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Synthesis of methyl isobutyl ketone from acetone over metal-doped ion exchange resin catalyst

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Abstract

The kinetics of one-step synthesis of methyl isobutyl ketone from acetone was studied in the presence of the bifunctional commercial ion exchange resin, Amberlyst CH28 over a wide range of temperature, total pressure and catalyst loading in a batch reactor. An activity-based kinetic model is proposed to predict the observed results, with the non-idealities of the liquid phase being described using the UNIQUAC method. Formation of mesityl oxide was found to govern the overall rate of reaction. Low reaction rates were observed at higher conversion, possibly due to a pseudo-equilibrium caused by reversible deactivation of the catalyst as a result of formation of water in the reaction system. Simultaneous removal of water during the course of the reaction may result in an enhanced conversion.

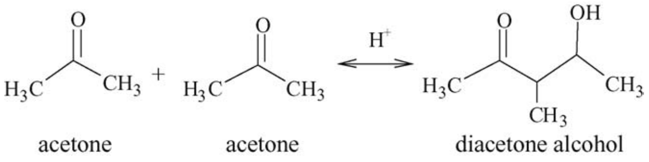
Keywords: Methyl isobutyl ketone; Bifunctional catalyst; Hydrogenation; Ion exchange resin; Acetone; Mesityl oxide

1. Introduction

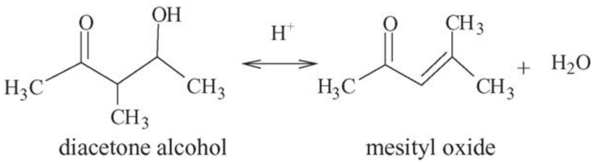
Cation exchange resins are popular solid acid catalysts for liquid phase reactions conducted under relatively mild conditions. Some excellent reviews on catalysis by cation exchange resin have appeared in the past [1,2]. However, not much information is available on catalysis with a bifunctional ion exchange resin catalyst, as it is a relatively new field. Multiple reactions involving acid catalysts followed by hydrogenation or dehydrogenation and vice versa are commonly encountered in many industrial processes. If the conditions for both the reactions are overlapping, one can advantageously perform them in a single step with a bifunctional catalyst. Aldol condensation followed by hydrogenation of dehydrated aldol is an important class of these reactions [3–5] for which such a bifunctional catalyst can be a potential candidate. An industrially important reaction of aldol condensation of acetone, followed by hydrogenation to methyl isobutyl ketone, has been studied in the present work.

Methyl isobutyl ketone is a widely used solvent in the pharmaceutical, coating and mining industries. It is also used in the manufacture of rubber antiozonants. Its synthesis from acetone in the presence of acidic and hydrogenation catalyst consists of three reaction steps. They are as follows:

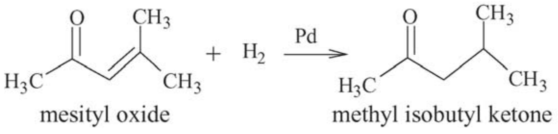
- Reaction 1:



- Reaction 2:



- Reaction 3:



Several references in the form of communications, research articles and patents are available in the literature on the synthesis of methyl isobutyl ketone from acetone.

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Nomenclature

a_i	activity of component i
E°	activation energy for reaction (kJ/mol)
k°	rate constant for reaction (kmol/(s g_{cat}))
k_{wtr}	adsorption coefficient of water
k_{act}	adsorption coefficient of acetone
M_{CAT}	mass of the catalyst (g)
n_i	number of moles of component i
$n_{Ac,0}$	initial number of moles of acetone
$n_{Ac,f}$	number of moles of acetone at any time t
r	rate of reaction (kmol/s)
S	selectivity towards methyl isobutyl ketone
T	Temperature (K)
x_i	liquid mole fraction of component i
X	conversion of acetone
Greek letters	
υ_i	stoichiometric coefficient for component i
Φ	objective function for optimisation

