Chem. Chem. Technol., 2025,
Vol. 19, No. 4, pp. 715–724

Chemical Technology

ISOMERIZATION OF GLUCOSE INTO FRUCTOSE OVER BASIC OXIDE CATALYSTS

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https://doi.org/10.23939/chcht19.04.715

Abstract. The isomerization of 10–30 % glucose aqueous solutions over several mixed basic oxides supported on γ-Al_2O_3 was studied at 90 °C and atmospheric pressure using batch and flow reactors. The catalyst samples were obtained by conventional impregnation method which is important for the development of the readily commercially available catalyst. It was found that the MgO–ZrO_2/Al_2O_3 catalyst with atomic ratio of Mg/Zr=4 and the deposited oxide phase content of 20 wt. % provides glucose conversion up to 19 % at 90 °C, with maximum fructose selectivity up to 100 % using the continuous flow fixed bed reactor. After 30 h of operation the deactivated catalyst has been regenerated by air calcination for 2 hours at 600 °C, restoring its activity and selectivity.

Keywords: fructose, isomerization of glucose, supported basic oxide catalysts.

1. Introduction

It is well known that fructose is widely used in the food industry as a dietary sweetener, which is almost 1.5 times sweeter than sucrose and 2 times sweeter than glucose.[1] Fructose is also a key starting compound for the synthesis of a wide variety of biobased value-added intermediates that can replace chemicals synthesized from the fossil feedstocks, *e. g.*, ethyl lactate,[2] methyl lactate,[3] levulinic acid,[4, 5] 2,5-dimethylfuran, caprolactam, maleic anhydride, 2,5-furandicarboxylic or adipic acid, *etc.*[5]

In terms of its free monosaccharide form, fructose is present in notable quantities only in honey (40 g/100 g) and a few fruits (apples 6–8 g/100 g, pears 5–9 g/100 g, grapes, dates, figs, and most berries).[6] Therefore, the use of this fructose as a raw material for the chemical industry is costly[7] and is not recommended. On the contrary, the fructose, obtained from glucose, being the most widespread monosaccharide in terms of biomass, as a building block of cellulose, starch, and glycogen,[8] could be a good candidate for the production of bio-based chemicals.

The isomerization of glucose into fructose is already a large-scale industrial process. Commonly, such a reaction is catalyzed by using immobilized enzymes.[9, 10] This is the largest process performed with about 1500 tons of immobilized enzymes, producing a glucose-fructose syrup (HFCS, high fructose corn syrup), with more than 10 million tons of product (dry matter) produced per year.[8, 9] However, this process requires considerable costs due to its long reaction time, expensive glucose isomerase, its temperature, pH sensitivity, and the need to use buffers and high-purity glucose solutions. In this context, the development of solid available catalysts able to perform the selective isomerization of glucose seems essential to advance biomass conversion.

A number of attempts have been made to investigate potential solid catalysts for fructose production. The yield of fructose obtained in aqueous solution, using a solid catalyst, is ca. 30 %, which is significantly less than in the case of enzymes (ca. 42 %). The yield of fructose is limited due to the reversibility of the isomerization (K_{eq} ~1 at 25 °C)[11] as well as the high reactivity of fructose, which undergoes subsequent transformations when using the catalyst. Currently, it is suggested that the most suitable catalysts for isomerization are solid Lewis acids[7, 11–18] and solid bases.[19–27] Recent publications put a focus on solid basic catalysts, being highly active and commercially available materials ready for use now.[24]

In our previous publications, it has been found that basic MgO–ZrO_2 catalysts provide for the fructose yield up to 30 % in the continuous mode at 90 °C and up to

35 % in an autoclave at 120 °C.[28, 29] These mixed oxide catalysts with different Mg/Zr atomic ratios have been prepared by calcination of hydroxides, obtained by coprecipitation from solutions of the corresponding salts.

However, the preparation of coprecipitated MgO–ZrO_2 catalyst is a somewhat more complicated procedure in comparison to the preparation of supported MgO–ZrO_2/Al_2O_3 catalysts synthesized by a simple impregnation method.[30]

Herein, we have presented the potential of MgO–ZrO_2/Al_2O_3 catalyst and some other basic oxides supported on commercially granulated γ-Al_2O_3 for the isomerization of glucose into fructose.

2. Experimental

2.1. Catalyst preparation and characterization

The catalysts were prepared using γ-Al_2O_3 (Ukraine), magnesium nitrate $Mg(NO_3)_2 \cdot 6H_2O$ (reagent grade), zirconium oxynitrate $ZrO(NO_3)_2 \cdot \times H_2O$ (reagent grade), calcium nitrate $Ca(NO_3)_2 \cdot 4H_2O$ (reagent grade) and aluminum nitrate $Al(NO_3)_3 \cdot 9H_2O$ (reagent grade). The reagents used in this study were purchased commercially in Ukraine. They were utilized as received without further purification.

The named samples with different mixed oxide content have been prepared by impregnation of aluminum oxide granules (fraction 0.5–2 mm) with calculated amounts of appropriate aqueous Mg, Zr, Ca, and Al salt solutions, followed by heat treatment as partly described in this article.[30] After preparation, the catalysts were dried at 110 °C and calcined at 600 °C for 2 h with a heating rate of 5 °C/min. These samples were designated as *x*MgO–*y*ZrO_2/Al_2O_3, where *x* and *y* correspond to supported oxide content in wt.% in terms of Al_2O_3.

