



Catalytic ketonization of propionic acid. Green chemistry in practice

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Abstract

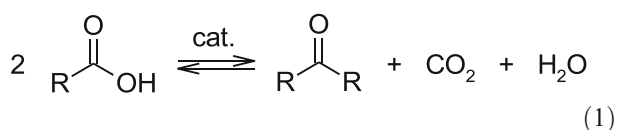
We present an experiment offered as a course for undergraduate students at our Faculty. During the laboratory classes, students synthesized 20%_{w.t.} MnO₂/Al₂O₃ catalyst, which is then used in the catalytic reaction—the propionic acid ketonization leading to 3-pentanone. The reaction is carried out in a flow system, in the presence of a solid catalyst bed, in the range of temperatures from 573 to 673 K. Students also perform thermodynamic calculations regarding the reaction. They estimate Gibbs free energy, then calculate equilibrium constant and the conversion of substrate—propionic acid.

Keywords Chemical education · Laboratory experiment · Fixed-bed flow reactor · Ketonization reaction · Catalysis

Introduction

Presented laboratory experiment consists of three main parts: catalyst synthesis (MnO₂/Al₂O₃—solid oxide catalyst), catalytic reaction (ketonization of propionic acid) and thermodynamic calculations (estimation of propionic acid conversion). The experiment complements the lecture and calculation exercises in chemical technology.

Ketonization reaction is a classical method of ketones synthesis (Eq. 1)—carboxylic acids undergo transformation into ketone, carbon dioxide and water [1]. This method of ketones' synthesis raises a legitimate interest as it is a one step reaction, no solvents are needed, and solid catalyst is used. It is an example of green chemistry process.



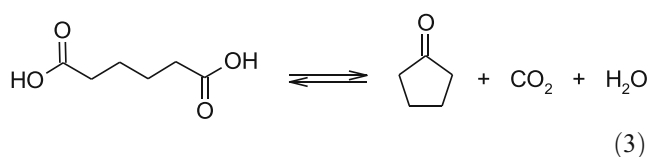
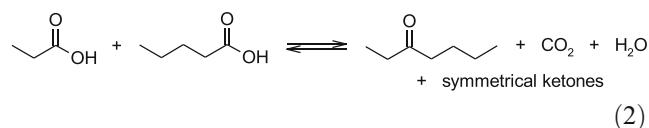
The ketonization reaction has been known since the mid-nineteenth century [2, 3]—at that time, it was a pyrolysis of metallic salts of carboxylic acids (no catalyst). Ketonization in

the presence of catalyst was introduced later and its first industrial application was the preparation of acetone [4]. For the last two decades it has aroused great interest due to biomass processing [5].

Depending on the substrate different ketones are obtained:

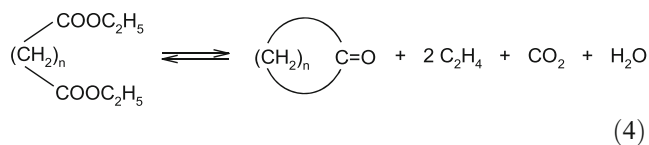
- symmetrical ketones (if only one acid is used as substrate—Eq. 1),
- unsymmetrical ketones (if two various carboxylic acids are used—cross ketonization—Eq. 2) [6, 7],
- cyclic ketones (dicarboxylic acids as substrates—cycloketonization—Eq. 3) [8].

The preparation of cyclopentanone in this way does not present any particular difficulties, unlike the preparation of other cyclic ketones. One must be aware that dicarboxylic acids are solids, which possess high melting points (> 373 K). It makes difficult to introduce them to the flow reactor. Hence, their esters can be used instead of the dicarboxylic acids—Eq. 4 [9, 10].



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Ketonization is catalyzed by metal oxides and zeolites [5]. Among metal oxides, ones the most active are: CeO_2 , MnO_2 , La_2O_3 .

Thermodynamics is an immanent feature of catalysis; in order to make students aware of this, we introduced elements of thermodynamics to the exercise. In this part of the exercise, the students' goal is to perform thermodynamic calculations and check if the reaction they are dealing with is thermodynamically favored. To achieve this goal, students use the group contribution method—the van Krevelen and Chermin method. This method is used for estimating Gibbs free energy values of formation of the compounds [11]. Knowledge (even superficial) of such methods seems to be important mainly due to the fact that not all thermodynamic data (for all chemical reactions) are available in the literature. Details concerning the method can be found in the supplementary materials (Student handout).

The presented experiment is a part of a technological block carried out in the same semester - lecture, exercises and laboratory (all these are obligatory for all students at our Faculty). Most often it is the first meeting of students with a flow reactor in a laboratory (at earlier stages, students work rather with batch or semibatch reactors). Students are already substantively (also computationally) prepared to work with the flow reactor.

During the experiment, the basic issues related to the heterogeneous catalysis and the use of flow reactors are discussed. Pedagogical goals are as follows:

- Students will be able to prepare a solid catalyst using dry impregnation method.
- Students will be able to conduct the catalytic reaction in flow conditions in a laboratory scale (in a flow reactor with catalyst fixed bed).
- Students will be able to determine the effect of reaction temperature on substrate conversion.
- Students will be able to apply van Krevelen and Chermin procedure for thermodynamic calculations.
- Students will be able to compare the results of thermodynamic calculations with the values obtained in a real experiment.

Experimental

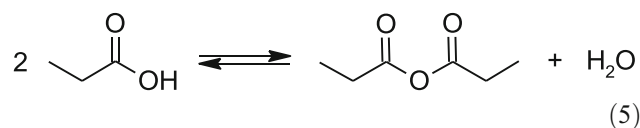
The experiment is planned for 3 students. It takes 2 days, 6 h each. Details are given in Instructor notes and Students Handout.

