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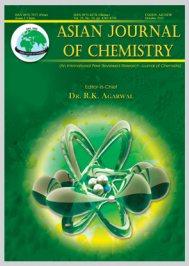

Synthesis of Allantoin Catalyzed by SO_4^{2-}/La_2O_3-SiO_2-ZrO_2

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Allantoin was synthesized using glyoxalic acid and urea as raw materials and La_2O_3-promoted solid acid SO_4^{2-}/SiO_2-ZrO_2 as catalyst. The present research focused on the effects of La_2O_3 doping amount, catalyst dosage, reactant ratio and reaction temperature and time on the yield of allantoin. The optimum condition for reactions is as follows: amount of catalyst, 2.5 g; doping amount of La_2O_3, 0.12 wt %; molar ratio of reactants $n_{(urea)}$: $n_{(glyoxylic\ acid)}$ = 4:1; reaction temperature, 75 ºC and reaction time, 5 h. The yield of allantoin at optimum condition was up to 46 %. The melting point determination, infrared spectroscopy and elemental analysis of the product confirmed that the obtained product is allantoin and the analysis indicated that the purity was 98.5 % or above.

Key Words: Synthsis, Allantoin, Solid acid, La_2O_3-promoted.

INTRODUCTION

Allantoin is widely used in the pharmaceutical, cosmetic, agricultural and biological engineering fields[1-5]. This compound is an important fine chemical product and its chemical synthesis is widely valued. Among all the methods to synthesize allantoin, studies have focused on the direct condensation of glyoxalic acid and urea[6-8].

The type of catalyst is the key for the direct condensation reaction of glyoxalic acid and urea. For this synthesis, liquid inorganic acid catalysts are currently vastly used as catalysts, inevitably causing defects during production, such as poor selectivity, side reactions, complicated post-treatment, serious equipment corrosion and serious waste acid emission. These conditions result in problems such as poor product quality, low yield, high production costs and severe environmental pollution[9-11]. Therefore, the development of a new green solid catalyst that is efficient, easy to recycle, reusable and environmental friendly is the new thrust of allantoin synthesis research. There have been efforts to develop new solid acids including super acids[12,13]. Currently, there are a number of solid acid-catalyzed reactions being industrialized, but research on solid acids for the synthesis of allantoin is still at the initial stage[14,15].

The introduction of multiple complementary metallic oxides enhances catalytic activity. Special electronic shells of rare earth elements have additional unpaired electrons and these atoms have higher magnetic moments and more energy transmission levels[16]. During incineration, the decomposition of ≡Zr-O-Zr≡ condensation polymer releases abundant energy. An energy level with a rich amount of La could absorb the energy released during the reaction. Thus, the energy of the surface of produced nanoparticles and the conglobation of these particles will be reduced. This phenomenon indicates that a proper degree of La doping could suppress the growth of the catalyst particle size, thus enhancing catalytic activity.

EXPERIMENTAL

Crystalline glyoxalic acid, urea, sulfuric acid, ethanol, pyridine, silver nitrate and other reagents were of analytical grade and purchased from the Chengdu Kelong Chemical Reagent Factory in China.

NEXUS 670 infrared spectrometer, USA Thermo Nicolet Co., Ltd; EA 3000 element analyzer, Italy EURO Co. Ltd.; X'Pert Pro MPD X-ray diffraction, PHILIPS Co. Ltd.; self-made thermostatic water bath with an accuracy of ± 1 ºC.

Preparation of solid superacid: A certain amount of zirconium oxychloride solid was weighed and then dissolved with distilled water to form a 0.1 mol/L solution. Silica sol was weighed at the ratio of SiO_2:ZrO_2 = 5:95 (mass ratio) and then dropped into the zirconium oxychloride solution. The mixture was blended until the solution became homogeneous. Ammonia was dropped into the solution as a precipitant until pH was adjusted to 9. The mixture was further stirred for 0.5 h and then aged for some time before filtration. The filter cake was washed repeatedly until no Cl^- ion could be detected in the 0.1 mol/L silver nitrate solution. The filter cake was then impregnated with a calculated amount of lanthanum nitrate, so that the mass ratios of La_2O_3 and SiO_2-ZrO_2 were 0.0, 0.04,

0.08, 0.12, 0.16 and 0.2 %. The products were dried and impregnated by sulfuric acid at the ratio of 1 mL/g for 1 h and then incinerated at 550 ºC for 3 h.

Synthesis of allantoin: A 100 mL three-necked flask equipped with a stir bar, a reflux condenser and a thermometer was placed in a thermostatic water bath. The water bath was adjusted to target temperature before urea and glyoxalic acid (10 g) solutions (total amount of water in the solution is 30 mL) were added sequentially. A certain amount of the catalyst was then added. After some reaction time, the flask was removed from the bath, cooled quickly and placed below 10 ºC for 6 h. Then, the solution was filtered to obtain crude allantoin, which was then recrystallized with hot water and oven dried at 100 ºC to obtain refined allantoin[17].