Diffraction patterns of the studied samples recorded on the DRON-4-07 diffractometer with CuKα radiation were identified by comparing with those from the JCPDS (Joint Committee of Powder Diffraction Standards) database.

The porous structure of the samples was studied using the nitrogen adsorption – desorption technique (Quantachrome Nova 2200e Surface Area and Pore Size Analyser). The specific surface area (S), total pore volume (V_Σ), and average pore radius (r_{av}) of the samples were calculated from the adsorption – desorption isotherms of nitrogen using the BET method.

The total content of base sites of prepared oxides was determined by inverse titration of 2,4-dinitrophenol adsorbed on the sample surface with KOH solution in the presence of bromothymol blue as an indicator. To perform this, 10 mL of 0.05 N solution of 2,4-dinitrophenol in toluene were added to 200–300 mg of the named sample and stirred for 30 min. The suspension was stored in closed glasses for over 24 h to establish equilibrium. The aliquots were titrated with 0.01 N solution of KOH. The computational error for content site determination is 0.05 mmol/g. The highest strength of base sites (H_max) was measured using the standard indicator method[31] following Hammett indicators (Aldrich): bromothymol blue (pK_{BH} =+7.2), phenolphthalein (pK_{BH} =+9.3), 2,4-dinitroaniline (pK_{BH} =+15.0), 4-chloro-2-nitroaniline (pK_{BH} = +17.2), and 4-nitroaniline (pK_{BH} = +18.4).

2.2. Catalytic tests

Glucose (production of Ukraine, commercially available) was used without further purification by means of aqueous solutions of glucose with a concentration of 10, 20, and 30 wt. %. The catalytic experiments were carried out in two ways: inside the batch reactor with stirring and in the flow reactor with a fixed catalyst layer. Batch catalytic tests were performed under autogenous pressure in a thermostated (glycerine bath) glass reactor (25 mL) using a magnetic stirrer for 0.5–3 hours at 90 °C. Then, the reaction was stopped by cooling the reactor in an ice bath, and the product was separated from the catalyst by filtering through a paper filter. The catalytic experiments were also performed in a fixed-layer continuous flow Pyrex reactor (i. d. 8 mm) inserted in an electric oven. The catalyst (1.0 cm^3, 0.6 g) was placed in the isothermal zone of the reactor. The glucose solution was fed using a pump Orion M 361 (Thermo Electron Corporation) with liquid hourly space velocity (LHSV) = 0.34–2.4 h^{-1}at 90 °C and atmospheric pressure.

^{13}C NMR spectroscopy (Bruker Avance 400, Germany) was used to identify products. To assign the observed peaks in the spectrum, the database of organic compounds spectra (SDBS, National Institute of Advanced Industrial Science and Technology, Japan, www.aist.go.jp) was used.

The product samples collected from the experiments were also analyzed by using Waters HPLC (Waters 1515 Isocratic HPLC Pump, Waters 717 plus Autosampler) equipped with a Waters 2414 RI detector (Waters 410 Differential Refractometer) and Aminex HPX-87H Ion Exclusion column (300×7.8 mm). The internal temperatures of the RI detector and column were 40 °C and 65 °C, respectively. The eluent was 0.004M aqueous solutions of H_2SO_4 at a 0.55 mL/min flow rate, and the total analysis time was 20 min. The product's concentration in received samples was defined by means of external calibration curves generated by using standard solutions with known concentrations.

3. Results and Discussion

Chemical composition, textural properties, strength, and concentration of base sites of synthesized catalysts are summarized in Table 1. Parameters of porous structure for initial aluminum oxide and used samples were calculated from nitrogen adsorption – desorption isotherms, the examples of which are shown in Fig. 1. All of them belong to type IV according to IUPAC classification, which is characteristic for mesoporous materials. Curves of pore size distribution (PSD) (inset of Fig. 1) also indicate it.

Thus, initial γ-Al_2O_3 has a surface area of 280 $m^2\ g^{-1}$ and contains mesopores with a size in the range of 2–14 nm and a maximum on the PSD curve of about 3.9 nm (Table 1). Deposition of basic oxides on alumina surface predictably leads to some decrease in the specific surface area, total pore volume, and mesopore volume, but their size remains almost the same (inset of Fig. 1, Table 1). The deposition of 10–20 wt. % mixed basic oxide on alumina surface, as a result, gives samples that are characterized by the basic sites with H_{max} from +9.3 to +17.

