

SINGLE CATION OXIDE HETEROGENEOUS CATALYSIS: HYDROGENATION OF PALM OIL AND GROUNDNUT OIL.

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ABSTRACT: Cobalt oxide and molybdenum oxide catalysts supported on activated carbon were used to catalyze the hydrogenation of groundnut oil and palm kernel oil respectively. Iodine value determination was used to measure the extent of hydrogenation in each reaction. Catalyst-support interaction was different for the two single cation oxide catalysts studied. In MoO₃ case, "unleached" supported catalyst exhibited higher hydrogenation activity than the "leached supported catalyst. The reverse was the case for leached and unleached supported CoO catalysts.

INTRODUCTION

In an earlier work by Kareem and Ojelabi, (1998), it was shown for the first time that CoMo (cobalt oxide/molybdenum oxide) supported on leached and unleached activated carbon can be used to hydrogenate natural oils. It does not follow however that the success observed when the dual-oxide CoMo, was investigated necessarily preclude inactivity of the individual cation oxides as catalyst. In this study therefore, CoO that showed higher hydrodesulfurization (HDS) activity than MoO₃ when investigated as single cation oxide catalyst (Kareem, 1999), is investigated for its hydrogenation (HYD) activity on a non-drying oil, palm kernel oil, while MoO₃ is investigated for its hydrogenation activity on groundnut oil, a drying oil. Effect of support leaching by HNO₃ prior to catalyst loading is also investigated. An extensive review by Davignon *et al.* (1980) of heterogeneous catalytic hydrogenation of natural oils commissioned by the Canadian government showed that even though the earliest published work dates back to 1953, no one has investigated the use of dual-cation oxides nor the individual single-cation oxides reported here for their hydrogenation activity before. A more recent review of heterogeneous hydrogenation of vegetable oils by Veldsink *et al.* (1997) confirmed the Canadian report and further indicated that Ni-based catalysts are most widely used in industrial hydrogenation. Consequently therefore, the possibility of the single cation oxide also exhibiting hydrogenation activity will be investigated along with the support pretreatment effect. Experimental design in this study will focus on investigation of CoO and MoO₃ as potential natural oil hydrogenation catalysts by interfacial contact mode in a reacting system at a high temperature and moderate pressure, without stirring.

METHODS AND MATERIALS

The materials and methods used for this study are similar to those in the previous work by Kareem and Ojelabi (1998) where in a step-wise mode, activated carbon support was sequentially impregnated with MoO₃ and then CoO before the final drying and calcination. Instead of the double loading method used in the previous investigation however, a single impregnation step was used to load the CoO catalyst on leached and unleached supports, followed by drying and calcination. The same impregnation step was then used to load MoO₃ catalyst on leached and unleached supports. To prepare CoO catalysts, 3.020g of activated coconut shell activated carbon (leached, or unleached) was impregnated with an aqueous solution containing 0.313g of cobalt carbonate. The sample was then dried at 120°C for 6 hours and then calcined for 6 hours at 500°C. Similar step was followed to impregnate (leached and unleached) coconut shell activated carbon with aqueous solution containing 1.200g of ammonium heptamolybdate.

Catalytic Hydrogenation

To evaluate the catalytic activities of the prepared catalysts, the methods employed for the oil catalytic hydrogenation and the iodine value determination were as reported in the previous work by Kareem and Ojelabi (1998). The hydrogenation reaction was carried out in an air -tight apparatus set-up. Hydrogen gas was generated in a conical flask by the action of zinc metal on predetermined amount of HCl. The hydrogen generation flask was connected with another conical flask (where hydrogenation reaction took place) by a flexible teflon tubing. The hydrogenation flask was placed on a sand bath maintained at 180°C, and the hydrogenation reaction lasted for 180 minutes. The iodine value of the reaction products (hydrogenated oil) was

tested using the standard Wij's method.

RESULTS

As in the previous experimental work, slight weight losses were recorded even in the once impregnated samples when experimental weights were compared with the theoretical weights. A 3% weight loss was recorded for CoO while that of MoO₃ was 2.3%. These figures are expectedly lower than those of the dual impregnated cation oxides previously reported as 6.81% (Kareem and Ojelabi 1998).

Tables 1 and 2 below give the iodine values for groundnut oil hydrogenation by CoO and palm kernel oil hydrogenation by MoO₃. The difference in the iodine values before and after hydrogenation is directly proportional to the level of hydrogenation that took place. The error margin in the iodine value differences is ± 0.05 . The listed values represent average readings for three experimental runs.

