

Kinetic Study of the Polycondensation of Acetone to Produce Isophorone Adopting Alumina and Magnesia as Catalyst

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Isophorone (3,5,5-Trimethyl-2-cyclohexene- 1-one) is an α,β -unsaturated ketone of remarkable industrial interest, produced as a consequence of the aldolic condensation of three acetone molecules. Isophorone is used extensively as a solvent in some printing inks, paints, lacquers, adhesives, vinyl resins, copolymers, coatings, finishes, and pesticides, in addition to being used as a chemical intermediate of organic synthesis. This important chemical molecule is produced both by an homogeneous catalytic process as well as an heterogeneous one. In the homogeneous catalysis isophorone is produced in liquid phase with a mixture of acetone, water and KOH (0.1%) at about 200 °C and 35 bar. In the heterogeneous process, acetone reacts over a catalytic bed at temperatures comprised between 200 and 300 °C and pressure of about 5 bar. The main advantages to operate in heterogeneous phase consist in the absence of a corrosive alkaline atmosphere, in the facility of separation of the catalyst from the reaction products and in its recovery. In this work has been adopted a continuous fixed bed reactor to study the heterogeneous production of isophorone using a moderately basic catalyst constituted by a 10% of magnesia (MgO) over alumina.

1. Introduction

As a result of the process of polycondensation of acetone, different intermediates of reaction can be identified. Some of these are the mesityl oxide and their isomer (isomesityl oxide), that are products of remarkable industrial interest because of they can be easily converted into methyl isobutyl ketone (MIBK). This chemical specie is widely used as solvent and is manufactured starting from the mentioned intermediates of the aldolic condensation process of acetone through a hydrogenation step. Processes conduced in vapour phase adopting a heterogeneous catalysis have been study using magnesium aluminated, zeolites ZSM-5 and catalysts as hydrate of metals and anhydrous oxides, but they are less used in industrial processes because are not sufficiently selective. The advantages to operate in heterogeneous phase consist in the absence of a corrosive alkaline atmosphere, in the facility of separation of the catalyst from the reaction products and in its recovery, beyond to the possibility to render the process more selective studying the opportunely composition of the catalyst. The mechanism of reaction in heterogeneous phase is analogous to that one in homogenous and it is described in Figure 1.

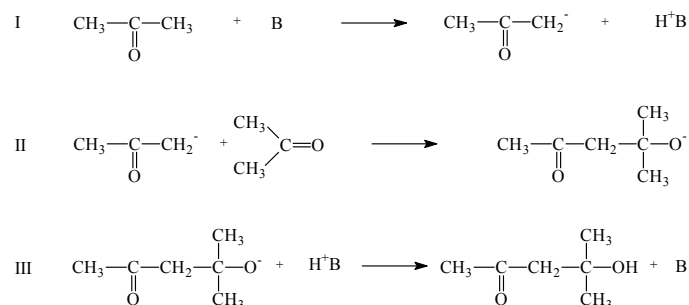


Figure 1. Mechanism of aldolic condensation. B represents the catalyst active basic site.

A study conducted with a C-13 NMR analysis has allowed to identify several products and co-products deriving from the condensation of acetone on one activated alumina. The reaction of condensation of acetone in phase vapor has been studied on a micro-reactor as reported by W. T. Reichle and using LiMgAl(OH) like catalyst. The outline of reaction verified through a series of pulsed steps with acetone and several reaction intermediates is illustrated in Figure 2.

In this research work a kinetic study of the acetone aldolic condensation process in a continuous fixed-bed reactor adopting catalyst constituted by magnesium oxide on γ -alumina, has been made. The choice of such catalyst has been made after a screening of different basic oxides supported on alumina with various active surface area.