Detection method: The melting point of allantoin was determined by the capillary tube method. Product content was determined using the Shanghai Q/WS-1-905-80 standard method.

RESULTS AND DISCUSSION

La content: The effects of La content on catalytic activity is shown in Fig. 1. A small amount of La loading on the surface of SO_4^{2-}/SiO_2-ZrO_2 improved the catalytic activity. The loading amount of 0.12 % resulted in the highest catalytic activity, with a 40.6 % yield. A small loading amount of La atoms alters the chemical state of the catalyst surface to enhance the electron-withdrawing ability of metal ions, increasing the acid density on catalyst surface. However, when the loading amount of La is too high, the catalytic activity will be reduced because La only serves as a co-catalyst which improves the activity of SO_4^{2-}/SiO_2-ZrO_2. However, La has no innate catalytic activity and a high amount of La will occupy surface active acid sites. This behaviour decreases the number of acid sites and, consequently, the catalytic activity[18].

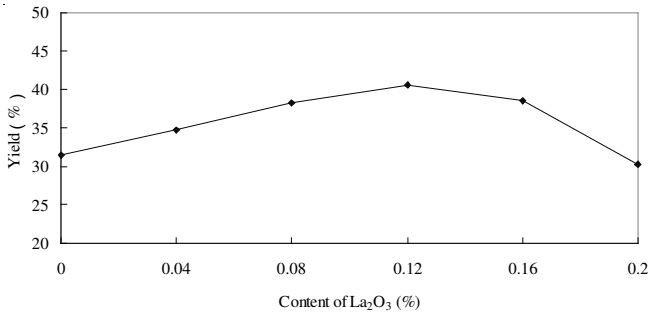

Fig. 1. Effect of La_2O_3 content on the yield

Amount of catalyst: SO_4^{2-}/SiO_2-ZrO_2 modified by 0.12 % La was used as catalyst in the experiments. The condition for the condensation reaction is as follows: molar ratio of urea and glyoxalic acid, 4:l; reaction temperature, 75 ºC and reaction time, 5 h. The effect of catalyst amount on the condensation reaction is shown in Fig. 2. Condensation reaction rate is greatly influenced by catalysts. Lesser catalysts will result in a slower reaction rate and longer equilibrium time. An increase in the catalyst amount results in an accelerated reaction rate and an increase in the yield of allantoin. When the catalyst

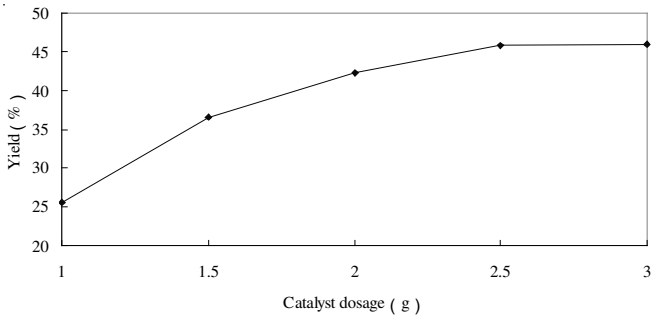

Fig. 2. Effect of catalyst dosage on the yield

was 2.5 g (3.7 % of the total mass of reactants), a relatively high product yield was achieved. Further increase in the catalyst amount only marginally increases the yield, but would add to the production cost. Therefore, the appropriate amount of catalyst should be 2.5 g, which will have a corresponding yield of 45.8 %.

Ratio of reactants: According to the reaction equation, the molar ratio of urea and glyoxalic acid should be 2:1. However, due to the reversible nature of condensation reaction, the direction of reaction could be controlled to favour product synthesis by increasing the ratio of one reactant. The condensation reaction was conducted at 75 ºC reaction temperature and 5 h reaction time. The effect of the ratio of reactants on the condensation reaction is presented in Fig. 3.

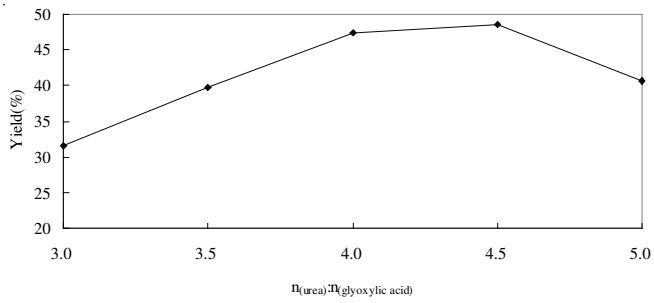

Fig. 3. Effect of molar ratio of reactants on the yield

The higher the ratio between urea and glyoxylic acid, the better the yield. However, an overly excessive urea would result in a decreased yield. A significantly excessive amount of urea reduces the concentration of glyoxylic acid, which in turn reduces conversion and yield. In addition, some of the excessive urea will blend into allantoin which will make post-treatment more difficult. The appropriate ratio of reactants should be $n_{(urea)}$: $n_{(glyoxylic\ acid)}$ or equal to 4:1 with a yield of 46.1 %.

