



## Continuous Synthesis of Triacetoneamine Over Cation-Exchange Resin

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A continuous process for the synthesis of triacetoneamine, which is the sole precursor of most hindered amine light stabilizers, from acetone and ammonia was carried out with NKC-9 cation-exchange resin in a fixed bed reactor. The plausible reaction mechanism was also discussed. The effect of different reaction parameters including molar ratio of reactants, gas hour space velocity and reaction temperature have been investigated to obtain the optimal conditions. The activity, selectivity and stability of the catalyst were demonstrated and a continuous process for production of triacetoneamine from acetone and ammonia has been established.

**Keywords:** Cation-exchange resin, Triacetoneamine, Acetone, Ammonia, Light stabilizer, Continuous process.

### INTRODUCTION

Triacetoneamine, which is known as 2, 2, 6, 6-tetramethyl-4-oxopiperidine and 2,2,6,6-tetramethyl-4-piperidone, is widely used as an intermediate for the production of antioxidants and stabilizers for polymeric materials. Triacetoneamine also represents a key intermediate in the preparation of the stable nitroxyl radicals of piperidine and pyrrolidine derivatives, which are used in spin labelling medicinal studies<sup>1-3</sup>.

Numerous methods have been developed for the preparation of triacetoneamine. Triacetoneamine can be prepared from acetone and ammonia in the presence of acidic catalysts. Suitable catalysts are Lewis acids, protonic acids and their salts with ammonia or with organic bases such as boron trifluoride, ammonium chloride or sulfuric acid. Other catalysts have also been reported for the preparation of triacetoneamine from acetone and ammonia, such as halogenated aliphatic hydrocarbon<sup>4</sup>, organic carboxylic acid halide<sup>5</sup>, dimethyl sulfate<sup>6</sup>, *p*-nitrotoluene<sup>7</sup> and aluminosilicates containing calcium<sup>8</sup>. The composition of the reaction mixture from the condensation of ammonia and acetone in the presence of calcium chloride<sup>9,10</sup> has been explored. This mixture includes triacetoneamine, acetone, diacetone alcohol and phorone, the composition of which depends highly on the method used and the ratio of the starting products. Triacetoneamine can also be obtained from phorone, diacetone alcohol and acetone, but all of these chemicals as starting materials have limitations due to their cost.

Up to now, the synthesis of triacetoneamine with a batch process in the autoclave has been widely employed in the

presence of ammonium nitrate as a catalyst. Although the yield of triacetoneamine is passable, the cost of production is high and a large number of sodium hydroxide must be used to absorb water produced during the reaction and neutralize the residual ammonium nitrate in the post-processing process which could lead to the pollution of the environment and the potential safety hazard of explosion. Therefore, environmental friendly manufacture of triacetoneamine is highly desirable and required.

The strong cation-exchange resins, which have been used commercially as solid acid catalyst in esterification<sup>11</sup>, hydration<sup>12</sup>, transesterification<sup>13</sup> and hydrolyzation<sup>14</sup>, have many inherent advantages, such as economy in operation by virtue of repeated utilization, negligible pollution of the environment and easy separation of the reaction products by decantation or filtration. Taylor and Milligan<sup>15</sup> studied the preparation of triacetoneamine by reacting acetone and ammonia with perfluorinated sulfonic acid polymer or perfluorinated alkyl sulfonic acid as catalysts. But the mechanism of the resin catalyzed reaction was seldom discussed.

In this work, the preparation of triacetoneamine from acetone and ammonia was carried out over NKC-9 cation-exchange resin in a fixed bed reactor. The reaction mechanism catalyzed by acidic resins was discussed. The reaction parameters including molar ratio of reactants, gas hour space velocity and reaction temperature were optimized using NKC-9 resin as a catalyst. The catalytic activity and stability of NKC-9 cation-exchange resin in the coupling reaction of acetone with ammonia were studied.

## EXPERIMENTAL

Acetone was obtained from Jiangtian Chemical Auxiliary Factory, Jiangtian, China. Macroporous strong acidic cation-exchange resin NKC-9, with an ion exchange capacity of 4.7 mol H<sup>+</sup>/kg, specific surface area of 77 m<sup>2</sup>/g, pore volume of 0.27 mL/g and average pore diameter of 56 nm, was purchased from the Chemical Plant of NanKai University. The catalyst consists of a styrene-divinylbenzene-based support to which sulfonic acid groups had been added as active sites. Divinylbenzene was used as a cross-linking agent, and the cross-link density was 7 %. The NKC-9 resin is a dry resin of H<sup>+</sup> type which can be directly used without any pre-treatment. The particle size of the catalyst is 0.4-1.25 mm and its maximum operating temperature is 100 °C.

