THE INDUSTRIAL CATALYSTS ENLARGED TESTS RESULTS IN THE BUTYNEDIOL-1,4 HYDROGENATION PROCESS

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Publication is devoted to carrying out of the butindiol-1,4 hydrogenation process enlarged tests. Results of the enlarged tests have shown that the process selectivity and product cleanness raises at use of alloy catalyst SKN-39 in the process of butindiol-1,4 hydrogenation. The tests have shown that the butanol exit grows much more slowly, i.e. from 2,3 up to 8,0% at work with alloy catalyst SKN-39. Comparing the data of alloy catalyst SKN-39 to industrial catalyst MNH advantage of the first catalyst is obviously observed. Their application in production allows to increase selectivity of process on butandiol by 18–27%, and stability in 1,5–2 times. SKN-39 catalyst possesses higher hydrogenating ability than industrial MHX. The productivity of process raises in 1,5–2,0 times, selectivity raises by 15–30%, and the target product possesses higher quality at the butindiol hydrogenation on the SKN-39 catalyst.

Keywords: butindiol-1,4, butandiol-1,4, nickel catalysts

The butynediol-1,4 hydrogenation kinetic regulations study is very significant in the practical relations, as, especially, this reaction has already been laid in the basis of the butanediol-1,4 obtaining industrial process.

So, it should quite necessary to be developed and to be implemented the most efficient and the most stable catalysts for the organic synthesis in the production for the modern production development. The high – performance steady – state and the stationary catalysts development for the hydrogenation process at the modern requirements level in the industry is the most significant, while, at the same time, it is the complex technical challenge, the final solution of which is resulted in the butanediol-1,4 increase in its yield and, in general, its obtaining process efficiency. That is why, it should be necessary the highly – efficiently catalysts, due to the special requirements just to the obtained substances purity for this process carrying out [1–3]. In this connection, the butindiol hydrogenation process study on the modified nickel catalysts is the most actual and relevant [4–6].

So, the laboratory researches have been shown, that, developed by us, the SKN-39 alloyed catalyst is displayed the highest activity, its selectivity, and its stability, and the MNX and the NX industrial catalysts – the smallest ones at the butindiol-1,4 hydrogenation NX [4]. At present, the SNK-39 from the alloyed catalyst has its industrial applications in a number of the hydrogenation processes, such as the oil aldehydes hydrogenation and the others. In this connection, the catalytic properties on the pilot installation have already been investigated by us, for the SKN-39 alloyed catalyst early introduction, which is also the highly – efficient catalyst in the butindiol-1,4 hydrogenation process. Thus, the MNX, NX, and SKN-39 catalysts enlarged and the integrated testing final results have already been given in the Tables 1–3.

Table 1

The MNX Various Catalysts Enlarged Tests Results, in the Butindiol-1,4 Hydrogenation Process. The Test Conditions: The Raw Materials Volume Flow Rate – 1 l./h., the Hydrogen Flow – 3 NM/h, pH – 7,0 – 9,…

The tests duration, h	The reactor temperature, t, °C	The weight hour space velocity h^{-1}	The hydrogen flow, nm^3/h	The BID concentration in charge stock, %	The hydrogenation products composition, %					The initial BID product yield, % mass	
					Butanol	OMA	BAD	BED	BID	Butanol	BAD
24	90	0,8	0,2	16,9	1,20	abs.	12,6	0,23	trace	7,1	74,8
80	90	0,8	0,2	16,9	1,65	abs.	11,3	0,27	0,10	9,8	66,9
160	90	0,8	0,2	16,9	2,17	0,31	11,5	0,13	abs.	12,9	68,4
200	90	0,8	0,2	16,9	1,97	0,47	11,3	0,2	abs.	11,7	68,4

Table 2

The NX Industrial Catalyst Enlarged Tests Results in the Butindiol-1,4 Hydrogenation Process. The Test Conditions: The Raw Materials Volume Flow Rate – 1 l./h., the Hydrogen Flow – 3 NM/h