Table 1. Effect of CoO Catalysis on Iodine Value of Groundnut Oil

Sample	Oil Iodine Value before HYD	Oil Iodine Value after HYD	Iodine Value Difference
Fresh oil	89.830	-	-
Control run (No Catalyst) (2hr run)	89.930	89.680	2.250
CoO on L/AC (1g, 2hr run)	89.830	53.210	36.720
CoO on UL/AC (1g, 2hr run)	89.930	55.160	34.770
L/AC (1g, 2hr run)	89.830	70.810	19.120
CoO on L/AC (2g, 2hr run)	89.930	37.990	51.940
CoO on UL/AC (2g, 2hr run)	89.930	38.160	51.770

L/AC = Leached activated carbon. UL/AC = Unleached activated carbon.

Table 2. Effect of MoO₃ Catalysis on Iodine Value of Palm Kernel Oil

Sample	Oil Iodine Value before HYD	Oil Iodine Value after HYD	Iodine Value Difference
Fresh oil	14.231	-	-
Control run (No Catalyst) (2hr run)	14.231	14.231	0.000
MoO ₃ on L/AC (1g, 2hr run)	14.231	10.780	3.433
MoO ₃ on UL/AC (1g, 2hr run)	14.231	9.771	4.442
MoO ₃ on L/AC (1g, 2hr run)	14.231	7.614	6.599

L/AC = Leached activated carbon. UL/AC = Unleached activated carbon.

DISCUSSION

As suspected, even though groundnut oil is a drying oil, it was still very difficult to hydrogenate it in the absence of a catalyst. It was also not possible to hydrogenate palm kernel oil in the absence of a catalyst. This confirms that a catalyst whether homogeneous or heterogeneous is definitely required for substantial hydrogenation to take place.

CoO that showed superior hydrodesulfurization activity when compared to MoO₃ in a previous investigation (Kareem, 1999), was chosen as the catalyst to hydrogenate groundnut oil with its high level of unsaturation. This is to confirm strongly whether or not MoO₃ with its lower HDS activity possesses the required hydrogenation activity to saturate the few double bonds, present and difficult to hydrogenate in the palm kernel oil. As shown in Table 1, CoO is indeed a good hydrogenation catalyst. Very significant reductions were catalytically effected in the iodine values of the groundnut oil hydrogenated. The most interesting aspect of this

study is that even leached (unloaded) activated carbon support itself turned out to be an active hydrogenation catalyst. Reasonable reduction in iodine value was observed as shown in Table 1.

In this study, the more difficult hydrogenation duty was matched with MoO_3 , the less active of the two catalysts investigated for the HDS reactions. MoO_3 also displayed significant hydrogenation activity as shown in Table 2. The three to six unit reduction in iodine value becomes major when it is realized that each unit decrease in iodine value is equivalent to theoretical consumption of 1 0.30m³ 112 per 100kg oil hydrogenated (Cocks and Van Rede, 1966).

In the case of CoO supported on leached and unleached activated carbon, leached support showed slightly better hydrogenation activity. This suggests possible opening of more pores in the support where adsorption can take place to facilitate hydrogenation reaction. On the other hand, for the supported MoO_3 catalyst, the unleached activated carbon as support showed slightly better hydrogenation activity than the leached activated carbon. The two conflicting findings suggest possible catalyst-support interaction, a phenomenon that can be further studied spectroscopically.

CONCLUSION

The two single cation oxide supported catalysts investigated are potential hydrogenation catalysts. In another study both catalysts (CoO and MoO_3) had been investigated for their HDS activity (Kareem, 1999). It does not have to follow, but based on the findings in that study, it was assumed that CoO would prove to be a better hydrogenation catalyst of the two. This will be so if the same catalytic sites are utilized for HDS and HYD reactions. Nevertheless, both catalysts showed significant HYD activity on their corresponding natural oils, lending support but not total proof for the oil/catalyst match-making made in this study.

This study further suggests strong catalyst-support interaction and should be further studied to optimize the hydrogenation activity of the catalysts.

The cation oxide catalysts investigated in this study are much cheaper than the fused metal catalysts currently employed in research studies and industrially for oil hydrogenation. Heterogeneously, if hydrogenation reaction mechanism is not mass transfer limited, then the cation oxide catalysts (both single and dual) should be extensively investigated as better substitutes for the currently favoured fused metal catalysts such as Raney nickel catalyst.

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