Table 1. Textural parameters and total base properties of the synthesized catalysts

Catalyst	Deposited phase, wt. % (Me atomic ratio)	S, $m^2\ g^{-1}$ BET)	V_Σ, $cm^3\ g^{-1}$	V_{me}, $cm^3\ g^{-1}$	r_{av}, nm	r_{me}, nm (BJH desorption pore radius)	H_{max}	Total content of base sites, mmol/g
5.6MgO–4.4ZrO_2/Al_2O_3	10 (4:1)	205	0.65	0.70	6.3	3.9	+9.3	1.2
11.3MgO–8.7ZrO_2/Al_2O_3	20 (4:1)	195	0,60	0.64	6.1	3.9	+15.0	1.5
11.5CaO–8.5ZrO_2/ Al_2O_3	20 (3:1)	150	0.52	0.56	6.9	4.0	+15.0	1.2
16.3CaO–3.7Al_2O_3/Al_2O_3	20 (4:1)	140	0.49	0.53	6.7	3.9	+17.0	1.3
15.3CaO–4.7Al_2O_3/Al_2O_3	20 (3:1)	145	0.50	0.54	6.9	3.9	+17.0	1.1
7.7CaO–2.3Al_2O_3/ Al_2O_3	10 (3:1)	155	0.55	0.59	6.7	3.9	+9.3	0.9
4.3CaO–6.2MgO–9.5ZrO_2/Al_2O_3	20 (1:2:1)	160	0.53	0.58	6.6	4.0	+9.3	1.2
20CaO/Al_2O_3	20	145	0.54	0.52	6.5	3.9	+17.0	1.1
Al_2O_3	–	280	0.78	0.84	5.9	3.9	–	–

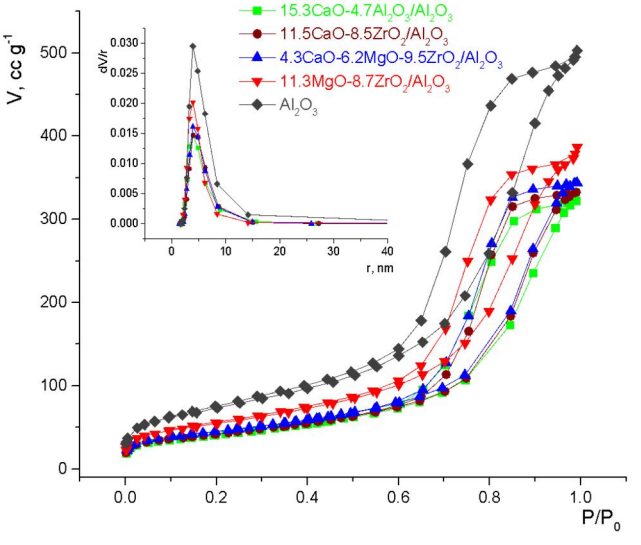


Fig. 1. Nitrogen adsorption-desorption isotherms and PSD curves for synthesized samples and initial γ-Al_2O_3

According to XRD analysis, all the synthesized supported oxides remain in the amorphous state. The diffractograms of supported samples, some of which are displayed in (Fig. 2), do not show characteristic peaks inherent to bulk crystal MgO, CaO, ZrO_2, and other basic oxides. All reflections (2θ = 36.5°, 46.1°, 66.6°) on XRD patterns of synthesized samples (Fig. 2) are due to a poorly developed crystalline phase of γ-Al_2O_3, which corresponds to the (311), (400), (440) crystal planes, respectively.

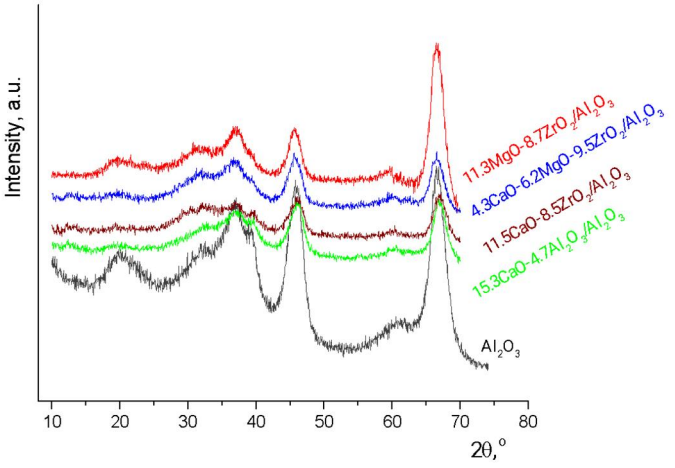


Fig. 2. XRD patterns of the synthesized samples after calcination at 600 °C for 2 h with initial γ-Al_2O_3

Table 2 shows the results of the conversion of 10 wt. % glucose solution on some studied catalysts at 90 °C in the batch reactor. Process temperature was based on data obtained from our previous studies and literature.[21–27] In our previous publications[28, 29] it was described that glucose isomerization on basic MgO-ZrO_2 catalysts should be carried out at 90 °C for about 2 hours, because the increase in time leads to the formation of by-products and the yield of fructose practically does not increase. The results of the tested catalysts shown in Table 2 are also consistent with this fact.

Table 2. Isomerization of glucose into fructose in batch reactors over various catalysts [a]

Catalyst	Reaction time, h	pH of product	Glucose conversion, %	Selectivity for fructose, %	Fructose yield, %
11.3MgO–8.7ZrO_2/Al_2O_3	0.5	7.2	19	99	19
	1	7.4	22	98	21
	2	7.5	23	97	22
	3	7.5	23	95	22
4.3CaO–6.2MgO-9.5ZrO_2/Al_2O_3	0.5	7.3	20	97	19
	1	7.5	26	96	25
	2	7.7	26	96	25
	3	8.1	27	92	25
15.3CaO–4.7Al_2O_3/Al_2O_3	1	7.8	29	83	24
	2	8.1	30	82	25
	3	8.5	30	80	24

Reaction conditions: 10 mL of 10 wt. % aqueous glucose solution, 100 mg catalyst, 90 °C, 500 rpm.

Further experiments of testing synthesized catalysts were carried out inside the flow reactor that is more acceptable for practice.

The pure γ-Al_2O_3 provides a low glucose conversion and fructose yield (<6 %) (Table 3, Fig. 3, *a*), confirming that it alone has no obvious contribution to the conversion of glucose under the studied conditions.

The highest conversion of glucose (47 %) was observed on 15.3CaO–4.7Al_2O_3/Al_2O_3 catalyst (Table 3, Fig. 3, *b*); however, the selectivity for fructose is not high

(58 %), and the product was brown in color with pH=8.6. In the chromatogram of this product (Fig. 3, *b*), in addition to peaks of fructose (10.77 min) and glucose (9.99 min), the peaks of by-products (8.45 min, 12.08 min, and 14.02 min), which could not be precisely identified, were recorded. It is known that basic catalysts can promote both isomerization and degradation of monosaccharides, glucose and fructose in particular.[20, 21]

Table 3. Isomerization of glucose into fructose in the continuous flow fix-bed catalytic reactor

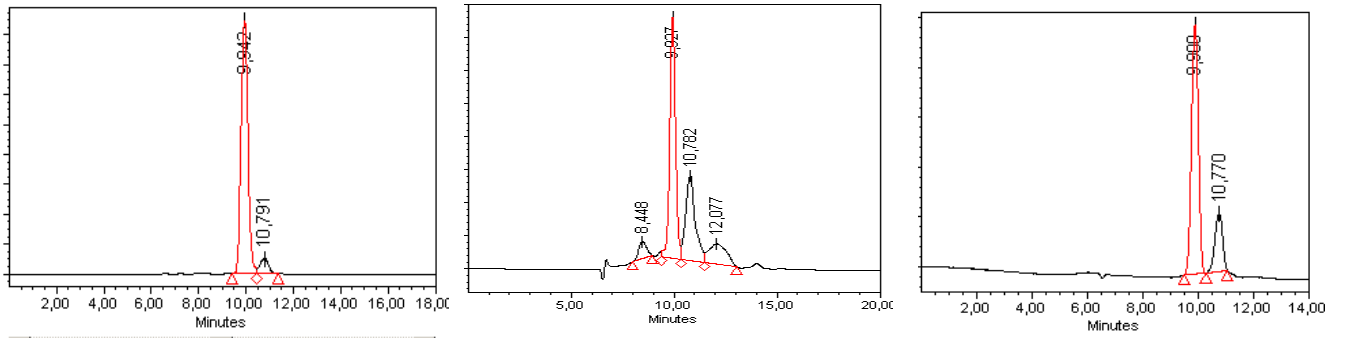
Catalyst	pH of product	Glucose conversion, %	Selectivity for fructose, %	Fructose yield, %
5.6MgO–4.4ZrO_2/Al_2O_3	7.1	16	~100	16
11.3MgO–8.7ZrO_2/Al_2O_3	**7.2**	**19**	**~100**	**19**
11.5CaO–8.5ZrO_2/Al_2O_3	8.2	37	61	22
16.3CaO–3.7Al_2O_3/Al_2O_3	8.7	51	49	25
15.3CaO–4.7Al_2O_3/Al_2O_3	**8.6**	**47**	**58**	**27**
7.7CaO–2.3Al_2O_3/ Al_2O_3	8.3	32	59	19
4.3CaO–6.2MgO–9.5ZrO_2/Al_2O_3	7.6	24	92	22
20CaO/Al_2O_3	8.7	45	52	23
Al_2O_3	6.8	7	~92	≤6

Reaction conditions: 10 wt. % aqueous glucose solution, 90°C, LHSV=1.0 h^{-1}, time-on-stream (TOS) =2 h

Isomerization of glucose into fructose is favorable in the presence of weak base sites of the catalyst and at low reaction temperature. The main by-products of glucose and fructose degradation, according to established reaction schemes,[20, 21] include dihydroxyacetone, glycolaldehyde, and organic acids (lactic, glycolic, glyceric, and formic acids), along with other products formed through subsequent breakdown and condensation reactions The signals at 171–182 p.p.m. are recorded in the ^{13}C NMR spectrum of products obtained on this catalyst (Fig. 4, curve 2) could indicate the formation of the above-mentioned acids and their salts with Ca^{2+} ions.

An alkaline environment (pH ≥ 8.2) of the products was observed for all tested CaO-containing catalysts (Table 3**)**, which may indicate certain Ca^{2+} ions leaching. The presented data are commensurate with the results,[25] where mixed oxide $Ca_3AlO_{4.5}$ (Ca Al-based hydrotalcite-derived) provided 50–68 % fructose selectivity inside the flow reactor at the same temperature of 90 °C. The authors[25] also reported that after the first run (TOS=4 h) a Ca^{2+} loss of ~5 % was detected.