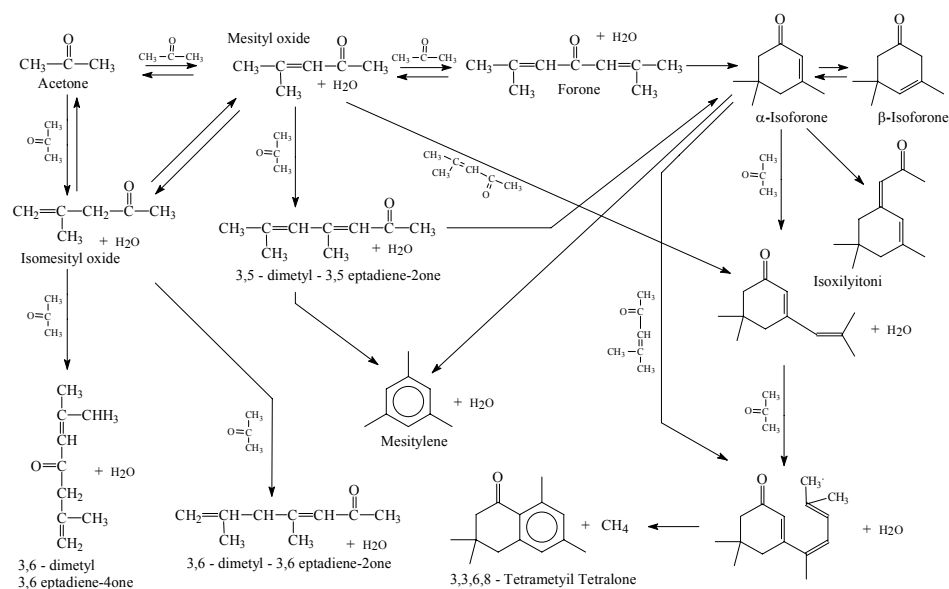


Figure 2. Global kinetic mechanism involved in the studied process.

2. Experimental

2.1 Chemicals

Acetone was purchased from Fluka Chemicals. The catalyst has been prepared on γ -alumina Calsicat E-149-SD (43 m²/g) starting from magnesium acetate (solution of 70 g/l of Mg). Produced pellets has been calcinated at 400 °C for 3 hours.

2.2 Apparatus

The reaction has been carried out using the equipment reported in Figure 3, and composed by an evaporator, an inlet pump, a tubular reactor, a condenser and system for the pressure regulation. The reactor is constituted by a tube of 40 cm of length for 1,2 cm of diameter (total volume is equal to 50 ml), axially crossed by a thermometric girdle for the temperature control. With this equipment it is possible to operate until temperatures of 500°C and pressures of 70 atm. Experimental runs have been conducted in a temperature range comprised between 250 and 420 °C, 5 atm of pressure, and acetone feeding with capacities comprised between 50 and 250 ml/h. The composition of the products has been analyzed every two hours for a total time comprised between 10 and 30 hours.

2.3 Analysis techniques

2.4.1 Gas Chromatography (GC)

Chemical properties of all products were determined by a Gas Chromatography (GC) device (Fisons Gc-8000) equipped with a “wide bore” column with poly(14% cyanopropyl/ 86% dimethylsiloxano) as fixed phase.

2.4.2 Karl Fischer

The amount of water present in a polymer sample was estimated by the Karl Fischer equipment (633 Karl Fischer-Automat and 645 Multi-dosimat), capable of measuring low concentration of water.

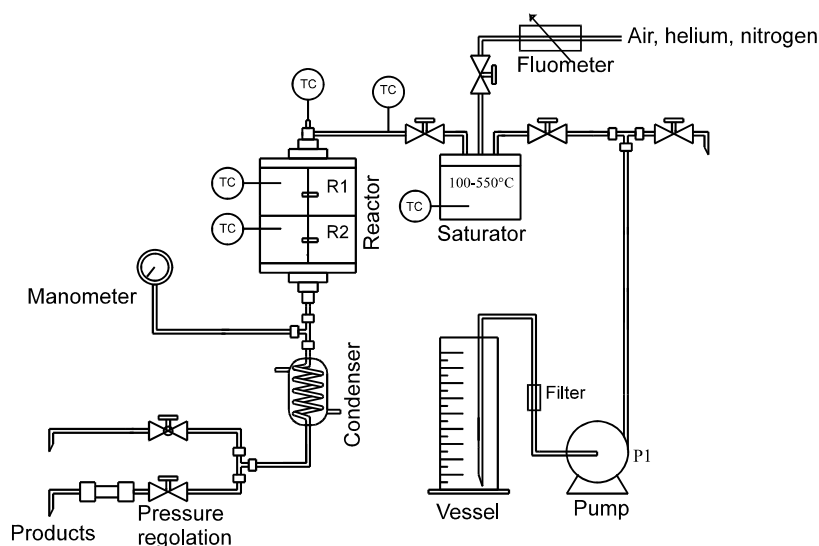


Figure 3. Equipment adopted for the experimental runs.

