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Oxydehydrogenation Of Succimide To Maleimide

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Abstract

Experiments describing oxydehydrogenation of succinimide-conversion to maleimide are presented. The experiments were performed in a quartz-glass reactor set-up, using atmospheric pressure. Temperatures used for the conversion ranged between 300 and 550°C and the airflow was 0.02 to 0.05 dm^3 per minute. Concentrations of succinimide in the experiments were 10, 100 or 200 grams of succinimide per liter of distilled water fed into the reactor tube. The flowrate was kept between 3.0 and 7.5 ml per hour. The iron-phosphate catalyst was calcinated at a temperature between 450 and 720°C for 7 hours. Sometimes a second calcination was performed in the reactor tube, occurring at 450 to 550°C and lasting for 2.5 to 3 hours.

Keywords:

Catalyst, iron-phosphate, calcination, succinimide, maleimide, reactor experiment, oxydehydrogenation, polymaleimide, fermentation

Introduction

Maleimide is a very useful raw material for synthesis of resins, medicines, and agricultural chemicals[1]. Maleimides have also acquired considerable importance as starting materials for the manufacture of high polymers. They can be polymerized by themselves or in combination with other suitable monomers, either by warming or by usage of catalyst. A polyaddition reaction of polymaleimides with organic polyamides is also known[2]. Given the importance of maleimides, it is necessary to develop advantageous and simple but also environmentally friendly processes for the production of maleimide.

Many different routes of producing maleimides have been tried during the years, the most popular being one described in US Patent No. **2,444,536**[3]. In this process maleamic acid is dehydrated with a dehydrating agent such as acetic anhydride to produce maleimide. Maleic acid is reacted with an amine compound, the resulting maleamic acid is then dehydrated in the presence of acetic anhydride and sodium acetate to perform an imidation reaction and obtain maleimide. Acetic anhydride is very expensive however, and the process requires one or more equivalents for the imidation reaction. A lot of water is needed for the separation and recovery of the maleimide that produces a large amount of wastewater containing acetic acid, and a considerable cost is needed to treat this water. For these reasons, this process is not suitable for industrial production of maleimide. The same process is described in US Patent No. **4,138,406**[2], using calcium, barium or strotium oxide, acetate or alcoholate as catalysts instead of nickel salts that are more widely used. US Patent No. **4,851,547**[1] also uses cyclic dehydration for the production of maleimide. Maleic anhydride is reacted with an amine to produce maleamic acid. The maleamic acid is then heated in a water-insoluble or water-immiscible inert organic non-polar solvent in the presence of a catalyst of an amine salt, which will cause dehydration and ring-closure. Kita *et. al* also wrote US Patent No. **4,786,738**[4] which talks about a similar process. Maleamic acids are subjucted to ring-closure imidation in an organic solvent capable of forming an azeotrope with water in the presence of an acid catalyst. The process is carried out in temperatures ranging from 120 to 250°C, and in presence of a compound consisting of at least one metal selected from the group consisting of zinc, chromium, cobalt, nickel, iron, aluminum, and palladium together with a stabilizer for the conversion to take place.

A different route for maleimide production is described in US Patent No. **4,122,076**[5]. The process was developed to avoid the handling of corrosive materials used in US Patent No. 2,444,536, to eliminate the need for recycling and precipitation problems, and to find environmentally friendly routes for the production of maleimide. The process produces maleimide by using the product of the Diels-Alder reaction between furan and maleic anhydride and reacts it with amine. The amic acid is then heated to form maleimide. Further heating of the imide product results in the furan being split off, leaving the imide of the particular amine precursor. The imide-containing products can then be easily isolated. In US Patent No. **4,132,715**[6], Roth presents a procedure for maleimide production that involves isomerization of the corresponding isoimides in the presence of specific catalysts. Catalysts involve mixtures of phenol and triethylamine. The process gives very pure crystals and good yields under mild conditions and the use of small amounts of catalysts.

In US Patent No. **5,973,166**[7] Farhad G.Mizori and Stephen M.Dershem presents a production route for maleimide that is environmentally friendly. They use certain amine salts to replace the polar, aprotic solvents used in the prior art for the cyclodehydration of maleamic acids. The use of these salts provide competitive reaction times and product yields relative to results obtained with the polar, aprotic solvents. The salts have the advantage of having no vapor pressure and therefore possibility to co-distill with the water produced by the cyclodehydration reaction. These salts can also be tailored to have desirable solubility characteristics that permit their easy removal from the reaction product. The amine salts are not destroyed during the cyclodehydration reaction and, therefore, can be efficiently recycled again and again.

