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Vapour-Phase Dehydrogenation of Ethanol using Heterogeneous Modified Kaolinite Catalyst

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Abstract- Vapour-phase dehydrogenation of ethanol to produce acetaldehyde using heterogeneous modified kaolinite catalyst was achieved in this work. The kaolinite was obtained from a local clay resource situated in Anambra State, Nigeria and was thermally modified. The effect of reaction temperature, catalyst loading and process duration were also investigated. The results obtained showed that while increase in reaction temperature and catalyst loading increased the conversion of ethanol, the effect of increase in catalyst loading was stronger. A decrease in conversion with time was also observed, indicating catalyst deactivation. The modified kaolinite was found to be an effective catalyst for the dehydrogenation reaction - a great boost for the green chemistry campaign.

Keywords- *acetaldehyde production, clay catalyst, dehydrogenation, green chemistry*.

I. INTRODUCTION

Relatively high yields of acetaldehyde have been obtained by the oxidation of dehydrogenation of ethanol over such catalysts as silver and vanadium – based catalysts in liquid phase oxidation [1]. Vapour-phase oxidative dehydration on copper oxide-chromium oxide catalyst on pumice as well as over neodymium oxide or samarium hydroxide has also given high yields of acetaldehyde [2]. Dehydrogenation of ethanol to ethanol over asbestos – supported copper catalyst activated by a small amount of cobalt and chromium have also been reported to give a maximum yield of 85% acetaldehyde and 9.6% ethylacetate at 548K. Simultaneous oxidation of a mixture of acetaldehyde and ethanol in the Vapour phase has also been reported to give good conversion. Other reports have showed a yield of 85 – 95% acetaldehyde by air – oxidation of ethanol with silver catalyst at 823K. The effect of different supported and unsupported copper-base catalysts for dehydrogenation has been reported [3]. It was found that 15% copper supported on silica gave the highest conversion of ethanol (76.7%) with an acetaldehyde selectivity of 90.4%. the catalyst was stable and conversion increased with increasing temperature up to 573K. At 623K, the catalyst was subject to quick deactivation caused by sintering of the copper particles.

Literature reports have also indicated the use of clay catalysts in numerous organic reactions including esterification reactions [4]. In particular, as part of a research into the utilization of local raw material resources, it has also been reported that modified montomorillonite and kaolinite clay gave good yields in the liquid-phase dehydrogenation of ethanol [5]. The use of clay catalysts provide better alternatives due to economic and environmental considerations relating to catalyst recovery [6,7]. Also these clay catalysts are eco-friendly and their reaction conditions are relatively mild.

In addition, given government stand on the exploitation of local resources to produce local raw materials, this work generated useful data for the production of catalysts from local clays, elucidation of reaction mechanism and reactor design. In particular, data on the effect of process parameters on the Vapour – phase dehydrogenation of ethanol using heterogeneous modified kaolinite from a local resource have been provided. These catalysts are expected to replace imported ones on the long run, thereby conserving foreign exchange and enhancing economic independence.

II. EXPERIMENTAL

Clay sample obtained from a local resource in Anambra State was crushed and sieved. Sample with particle size in the range of -20 to + 50 mesh size (particle size in the range of 0.297 – 0.841μm) were thermally activated in a furnace at 673K for four hours and used for the dehydrogenation reaction. Ethanol of analytical grade was used without further purification.

A batch reactor consisting of a two-necked round bottom flask of 250 cm^3 capacity, fitted with a catalyst chamber immersed in a heated sand bath at the appropriate temperature, a condenser and a sampling device was used. 100ml of ethanol was put into the two-necked flask and heated to the appropriate temperature for the run. The Vapour generated was channeled into the catalyst chamber where the dehydrogenation occurred. The product stream was subsequently condensed. Samples were drawn at time intervals and analysed using ABBE – 60 refractometer. All the runs were carried out in a similar manner using the following ranges of process variables: catalyst loading (g) - 0, 20, and 40g respectively; temperatures 473, 523 and 573K respectively. The effect of catalyst loading, temperature and process duration (min) on the dehydrogenation reaction was evaluated.