3. Results and Discussion

Kinetic studies have been conducted at 400°C and 5 atm, changing the residence time in the reactor between 0.5 and 10 s opportunely modifying the capacity of feeding and the volume of catalyst as reported in Table 1.

Table 1. Acetone feed, Catalyst weight, reactor volume and residence time adopted in the experiments.

| Run | Acetone feed (ml/h) | Catalyst weight (g) | Reactor volume (ml) | Residence time (s) |
|-----|------------------------|------------------------|------------------------|-----------------------|
| 1 | 250 | 5 | 5 | 0.478 |
| 2 | 250 | 10 | 10 | 0.956 |
| 3 | 200 | 10 | 10 | 1.196 |
| 4 | 150 | 10 | 10 | 1.595 |
| 5 | 100 | 10 | 10 | 2.392 |
| 6 | 50 | 10 | 10 | 4.783 |
| 7 | 50 | 20 | 20 | 9.567 |

In order to verify the presence of diffusional limitations they have been realized three tests at same time residence, but with different linear velocity of vapors in the reactor as reported in Table 2.

Table 2. acetone conversion, mesityl oxide yield and isophorone yield at different vapors linear velocity

| Acetone (ml/h) | Reactor volume | Residence Time (s) | Linear Velocity | Acetone Conversion | Mesityl oxide yield | Isophorone yield |
|-------------------|-------------------|-----------------------|--------------------|-----------------------|------------------------|---------------------|
| 50 | 2.5 ml | 1.196 | 1.18 cm/s | 18.5 % | 9.30 % | 3.85 % |
| 100 | 5 ml | 1.196 | 2.37 cm/s | 18.8 % | 9.25 % | 3.9 % |
| 200 | 10 ml | 1.196 | 4.75 cm/s | 18.85 % | 9.15 % | 4.0 % |

Observing the acetone conversion values, the yield to mesityl-oxide and to isophorone, it can be noticed as the production of these compounds is not minimally influenced by the linear velocity of vapors inside the reactor, indicating the absence diffusional inter-particle limitations. Vice versa the absence of diffusional intra-particle limitations has been verified carrying out two tests varying the size-particle of catalyst, that is on spheres of 2-3 mm of diameter in the first case and 0.5 mm of diameter in the second. Results of this test are showed in Table 3.

Table 3. Effect of different catalyst particle-size in the products distribution

| % peso | Allumina Calsicat E-149SD + 10% MgO | |
|------------------|-------------------------------------|--------|
| | 2-3 mm | 0.5 mm |
| Acetome | 73.92 | 73.9 |
| Mesityl oxide | 9.54 | 3.68 |
| Isomesityl oxide | 3.73 | 9.83 |
| Mesitylene | 0.42 | 0.40 |
| Phorone | 0.31 | 0.30 |
| Isophorone | 5.43 | 5.71 |
| Isoxylitoni | 0.39 | 0.40 |
| Tetralone | 0.38 | 0.37 |
| Unknowns | 1.65 | 1.11 |
| Water | 4.23 | 4.30 |

Comparing values of composition of the products obtained in the two different cases it is possible to observe a perfect coincidence in the products distribution, confirming the absence of diffusional intra-particle limitations.

After the confirmation of the absence of diffusional limitations it has been possible to estimate the evolution of the reaction as a function of the residence time in a perfect chemical regimen (Table 1). Results of the experimental runs are reported in Figure 4.

