

HYDROGENATION OF *THEVETIA PERUVIANA* SEED OIL USING COBALT OXIDE-MOLYBDENUM OXIDE CATALYST SUPPORTED ON ACTIVATED CARBON

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ABSTRACT: Laboratory prepared cobalt oxide-molybdenum oxide on egg-shell activated carbon was used to hydrogenate *Thevetia peruviana* seed oil. Dual impregnation method was used to load the oxides on the activated carbon support. The extent of hydrogenation was determined from the iodine values of fresh and the hydrogenated oil. Significant catalyst-support interaction was observed that can be explained by the different support type and treatments. Activated carbon and silica were used as supports. Activated carbon by itself displayed hydrogenation activity.

INTRODUCTION

A natural oil extracted from *Thevetia peruviana* plant otherwise known as yellow oleander plant was used in this study. The seed has been reported to contain 62% oil and about 37% protein. Defatted seed cake contains two glucosides, peruvoside and revoside. *Thevetia peruviana* seed oil (TPSO) is used in India for the treatment of topical skin diseases (Kirk, 1964; Oyelowo, 1997).

Oils are classified into three major groups, namely, Drying, Non-drying and Semi-drying oils. The drying oils possess the highest level of unsaturation, followed by the semi-drying and non-drying oils respectively. In these oils, unsaturation is proportional to the number of double bonds, a property that will be made use of in this study.

Most of these oils have inherent rancid property that manifests as the shelf life prolongs. The technical solution is to hydrogenate the oil to reduce odour and colour, improve stability, and to increase the melting point. As the hydrogenated oil acquires these properties, it loses its fluidity and may form semi-solid or solid product at room temperature depending on the level of hydrogenation.

Even though this study aims to achieve the objectives stated above, there are studies suggesting that high level of unsaturation in oils help lower the cholesterol level in human body when consumed (Stinson, 1988). Hydrogenation of oil can be carried out using homogenous or heterogeneous route. Hydrogenation reaction is an extremely slow process and is used mostly for converting carbon-carbon double bonds to carbon-carbon single bonds.

Although the hydrogenation reaction is exothermic and appears simple, its rate is negligible in an uncatalyzed reaction, even at elevated temperature. In homogeneous hydrogenation reactions, Wilkinson's catalyst is used. This catalyst is an organic complex of transition metals like rhodium or iridium. The solubility or homogeneous nature of the catalyst creates catalyst-from-product separation problem when the hydrogenation reaction is completed.

As can be indicated by the conversion of alkane to alkene, hydrogenation reaction is quantitative. In converting one molecule of the alkene to alkane, one molecule of hydrogen is consumed. Hydrogenation reaction can thus be used analytically by measuring hydrogen consumption volumetrically. Hydrogenation reaction is exothermic, a consequence of the formation of two stronger sigma bonds (C-C) from the breakage of one sigma bond (H-H) and one pi bond (C=C). For most of the alkenes the heat of hydrogenation is close to 7.17 kJ per each double bond in the compound (Morrison and Boyd, 1987).

Typically and commercially, metal catalysts of platinum, palladium or nickel are used for hydrogenation reactions. The goal of this study is to investigate the use of mixed oxides of cobalt and molybdenum for the hydrogenation of TPSO.

For commercial hydrogenation of oils, Raney nickel catalyst is most preferred. It involves a complex reaction mechanism. Raney nickel catalysts are alkaline and may be used for hydrogenations that are not adversely affected by basic conditions. They are deactivated by acids (Rase, 1997; McGraw, 1990; Kirk, 1964; Furnish *et al*, 1991). The catalyst investigated in this study is not new to the chemical industry. It has not been investigated for natural oil hydrogenation, but is predominantly used in the petroleum industry for hydrotreating processes. It is often used as dual-oxide of molybdenum and another transition metal Ni, Co or Pb. The other transition metals have catalytic activity lower than that of molybdenum individually, however, when smaller proportions of these transition metals are compounded along with molybdenum oxide, the other metal oxide acts to produce better activity, stability or selectivity for the desired reaction (Miranda and Kareem, 1988; Delman, 1989).

Cobalt oxide/molybdenum oxide dual catalysts on γ -alumina, or CoMo/ γ -Al₂O₃, or CoMo as it is usually called in the industry, can meet at least five different hydrotreatment requirements, namely; hydrodesulfurization (HDS), hydrodenitrogenation (HDN), hydrogenation (HYD), hydrodeoxygenation (HDO), and hydrocracking (HCG). The investigation of its HYD catalytic activity is what this study focuses on, to see whether and to what extent a natural oil (TPSO) could be hydrogenated by CoMo.