Stephen S. Hupp has performed conversion of succinimide to maleimide in US Patent No. **4,515,965**[8], where he claims a process for production through vapor phase oxydehydrogenation. This was made over an iron phosphate catalyst that also may contain one or more alkali metals and alkaline earth metal components. A mixture of succinimide, air and water was mixed in ratios of 1:0.1:1 to 1:5:50 respectively. The reaction was run at temperatures spanning from 300 to 550°C, and the catalyst was preferably calcinated at a temperature between 300 and 600°C at a pressure of 0.1 to 10 atmospheres. The calcinations were performed for one hour or more. The same reaction conditions were claimed in a different US Patent of Hupp, Patent No. **4,520,206**[9]. In this process a succinimide solution is vaporized and passed over a heterogeneous catalyst composed of copper, phosphorous, vanadium or molybdenum and oxygen. The catalyst was treated to the same conditions in this experiment as in the one described in Patent No. 4,515,965.

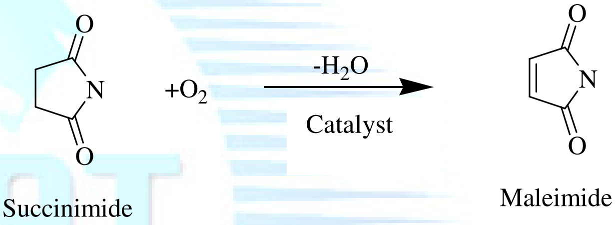

Figure 1. The conversion of succinimide to maleimide.

Experimental Methods

Preparation of the Catalyst

The catalyst used in the oxydehydrogenation experiments was an iron phosphate powder that was bought commercially from Aldrich. No promoter or any other additives were used when preparing the catalyst. The catalytic system is simple and very efficient. The only treatment that was made to activate the powder as a catalyst was to calcine it in a muffler furnace (Thermolyne, Type 1400 Furnace, Model number FB1415M). The catalyst was calcinated in a temperature between 450 and 720°C for 7 hours, followed by a second calcination in the reactor tube before usage at a temperature between 450 and 550°C for 2.5 to 3 hours with airflow of 0.05 dm^3 air per minute. Experiments with the catalyst only calcinated once were also attempted. The catalyst for these experiments was calcinated at 500 to 600°C for 7 hours.

Catalyst testing

An experimental set-up as previously described was used to test the reaction conditions. The catalyst was placed in a one-meter long quartz reactor tube. The reactor tube was made with a glass frit half way down the reactor tube, so that the catalyst and the glass beads could rest in the desired location. The reactor tube was used together with a three-zone furnace (Applied Test Systems Inc., Series 3210) with a maximum temperature of 900℃. Each segment of the furnace is independently controlled using Digi-Sense temperature controllers (Model 89000-10, marketed by Barnant Company, Barrington, IL). A syringe infusion pump was used to feed the succinimide solution into the top of the reactor tube (Cole-Parmer Instruments Series no 74900). The syringe pump had adjustable flowrates and capacity to handle different sizes and types of syringes. To prevent contamination on the glass frit, glass wool was placed below the catalyst in the reactor tube. Glass beads were used to create a uniform flow of the feed onto the catalyst. The beads were placed on top of the catalyst, loosely packed with a height of one to two inches. Nitrogen gas was used as an inert carrier of the succinimide solution through the reactor tube. Air was added to the nitrogen flow, to help the conversion (regular chemistry grade air cylinder). The airflow was controlled by a Cole-Parmer flow meter (Model no 33116-00, serial no 3298). The vapors leaving the reactor condense at room temperature and are further cooled and collected in a cold finger.

Product Analysis

Analysis of the product was made on a VXNMR 300. H^1 nuclear magnetic resonance provided simple means to determine the product composition and the concentrations of the different substances. Samples were taken from the uniform product solution and the water was removed by using a rotatory evaporator. The solid product was then dissolved in D_2O to make the analysis. Figures 2 and 3 show examples of spectra taken of product solutions.