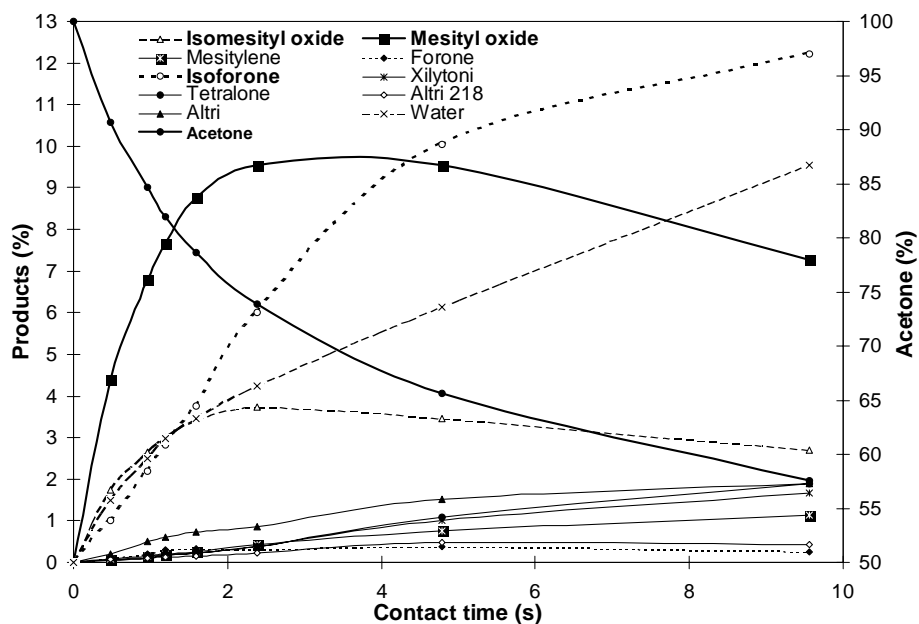


Figure 4. Products distribution and acetone consumption as a function of the residence time.

4. Conclusion

Production of Isophorone (3,5,5-Trimethyl-2-cyclohexene- 1-one) as a consequence of the aldolic condensation of three acetone molecules has been studied. It has been found that the conversion of acetone is enhanced increasing the residence time (Figure 5); at the same time it was found that the selectivity to mesityl oxide is decreased and that to isophorone is increased (Figure 6). Moreover it was found that the global selectivity (that is the selectivity to isophorone, mesityl oxide and iso-mesityl oxide) remains almost constant (around to 90%, as possible to see in Figure 7) until a contact time of approximately 2.5 s, after that, the global selectivity drastically diminish because of the formation of large amount of undesired co-product (isoxilioni, tetralone, etc). The yield total obtained multiplying the conversion by the total selectivity is augmented increasing the contact time (Figure 8).

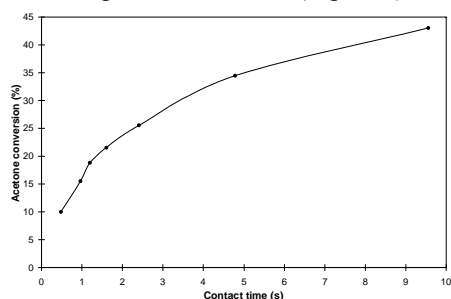


Figure 5. Acetone conversion as a function of the contact time.

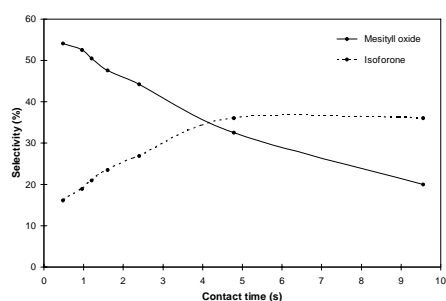


Figure 6. Selectivity to mesityl oxide and to isophorone vs contact time.

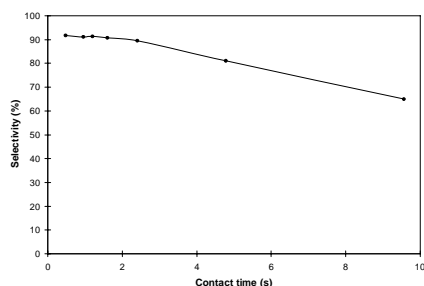


Figure 7. Global selectivity as a function of the contact time.

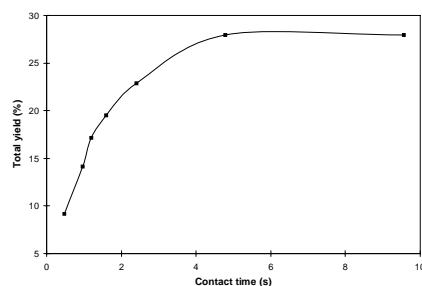


Figure 8. Total yield as a function of the contact time.

5. References

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