The duration, h	The reactor tempera-ture, t, °C	The initial raw material composition, % mass			The hydrogenation products composition, % mass			The product yield from the initial one			
								BID, %		BID + BAD, %	
		BID	BAD	Total in water solution	Butanol	BAD	BED	Butanol	BAD	Bu-tanol	BAD
80	90	14,93	32,30	47,23	0,52	42,65	0,18	3,5	69,3	1,1	90,3
80	90	same	same		1,06	43,05	0,15	7,1	72,0	2.2	91,1
112	110	«»	«»	«»	2,13	42,53	0,18	14,3	69,1	4,5	90,0
110	110	15,36	28,07	43,43	2,11	35,89	0,18	13,7	50,9	4.9	82,6
208	110	same	same		1,91	32,92	0,13	12,4	31,6	4.4	75,8
256	120	17,17	32,65	49,82	2,57	38,30	0,09	15,0	32,9	5.2	76,9
288	120	same	same		2,78	34,14	0,34	16,2	8,7	5,6	68,5

Table 3

The SKN-39 Industrial Catalyst Enlarged Tests Results in the Butindiol – 1,4 Hydrogenation Process

The tests dura-tion, h	The reac-tor tem-perature, t, °C	The weight hour space velocity, h^{-1}	The hy-drogen flow, nm^3/h	The BID concentra-tion in the in initial raw mate-rial, %	The hydrogenation products composition, %					The initial BID product yield, % mass	
					Buta-nol	OMA	BAD	BED	BID	Buta-nol	BAD
24	80	0,6	1,0	14,3	0,11	abs.	13,7	0,16	0,04	3,1	97,7
80	80	0,6	1,0	14,4	0,12	abs.	14.3	0,07	0,02	4,3	99,4
112	80	1,5	3,0	13,9	0,10	abs.	13,7	traces	traces	5,3	99,1
160	80	1,5	3,0	30,0	0,17	abs.	27,7	traces	abs.	7,3	92,5
248	60	1,0	0,2	15,0	1,67	abs.	14,4	traces	abs.	11,1	96,0
320	100	1,0	0,2	15,0	1,20	0,27	13,0	0,26	0,25	8.0	86,9

N o t e : BAD – butanediol-1,4; BID – butynediol-1,4; BED – butenediol-1,4; OMA – oxibutyl aldehyde.

So, it can be seen from the Tables 1–3 data, that the selectivity by the butanediol-1,4 at the butynediol-1,4 hydrogenation on the SKN-39 alloyed catalyst has been made up 86,9 %, which is 18 % higher, than at the MNX industrial catalyst. So, the selectivity by the butanediol is equal to 68,4 %, under the similar conditions of the last catalyst work. For all this, the SKN-39 catalyst work duration has been made up 320 hours, while the MNX industrial catalyst operation time is much less, that is why, it has been made up only 200 hours. The butynediol-1,4 hydrogenation products chromatographic analysis has been shown, that the butanol yield, having had the production by – product, with the hydrogenation process duration increase, to the greatest extent, is being increased on the MNX (e.g. nickel/kaolin) and the HX (e.g. nickel/Cr_2O_3) catalysts. So, at the process duration, which is equal to 288 hours, the butanol yield on the NX catalyst has been made 16,2, and on the SKN-39 – 8,0 %. At the same time, the butanol yield on the MNX catalyst is being increased up to 30,6 % at the butynediol hydrogenation during 200 hours. So, the tests have been shown, that the butanol yield is being grown much slower, e.g. from 2,3 up to 8,0 %, at the working with the SKN-39 alloyed catalyst. Having compared the SKN-39 alloyed catalyst data with the MNX industrial catalyst, it is clearly observed the first catalyst advantage. Their application in the production is quite able to be increased the process selectivity by the butanediol for 18–27 %, and its stability in 1,5–2 times. So, the SKN-39 catalyst is possessed a higher hydrogenating capacity, than the MNX industrial one. The γ-hydroxybutyric aldehyde has been absent, and the butenediol – the intermediate product, and the butynediol – the raw materials have been, or have been absent, at butynediol-1,4 hydrogenation at the alloyed catalysts with the hydrogen low flow in the hydrogenation product. At the same time, in the hydrogenation product, having obtained after the butynediol-1,4 hydrogenation, the γ-hydroxybutyric aldehyde, the BED, and the BID have been present at the industrial catalyst.

Thus, the process performance is being increased in 1,5–2,0 times, the selectivity – for 15–30 % at the butynediol hydrogenation at the SKN-39 catalyst, and the end product has a higher quality (e.g. the product purity is being increased by, at least, for 2–3 %, in comparison with the MNX industrial catalyst).

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