



Towards a more sustainable production of triacetoneamine with heterogeneous catalysis



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ABSTRACT

The acid-catalyzed condensation of acetone and ammonia to directly produce 2,2,6,6-tetramethyl-4-piperidone (triacetonamine) was studied under both homogeneous and heterogeneous catalysis. The selectivity to the desired product was affected by the presence of a complex reaction network involving several kinetically parallel and consecutive reactions, leading to by-products such as diacetonealcohol, diacetoneamine, mesityl oxide, acetone, and 2,2,4,6-tetramethyl-2,5-dihydropyridine. The latter was the most undesired by-product, since its formation was irreversible. Key elements in achieving high selectivity in the direct synthesis of triacetoneamine were the molar feed ratio between acetone and ammonia, and the amount of water in the reaction medium; in fact, water was found to play an important role in the transformation of the intermediate acetone into triacetoneamine. Compared with homogeneous catalysis, the selectivity achieved by the use of the heterogeneous H-Y zeolites was controlled by means of a proper selection of the zeolite features. In fact, the use of a highly hydrophilic H-Y zeolite made it possible to achieve the same selectivity as that obtained under homogeneous catalysis conditions, with the additional advantage of using an easily separable and reusable catalyst, which showed no deactivation.

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1. Introduction

2,2,6,6-Tetramethyl-4-piperidone (triacetonamine, TAA) is the key intermediate for the synthesis of polymer light stabilizers HALS (Hindered-Amines-Light-Stabilizers) [1,2]; their ability to efficiently interrupt polymer degradation by radical scavenging is based on the sterically hindered amine functional group, which is able to form stable N-oxides as active intermediates (Denisov cycle). TAA is also used in the synthesis of drugs, nitroxyl radicals of piperidine, and pyrrolidone derivatives [2]. For instance, by the oxidation of TAA or its derivatives, the corresponding tetramethylpiperidine-N-oxide, called TEMPO, is formed; the latter may be used as a polymerization inhibitor, molecular weight regulator, or oxidation catalyst.

In literature, various procedures are reported for the synthesis of TAA, with the most important being: (i) the direct condensation of acetone and ammonia (Scheme 1) [3–8], and (ii) the two-step process comprising the synthesis of 2,2,4,4,6-pentamethyl-1,2,5,

6-tetrahydropyrimidine (acetone, ACTN), carried out at room temperature, and the reaction of the separated ACTN with acetone or water to yield TAA [9,10]. Patent literature describes various catalysts for these reactions, such as homogeneous Lewis and Brønsted acids (CaCl₂, ZnCl₂, NH₄Cl, AlF₃, and BF₃, used especially in the second step of the two-step process) [10–13], sulfonated resins (Amberlyst® and Nafion®) [14] and *p*-nitrotoluene [15]. In the one-pot process, the catalysts used industrially are based on homogeneous systems (such as CaCl₂, NH₄NO₃ or NH₄Cl), because of their better performance, although the use of a heterogeneous system might offer two advantages: an easier separation of the catalyst from the reaction medium, and fewer problems related to product contamination. On the other hand, the heterogeneous catalyst should be easily regenerable and show constant performances during repeated uses or long time spans in the continuous-flow mode; in this respect, inorganic solid acids are preferable over organic resins.

Table 1 summarizes the yields to TAA reported in literature, using various catalysts and procedures. It is shown that the reaction of ACTN transformation into TAA – the second step in the two-step process – can be carried out with a remarkable yield, by using a Lewis or a Brønsted acid catalyst, depending on the reaction conditions used. The stoichiometry for the transformation of ACTN into TAA involves the elimination of either NH₃ replaced with H₂O, or

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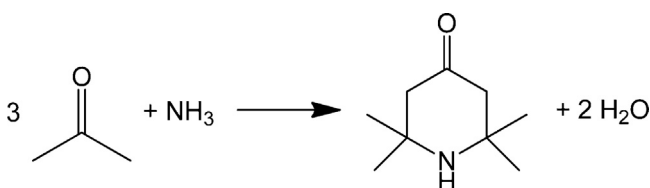
Table 1
Main catalysts and TAA yield in the two-step and one-pot process.

References	Starting materials	Catalyst	TAA yield (mol%)
[10]	ACTN, acetone	BF ₃ ; NH ₄ Cl	95; 95 (wt.%) ^a
[11]	ACTN, acetone (+ water)	p-Toluenesulphonic acid salt of ACTN	91
[6]	ACTN, acetone	Acetyl halide	^b
[13]	Acetone, NH ₃	Acid ion exchanger, in continuous fixed-bed reactor	25 ^c
[3]	Acetone (+ methanol), NH ₃	CCl ₄	26 ^c
[4]	Acetone (+ methanol), NH ₃	Organotin halides; cyanuric halides	36; 39 ^c
[5]	Acetone, NH ₃	CaCl ₂ ·2H ₂ O; NH ₄ Cl; CaCl ₂ ·2H ₂ O + NH ₄ Cl	20; 24; 28 ^c
[14]	Acetone, NH ₃	Perfluorinated sulphonic acids (Nafion®)	25 ^c
[8]	Acetone, NH ₃	Dimethyl sulfate	28 ^c
[12,16]	Acetone, NH ₃	CaY + NH ₄ NO ₃	22 ^c

^a wt and mol yield, calculated with respect to initial ACTN, are very similar, because of the very similar MW of ACTN and TAA.