**General procedure:** The condensation of acetone and ammonia was carried out in a tubular, fixed-bed reactor with an inner diameter of 15 mm and a length of 660 mm, which was loaded with 40 mL catalysts. Acetone was dosed into the reactor by a syringe pump. The flow rate of ammonia gas was set by mass gas flow controller. The temperature in the reaction zone was measured with a thermocouple loaded in the center of the tube and regulated by a PID cascade controller.

**Detection method:** The composition of the reaction mixture was determined by GC with a 30 m SE-54 capillary column. The GC-MS (Polaris Q, Thermo Finnigan, America) used to confirm the components of the reaction mixture was performed on a HP-5 capillary column (30 m × 0.25 mm, 0.2 μm film thickness) equipped with an ion trap MS detector.

## RESULTS AND DISCUSSION

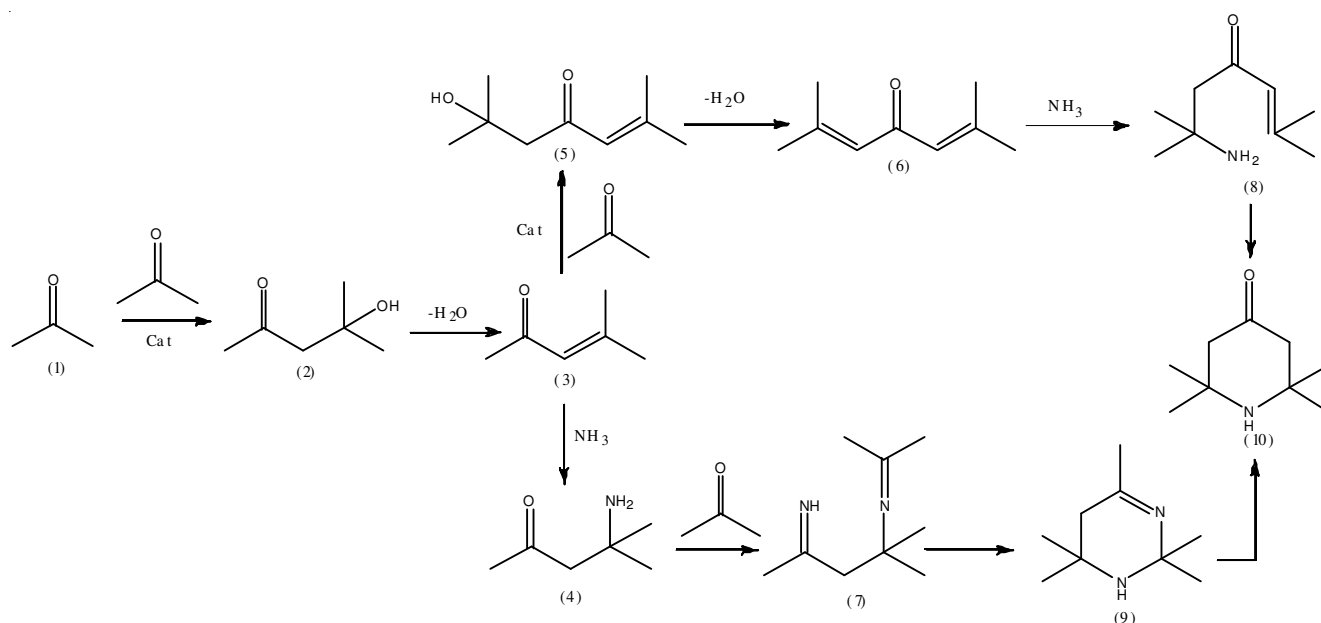
**Reaction parameters:** The reaction parameters, including molar ratio of reactants, gas hour space velocity (GHSV) and reaction temperature, were optimized. From the GC-MS results of the reaction mixtures, the plausible mechanism for the condensation of acetone with ammonia had been demonstrated, which is shown in **Scheme-I**. Most of the intermediates and products had been detected. The aldol condensation of acetone, which is catalyzed by acidic resin, leads to diacetone alcohol

(2). Diacetone alcohol dehydrates to give mesityl oxide (3), which reacts with another acetone to yield phorone (6). Furthermore, mesityl oxide (3) can also react with ammonia and acetone over acidic resin to give acetone (9). Triacetonamine (10) is eventually obtained through phorone (6) and acetone (9). As is shown in **Scheme-I**, NKC-9 resin is an effective catalyst for the condensation of acetone with ammonia. In order to improve the selectivity of triacetonamine, reaction parameters were optimized.

