

INVESTIGATIONS IN THE FIELD OF DIOLS
AND CYCLIC ETHERS. XXX*

Preparation of Methyl Ethyl Ketone and Butyraldehyde
from Butanediol-1,3 in Gas Phase

By

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The dehydration of butanediol-1,3 was investigated in continuous system in the presence of copper catalysts applied onto aluminium oxide and silica carriers in gas phase, between 150 and 350°C. Similarly to the Cu—Al catalysts the main directions of the reaction are the formation of methyl ethyl ketone and butyraldehyde. The optimum parameters of the preparation of both oxo compounds were also studied. Maximum yield (73% of methyl ethyl ketone and 24% of butyraldehyde) can be achieved on Cu—SiO₂ catalyst at 250°C. The cycle time and durability of the catalyst in the process investigated can be considered as satisfactory.

Two papers [1, 2] on our investigations in connection with the dehydration of butanediol-1,3 were published up today. As a result of these investigations, it could be proved that the transformation of butanediol-1,3 into butyraldehyde takes place most easily in the presence of Cu—Al catalyst. One of the purposes of the authors was to prepare a catalyst suitable for selective dehydration of butanediol-1,3 affording the possibility of economic preparation of methyl ethyl ketone. Seven different catalysts were tested, however, beside methyl ethyl ketone, also butyraldehyde was obtained in each case.

Since the catalyst containing copper proved to be the best in the course of the investigations, it was our aim to study the effect of copper catalysts applied onto different carriers. The question to be solved was not only whether the catalytic effect is to be attributed to the Raney skeleton or the copper itself, but our purpose was to prepare active catalysts the cycle time and durability of which is suitable for the preparation of methyl ethyl ketone. Namely, the regeneration of catalysts of Raney type is known to be uneconomical, whereas copper catalysts on the suitable carrier can easily be regenerated by means of air oxidation and subsequent reduction by hydrogen in the catalyst space itself.

In the course of the experimental work the transformation of butanediol-1,3 on Cu—Al₂O₃ and Cu—SiO₂ catalysts (the latter prepared in two different ways)

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was investigated as a function of space velocity and temperature. The results of the experimental data are given in Figures 1 and 2.

Our experiments proved that, first of all, it is the form of the copper rather than the Raney skeleton which is responsible for the dehydration of butanediol-1,3 to oxo compounds. It can be seen from the two Figures that in the case of silica carrier the yield of the oxo compounds is higher than on Al_2O_3 carrier. This can be explained by the circumstance that the dehydration of butanediol-1,3 is catalyzed also by the Al_2O_3 itself. This is, however, not a one-way process, the secondary

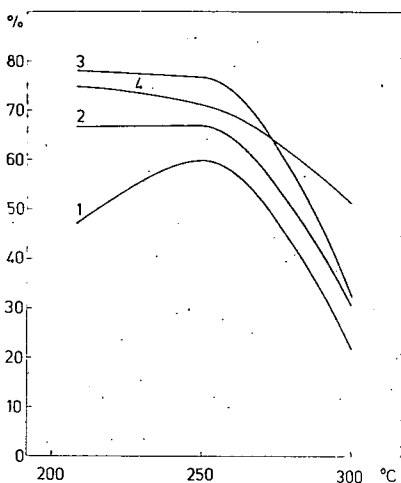


Fig. 1. Dependence of the conversion of butanediol-1,3 into methyl ethyl ketone and butyraldehyde in the presence of $\text{Cu}-\text{Al}_2\text{O}_3$ catalyst as a function of temperature and feeding. 1. 4 ml/hour; 2. 6 ml/hour; 3. 12 ml/hour; 4. 22 ml/hour.

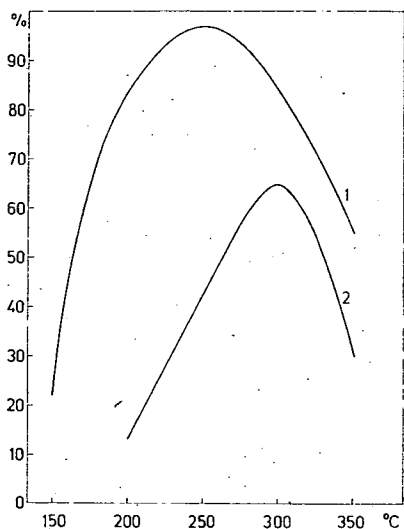


Fig. 2. Dependence of the conversion of butanediol-1,3 into methyl ethyl ketone and butyraldehyde as a function of temperature, on different $\text{Cu}-\text{SiO}_2$ catalysts. 1. catalyst prepared from copper(II) nitrate; 2. catalyst prepared from basic copper carbonate. Rate of feeding: 4 ml/hour.