Results and Discussion

Catalyst Results

The catalyst used in the experiments was an iron-phosphate powder purchased from Aldrich. The temperatures studied were 300, 350, 400, 500 and 550°C and airflow that were used were 0.02 and 0.05 dm^3 air per minute. Concentration of succinimide in the reactant solution was 10, 100 or 200 grams of succinimide per liter of distilled water, and the flowrate of the solution was between 3.0 and 7.5 ml of solution per hour. The flowrate determines the contact time of the succinimide with the catalyst, meaning that a high flow rate gives a shorter contact time. Pressure and flowrate of nitrogen gas was kept constant. The treatment of the catalyst was varied, the temperature at which the iron-phosphate powder was calcinated was between 450 and 720°C for 7 hours. In some cases a second calcination was performed in the reactor tube, the temperature was varied between 450 and 550°C, airflow was 0.05 dm^3 of air per minute during 2.5 to 3 hours.

Conversions of up to 89% were achieved for the reaction of succinimide to maleimide. The selectivity towards maleimide depends a lot on the temperature used in the experiment, the higher the temperature used the more byproducts are produced. The temperature is also important for the achieved conversion, giving higher conversion at temperatures of 350°C and above. The airflow could not be determined to have any impact on the achieved conversion. With the flowmeter used for the experiments there were not many options of lower flowrates since it regulated the flow in dm^3 per minute. The concentration of the succinimide solution did not seem to have any impact on the conversion, preferably a solution with higher concentration should be used to utilize the process to the fullest. Experiments were made with concentrations up to 200 grams of succinimide per liter of distilled water. The calcination conditions for the catalyst were varied as well. Temperatures between 450 and 720°C were used for 7 hours. Sometimes a second calcination was used, but no difference in the conversions could be determined due to the second calcination. Therefore one calcination is considered to be enough and preferred since less time and energy is spent on the preparation of the catalyst. The initial calcination temperature could not be determined to have any effect on the final conversion, although a catalyst calcinated at a lower temperature, 450 to 600°C, might have a longer lifetime in the reactor tube.

The catalyst was tested for the conversion obtained and the selectivity towards maleimide. Temperatures that were examined were 300, 350, 400, 500 and 550°C with airflow 0.02 to 0.05 liters per minute, succinimide concentration of the solution was 10, 100 or 200 grams per liter of water and flowrate between 3.0 and 7.5 ml per hour. The iron phosphate works very well as a catalyst for the proposed reaction. Considering the different conversions that were achieved with the same conditions the long runs can be seen as more reliable, they have been run for many hours with the same conditions and the conversion is an average for the total conversion over the whole experiment. More impurities were formed when running experiments at higher temperatures, and the catalyst did not last as long at the higher temperatures. It appeared the catalyst was poisoned, it changed color drastically when the conversion went down. Results from conversion of succinimide to maleimide can be seen in Table 1 and Figure 4.

Seen in Figure 4 is a diagram of the conversion between succinimide to maleimide at three different temperatures. The results show very clearly that the 350°C experiment gave much higher conversion then seen in the 300°C runs. The 400°C experiments gave good conversions, but after the first couple of runs a byproduct was the major product. The byproduct was thought to be polymaleimide, a sticky, red compound that precipitated in the reactor tube. Therefore, the good conversion did not last for very long at 400°C and lower temperatures are suggested for production of maleimide.

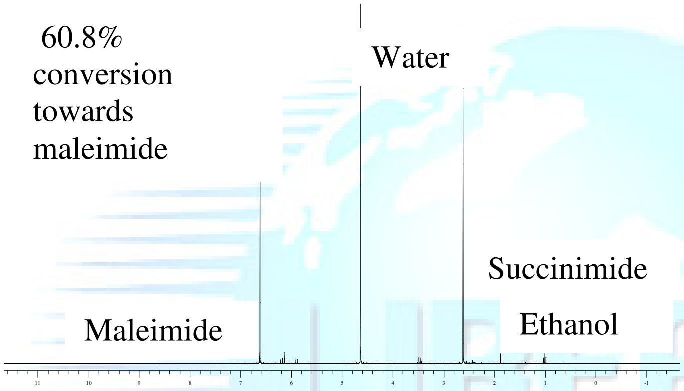

Figure 2. NMR spectrum of succinimide conversion to maleimide containing impurities.

