Wavelength (nm)

**Figure 3**. 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.



**Scheme 1**. Hydrogenation of methyl orange.

The experiment performed with leached activated carbon provided the best result for the hydrogenation process; this was observed through the change in absorbance and the presence of a faint pink-yellowish color.



**Figure 4**. UV-visible spectra of methyl orange (MO) solution (0.0199 mM) and the sample obtained after the hydrogenation reaction experiment. I = UV-visible spectra of methyl orange (MO) solution (0.0199mM). II = UV-visible spectra of hydrogenated ethyl orange (MO) solution (0.0199 mM) using catalyst B. III = UV-visible spectra of hydrogenated methyl orange (MO) solution (0.0199 mM) using catalyst A.

## Conclusion

Both the leached and unleached activated carbon has great effects on the hydrogenation process. The hydrogenation reaction was conducted at a low temperature (110°C) in order 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]. A temperature between 500-1,000 °C, which imposes a very high pressure into the system, would be more effective.

# **References and Notes**

- [1] Gupta, V. K.; Sharma, S.; Yadav, I. S, Mohan, D. J. Chem. Technol. Biotechnol. 1998, 71, 180.
- [2] Housecroft, C. E.; Constable, E. C. An Introduction to organic, inorganic and physical chemistry. 2<sup>nd</sup> ed. New York: Prentice Hall, 2003, p. 867.

- [3] Vinod, V. P.; Anirudhan, T. S. J. Sci. Ind. Res. 2002, 61, 128.
- [4] Burleigh, M. C.; Markowitz, M. A.; Spector, M. S.; Gaber, B. P. Environ. Sci. Technol. 2002, 36, 2515.
- [5] Darwish, N. A.; Halhouli, K. A.; Al-Dhoon, N. M. Sep. Sci. Technol. 1996, 31, 705.
- [6] Singh, K. P.; Mohan, D.; Sinha, S.; Tandon, G. S.; Ghosh, D. Ind. Eng. Chem. Res. 2003, 43, 1965.
- [7] Flock, C.; Bassi, A.; Gijzen, M. J. Chem. Technol. Biotechnol. 1999, 74, 303.
- [8] Srinivasan, K. R.; Ramadevi, A. Ind. J. Environ. Hlth. 1998, 30, 303.
- [9] Sankaran, N. B.; Anirudhan, T. S. Indian J. Eng. Mater. Sci. 1999, 6, 229.
- [10] Topsøe, H.; Clausen, B. S.; Topsøe, N. Y.; Pedersen, E. *Ind. Eng. Chem. Fundam*. 1986, 25, 25.
- [11] Muralidhar, G.; Massoth, F. E.; Shabtai, J. J. Catal. 1984, 44.
- [12] Blanchard, P.; Payen, E.; Grimblot, J.; Le Bihan, L.; Poulet, O.; Loutaty, R. J. Mole. Catal. A-Chem. 1998, 135, 143.
- [13] Singh, K. P.; Mohan, D.; Sinha, S.; Tandon, G. S.; Ghosh, D. Ind. Eng. Chem. Res. 2003, 42, 1965.
- [14] Ramirez, J.; Fuentes, S.; Diaz, G.; Vrinat, M.; Breysse, M.; Lacroix, M. Appl. Catal. 1989, 52, 211.
- [15] Radovic, L. R, Moreno-Castilla, C., Rivera-Utrilla, J. In: Radovic, L. R. eds. Carbon materials as adsorbents in aqueous solutions. Chemistry and Physics of Carbon, 27, New York: Marcel Dekker, Chapter 4, p. 227, 2000.
- [16] Urbano, F. J.; Marinas, J. M. J. Mol. Catal. A-Chem. 2001, 173, 329.
- [17] Talukdar, A. K.; Bhattacharyya, K. G. Appl. Catal. A-Gen. 1993, 96, 229.
- [18] Zazo, J. A.; Casas, J. A.; Mohedano, A. F.; Gilarranz, M. A.; Rodriguez, J. J. Environ. Sci. Technol. 2005, 39, 9295.
- [19] Topsøe, H.; Clausen, B. S.; Massoth, F. E. In: Anderson, J. R.; Boudard, M., eds. Catalysis-science and technology, Berlin: Springer, 11, 1996.
- [20] Kabe, K.; Ishihara, A.; Qian. W. Hydrodesulfurization and hydro-denitrogenation. Tokyo: Kodansha, 1999.
- [21] Topsøe, H.; Clausen, B. S. Catal. Rev.-Sci. Eng. 1984, 26, 395.
- [22] Candia, R.; Sørensen, O.; Villadsen, J.; Topsøe, N.; Clausen, B. S.; Topsøe, H. Bull. Soc. Chim. Belg. 1984, 93, 763.
- [23] Van Veen, J. A. R.; Gerkema, E.; Van der Kraan, A. M.; Knoester, A. J. Chem. Soc. Chem. Commun. **1987**, 1684.
- [24] Van Veen, J. A. R.; Gerkema, E.; Van der Kraan, A. M.; Hendriks, P. A. J. M.; Beens, H. J. Catal. 1992, 133, 112.
- [25] Louwen, S. P. A.; Prins, R. J. Catal. 1992, 133, 94.
- [26] Medici, L.; Prins, R. J. Catal. 1996, 163, 94.
- [27] Prins, R.; de Beer, V. H. J.; Somorjai, G. A. Catal. Rev. Sci. Eng. 1989, 31, 1.
- [28] Chianelli, R. R.; Daage, M.; Ledoux, M. J. Adv. Catal. 1994, 40, 177.
- [29] Whitehurst, D. D.; Isoda, T.; Mochida, I. Adv. Catal. 1998, 42, 345.
- [30] Breysse, M.; Portefaix, J. L.; Vrinat, M. Catal. Today. 1991, 10, 489.
- [31] Papadopoulou, Ch.; Vakros, J.; Matralis, H. K.; Kordulis, Ch.; Lycourghiotis, A. J.

Col. and Inter. Sci. 2003, 261, 146.

[32] Sadhana, S. R.; Nidhi, D.; Nitin, K. L.; Kagne, S.; Sukumar, D. *Int. J. of Hydrogen Energy*. **2007**, *32*, 2776.

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