Reaction temperature: The reaction was conducted under different temperatures. The following condition was established to study the temperature effect on yield: ratio of reactants, $n_{(urea)}$:$n_{(glyoxylic\ acid)}$ = 4:1; reaction time, 5 h and amount of the catalyst SO_4^{2-}/La-SiO_2-ZrO_2, 2.5 g. The result is shown in Fig. 4. At a temperature below 80 ºC, with increasing temperature, the reaction was hastened and yield increased. However, when the temperature was further increased, the poor stability of allantoin resulted in easy disintegration at higher temperature. The final colour of the reaction solution was darker and brown at high temperature. To prevent the disintegration of allantoin,

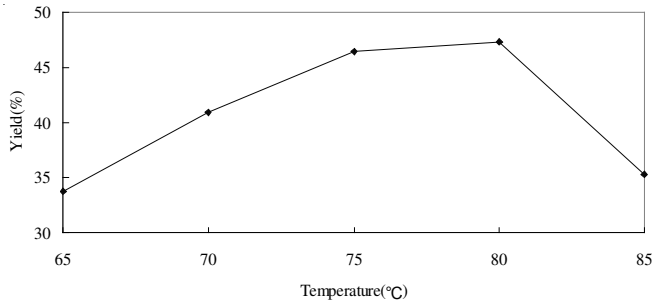

Fig. 4. Effect of reaction temperature on the yield

the optimized temperature for the reaction should be 75 ºC with a yield of 46.3 %.

Reaction time: To study the effect of reaction time on yield, the reaction temperature was set at 75 ºC, ratio of reactants was $n_{(urea)}$:$n_{(glyoxylic\ acid)}$ at 4:1 and 2.5 g of 0.12 % La-modified La-SiO_2-ZrO_2 was used as catalyst for the condensation reaction. The result is shown in Fig. 5. With an increase in the reaction time, the yield also increased. However, when the reaction time was beyond 5 h, the increase in the yield became negligible and yield decreased when reaction time was longer than 6 h. This behaviour may be due to the instability of allantoin resulting in the disintegration of this compound under prolonged heating in a water solution. Thus, the optimum reaction time should be 5 h with a yield of 46.1 %.

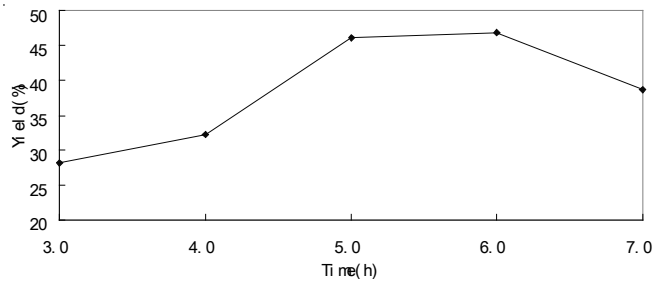

Fig. 5. Effect of reaction time on the yield

Melting point determination: The synthesized allantoin was a white crystalline powder. To ensure that the final products catalyzed by different catalysts were the same compound, their melting points were determined *via* capillary method after they were recrystallized. The range of their melting points was 225-228 ºC, mainly consistent with the literature value of 225-238 ºC. Some of the products broke down while being melted.

IR analysis: There are absorption peaks of secondary amide groups (-NH) at 3338, 3345 and 1603 cm^{-1}. There are absorption peaks of carbonyl groups (-C=O) at 1781, 1716 and 1655 cm^{-1}. There is also an absorption peak of (-N-C) at 1532 cm^{-1} and a (-C-H) absorption peak at 2761 cm^{-1}. The peak of deformation vibrations of amide groups over-lapped with -C=O peaks. The data were mainly consistent with the standard spectra provided by Acros Organics Co. Ltd.

Elemental analysis: Elemental analysis was performed on refined allantoin as follows: Measured value (Theor. value) %: C 30.40 (30.39), H 3.84 (3.82), N 35.41 (35.43).

The measured values of each element of refined allantoin were greatly consistent with the theoretical values of allantoin.

Content measurement: Product purity measured with Shanghai Q/WS-1-905-80 standard methods was 98.5 %, consistent with the mass fraction requirement (98.5-101.0 %).

Conclusion

The optimum process condition for the condensation reaction of urea and glyoxylic acid catalyzed by SO_4^{2-}/La_2O_3-SiO_2-ZrO_2 catalyst was as follows: amount of catalyst, 2.5 g; molar ratio of reactants, $n_{(urea)}$:$n_{(glyoxylic\ acid)}$, 4:1; reaction temperature, 75 ºC and reaction time, 5 h. At optimum conditions, the maximum yield of allantoin was up to 46 %. The products were proved to be allantoin by IR and elemental analysis. The measured melting points were within 225-228 ºC and purity was measured at 98.5 %, consistent with the pharmaceutical standard of 98.5-101.0 % purity.

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