However, the use of bifunctional catalyst for one-step synthesis is gaining importance and substantial work has been reported with different metals from Groups VIII and IB of the Periodic Table like Pd, Cu and Pt on acid supports. Table 1 gives a review on the previous studies on this system with bifunctional catalysts. It is clear from Table 1 that Pd is the most widely used metal for this system with almost all types of acid/base catalytic supports like alumiosilicates, zeolites, metal oxides and ion exchange resins. Different catalysts, like Pd-ZSM-5 [24], Pd–C–Nb_2O_5 [12,13] and Pd–CuO/MgO/SrO [8] in liquid phase and Pd-H-ZSM-5 [37], Cu–MgO [26] and Pd-CS-H-ZSM-5 [16] in gas phase, have been studied. They show conversions of acetone in the ranges 20–40% and 40–60% and selectivity towards methyl isobutyl ketone of ~90% and 30–80%, respectively. It is reported that the catalyst used in the present work gives a conversion as high as 50% with 90% selectivity towards methyl isobutyl ketone in a liquid phase reaction [45]. The supports other than ion exchange resins need pre-treatment; indeed, the performance of these supports is sensitive to the method and conditions of the pre-treatment. Moreover, the reaction conditions are more severe than those with ion exchange resins without much improvement in conversions and selectivities. Ion exchange resins are more popular than traditional supports for low temperature operations due to the ease of separation, less pre-treatment and high acid strength. A commercial bifunctional ion exchange resin, Amberlyst CH28, has been designed for such performance and has been investigated in the present work.

Ion exchange resin can be loaded with desired metal ions by contacting an aqueous solution of the metal ion with the hydrogen form of the cation exchange resin in a batch or continuous mode. Typically, the metal ion will be provided in the form of a metal salt, such as chlorides, bromides, nitrates, sulphates and acetates. The detailed procedure for preparation for such catalysts can be found elsewhere [9].

In spite of a lot of literature on the present system, very little work is reported on commercial metal-ion exchange resins as a catalyst. Nicol and du Toit [45] have successfully performed reactions with the same catalysts in a laboratory-scale trickle bed reactor. A couple of patents from Catalytic Distillation Technologies [50–53] claim the use of catalytic distillation for enhanced conversion of acetone to methyl isobutyl ketone preferably catalysed by metal-ion exchange resin as a catalyst. Systematic kinetic studies and a reliable kinetic model are necessary to design an industrial reactor; the present work is undertaken to provide inputs in this regard.

2. Experimental

2.1. Materials

Acetone (99.5%), methyl isobutyl ketone (99%) and methyl ethyl ketone (99.5%) were obtained from Merck Ltd., India. Rohm and Haas, France, supplied the catalyst Amberlyst CH28. The properties of catalyst are given in Table 2. Before its use, the catalyst was dried in an oven at 353 K for 3 h.

2.2. Apparatus and procedure

A stainless steel autoclave from Parr Instrument Company, USA, with a capacity of 3×10^{-4} m^3, equipped with an online temperature monitoring and control facility was used for conducting all the batch reactions. Before feeding to the reactor, each catalyst was washed with acetone in order to remove the moisture present, if any. The desired quantities of the catalyst and reactants (100 g of acetone in all runs) were charged to the reactor. The reactor and gas lines were flushed with hydrogen in order to remove the air present in the empty space in the reactor and lines. The reaction mixture was heated up to the desired temperature with slow stirring. As the reaction temperature was reached, the speed of agitation was increased up to the desired level and the corresponding time was regarded as the zero reaction time. The samples were withdrawn at different time intervals to study the kinetics of the reaction. In all the runs, the reaction volume was about 8×10^{-5} m^3.

2.3. Analysis

The reactants and products were analysed using a gas chromatograph (GC-MAK-911) equipped with a flame ionisation detector (FID). A 25 m long capillary column BP-1 (SGE, Australia) was used to separate the different components in the reaction mixture using methyl ethyl ketone as an external standard. The column temperature was maintained at 373 K isothermally. The various components in the reaction mixture and the separated products were characterized by authentic samples.