

SELECTIVITY OF METAL ALLOY CATALYSTS IN THE HYDROGENOLYSIS OF 2-METHYLOXACYCLOALKANES UNDER PRESSURE

By

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The catalytic hydrogenolysis of propylene oxide, 2-methyloxacyclobutane, 2-methyltetrahydrofuran and 2-*n*-propyltetrahydrofuran under pressure leads to the formation of primary and secondary alcohols. The selectivity of the hydrogenolysis depends on the number of atoms in the ring and on the catalysts used (Ni/Al, Cu/Al and Ni/Zn). The mechanism of the transformations and the selectivities of the catalysts can be brought into correlation with the different chemisorption properties of the alloy catalysts.

We accounted earlier [1] on our investigations of the behaviours of propylene oxide (I), 2-methyloxacyclobutane (II), 2-methyltetrahydrofuran (III) and 2-*n*-propyltetrahydrofuran (IV) on Raney-type catalysts (Ni/Al, Cu/Al, Ni/Zn) at 50 atm, in the temperature range 200—300 °C, in a continuous system.

It was found experimentally that the Cu/Al catalyst exhibited considerable activity and selectivity in the hydrogenolyses of I and II and only primary alcohols were formed. At the same time the hydrogenolysis of III was much slower and gave rise to a number of products. In contrast, the Ni/Al catalyst proved selective in the hydrogenolyses of III and IV, only secondary alcohols being formed, whereas in the case of I and II the hydrogenolysis took place in two directions. The effect of Ni/Zn catalyst was more similar to that of Cu/Al than to the Ni/Al, for 1-butanol was formed in the hydrogenolysis of II.

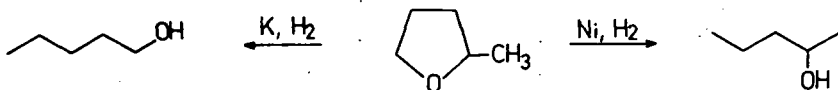
Besides showing the important role of the second metal in the development of the catalytic properties of the Raney-type catalysts, the sharp difference in selectivity between Ni/Al and Ni/Zn catalysts can lead to further significant conclusions.

In the publication mentioned [1] only the experimental observations were reported without dealing with their explanation.

The cause of the ring size and catalyst-dependent differences in the direction of the hydrogenolysis of 2-methyloxacycloalkanes under pressure is to be sought in the mechanism of the transformations. Special investigations in order to clear up the mechanisms of the processes were not performed, and accordingly only literature data can be relied upon in the interpretation of these transformations. Experimental

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observations of other authors, too [2], draw attention to the sharp difference in selectivity between certain catalysts in the hydrogenolysis of III:



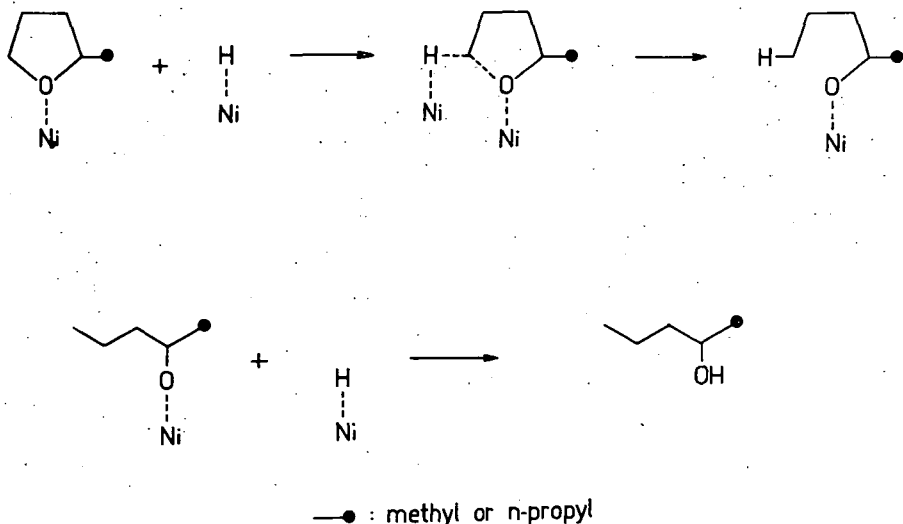
where $K = \text{CuO} \cdot \text{Cr}_2\text{O}_3$.