Practically, 100 % selectivity towards fructose at 19 % glucose conversion was provided by 11.3MgO–8.7ZrO_2/Al_2O catalyst (Table 3). Only peaks of fructose (10.77 min) and glucose (9.99 min) were recorded in the chromatogram (Fig. 3, *c*) and their corresponding signals in the ^{13}C NMR spectrum (Fig. 4, curve 3), in terms of the product obtained on this catalyst. The product had a pH value of 7.2 which indicated a very little leaching of Mg^{2+} ions and the stability of this mixed oxide catalyst accordingly. The authors[23] who studied glucose isomerization in aqueous media over coprecipitated MgO–ZrO_2 mixed oxides prepared with different Mg/Zr atomic ratios also noted the insignificant leaching of Mg^{2+} during the consecutive runs.



Al_2O_3 a | 15.3CaO–4.7Al_2O_3/Al_2O_3 b | 11.3MgO–8.7ZrO_2/Al_2O c

Fig. 3. Chromatograms of the products obtained on studied catalysts

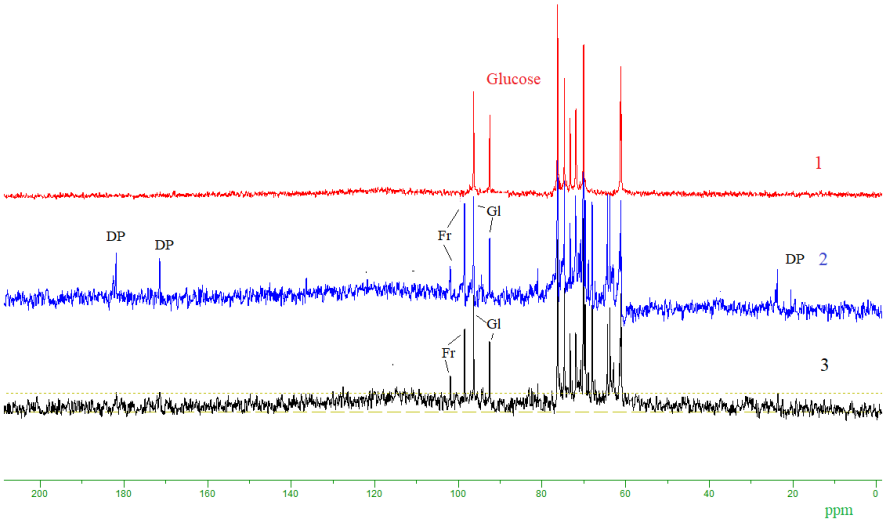


Fig. 4. ^{13}C NMR spectra of glucose (10 wt. % water solution) (1) and product obtained at 90 °C on 15.3CaO–4.7Al_2O_3/Al_2O_3 (2) and 11.3MgO–8.7ZrO_2/Al_2O_3 (3) catalysts (LHSV= 1 h^{-1}, TOS=2 h; *Fr – fructose, Gl – glucose, DP – degradation products*)