^b Weight yields higher than 100% were claimed, probably referring to some unspecified TAA salt.

^c Molar yield, calculated after the multiplication of the number of TAA moles by the factor 3.



Scheme 1. TAA synthesis stoichiometry in the one-pot process.

2-iminopropane (dimethylketimine) replaced with acetone. Therefore, the reaction can be carried out in any of three ways: in the presence of at least an equimolar amount of water, in the presence of excess acetone and without water (the preferred procedure), or with both acetone and water [6,10,11].

The case of the one-pot reaction is different, since several equilibria establish in the presence of acetone (or diacetonealcohol) and ammonia, and most reactions involved are equilibrium-limited. In fact, in most cases, the yield to TAA reported is in the range of 20–30%. Worthy of note is the outstanding TAA selectivity, higher than 95%, with a 22% yield: it was obtained by combining a very large amount of NH₄NO₃ (used both as a catalyst and as an ammonia source) with Ca-exchanged HY zeolite catalysts [12,16].

As shown in Scheme 1, water is not needed in the overall reaction stoichiometry, and in fact gaseous ammonia is typically used in industrial processes. On the other hand, a NH₄OH aqueous solution may also be used [16], clearly increasing the process safety, while the actual role of water on the reaction mechanism, as well as on yield and selectivity, has not yet been investigated in detail.

Despite the industrial importance of this compound, very little information is available in literature on the mechanism of TAA formation and the role of the main reaction parameters. We decided to investigate this reaction under both homogeneous and heterogeneous catalytic conditions; the final aim was that of designing a heterogeneous catalyst for the one-pot synthesis of TAA, using a NH₄OH aqueous solution as the ammonia source, and a properly selected and fully reusable solid acid catalyst, without the need for homogeneous co-catalysts.

2. Experimental

The following reactants and products were used for the reaction: Acetone (Chromasolv® Sigma–Aldrich), Ammonium Hydroxide 28–30 wt% (Sigma–Aldrich), Ammonium Chloride (99.5%+ Sigma–Aldrich). The zeolites were provided by TOSOH: HSZ-330HUA (HY zeolite SAR 6) 584 m²/g (from catalogue 550 m²/g), HSZ-390HUA (HY zeolite SAR 200) 814 m²/g (from catalogue 750 m²/g), and HSZ-360HUA (HY zeolite SAR 15, from catalogue 550 m²/g). The H-β zeolite was supplied by Süd-Chemie (sample SN308 H/00, SAR 150). The ammonium-Y zeolite (SAR 15) was

prepared by first exchanging the H-zeolite with Na⁺ (treatment with a 2 M NaCl solution at 80 °C and pH adjusted at 10–11 with NaOH); then after filtration and drying at 110 °C, Na-zeolites were treated with 2 M NH₄Cl solution overnight and dried again at 110 °C.

For reactivity experiments, in a typical batch test, 2.3 g of acetone and a variable quantity of NH₄OH (30 wt%, aqueous solution) were loaded into a Teflon-capped test tube equipped with a magnetic stirrer. The mixture was homogenized at room temperature for 2–3 min and then the catalyst, either an ammonium salt (0.046 g) or a zeolite (0.23 g), was quickly added. The process was carried out at 65 °C while stirring at about 500 rpm. Diffusional limitations were excluded by means of preliminary experiments, carried out by varying the mixing speed.

Molar yields were calculated by dividing the concentration of a defined product by the initial molar concentration of acetone, normalized with respect to the number of C atoms. Molar selectivities were calculated by the ratio between the yield to a specific compound and acetone conversion.

A continuous flow reactor with internal recirculation was also used for short-lifetime experiments; 3.0 g of zeolite in the form of extrudates (sample H-β 303 H/02, delivered by Süd-Chemie), were loaded, while a make-up feed consisting of acetone and NH₄OH aqueous solution in the desired molar ratio was introduced, and an analogous volumetric feed containing unconverted reactants and products was purged out from the reactor. The make-up/purge flows and the internally recirculated volumetric feed (withdrawn from the liquid buffer with an average composition equal to that of the purge stream) were set up in order to develop an overall reaction contact time of around 30 min.

At the end of the reaction, the mixture was analyzed by means of a Thermo Focus GC gas-chromatograph equipped with a FID detector and Agilent HP-5 column, using *n*-decane as the internal standard. Analysis conditions were: 50 °C for 2 min, 10 °C/min up to 280 °C, and 5 min at 280 °C.

3. Results and discussion

3.1. Determination of the reaction scheme in homogeneous catalysis

We first carried out a kinetic study at 65 °C, using an acetone-to-ammonia molar feed ratio equal to 4.0 and a catalyst-to-acetone weight ratio equal to 0.02, with a reaction time ranging from 0 to 120 h. Ammonium hydroxide (30 wt% aqueous solution) was used as a source of ammonia, and ammonium chloride as the catalyst. The reaction products, shown in Scheme 2, were: diacetonealcohol (DAA), diacetoneamine (DAAM), mesityl oxide (MO), acetone (ACTN), triacetoneamine (TAA), and

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