The design of this study will be based on the investigation of inter-facial hydrogenation of the oil, catalyzed by CoMo catalyst, at a high temperature, moderate pressure, without stirring. The proposed scheme is that oil (containing some unsaturated fatty acids) will adsorb on the catalyst surface, followed by hydrogen adsorption from the gas phase to the catalyst surface, there will be molecular cleaving of hydrogen into atoms before subsequent hydrogenation reaction.

MATERIALS AND METHODS

All the chemicals used were from laboratory reagents (imported) stock, purity (> 99.9%), purchased from BDH Chemicals Ltd. Poole England. Activated carbon supported catalysts were synthesized according to the procedure of Kareem (1988) using locally available carbonaceous matter (egg shell) for catalyst support preparation.

Eggshell Activated Carbon Production

Dried eggshell (100g) was placed in a perforated tin. The perforated tin was placed in a muffle furnace where the eggshell was destructively burnt. The burnt eggshell was ground with pestle and mortar and then sieved to 90mm particle size.

Concentrated nitric acid was used to leach a portion of the sieved particle, the other portion was left unleached. The leached portion was washed with water to remove the residual acid. This was confirmed using blue litmus paper.

The leached and unleached portions were then placed in different evaporating dishes and placed in the muffle furnace at 800°C for one and half hours to dry and activate the particles.

Synthesis of Activated Carbon Supported Catalysts

Two sets of catalysts were prepared one with leached activated carbon support, the other with the unleached portion. Double impregnation method was applied in both cases to incorporate MoO₃, followed by CoO into the support.

The leached activated carbon particle (3.116g) was soaked with an aqueous solution containing 1.019g of ammonium heptamolybdate (NH₄)₆Mo₇O₂₄.H₂O, in distilled water. The aqueous solution was added to the support dropwise and just enough distilled water to soak the support was used in preparing the solution. The impregnated support was first dried at 120°C for six hours, and then calcined for four hours at 500°C. After allowing the heptamolybdate impregnated support to cool down, 0.330g cobalt carbonate dissolved in enough distilled water to soak the support was added dropwise to cool the impregnated support. The impregnated support was again dried at 120°C for six hours, and calcined at 500°C for six hours.

The dual oxide impregnated catalyst was allowed to cool and then stored in an airtight container pending hydrogenation activity determination.

Catalytic Hydrogenation

To carry out catalytic hydrogenation of the oil a conical flask with an outlet was connected to another conical flask using glass tubes thrust into the flasks, and flexible teflon tubing. Hydrogen is generated in the first flask, and catalytic hydrogenation took place in the second flask. The conical flasks were well corked using rubber bungs. A burette was connected to the hydrogenation flask through a second hole drilled into the rubber bung. The burette was clamped to a retort stand. The hydrogenation flask was immersed in a sand bath. To generate hydrogen, 22g of zinc metal was placed in 60ml 0.6M dilute hydrochloric acid. 1g of the catalyst was weighed and poured into the hydrogenation flask. Both flasks were corked, all joints and connections were then tested for leaks. The empty burette was opened for 45 minutes to purge the whole system with hydrogen of other gases. After purging, the burette tap was closed and the catalyst in the hydrogenation flask was activated with hydrogen for 75 minutes. While the catalyst activation was being done, the sand bath temperature was maintained at 320°C. After activating the catalyst, the sand bath temperature was reduced to and maintained at 180°C. The burette was filled with TPSO and 10ml of TPSO was then introduced into the hydrogenation flask. The hydrogenation reaction was carried out at 180°C for 120 minutes, after which the sand bath was removed and the reaction mixture allowed to cool. The content of the hydrogenation flask was poured into an air-tight bottle. The oil was separated from the catalyst by decantation and through filter paper, then kept in an air-tight bottle pending iodine value determination.

Iodine Value Determination

The iodine value of the oil was determined before and after hydrogenation. The Wijs' method was followed to determine iodine value (Pearson, 1976).

In the unleached samples (only) during hydrogenation, the natural colour of TPSO progressively turned darker, taking on the black colour of the support, and viscosity was observed to be progressively getting higher, the fluidity motion of TPSO progressively getting lard-like or more viscous.

There was a significant aroma (oil smell) reduction in all the hydrogenated products. The reduction can be attributed to the use of porous supports in the catalytic hydrogenation process.

