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Catalytic isomerisation of α-pinene oxide to campholenic aldehyde using silica-supported zinc triflate catalysts

I. Kinetic and thermodynamic studies

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Abstract

Three silica-supported zinc triflate ($Zn(CF_3SO_3)_2$) catalysts have been studied in a batch reactor for performing isomerisation reaction of α-pinene oxide to campholenic aldehyde. Reaction order was evaluated from the obtained experimental data by using an integral method of data analysis. Reaction rate constants were obtained at different temperatures and activation energies using each catalyst determined. Different catalyst loadings and supports were tested in this study: 0.05 mmol/g Zn-triflate/K60 (Catalyst 1), 0.01 mmol/g Zn-triflate/K100 (Catalyst 2) and 0.05 mmol/g Zn-triflate/HMS_{24} (Catalyst 3).

Various methods for determining heat of reaction were used in order to calculate thermodynamic parameters. Heat of α-pinene oxide to campholenic aldehyde isomerisation reaction was estimated as −73.2 kJ/mol.

Keywords: α-Pinene oxide isomerisation; Campholenic aldehyde; Kinetics; Reaction order; Heat of reaction; Activation energy

1. Introduction

The future growth of the fine, pharmaceutical and speciality chemical industries are expected to depend heavily on the development of new more environmentally friendly technologies. Manufacturing in those areas has commonly been associated with the accumulation of large quantities of hazardous waste resulting from the use of mineral acids and Lewis acids used as catalysts [1–3]. A further serious problem is encountered in the selectivity to desired product, which demands control of isomer formation and minimisation of high molecular weight species.

In the past decade there have been serious efforts in the search for heterogeneous catalysts that would not only enhance reaction rates and product selectivity, but eliminate the problem of separating product from catalyst. An important industrial example, from the field of fine chemicals, is the rearrangement reaction of α-pinene oxide (3-Oxatricyclo [4.1.1.0(2,4)] octane, 2,7,7-trimethyl-) to campholenic aldehyde (Fig. 1). Campholenic aldehyde is a key intermediate in the synthesis of santalol, the main constituent of natural sandalwood oil. Currently, a homogeneous catalyst is used for the rearrangement, but selectivity is only moderate and represents optimisation to aldehyde in a reaction that can lead to the formation of more than 100 different products depending on reaction conditions [4–6]. Some of the recent attempts to develop heterogeneous catalysts for this reaction have involved the use of mixed oxide solid acids [7], US-Y zeolites [6,8] and Ti-Beta [9]. Depending on reaction conditions selectivities towards campholenic aldehyde of 55–94% have been reported.

Wilson et al. have developed new solid acid catalysts based on silica-supported zinc triflate, which have been reported as being active and reasonably selective in the rearrangement reaction of α-pinene oxide to campholenic aldehyde [10]. Additional benefit of these catalysts is that they can be recycled without loss of selectivity towards the aldehyde. Our intention to use this type of catalyst in an intensified reactor led us to an investigation of a batch reaction process, initially in order to compare conventional batch process with an intensified process, namely a spinning disc reactor (SDR) [11,12].

The main problem of having such an active catalyst for α-pinene oxide rearrangement reaction is that the products formed are themselves highly reactive, and consecutive reactions

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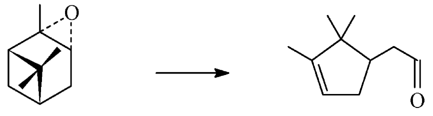
Nomenclature

a	polynomial constant
A	pre-exponential factor (Arrhenius equation)
b	polynomial constant
c	polynomial constant
C_x	concentration of component x (mol/m^3)
ΔC_P°	standard molar heat capacity (J/(mol K))
E_a	activation energy (kJ/mol)
ΔG	Gibbs free-energy change (J/mol)
ΔG_T°	standard enthalpy (kJ/mol)
HMS$_x$	hexagonal mesoporous silica, with pore size x
k	rate constant (s^{-1} g^{-1})
K	equilibrium constant
KX	K stands for Kiesel (silica), X for pore size
n	reaction order
r_A	reaction rate (s^{-1} g^{-1})
R	universal gas constant = 8.314 (J/(mol K))
R^2	fitting factor
ΔS_T°	standard entropy (J/mol)
t	reaction time; time (s)
T	temperature (K)

Subscripts

f	formation
int	integral



α-pinene oxide

campholenic aldehyde
(2,2,3-trimethyl-3-cyclopentenacetaldehyde)

Fig. 1. Rearrangement reaction of α-pinene oxide to campholenic aldehyde.

will decrease the observed selectivity towards campholenic aldehyde. In other words, reaction is not as simple as presented in Fig. 2.

Simplified reaction paths look like those presented in Fig. 3, where at the same time many parallel and consecutive reactions are taking place.

Therefore, it is very important not only to "direct" reaction towards forming campholenic aldehyde (B), but to stop the reaction at that point. It is hoped that this can be achieved by use of novel catalysts and/or intensified technologies [13]. Furthermore, it is also expected that by use of alternative intensifying reactors "greener" process with improved selectivity will be accomplished. Results of our investigation into using these catalysts immobilised on the surface of an intensified reactor are also available in a separate publication [14].

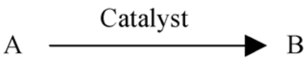


Fig. 2. Schematic of the reaction: (A) α-pinene oxide and (B) campholenic aldehyde.

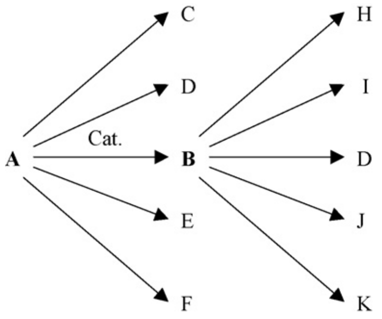


Fig. 3. Schematic of simplified reaction paths.

Lack of kinetic and thermodynamic data in the literature for this particular reaction led us to believe that this paper could be particularly useful as a benchmark and guidance. Recent report by Neri et al. [15] was the first publication regarding reaction kinetics that the authors are aware of.

1.1. The rate equations

As catalytic reactions have great importance in the industrial application, considerable effort has been made in developing theories from which kinetic equations can be realistically developed [16]. If it is considered that the reaction takes place on an active site on the surface of the catalyst, three steps are viewed to occur successively at the surface:

1. A molecule is adsorbed onto the surface and is attached to an active site.
2. The molecule then reacts either with another molecule, or it simply decomposes while on the site.
3. Products are desorbed from the surface, which subsequently frees the site.

All the three steps mentioned above may be regarded as jointly constituting the catalytic reaction and are all chemical in nature. There are two additional steps that involve transport of reactant(s) to the catalyst (before it is adsorbed) and transport of product(s) away from the catalyst (after being desorbed) and are physical processes. This is a diffusion process and the phenomenon is called mass transport or mass transfer. Diffusion limitation at the external surface of catalyst is recognised by the following characteristics [17]:

1. The rate is proportional to the catalyst weight (or to the concentration of the active component) raised to a power less than unity, which in the limit may be zero.
2. The rate is increased by improving the movement of the gas or liquid with respect to catalyst.
3. The temperature coefficient is low and the apparent activation energy may be as low as 10–15 kJ/mol.

Reactions whose rate is truly governed by a chemical step show the following characteristics: