GAMMA-ALUMINA MODIFIED BY ACIDIFICATION AS AN ACIDIC CATALYST FOR PETROCHEMICAL PROCESSES

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Abstract. The catalytic efficiency of a commercial γ-Al_2O_3 as a reference heterogeneous acidic catalyst for organochemical processes and that of a γ-Al_2O_3 acidified with hydrochloric acid or with dilluted sulphuric acid is compared. The reference γ-Al_2O_3 shows the lowest activity. γ-Al_2O_3 acidified with dilluted hydrochloric acid or sulphuric acid furnishes proof of a high activity. On the other hand a catalyst acidified using hydrochloric acid needs not only to be reactivated by e. g. the burn out of the organic sediments and coke but repeatedly activated with hydrochloric acid. On the other hand a catalyst acidified with dilluted sulphuric acid can get rid off organic settlements by reactivation already. It preserves its high activity more than 2000 h that was proved both in the course of the skeletal isomerisation of n-butenes in the C4 pyrolysis residual fraction to isobutene and the dehydration of C4 alkanols conjugated by position and skeletal isomerisation of C4 alkenes as well. Using this effective catalyst a high dehydration selectivity of 1,4-butane-diol to tetrahydrofuran, arylalkylation of phenol with unsaturated dimers of alpha-methylstyrene to cumylphenol was reached. The results and possibilities of other applications of heterogeneous catalysts acidified in the above way in other organochemical processes are discussed.

Key words: gamma-alumina, acidification, hydrochloric acid, sulphuric acid, arylalkylation, dimers of alfa-methylstyrene, phenol, isomerisation, n-butenes, isobutene, 1,4-butanediol, tetrahydrofuran

Strong, mainly mineral acids have been long known [1, 2] as catalysts for organic reactions such as dehydrations, etherifications and esterifications, acetylations, alkylations, arylalkylations, isomerisations, oligomerisation particularly of alkenes and so on. Those catalysts are to be removed from the reaction products that requires another demanding technological operation. Besides there show difficulties in their further use in their disposal in a way that is not dangerous from the environment point of view. The changeover to heterogeneous catalysts, mainly in finding out the possibility to use them as acid catalysts of polyelectrolytes – cationic exchangers (in H-form) [3-5] presented an important progress. But their durability, mainly when used at higher temperatures is rather short and their regeneration is troublesome. So for the reactions requiring higher reaction temperature heterogeneous acidic catalysts based on natural and synthetic alumosilicates, mainly on zeolites [3-6] which can be applied appropriately not only in suspension, in bed, but also in treading can mean a solution. In most cases they are less active or their preparation is demanding and for this reason expensive.

We have for longer been interested in [7–12] alumina activated by various mineral acids, mainly hydrogen halides, alkylhalogenides, inorganic salts and silica compounds. This shows increased acidic properties and is suitable even for the skeletal isomerisation of alkenes at a temperature of 300 – 600 °C [12, 13]. There was also proved, while the commercial γ-Al_2O_3 has a rather low isomerisation activity in the isomerisation of n-butenes to isobutene, γ-Al_2O_3 activated with hydrochloric acid has a considerably higher activity but a low durability. Its re-

activation requires not only to use coke and carbon compounds burnt out but even a repeated „acidification" with hydrogen chloride [12, 13]. Nevertheless, γ-alumina acidified only with dilluted sulphuric acid applied for skeletal isomerisation of n-butenes at a temperature of about 450 °C the reactivation in the duration of 1 hour in 6 – 8 h intervals will do without repeated acidifications [12, 13], using dilluted sulphuric acid. There was to be expect a similar catalyst having a convenient durability will be efficient in further reactions catalysed with acids.

Experimental Section

Materials and catalysts. *α-methylstyrene dimers (from „phenol pitches", as a by-product generating in phenol production an acetone by so called cumene method), obtained from the fraction having the boiling point 160 – 195 °C/2,67 kPa and after the removal of 2-cumyl phenol by washing with aqueous NaOH with a concentration of 10 % wt. have the following composition (wt %): 2,4-diphenyl-methyl-1-pentene = 79.2 (1-DPP), trans-2,4-diphenyl-4-methyl-2-pentene = 14.9 (2-DPP); acetophenon = 0.4; α-methylstyrene = 0.1 and dimethylphenylcarbinol = 0.1.*

The residual pyrolysis C_4-fraction (after the extraction of 1, 3-butadiene and the use for production of methyl-tertiarybutylether), and so called raffinate 2 of the composition (wt %): propane = 0.3; propene = 0,22; isobutane = 6.64; n-butane = 17.82; 1-butene = 50.1; isobutene = 2.31; trans-2-butene = 14.10; cis-2-butene = 8.14; 1,3-butadiene = 0.10; C_5-hydrocarbons < 0,1. Nitrogen having the purity of 99.9 %.

n-Butanol, isobutanol, tertiary-butyl alcohol, 1,4-butanediol were of p. a. purifty. Hydrochloric acid had a concentration of 36 wt % and the sulphuric acid 100·% and nitric acid was of p. a. purity. γ-Al$_2$O$_3$ with the admixtures of 0.07 % Fe$_2$O$_3$; Na$_2$O and K$_2$O = 0.04 wt %; granulation of 3-4 mm; bulk density = 785 kg.m^{-3}; specific surface (by S$_{BEP}$) = 234 m^{2}g^{-1}, lost in burning out at 600 °C = 5,9 wt %.

Activated – acidified γ-Al$_2$O$_3$ prepared from the given γ-Al$_2$O$_3$ after its pores were released (by heating and evacuation) followed by impregnation using dilluted aqueous mineral acids or their ammonium salts similarly as in [10 and 13].

Procedure

Nitrogen in an amount of 12 cm^3 cm^{-3} h^{-1} was weighed into a reactor from heavily meltable glass including catalyst in an amount of 50 cm^3 (whereby under and over the catalyst there were 30 cm^3 of glass rings ancered on glass cotton) with an electrically heated jack, outfitted with temperature control. Then it was gradually heated to the required temperature, kept on it at a deviation of ± 2 °C. Then there was begun with the addition of the raw materials. The gas mixture was exhausted from the reactor through a water cooler and liquid separator through the gas meter, analysed by GC, and by liquid-gas chromatography [11, 15]. The other data are presented together with the results.

Results and Discussion

Table 1 compares the results of phenol arylalkylation with dimers of alpha-methylstyrene on commercial γ-Al$_2$O$_3$ (catalyst I), on γ-Al$_2$O$_3$ modified by acidification [14] using aqueous hydrochloric acid (catalyst II), with 5 wt % concentration (catalyst III), with 5 wt % concentration, as well as activated by aqueous sulphuric acid having a concentration of 0.5 wt % (catalyst IV) and with aqueous ammonium sulphate having a concentration of 0,6 wt % (catalyst V). The acidification was performed after preheating and evacuation, e. g. 50 g of γ-Al$_2$O$_3$ with 100 g of the water solutions of acids having a concentration of 5 wt %, and with 400 g of water solutions with the concentrations of the acids 0.5 wt %.

The same technological conditions were used for all catalysts : reaction temperature, injection of phenol mixtures with unsaturated dimers of alpha-methylstyrene, mol. ratio: phenol/dimers of alpha-methylstyrene = 1.46, the injection of the mixture to the catalyst: 0.16 g.cm^{-3}h^{-1} and the nitrogen flow of 12 cm^3.h^{-1}) and the time of the single experiments 4 h.

The results obtained also by liquid-gas chromatography given in Table 1 prove the commercial γ-Al$_2$O$_3$ to have the lowest efficiency.

But in short time experiments practically all the acidified catalysts showed a rather high effectivity. As already mentioned, important differences can be seen in their longer use. From the technical point of view interesting is the finding, the

Table 1. Influence of the catalyst type based on γ-Al$_2$O$_3$, and modified by acidifying the γ-Al$_2$O$_3$ for the arylalkylation of phenol with unsaturated dimers of alpha-methylstyrene to cumyl phenols

Catalyst	Temperature [^{0}C]	Conversion [%]		Selektivity to cumyl phenols [%]	
		unsaturated dimers of α-methylstyrene	of phenol	dimers of α-methylstyrene	of phenol
I.	140	3,1	0,2	9,7[a]	44,3
I.	160	4,9	0,8	41,8[a]	77,6
I.	180	6,1	1,6	61,8[a]	96,0
II.	140	39,9	11,8	89,8[a]	98,5
II.	160	45,5	16,2	92,4[a]	85,5
II.	180	75,1	17,2	68,6[a]	100
III.	140	36,6	7,9	63,2[a]	99,9
III.	160	85,2	19,2	65,7[a]	97,9
III.	180	97,6	23,1	69,1[a]	100
IV.	140	46,5	13,5	86,7[a]	99,9
IV.	160	59,6	18,7	91,5[a]	97,6
IV.	180	96,0	28,5	86,7[a]	100
V.	140	47,3	13,8	87,2	99,9
V.	160	59,9	19,1	92,1	97,9

[a] The residue in the selectivity up to 100 % of the converted unsaturated dimers is the selectivity to 1,1,3-trimethyl-3-phenylindan.

same takes place practically in one technological stage of the course as „monomerisation", it means the decomposition of unsaturated dimers of α-styrene to α-methylstyrene followed by the aralkylation of phenols to cumyl phenols:
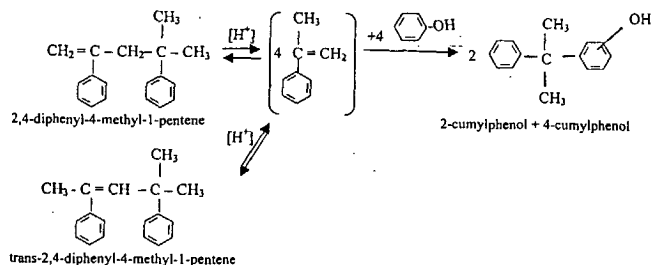
The side-reaction gives from the intermediary products generating in course of the decompo-sition of the unsaturated dimer of alfa-methylstyrene also saturated dimer 1,1,3-trime-thyl-3-phenylindan, as this mechanismus was explained in the phenyl arylalkylations carried out with α-methylstyene and its dimers over alumosilicate catalysts [15]. Figure 1 shows the results of the selective isomerisations reached on the three catalysts given and the conversion of n-butenes as well as the selectivity to isobutene.
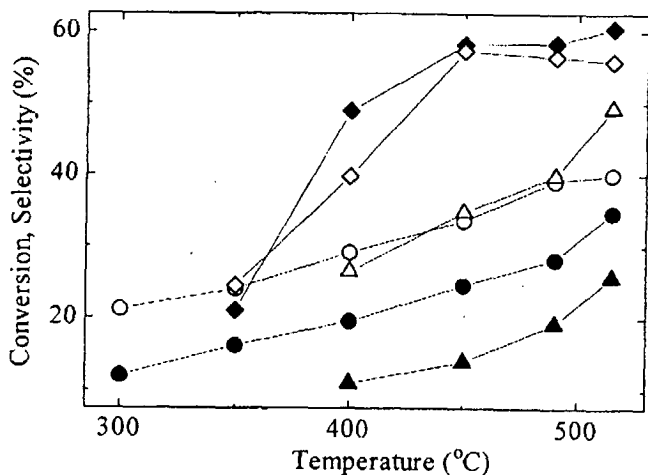

Figure 1. Conversion (full symbols) of butenes and selectivity (empty symbols) to the formation of isobutene after 1 h experiments in the skeletal isomerisation of n-butenes over the commercial γ-Al$_2$O$_3$ (catalyst I, circles), on γ-Al$_2$O$_3$ modified by acidification using aqueous hydrochlorid acid (catalyst II, up triangles), with 5 wt.% concentration, activated γ-Al$_2$O$_3$ aqueous H$_2$SO$_4$ (catalyst III, diamonds); GHSV = 1±0,07 g.cm^{-3}.h^{-1}; each experimental point was obtained over the fresh cat. after 1 h of the experiment.

Figgures 2 and 3 show the results of the durability of catalyst IV and V that is presented in the conversion of n-butenes and the selectivity to isobutene as well as further hydrocarbons as published in [16].

A long durability was observed only in case of the catalysts IV and V. The others (II and III) needed acidification besides reactivation.