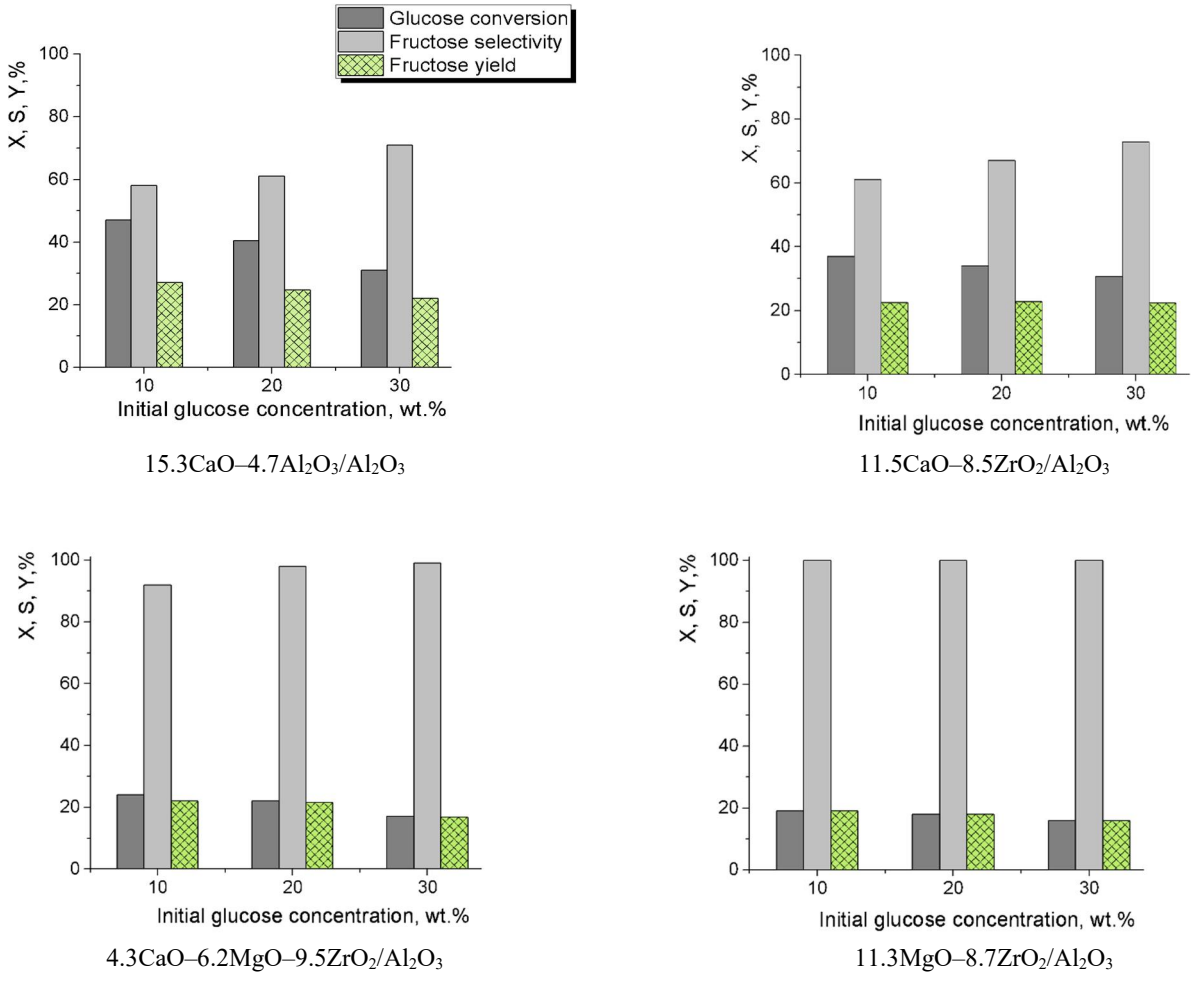


Fig. 5. Formation of fructose on tested catalysts using different initial glucose concentration (LHSV=1.0 h^{-1}, TOS=2 h)

The results on the influence of glucose solution concentration in terms of the yield of fructose are presented in Fig. 5. As the concentration increases from 10 to 30 %, glucose conversion decreases to some extent for all tested samples. So, for example, on 15.3CaO–4.7Al_2O_3/Al_2O_3 catalyst, the conversion decreases from 47 to 31 %. However, due to the increase in selectivity, the yield of fructose decreases to a lesser extent from 27 to 22 %. At the same time, the fructose yield on the most selective 11.3MgO–8.7ZrO_2/Al_2O catalyst decreases from 19 to 16 %. This makes it possible to use more concentrated solutions and obtain more of the target product per unit of time, which is beneficial for an industrial production of fructose.

The increase of fructose selectivity together with an increase of the initial glucose concentration was observed during the study of the isomerization process on several basic catalysts, in particular Mg–Al hydrotalcites,[21] MgO-ZrO_2 mixed oxides,[23] MgO-doped ordered mesoporous carbon.[27] The authors assume[23] that the lower fructose selectivity at low glucose concentration is likely due to the degradation of the formed fructose on the basic sites by subsequent side reactions because fructose is more reactive than glucose. Thus, the high initial concentration of glucose minimizes these undesirable side reactions, leading to high fructose selectivity. Our results confirm this fact.

Decreasing the LHSV values and, accordingly, the load on the catalyst increases the contact time, which leads to the formation of a higher content of by-products and, accordingly, to a decrease in fructose selectivity (Table 4). As can be seen from the results presented in Table 4, for all studied catalysts a decrease of glucose conversion was observed at increasing LHSV values.

Table 4. Isomerization of glucose into fructose on several catalysts inside the flow fixed-layer reactor at different load on a catalyst

LHSV, h^{-1}	Contact time, min	Load on a catalyst, mmol Gluc/g_{cat}/h	Glucose conversion, %	Fructose selectivity, %	Fructose yield, %	Fructose productivity of the catalyst, mmol/g cat/h
15.3CaO–4.7Al_2O_3/Al_2O_3						
0.3	200	0.83	49	53	26	0.22
0.5	120	1.39	42	61	25	0.34
1.0	60	2.78	**31**	**71**	**22**	0.61
1.5	40	4.17	23	73	17	0.71
2.4	25	6.67	19	78	15	1.00
11.5CaO–8.5ZrO_2/Al_2O_3						
0.3	200	0.83	39	61	24	0.20
0.5	120	1.39	34	68	23	0.32
1.0	60	2.78	**30.6**	**72.8**	**22**	0.61
1.5	40	4.17	23	78	19	0.85
2.4	25	6.67	17	82	14	0.93
4.3CaO–6.2MgO–9.5ZrO_2/Al_2O_3						
0.3	200	0.83	24	86	21	0.17
0.5	120	1.39	20	94	19	0.26
1.0	60	2.78	**17**	**97**	**16.5**	0.46
1.5	40	4.17	12	99	12	0.50
2.4	25	6.67	11	100	11	0.73
11.3MgO–8.7ZrO_2/Al_2O_3						
0.3	200	0.83	20	96	19	0.16
0.5	120	1.39	18	98	18	0.25
1.0	60	2.78	**16**	**100**	**16**	0.44
1.5	40	4.17	12	100	12	0.50
2.4	25	6.67	10	100	10	0.67

Reaction conditions: 30 wt. % aqueous glucose solution, TOS=2 h.