Reagents. Al_2O_3 (Degussa C, $S_{\text{BET}} = 103 \text{ m}^2/\text{g}$, grain diameter 0.5–1.0 mm), $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Fluka, > 97%), propionic acid (BDH, b.p. 141 °C, purified by distillation).

Catalyst preparation (20%_wt $\text{MnO}_2/\text{Al}_2\text{O}_3$). Aluminium oxide was calcined at 873 K in a muffle furnace during 5 h. After cooling down, 1 g of Al_2O_3 was impregnated with a water solution of manganese (II) nitrate (0.722 g $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, 1.6 cm³ H_2O). As prepared pre-catalyst was dried at 353 K during 1 h. Then it was poured into the flow reactor (the same in which the reaction would be performed; internal diameter: 10 mm, height: 265 mm), where it was calcined in stream of air at 723 K during 3 h.

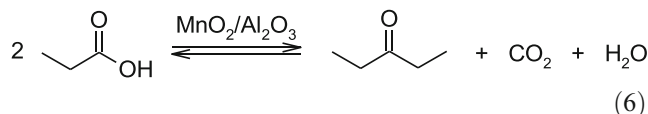
Catalytic reaction was performed in the flow reactor (mentioned above) at temperatures between 573 and 673 K. The substrate stream was fed continuously, LHSV = 3 cm³/(g·h). The reaction mixture was cooled in a condenser and collected. Three samples were taken at three temperatures: 573, 623, and 673 K. Before each sample was taken, the foreruns were collected (first—during 45 min, the last two—10 min). Collection time for analytical samples—10 min.

Analytics. Samples were titrated with 0.0100 M KOH in the presence of phenolphthalein as indicator. This allowed to determine the amount of propionic acid which did not undergo ketonization reaction. At the lowest reaction temperature (573 K), propionic anhydride can be formed (Eq. 5). During the titration it hydrolyzes. It is possible to measure the amount of the anhydride—the titration should be conducted not till the first color of the solution, but till the constant color of solution (1 min without the discoloration).



Results and discussion

Students carried out a ketonization reaction of propionic acid. The products of this reaction are 3-pentanone, carbon dioxide, and water:



In Table 1 you can find:

- the Gibbs free energy values estimated using the van Krevelen and Chermin method,
- and the reaction equilibrium constant, and
- conversion rates of propionic acid calculated on their basis.

Table 1 Estimated Gibbs free energy (ΔG_r), equilibrium constant (K) and propionic acid conversion (α) in the function of temperature. $P = 0.1$ MPa

T [K]	ΔG_r [kJ/mol]	K	α [%]
573	-16.576	32.44	95.3
623	-24.237	107.7	97.3
673	-31.625	284.9	98.3

The values of Gibbs free energy are negative in the range of temperatures taken into the account in calculations. As the reaction temperature increases, ΔG_r decreases and the conversion of the substrate increases. Estimated conversion values are all above 95%. The maximum estimated conversion value is 98.3% in 673 K.

Table 2 Sample results obtained by students (years 2016–2019). Catalytic ketonization of propionic acid over 20% $\text{MnO}_2/\text{Al}_2\text{O}_3$, gas phase reaction, flow reactor with solid catalyst bed. LHSV = $3 \text{ cm}^3/(\text{g}\cdot\text{h})$. The influence of temperature on substrate conversion

Students group no.	T [K]	α [%] ^a	Students group no.	T [K]	α [%]
1	573	64.0	9	573	19.6
	623	89.3		623	98.4
	673	97.3		673	99.2
2	573	37.5	10	573	40.6
	623	97.7		623	79.7
	673	99.4		673	98.6
3	573	60.3	11	573	42.1
	623	94.5		623	78.9
	673	99.3		673	98.0
4	573	57.5	12	573	75.0
	623	95.0		623	80.8
	673	99.4		673	99.0
5	573	37.8	13	573	45.3
	623	83.8		623	83.1
	673	98.6		673	98.0
6	573	56.3	14	573	92.6
	623	79.9		623	97.7
	673	97.2		673	99.2
7	573	64.3	15	573	27.5
	623	88.1		623	98.4
	673	97.9		673	99.2
8	573	48.9	16	573	26.8
	623	75.5		623	98.6
	673	98.6		673	99.3

^a propionic acid conversion

In Table 2 we present the conversion of propionic acid values obtained by students. The experiment was planned in such a way that the students measured only the degree of substrate conversion (substrate loss). They did not check the yield of 3-pentanone. At the lowest temperature (573 K), they found the conversion of propionic acid far away from estimated—even around 20%, in comparison to theoretical value—95.3% (Table 1).

The results obtained by students vary (especially at 573 K). This is most likely due to lack of laboratory skills (setting and maintaining the right temperature seem particularly tricky). The reaction rate is strongly dependent on the temperature. Slight variations at lower temperatures result in large differences in substrate conversion. Therefore, at higher temperatures, such a difference is not so visible—the reaction rate is so high that small temperature differences do not have such an impact on the substrate conversion.

At the highest temperature, the experimental values of conversion are close to the calculated values. The calculated values are only estimates, and are therefore in some cases lower than the experimental values.

Conclusions

The described laboratory experiment allows students to familiarize themselves with the methods of organic synthesis under flowing conditions and compliant with the principles of green chemistry. Students also perform thermodynamic calculations related to the studied reaction. The reaction is thermodynamically favored. The calculation results are confirmed by the results obtained in the laboratory.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s41981-021-00149-2>.

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Declarations

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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