Textured Catalysts for Hydrothermal Reactions

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Introduction

Historically there has been a need for catalysts which are stable both physically and performance wise for use in liquid water and at elevated temperatures and pressures. The need for hydrothermally stable catalysts is of particular need for catalytic processing of renewables where the feedstocks, generally non-volatile, would normally be presented in aqueous solution. In other cases such as the purification of terephthalic acid and hydrogenation of maleic acid, processing in aqueous solutions is the only viable means of conducting catalytic reactions.

Unfortunately liquid water at temperatures in the 100-300 ^{o}C range is quite aggressive and easily capable of dissolving or causing substantial loss of physical integrity of conventional alumina, silica-alumina and similar supports. Liquid water at these severe conditions is also capable of initiating sintering and even solubilizing active metals. These processes essentially eliminate silica, alumina and silica-alumina as supports for hydrothermal reactions. To overcome these problems, it is the industrial convention to use activated carbon as the support for reactions conducted in liquid water [1,2]. Carbon is robust in liquid water at high temperatures and at from low to high pH but it is not a completely ideal catalyst support for hydrothermal conditions. It has been found that many catalytic metals, once reduced, are not tightly bound to a carbon surface. During catalytic operation these metals move about and sinter, reducing catalytic activity. This is a particular problem for fixed bed catalytic processes as it is costly to replace sintered and deactivated catalyst with fresh. To reduce this negative effect, catalyst manufacturers typically limit the amount of metal on fixed bed catalysts to a maximum of about 1% by weight. Although moderately effective, this approach limits the ultimate catalytic activity which may be achieved.

In this work we discovered that the addition of a texturizing component in the form of specific metal oxides to the carbon – active metal catalyst improves both activity and lifetime without sacrifice of selectivity [3].

Materials and Methods

Catalytic hydrogenations were conducted in a 300cc Parr Autoclave equipped with stirring, an internal thermocouple, automated temperature control, gas addition and pressure regulation capability and liquid sampling via a dip tube. Product analysis was conducted by withdrawing samples periodically over time and quantification of product via HPLC and GC methods. Catalyst characterizations were performed by XRD, scanning electron microscopy and EDAX and chemisorption. Textured catalyst samples were prepared by the incipient wetness technique using carbon supplied by Engelhard Corp. (20x50 mesh, CTC% = 120, Iodine # approximately 1000). The metal components were used in the form of nitrates supplied by chemical supply houses. The comparative standard commercial catalyst sample was supplied by Engelhard Corp. and was stated to have been prepared on the same carbon as was used to prepare the textured catalysts.

Results and Discussion

We have found that by adding texturizing, that is stabilizing, oxidic components, especially ZrO_2 or TiO_2, to carbon supported catalysts it is possible to achieve higher activity and hydrothermal stability than comparable catalysts without the oxide present. This has been found to be particularly useful for Palladium and Rhodium containing catalysts. It has also been found that one preferred method of adding the oxide component is as a sol or colloid and adding it simultaneously with the active metal component. SEM/EDAX shows that one effect of adding the oxide component is to easily and effectively place the active metal component at or very near the exterior surface of the catalyst particle.

One useful comparison is the aqueous phase hydrogenation of a 20% solution of succinic acid to GBL at 225 ^{o}C and 2500 psig Hydrogen pressure using a 2.5% Pd / Carbon catalyst textured with ZrO_2 and also a standard commercial 2.5% Pd on carbon catalyst. Both catalyst were reduced in the same fashion with 20% hydrogen at 120 ^{o}C for 4 hours before testing.

The results are presented in Figure 1 and clearly show that the textured catalyst containing ZrO_2 is considerably more active but with little effect on selectivity when compared to essentially the same catalyst without texturizing.

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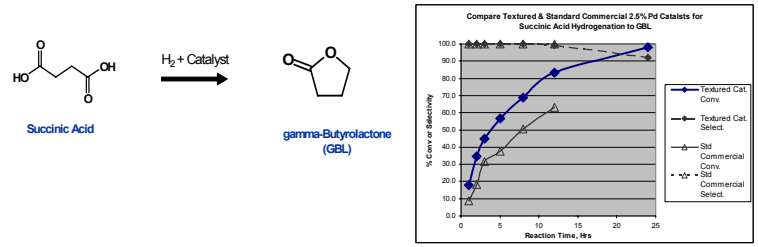

Figure 1

Characterization of the catalysts before and after use shows much less sintering for the texturized catalyst. Similar results were also obtained for two 5% Rhodium – based catalysts. Heineke, et. al, [4] found that addition of $TiCl_4$ to preparations of Pt on graphite improved the rate and selectivity for production of hydroxyl amine from NO. However, Heineke's preparation method using organic solvents and air sensitive $TiCl_4$ is much more complex and expensive than the simple approach we report here.

Significance

The observations we report here permit preparation of catalysts especially useful in the catalytic processing of renewable feedstocks in aqueous solutions.

References

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3. Werpy, T.A., et. al., US 6,670,300 and WO 02/102511.
4. Heinke, et. al., 2,191,360.