The stability of basic solid catalysts during the reaction of isomerization of glucose into fructose in an aqueous medium is a known problem. The reasons for this are the leaching of ions Mg^{2+} [21,22] or Ca^{2+} ions[25] and the accumulation of adsorbed sugar degradation products on the surface of the catalyst. The stability of supported catalysts with time on stream was studied at 90 °C during a period of 30 h (Fig. 6). Then, to eliminate the adsorbed by-products, deactivated catalysts were regenerated by calcination in air at 600 °C, 2 h.

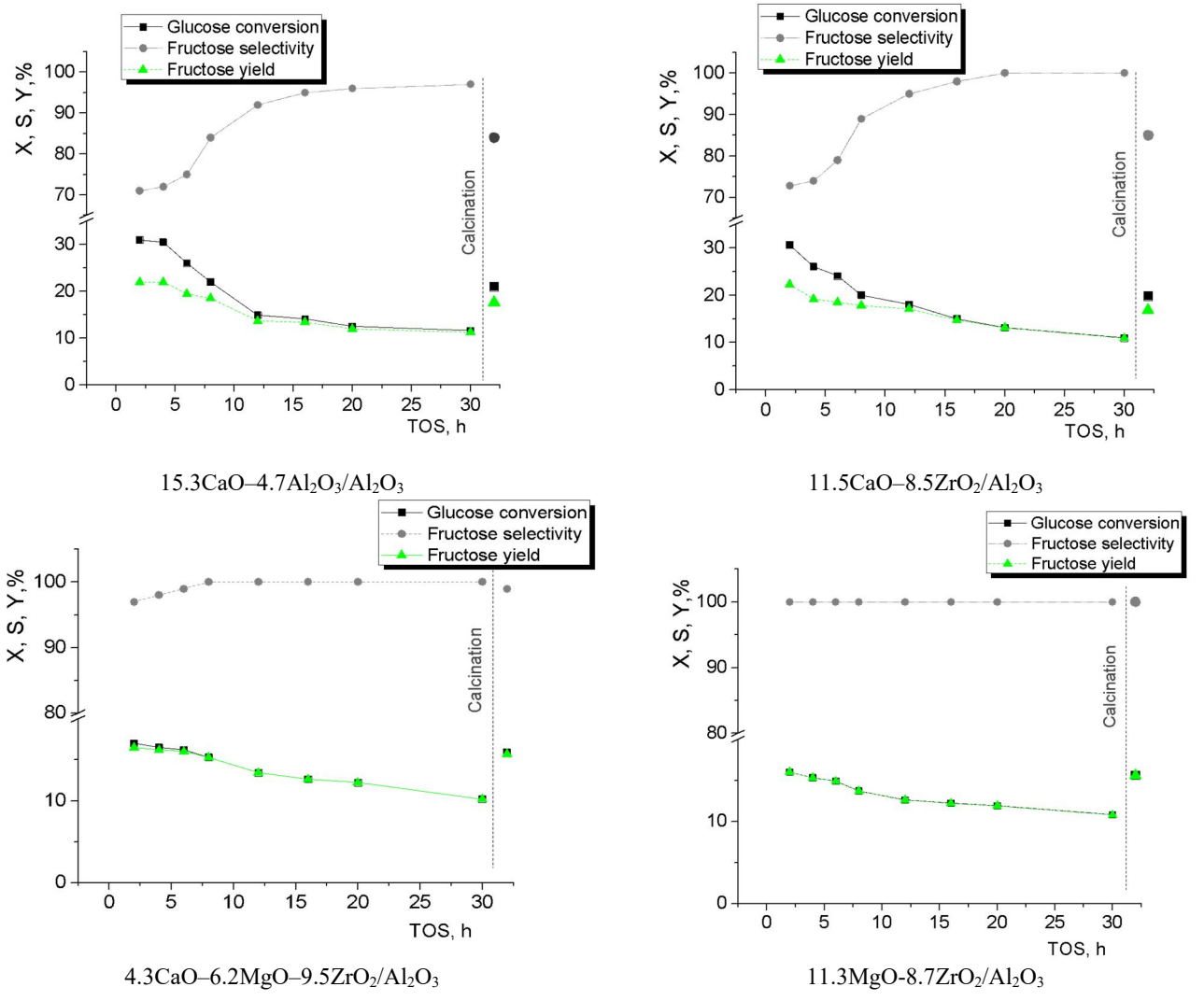


Fig. 6. Fructose formation in the continuous time-on-stream on studied catalysts (30 wt. % aqueous glucose solution, LHSV=1.0 h^{-1})

The obtained results indicate a slow deactivation of all synthesized catalysts, as glucose conversion gradually decreases during 30 h. course (Fig. 6). For CaO-containing samples with stronger basic sites, this process occurs more intensively (especially in the first 12 hours). The most active $16.3CaO–3.7Al_2O_3/Al_2O_3$ catalyst initially provides a glucose conversion of 31 %, after 12 hours – 15 %, and after 30 hours it remains at the level of 12 %. At the same time, the fructose selectivity gradually increases from 71 to 97 %. After regeneration, this catalyst partially restored its activity and provided 16 % glucose conversion, which is higher compared to the initial fructose selectivity of 94 %.