RESULTS

From the volume of hydrogen generated and the fixed volume of the wares used, the hydrogenation reaction took place at mild pressure of about 50 psig, and temperature of about 180°C. Bubbling was noticed in the hydrogenation flask while the experiment was on. Table 1. Indicates about 7% weight loss in the impregnated sample when compared with theoretically expected weight.

Table 1: Catalyst Loading; Experimental and Weights Calculated

	Experimental	Theoretical
Wt. Of Heptamolybdate	1.010g	1.019g
Wt. Of cobalt carbonate	0.330g	0.330g
Wt. Of support (leached)	3.116g	3.116g
Wt. Of MoO ₃	(0.8310 – x ₁)g	0.83g
Wt. Of CoO	(0.208 – x ₂)g	0.208g
Catalyst wt	3.872	4.155g
Wt. % difference	= 6.81%	

MoO₃ and CoO are derived from the thermal decomposition of ammonium heptamolybdate and cobalt carbonate respectively.

Theoretically, the quantitative amount of MoO₃ and CoO expected can be calculated based on the amount of their precursors used.

However, the impurities contained in these precursors will affect the experimental weights of the oxides obtained. Besides, CoCO₃ in the chemical catalog is listed as CoCO₃ · x H₂O suggesting that it can hydrate before use, during storage. The purity of the precursors was not redetermined neither was CoCO₃ dried (for fear of pre-experimental decomposition) before its sequential impregnation on the activated carbon support.

x₁ accounts for weight loss attributable to ammonia heptamolybdate impurity, while x₂ accounts for weight loss attributable to cobalt carbonate impurity and the undeterminable water of crystallization.

Consequently, the experimental catalyst weight is expected to be less than the calculated/theoretical weight.

The weight loss could be further attributed to power deposit in the product dish, burn off impurities and/or possible over calcination. The reduction in iodine value indicates the level of hydrogenation achieved. TPSO belongs to the non-drying oil group, having low iodine values and hence low unsaturation level. Because of their low iodine values, they are consequently least reactive and can therefore be a good measure of catalyst efficiency, since they are difficult to hydrogenate. The difference in the iodine values before and after hydrogenation is directly proportional to the level of hydrogenation that took place.

Table 2: Effect of Catalysts on Iodine Values of Oil

Sample	Oil Iodine Value before(HYD)	Oil Iodine value after(HYD)	Iodine Value difference
Fresh Oil	12.690	-	-
Control Run (No catalyst) (2 hr. run)	12.690	12.690	0
CoMo on L/AC (1g, 2 hr. run)	12.690	8.493	4.197
CoMo on UL/AC (1g, 2 hr. run)	12.690	7.614	5.076
UL/AC only (1g, 2 hr. run)	12.690	6.931	5.759
CoMo on SiO ₂ (1g, 2 hr run)	12.690	1.171	11.519

L/AC = Leached activated carbon; UL/AC = unleached activated carbon

Triple runs of each experiment was carried out, the values tabulated in Table 2 are average values. The Wij's method used in determining iodine values can introduce measurement error into the iodine values only through the titre values measurement in the burette used. The error margin specified in the next section represents measurement/calculation error.

DISCUSSION

A unit decrease in iodine value is equivalent to theoretical consumption of 10.33 H₂ per 100kg oil hydrogenated (Cocks and van Rede, 1966). As shown in Table 2, in the absence of a catalyst, hydrogenation of TPSO was impossible or very negligible, as the Iodine value test could not detect any change. The error margin in the iodine value differences is + 0.05. CoMo on leached and unleached activated carbon supports both registered significant hydrogenation activity. The most interesting aspect of this study is that the laboratory synthesized activated carbon support itself turned out to be an active hydrogenation "catalyst".

This is evident in the hydrogenation activity displayed by the leached and unleached activated carbon support and supported further by what appears to be an indication of catalyst-support interaction when the whole result in Table 2 is considered. The result shown for CoMo on SiO₂ further indicates the significant role that the catalyst-support interaction played on the hydrogenation rate obtained. SiO₂ being a non-reactive, less interactive support showed higher (HYD) rate than that displayed by CoMo on the activated carbon supports (leached and unleached).

CONCLUSION

CoMo (on leached and unleached activated carbon supports) can be used as a natural oil hydrogenation catalyst. The support used in loading CoMo has a strong effect on the catalytic hydrogenation activity. Activated carbon, though investigated in this work as a possible support, turned out to be a promoter of the hydrogenation reaction. From the results obtained, strong catalyst-support interaction influenced the hydrogenation activity of CoMo when supported on activated carbon. Overall, supported CoMo in all the experiments displayed significant hydrogenation activity.