No explanation of the different transformations was given.

In the course of our experimental work, it became evident that the effects of the Raney-type copper and nickel catalysts on the direction of hydrogenolysis of the various oxacycloalkanes are different. Although the interpretation may be approached in a number of ways, in our view the determining factor is the difference in chemisorption properties of the metals:

On nickel a very rapid chemisorption of hydrogen, not activated or characterized by a low activation energy, can be observed, while hydrogen is not chemisorbed at all on copper below 0°C [3], and certain observations indicate that it is practically not adsorbed up to 300°C [4].

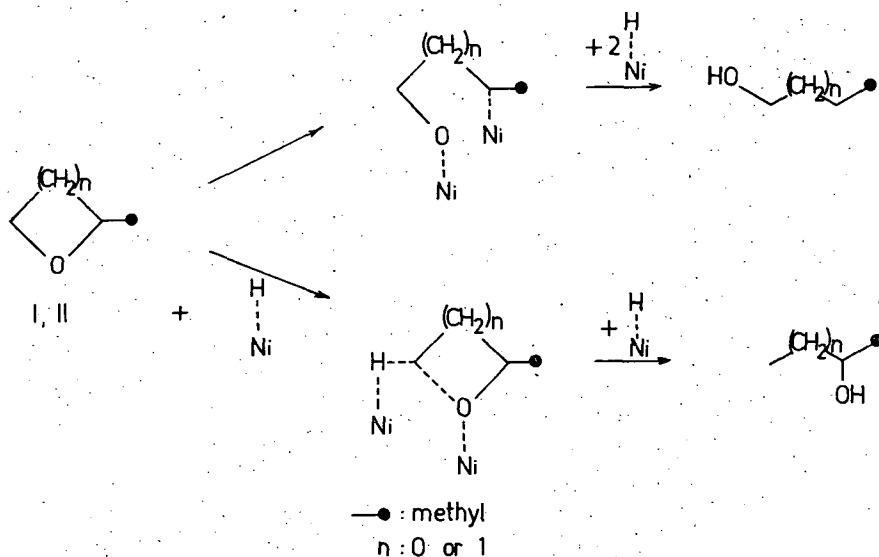
On this basis, in the case of Ni/Al the process is initiated by the chemisorbed hydrogen; this takes place obviously with higher rate on the less spatially-screened primary carbon atom. This transformation is accompanied by the formation of secondary alcohols:



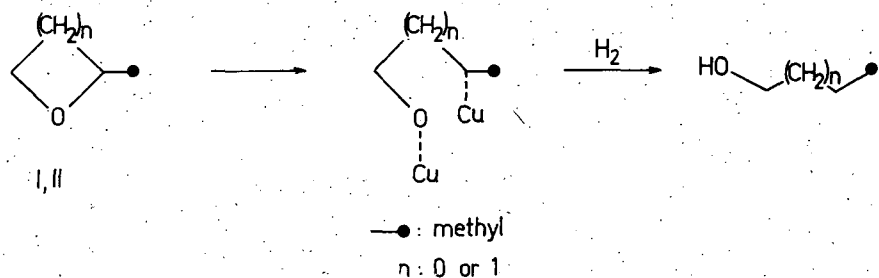
This mechanism is also supported by the fact that if the substituent is increase in size then the rate of formation of the secondary alcohols rises considerably [1].

Since the epoxides and oxethanes are strained systems, on their chemisorption on a Ni/Al catalyst the C—O bond adjacent to the substituent splits. Consequently,

in the hydrogenolyses of **I** and **II** on Ni/Al the formation of both alcohols is observed.