The catalyst $4.3CaO–6.2MgO–9.5ZrO_2/Al_2O_3$, with the lowest CaO content among the studied samples, lost activity to a lesser extent. The initial glucose conversion of 17 % with a fructose selectivity of 97 % after 8 hours under the studied conditions decreased to 15 % and after 30 hours to 10 %. The fructose selectivity at the same time increased, and after 8 hours of

continuous process over this catalyst reached almost 100 %. After regeneration, this catalyst recovered its activity to a much greater extent than the 16.3CaO–3.7Al_2O_3/Al_2O_3 catalyst, providing for 16 % glucose conversion, also with a higher fructose selectivity of 99 % than at the beginning of its operation (97 %).

It can be assumed that the irreversible loss of the initial activity of CaO-containing catalysts, as it is,[25] is due to the leaching of a certain part of Ca^{2+} ions. The loss of strong base sites leads to decreased glucose conversion while enhancing fructose selectivity, as the base-catalyzed degradation of fructose is significantly suppressed.

On the 11.3MgO–8.7ZrO_2/Al_2O_3 catalyst, the maximum selectivity for fructose did not change during 30 h of operation, although the glucose conversion and fructose yield gradually decreased from 16 to 11 % accordingly (Fig. 6). After regeneration, this catalyst almost completely restored its activity and provided 16 % glucose conversion. This means that the decrease in the efficiency of the catalyst occurred mainly not due to the leaching of magnesium ions, but rather due to the blockage of the active sites resulting from the strong adsorption of by-products on its surface. The latter is proved by the brown color that the catalyst acquired during catalytic experiments, which disappeared after calcination.

Thus, CaO-containing catalysts with stronger bases initially provide for higher glucose conversion but with lower fructose selectivity. The formation of by-products leads to the faster deactivation of these catalysts. The presence of acids among the by-products, in particular lactic acid, which is a typical by-product of carbohydrate destruction when mixing with bases, promotes the leaching of Ca^{2+} ions. This leads to a partial loss of catalyst activity that is not restored after regeneration by calcination. In the case of the MgO–ZrO_2/Al_2O_3 catalyst with lower strength of basic sites, glucose conversion is lower but more selective in terms of fructose. The absence of acidic by-products contributes to a greater catalyst stability.

4. Conclusions

A series of alumina-supported mixed oxides prepared by impregnation of γ-Al_2O_3 with appropriate aqueous Mg, Zr, Ca, and Al salt solutions followed by heat treatment, was studied as catalysts to be used in the process of glucose isomerization into fructose at 90 °C and atmospheric pressure using 10–30 % aqueous glucose solutions. The obtained results demonstrated that the basicity of the catalyst plays a key role in the reversible glucose isomerization reaction, accompanied by the formation of by-products of the breakdown of glucose and fructose, including lactic acid. The catalysts with CaO, which increase strong basicity, promote sugar degradation reactions resulting in the increased glucose conversion, but at the expense of decreasing fructose selectivity, while catalysts with medium basic sites, attributed to MgO-ZrO_2, are more selective towards fructose.

It was found that the MgO–ZrO_2/Al_2O_3 catalyst with a molar ratio of Mg/Zr=4 and the deposited oxide phase content of 20 wt. % provides glucose conversion up to 19 %, with maximum fructose selectivity up to 100 % when using the flow reactor. The possibility of processing of concentrated (30 %) glucose solutions at 90 °C with a catalyst productivity up to 0.7 mmol fructose/g_{cat}/h was presented. After 30 h processing, the MgO–ZrO_2/Al_2O_3 catalyst has been regenerated by calcination in air for 2 hours at 600 °C, which restored its activity and selectivity.

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Received: March 12, 2025 / Revised: May 22, 2025 / Accepted: June 05, 2025

ІЗОМЕРИЗАЦІЯ ГЛЮКОЗИ У ФРУКТОЗУ НА ОСНОВНИХ ОКСИДНИХ КАТАЛІЗАТОРАХ

Анотація. *Досліджено процес ізомеризації 10–30 % водних розчинів глюкози на кількох основних оксидних каталізаторах у періодичному та проточному режимах за температури 90 °C та атмосферного тиску. Основні змішані оксиди синтезовано методом просочення комерційного гранульованого γ-Al_2O_3 розчинами відповідних солей з подальшим термообробленням, що важливо для розроблення простого та дешевого каталізатора цільової реакції. Встановлено, що каталізатор MgO–ZrO_2/Al_2O_3 із мольним співвідношенням Mg/Zr = 4 і вмістом осадженої оксидної фази 20 мас. % у проточному реакторі забезпечує конверсію глюкози до 19 % за максимальної селективності за фруктозою до 100 %. Цей каталізатор після 30 год безперервної роботи можна регенерувати прожарюванням на повітрі протягом 2 год за 600 °C без втрати активності та селективності.*

Ключові слова*: фруктоза, ізомеризація глюкози, оксидні каталізатори.*