III. RESULTS AND DISCUSSION

The ethanol conversion obtained at different temperatures and catalyst loadings are shown in Tables I and II while the effects of the process variables on conversion are depicted in Figs. 1 – 8. The effect of temperature on conversion of ethanol in the production of acetaldehyde as shown in Fig. 1 indicated that there was a proportionate increase in conversion at the three temperatures. The temperature effect seemed to be evenly scaled with respect to the reaction temperature with conversion at 573K being markedly pronounced and higher than at the lower temperatures as seen in Figs. 2 and 3. Similarly, conversion increased with increase in catalyst loading. Comparatively, the effect of catalyst weight on conversion at various temperatures showed a progressive increase with catalyst loading and reaction temperature as seen in Figs. 5 -8. The increase in conversion increased very sharply at the highest catalyst loading.

On the other hand, the duration of the reaction had very little effect on conversion as can be seen from Figs. 1 – 7. This was attributed to the fact that the Vapour phase dehydrogenation reaction was a continuous flow reaction, whose products were removed at regular intervals. In the absence of catalyst deactivation and temperature fluctuations, the amount of reactant converted at equal time intervals should remain constant. However, it was observed from Figs. 1 -7 that conversion decreased slightly with time, which indicated a mild catalyst deactivation, reducing its effectiveness in the dehydrogenation reaction.

IV. CONCLUSION

The effect of process duration, reaction temperature and catalyst loading has been investigated in the vapour phase dehydrogenation of ethanol using heterogeneous modified kaolinite catalyst from a Nigerian clay resource. While it has also been reported that the use of heterogeneous modified montomorillonite clay catalyst affords more promising conversion and yield for this reaction, it is worth noting that even heterogeneous modified kaolinite could also be used and conversion and yield improved through reaction engineering.

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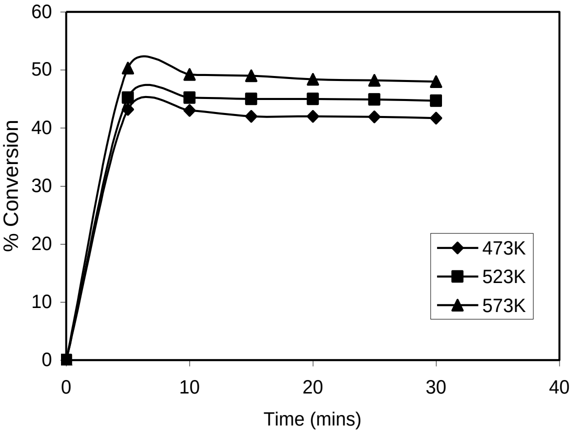