We have carried out a profound search [17] of the dehydration of C$_4$ alcohols as well, conjugated by sceleton isomerisation of intermediary alkenes over inactivated γ-Al$_2$O$_3$ (Cat. I)
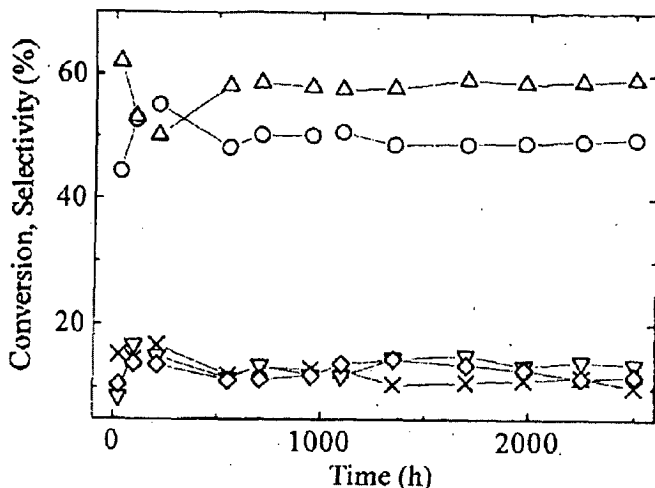

Figure 2. Conversion (circle) and selectivity to iso-butene (up triangle), C$_2$-C$_3$ hydrocarbons (down triangle), C$_5$ hydrocarbons (diamonds), and butanes (cross) over catalyst cat. **IV** (γ-Al$_2$O$_3$ activated with sulphuric acid) vs. time, after 1 h experiments fresh/reactivated catalyst at GHSW = 0,6 ± 0,05 g.cm^{-3}.h^{-1}, 450 ± 5 °C; the catalyst was reactivated with air.
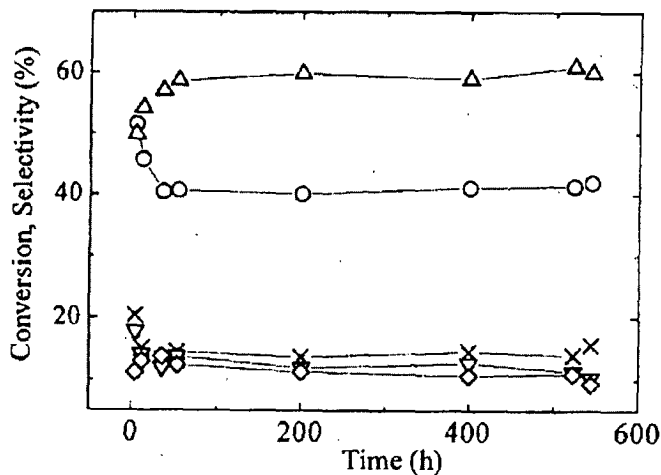

Figure 3. Conversion (circle) and selectvity to iso-butene (up triangle), C$_2$ – C$_3$ hydrocarbons (down triangle), C$_5$ hydrocarbons (diamonds), and butanes (cross) over the catalyst cat. **V** (salinised γ-Al$_2$O$_3$ with aqueous solution of ammonium sulphate having a concentration of 0,6 wt.%) vs. time after 1 h over fresh/reactivated at GHSV = 0,06 ± 0,05 g.cm^{-3}.h^{-1}, 450 ± 5 °C; the catalyst was reactivated with air.

and activated γ-Al$_2$O$_3$ (Cat. IV). The results reached are given in Table 2 and 3, the influence of the loading on catalyst IV reached at a temperature of 472 + 2 °C is shown in Figure 4.

The results show not only the dehydratation of butanols, but the sceletal isomerisation of intermediary alkenes and an approchment to thermodyamical equilibrium values that we devoted greater attention to [17].

It was found, at such a high temperature commercial alumina (catalyst I) is effective enough even if the isomerisation rate is higher with catalyst II.