It is significant whether activated carbon support is leached or not before the catalyst is loaded. For this work, unleached support displayed higher hydrogenation activity. Silica support is better than activated carbon support for CoMo loading in natural oil hydrogenation.

An advantage realized in using CoMo on activated carbon support (leached and unleached) over Raney Nickel is that cobalt carbonate and ammonium heptamolybdate are relatively cheap compounds (\$80/kg and \$60/kg respectively) compared to Raney Nickel selling for \$200/kg.

Raney Nickel is supplied as 50% slurry in water, requiring post operation separation of oil from the catalyst and further separation of water from the hydrogenated oil. The additional separation of water from hydrogenated oil is not required when CoMo on activate carbon (leached and unleached) is used.

The biggest process advantage of using CoMo on activated (leached and unleached) over Raney Nickel is that, even though both catalyst are heterogeneous, when activated carbon support is used and CoMo is dispersed on its surface, through dispersion phenomenon, thin layers of active catalyst can be spread over the very high specific surface area of the support.

The large pores in the activated supports facilitate rather easy, mass transfer aided hydrogenation reaction. In the Raney Nickel catalyst, the porosity is very low, the metal surface area therefore reduces or limits possible oil/catalyst inter-facial contact to a minimum depending on the particle size used. The smaller the particle size, the higher the oil/catalyst interfacial contact, however the more complex is the process constraints encountered and the post hydrogenation separation of catalyst particles from oil.

Moreover, because active catalyst is dispersed on activated carbon support in ratio of about 1:3, expensive active catalyst precursors are further stretched by using locally or easily available materials like egg or coconut shell as support.

Industrially, supported CoMo is very cheap because practically all the refineries in the world utilize the catalyst, they are safe and easy to handle since activation is done in-situ as in this experiment. Raney Nickel however is very difficult to handle because of the slurry nature of its supply. Many processing constraints are posed by its use, such as pH adjustment, water/oil separation, etc. Raney Nickel in fine mesh size is a suspect cancer agent, it is also a flammable solid.

That this study is able to establish reasonable hydrogenation of natural oil using CoMo on activated carbon support, suggests that it can be an alternative to the process constraints-afflicted Raney Nickel catalyst.

REFERENCES

1. Cocks L. V., and Van Rede, C., Laboratory Handbook for Oil and Fat Analysis, Academic Press, London, 241 – 260, 1966.
2. Delman, B., "Advances in Hydropurification Catalysts and Catalysis", D. L. Trimm *et al* (Editors), Catalysts in Petroleum Refining, (1989), 11 – 32.
3. Furnish, B. S., Hannaford, A. J., Smith, P.W.G., and Tatchell, A. R., Vogels Textbook of Practical Chemistry, 5th Edition, (1991), 87 – 92.
4. Kareem, S. A. (1988), "Ternary Molybdenum Chalcogenides for Hydrodesulfurization", Ph.D. Dissertation, University Microfilms International No. 8953323, Ann Arbor, USA.
5. Kirk Othmer Encyclopedia of Chemical Technology, 2nd Edition, vol. 4, (1964), 565 – 570.
6. Kirk Othmer Encyclopedia of Chemical Technology, 2nd Edition, vol. 8, (1964), 776 – 785.

7. McGraw Hill Encyclopedia of Science and Technology, vol. 8, McGraw Hill, N. Y., (1990), 425 – 428.
8. Miranda R., and Kareem, S. A., (1988), “Supported and Sulfided Pb-Mo oxides: Active and Stable Hydrotreatment Catalysts, Catalysis Letters, (1988), 217 – 222.
9. Morrison, R. T., and Boyd, R. N., (1987), Organic Chemistry, 5th Edition, Allyn and Bacon, Inc. Boston, 303 – 307.
10. Oyelowo, E. A., “Epoxidation of *Thevetia Peruviana* Seed Oil”, 1997 B.Sc. Thesis, University of Ilorin, Nigeria.
11. Pearson, D., The Chemical Analysis of Foods, 7th Edition, Edinburgh, Churchill Livingstone, 488 – 491, (1976).
12. Rase, H. F., (1977), Chemical Reactor Design for Process Plants, vol. 2, John Wiley, N. Y., 161 – 178.
13. Stinson, S. C., (1988), “Drug Industry Steps up Fight Against Heart Disease”, Chemical and Engineering News. Vol. 66, No 40, 35 – 70.