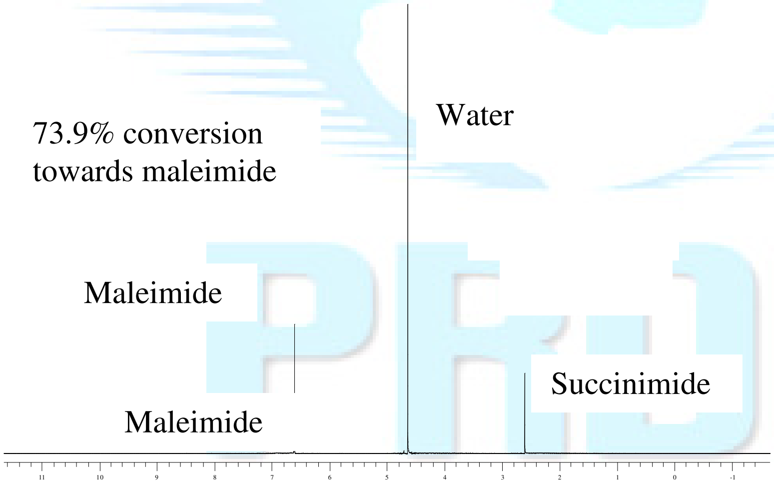

Figure 3. NMR spectrum of succinimide conversion to maleimide without impurities.

Conversion [%]	Temperature [C]	Impurities
32.4	300	no
84.1	350	no
86.8	350	no
75.2	350	no
65.8	350	no
21.5	400	yes
60.3	425	yes
<89.3	475	yes
70.2	500	no
<64.6	500	yes

Table 1. Conversion of succinimide to maleimide at different temperatures.

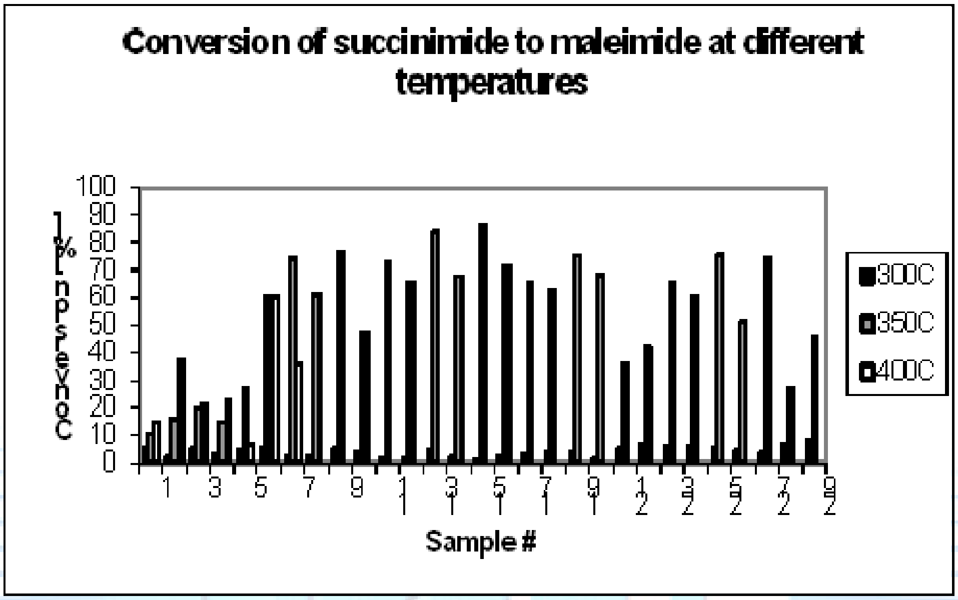

Figure 4. Conversion from succinimide to maleimide at different temperatures.

Conclusions

From the results obtained in the different experiments, it can be determined that iron-phosphate is a very efficient catalyst for the conversion of succinimide to maleimide.

Very high conversions and 100% selectivity are seen in many experiments, even though byproducts are seen in others. The system is very sensitive to high temperatures, giving byproducts in those experiments only. The byproducts and short lifetimes of the catalyst is mostly seen in experiments using temperatures of 400°C and over. Byproducts were sometimes seen in experiments with 350°C also, but the catalyst always lasted for much longer in those experiments. When using 300°C as the reaction temperature, the conversions achieved were very low. The conversions for a typical 300°C-run is below 15%, although good conversions were seen when the temperature was varied between 300, 400 and 500°C in the same run, using a couple of hours for each temperature before changing to the next one. After considering all the parameters, it was concluded that 350°C was the optimum temperature for the conversion. A good conversion, over 70%, is achieved with minor amounts of byproducts produced. The catalyst lasts for a long time in this temperature, much longer then were seen in the 400°C-experiments.

The airflow and the succinimide concentration do not seem to have a significant impact on the conversion result. A relation between the flowrate of the succinimide solution and the conversion towards maleimide could not be determined. The flowrates used in the experiments were between 3.0 and 7.5 ml per hour.

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