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## ACTIVITY OF MODIFIED CATALYSTS IN HYDROGENATION OF XYLOSE TO XYLITOL

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Xylitol and its derivatives are widely used in many branches of industry. One of the methods of obtaining xylitol is the catalytic hydrogenation of the xylose present in the hydrolysates of agricultural wastes.

In laboratory practice and also in the chemical industry, the skeletal alloy catalysts developed by Raney and by A. A. Bagg [1, 2] have come into wide use. In numerous publications, catalysts for the hydrogenation of monosaccharides and, especially, glucose and xylose are described in which to Raney nickel are added alloying components - chromium, titanium, molybdenum, magnesium, cobalt, palladium, etc. - which frequently not only raise the activity and selectivity of the catalyst but also make it more resistant to poisoning by various impurities and to changes in the parameters of the process [3, 4].

We have investigated the influence of modifying additives on the activity of a nickel-aluminum catalyst. A number of laboratory modified catalysts have been prepared. Leaching out was carried out with 10% solution of caustic soda at  $95 \pm 3^\circ\text{C}$ , the degree of elimination of aluminum being 40%.

The catalysts were tested in a 0.25-liter Bergius autoclave. A 15.6% aqueous solution of xylose was subjected to hydrogenation. The ratio of catalyst to xylose solution was 1:25. Hydrogenation was performed at  $100^\circ\text{C}$  and a pressure of hydrogen of 10 MPa, and the process was considered complete when there was no further absorption of hydrogen for an hour. The results obtained are given below; an industrial nickel-titanium catalyst was tested beforehand as standard:

Catalyst	Time of hydrogenation, h	Dry matter, %	Reducing substances, %	pH
Al-Ni-Ti (ind.)	8	15.2	0.21	5.5
Al-Ni-Cd	3	15.2	0.08	5.8
Al-Ni-Mo	3	15.2	0.06	6.1
Al-Ni-Ce	2	15.4	0.04	5.9
Al-Ni-La	2	15.2	0.09	5.6
Al-Ni-Mn	3	15.5	0.09	5.8
Al-Ni-Cr	5	15.6	0.12	5.6
Al-Ni-Mo-Cd	4	15.6	0.10	5.4

In the hydrogenation of xylose in the Bergius autoclave the industrial nickel-titanium catalyst did not exhibit a high activity. The inclusion of modifying additives in it led to a rise in activity and the residual amount of reducing substances (determined by the Makken-Shoorlya method) fell, which indicated a fairly high hydrogenating capacity of the modified catalysts. Simultaneously, the hydrogenation time was shortened from 8 to 2-5 h.

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The most appreciable effect of modification was shown on promotion with metallic cerium: the amount of reducing substances in the hydrogenate fell by a factor of 5 and the time of hydrogenation by a factor of 4.

An improvement of known industrial catalysts by modification has permitted a rise in the selectivity of their action and a shortening of the reaction time with the production of high-quality xylitol.

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#### GLUCOFRUCTANS OF *Cousinia polycephala*

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The main polysaccharides of the roots of *Cousinia* are glucofructans [1, 2]. We have studied the structure of the glucofructans isolated from the roots of *C. polycephala* Rypr. [3]. The glucofructans were dissolved in hot water (10% solution, 80°C). On standing, a precipitate of the aqueous fraction (AF) deposited with a yield of 51%. The mother solution was concentrated and precipitated with ethanol to give an ethanolic fraction (EF) with a yield of 38%.

Gel chromatography on Sephadex G-75 showed that the aqueous and ethanolic fractions consisted of polydisperse polymers the molecular masses of which ranged from 12,000 to 21,000 and from 10,000 to 18,000, respectively. In order to obtain a homogeneous polysaccharide, the aqueous and ethanolic fractions were fractionated by precipitation from water (2% solution) with ethanol (Table 1).

Since AF-III, AF-VIII, and EF-VII formed the bulk of the polysaccharides, we studied their structures. Fructose and traces of glucose were detected in the products of the complete hydrolysis of the three polymeric fractions. By a standard method [4], 98.0, 96.2, and 98.3% of fructose were detected in the glucofructans AF-III, AF-VIII, and EF-VII, respectively. The values of  $[\alpha]_D^{22}$  (c 1.0; H<sub>2</sub>O) were as follows: -36.5° (AF-III), -39.3° (AF-VIII), and -37.2° (EF-VII). The negative values of the specific optical rotation confirmed the  $\beta$ -configuration of the glycosidic bonds of the fructose residues.

In the products of the Smith degradation of all the samples, PC showed the presence mainly of glycerol with very small amounts of fructose, which may indicate the presence of both 2  $\rightarrow$  1- and 2  $\rightarrow$  6-bonds between the fructofuranose residues and a small number of branches.

The glucofructans AF-III, AF-VIII, and EF-VII were methylated by Hakomori's method [5]. The completeness of methylation was checked by IR spectroscopy. The following methylated sugars were detected in the hydrolysates of all three completely methylated polysaccharides by TLC [in the benzene-acetone (2:1) system] and GLC (in the form of methyl glycosides): 2,3,4,6-tetra-O-Me-D-glucose; 1,3,4,6-tetra-O-Me-D-fructose; and 3,4,6-tri-O-Me-D-fructose (the main product), together with a very small amount of di-O-Me-fructose.

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