transformation of the main product being catalysed at the same time. The experimental data also show that the activity of the catalyst prepared from copper(II)nitrate is significantly higher than the activity of that prepared from basic copper carbonate. The degree of formation of the oxo compounds changes with the temperature according to a maximum curve. This fact shows not only that the main products may decompose at higher temperature but, chiefly, that the fragmentation rate of butanediol-1,3 also increases with increasing temperature:

Butanediol-1,3, also in the form of an aqueous mixture, proved to be a suitable starting material for the production of methyl ethyl ketone. This is important because in this way the raw, dilute butanediol-1,3 solution, prepared from propylene by Prins reaction, can also be used for the preparation of methyl ethyl ketone and butyraldehyde.

As the preparation of copper catalysts of long lifetime, which can also be well regenerated, was the aim of our research work, experiments were carried out to establish the cycle time and durability of the Cu—SiO₂ catalyst. The fatigue-tests of catalysts were made with 22 ml catalyst space. It can be stated from our experimental data that the activity of the catalyst decreases by one half after feeding in 500 ml of butanediol. The space velocity was 22 ml/hour. After the regeneration of the catalyst it could be proved that, under the circumstances given in the experimental part, the catalyst stands a great number of regenerations, and so its durability proved satisfactory.

Experimental

Butanediol-1,3

A product of technical grade (Chemische Werke Hüls) was used for the investigations.

Preparation of Cu—Al₂O₃ catalyst

RB-13 Al₂O₃ prepared by the Research Institute of Organic Chemical Industry (Szervesvegyipari Kutatóintézet), Budapest, was used as carrier. The aluminium oxide of 2—4 mm particle size was washed with 10% hydrochloric acid solution to remove the possibly present basic impurities, then it was dried at 250°C. For the preparation of the copper catalyst, the carrier was allowed to stand in 15% copper(II)nitrate solution for 24 hours. The impregnated catalyst was dried, reduced, and activated in hydrogen stream in a tube reactor at 250°C for 3 hours.

Preparation of Cu—SiO₂ catalysts

Commercial granulated silica gel carrier of 2—4 mm particle size was allowed to stand in 15% copper-(II)nitrate solution for 24 hours. After filling into the tube reactor the catalyst was dried, then activated in hydrogen stream at 250°C for 3 hours.

The other copper—silica gel catalyst was prepared similarly to the above, with the following modifications. 420 g of granulated silica gel of 2—4 mm particle size was brought together with a solution of 120 g of basic copper carbonate in 2 litres conc. ammonium hydroxide. It was dried on water bath and evaporated under stirring. The activation was carried out similarly to the above catalyst.

Dehydration of the butanediol-1,3 was studied on the apparatus described in [1]. The product obtained was subjected to distillation. Since it is very difficult to separate the methyl ethyl ketone from butyraldehyde by distillation, the composition of the oxo mixture was established by means of gas-liquid chromatography. The β , β' -oxydipropionitrile ether proved to be the best liquid phase for separation of the two isomeric oxo compounds. Using this liquid phase a column length of 1 m is sufficient.

The regeneration of the catalysts was performed in air stream at 350—400°C for 3—4 hours. The oxidation was followed by a reduction with hydrogen at 250—300°C.

References

- [1] *Bartók, M., B. Kozma: Acta Phys. et Chem. Szeged 9, 116 (1963).*
[2] *Zalotai, L., M. Bartók: Acta Phys. et Chem. Szeged 14, 47 (1968).*

ИЗУЧЕНИЕ ХИМИЧЕСКИХ ПРЕВРАЩЕНИЙ ДИОЛОВ И ОРГАНИЧЕСКИХ
ОКИСЕЙ ХХХ ПОЛУЧЕНИЕ МЕТИЛЭТИЛКЕТОНА И МАСЛЯНОГО
АЛЬДЕГИДА ИЗ БУТАНДИОЛА-1,3 В ПАРОВОЙ ФАЗЕ

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Нами была изучена дегидратация бутандиола-1,3 на медном катализаторе нанесенной на окись алюминия и кремния при температуре 150—350°C в паровой фазе на проточной лабораторной установке. Главным направлением превращения, как и в случае катализатора скелетной меди, является образование метилэтилкетона и масляного альдегида. Также были изучены оптимальные условия получения этих соединений. Максимальные выходы (73% метилэтилкетона и 24% альдегида) были достигнуты на медном катализаторе нанесенной на окись кремния при температуре 250°C. Время цикла работы и срок службы катализатора являются удовлетворительными в изученном процессе.