**Effect of molar ratio of acetone to ammonia:** The effect of molar ratio of acetone to ammonia was examined over the range of 1.5:1 to 9:1 and the results are listed in Table-1. The molar ratio of acetone to ammonia was controlled by changing the flow rate of acetone while the flow rate of ammonia was constant. As the molar ratio of acetone to ammonia was increased from 1.5:1 to 6:1, the conversion of acetone increased from 38.2 to 59.5 % and the selectivity of triacetonamine increased from 51.3 to 66.8 %. However, when the molar ratio of acetone to ammonia was over 6:1, the conversion of acetone and selectivity of triacetonamine decreased. It is obvious that the enhancement of molar ratios of acetone to ammonia facilitate the formation of triacetonamine. However, higher molar ratios of acetone to ammonia may bring about the production of more aldol condensation products so preventing triacetonamine formation with high selectivity. The maximum selectivity of triacetonamine was obtained at a 6:1 molar ratio of acetone to ammonia as shown in Table-1. It is obvious that 6:1 could be selected as the optimum molar ratio of acetone to ammonia.

Molar ratio of acetone to ammonia	Conversion of acetone (%)	Selectivity of triacetonamine (%)
1.5:1	38.2	51.3
3:1	42.7	59.4
6:1	59.5	66.8
9:1	52.2	63.2

Reaction condition: temperature = 60 °C; GHSV = 20.7 h<sup>-1</sup>



**Scheme-I:** Plausible mechanism for the condensation of acetone with ammonia

**Effect of gas hour space velocity (GHSV):** Variation of GHSV on the condensation reaction of acetone and ammonia over NKC-9 was studied in the range of 10.35-41.40 h<sup>-1</sup> and the results are given in Table-2. The conversion of acetone and selectivity of triacetoneamine decreased with an increase of GHSV due to the decrease in the contact time between reactants and active sites of the catalyst. The maximum selectivity of triacetoneamine was obtained at a GHSV of 20.7 h<sup>-1</sup>.

TABLE-2  
EFFECT OF GHSV ON THE REACTION OVER NKC-9 RESIN

GHSV (h <sup>-1</sup> )	Conversion of acetone (%)	Selectivity of triacetoneamine (%)
10.35	47.4	59.5
20.70	59.5	66.8
31.05	55.0	56.1
41.40	48.0	50.0

Reaction condition: molar ratio of acetone to ammonia = 6:1; temperature = 60 °C

**Effect of reaction temperature:** The reaction was examined at a temperature range from 50 to 70 °C and the results are given in Table-3. The selectivity of triacetoneamine was enhanced with the increase of temperature from 50 to 60 °C. However, as the temperature was increased from 60 to 70 °C, the selectivity of triacetoneamine decreased significantly. The maximum selectivity of triacetoneamine was observed at 60 °C. As the condensation of acetone with ammonia is an endothermic reaction, the enhancement of reaction temperature can promote this reaction. However, higher temperature may result in high-boiling byproducts. Therefore, 60 °C was chosen to be the reaction temperature.

TABLE-3  
EFFECT OF TEMPERATURE ON THIS  
REACTION OVER NKC-9 RESIN

Temperature (°C)	Conversion of acetone (%)	Selectivity of triacetoneamine (%)
50	43.7	31.1
55	48.2	43.8
60	59.5	66.8
65	57.3	40.5
70	55.6	16.7

Reaction condition: Molar ratio of acetone to ammonia = 6:1; flow rate of acetone = 0.26 mL/min, GHSV = 20.7 h<sup>-1</sup>

**Lifetime of the NKC-9 resin:** The continuous synthesis of triacetoneamine from acetone and ammonia proceeded effectively over NKC-9 resin in a fixed bed reactor. The lifetime of the NKC-9 resin was studied under the optimum conditions over 200 h. During this process, the NKC-9 resin demonstrated good stability and the selectivity of triacetoneamine remained around 60%, indicating that NKC-9 resin could be used for large-scale industrial.

## Conclusion

A continuous process for the production of triacetoneamine from acetone and ammonia over NKC-9 resin had been established in this work. NKC-9 resin exhibits good activity, selectivity and stability during this continuous process. Higher conversion of acetone (about 60 %) and better selectivity of triacetoneamine (about 67 %) were obtained by NKC-9 resin under 6:1 acetone to ammonia molar ratio, 0.26 mL/min acetone flow rate and 60 °C reaction temperature. This process could be economically applied for large-scale industrial production of triacetoneamine.

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