Figure 1. Effect of Temperature on Conversion at 0g Catalyst Loading

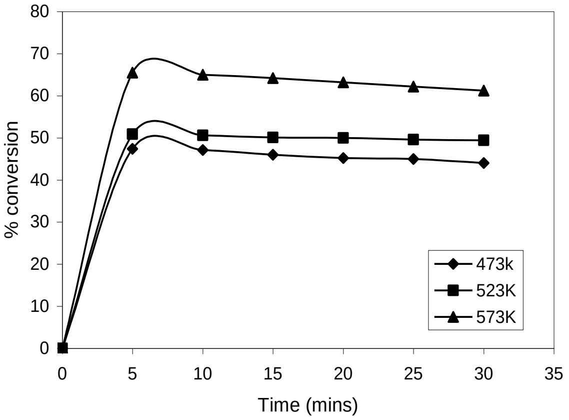

Figure 2. Effect of Temperature on Conversion at 20g Catalyst Loading

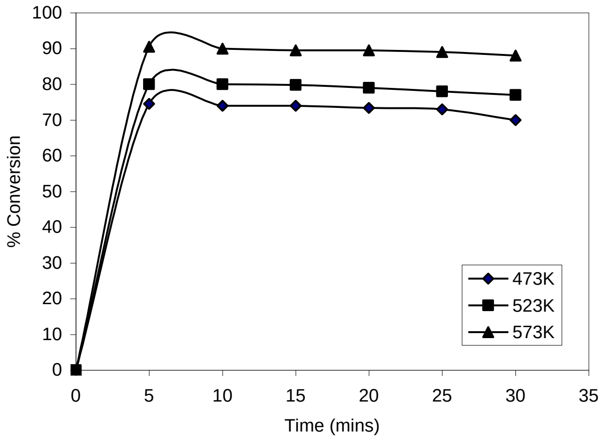

Figure 3. Effect of Temperature on Conversion at 40g Catalyst Loading

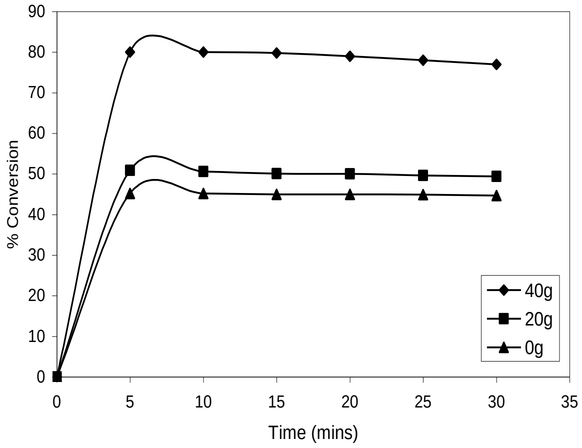

Figure 6. Effect of Catalyst Loading on Conversion at 523K

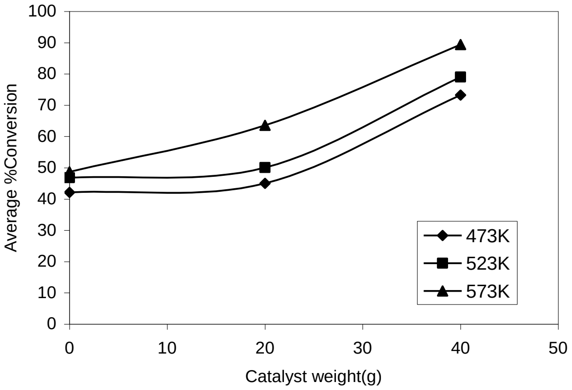

Figure 4. Effect of Catalyst Loading on Average Conversion

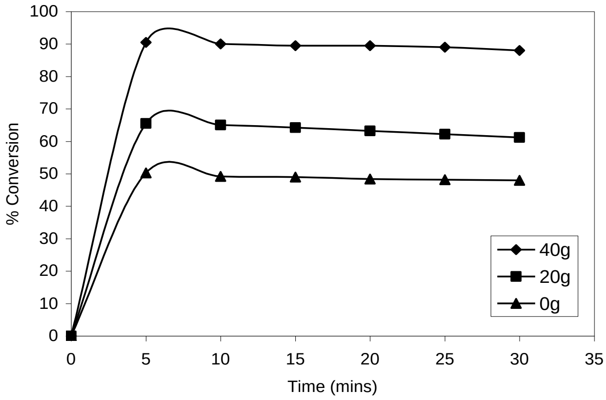

Figure 7. Effect of Catalyst Loading on Conversion at 573K

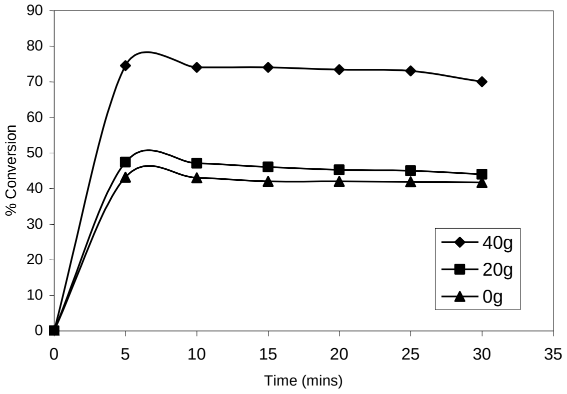

Figure 5. Effect of Catalyst Loading on %Conversion at 473K

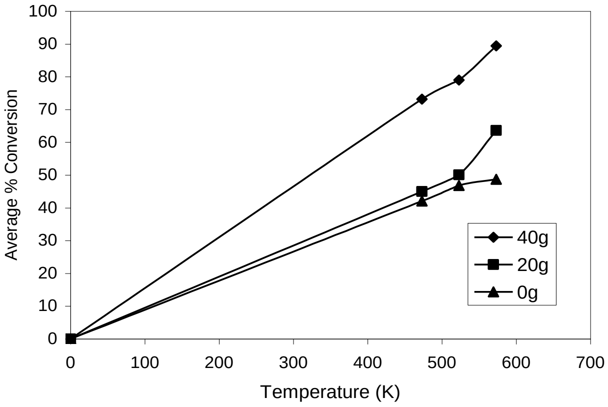

Figure 8. Effect of Temperature on Conversion