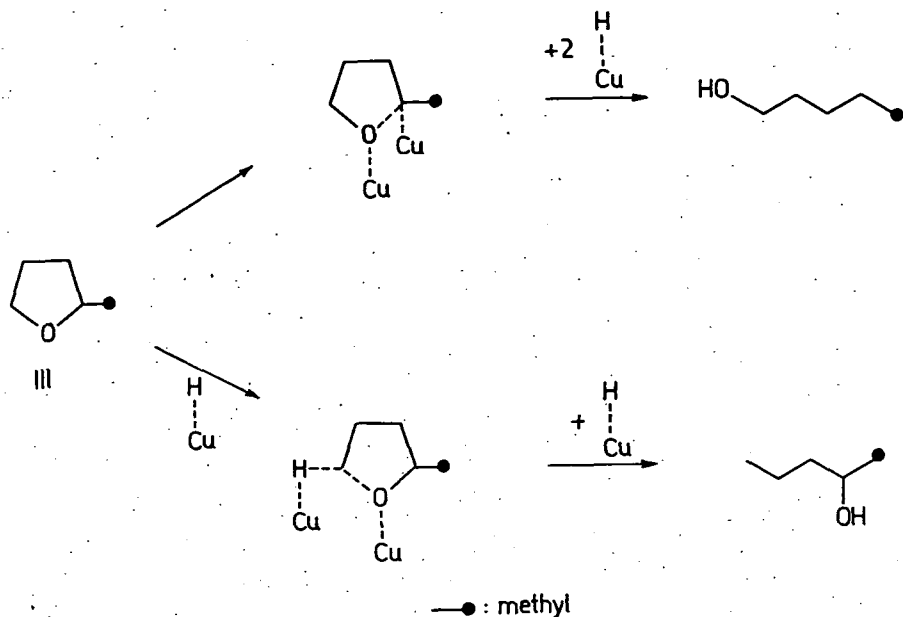


The hydrogenolyses of the epoxides and oxethanes on Cu/Al can be interpreted on the basis of the following reaction scheme:



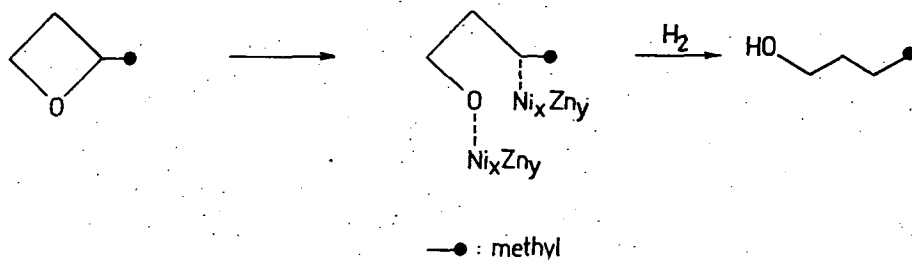
As a result of the inductive effect of the substituent on the ring, the C—O bond adjacent to the substituent splits on the chemisorption of the substrate; attack by hydrogen from the gas phase leads to the formation of primary alcohols.

As a consequence of the significantly higher stability of the ring, a more elevated temperature is required for the hydrogenolysis of 2-methyltetrahydrofuran (**III**). Further, above 300 °C the hydrogen is chemisorbed by copper, too. These effects have the result that the formation of both alcohols is observed on the hydrogenolysis of **III** on Cu/Al:



At 300 °C on Cu/Al the presence of chemisorbed hydrogen is also indicated by the experimental fact that in addition to the two pentanol isomers, pentane was formed, too, as a result of further hydrogenolysis [1]. Such a transformation takes place only in the presence of chemisorbed hydrogen or nascent hydrogen.

The special nature of the Ni/Zn catalyst can be explained in that during the alloying a phase or phases are produced, the catalytic characteristics of which resemble those of Cu/Al. On alloying with zinc the *d*-orbital of nickel can be filled; it appears that the Ni/Zn phase thus formed no longer chemisorbs hydrogen under the experimental conditions employed:



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СЕЛЕКТИВНОСТЬ СКЕЛЕТНЫХ КАТАЛИЗАТОРОВ
ПРИ ГИДРОГЕНОЛИЗЕ 2-МЕТИЛ-ОКСА-ЦИКЛОАЛКАНОВ ПОД ДАВЛЕНИЕМ

М. Барток, Р. А. Караханов

Каталитический гидрогенолиз под давлением пропиленоксида (I), 2-метил-оксациклобутана (II), 2-метил-тетрагидрофурана (III) и 2-*n*-пропил-тетрагидрофурана (IV) приводит к образованию первичных и вторичных спиртов. Селективность гидрогенолиза зависит от числа членов цикла и применяемых катализаторов.

Обнаружена корреляция между механизмом превращений, селективностью катализаторов и различиями в хемисорбционных свойствах катализаторов из металлических сплавов.