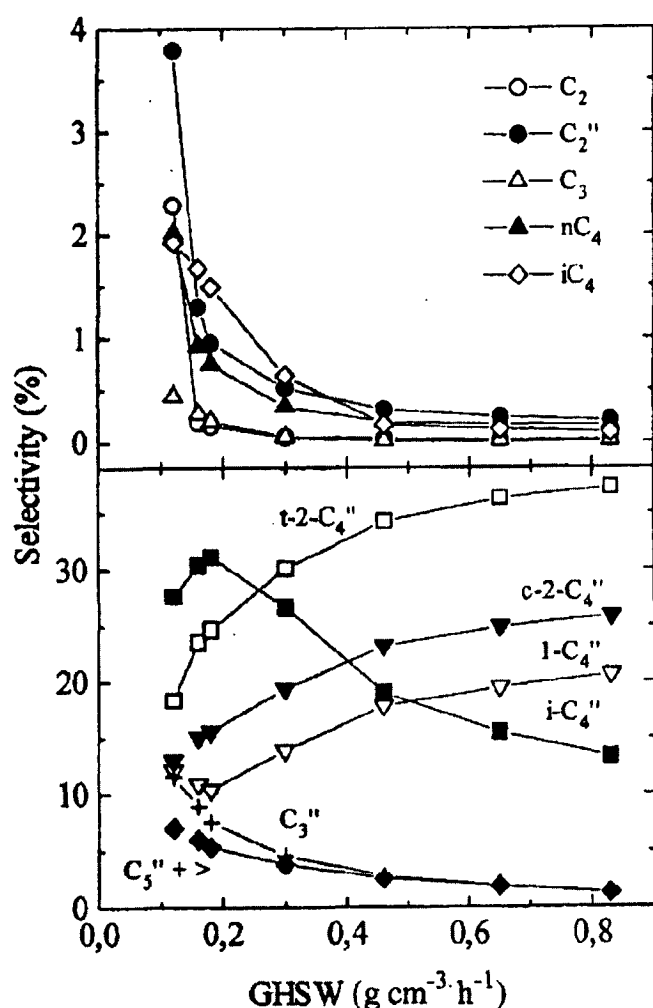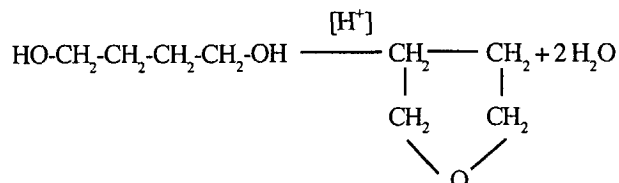The comparison od the dehydration of 1,4-butane diol on tetrahydrofuran if of impotance

Figure 4. Effect of loading (GHSW) in the total dehydratation of n-butanol accompanied by the isomerisation and other reactions (acidified γ-Al$_2$O$_3$: the catalyst IV: atmosferic pressure; T = 472 ± 2 °C).

$$HO\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}OH \xrightarrow{[H^+]} \begin{array}{c} CH_2 \underline{\quad\quad} CH_2 + 2\,H_2O \\ | \qquad\qquad | \\ CH_2 \qquad CH_2 \\ \diagdown \quad \diagup \\ O \end{array}$$

over three different solid acidic catalysts is of importance too, that is on cation exchanger in H-form (Amberlyst 36), commercial γ-Al$_2$O$_3$ (cat. I) and over an acidified catalyst (IV). The reaction conditions and results reached are given in Tab. 3.

A higher activity of catalyst IV in comparison to I enables to use a lower temperature in the course of the dehydration at a positive influence on the selectivity increase or the efficiency of the dehydration reactor.

It was similarly found, the increase of the activity of other catalysts is possible, not only with γ-Al$_2$O$_3$ but with aluminosilicates as well, which,when activated in this way, can be more efficient at the catalytic cracking of vacuum distillates of rude oil and other catalysed processes catalysed by solid acids. The palette of efficient catalysts available technically and from the expensivity point of view, besides zeolites of different structures [7], ZrO$_2$/SiO$_2$ and others [8] can be enlarged.

Conclusions

The results presented as well as further our works cited are to prove the convenience of an essential increase of the acidity of γ-Al$_2$O$_3$ via acidification with dilluted sulphuric acid, and ammonium sulphate respectively. Such an acidification in comparison to the acidification when using halogenes, and hydrogen halides respectively, shows a distinguished stability enabling a long durability of such an acidic catalyst. The acidification process presenting good results can be used for the acidification of other solid catalysts on aluminosilicate and on aluminosilicato-metallic basis as well.

Table 2. Selectivities to products in the dehydration of butanols accompanied with the isomerisation and other transformation reactions (GHSV = 0,18 ± 0,02 gcm^{-3}h^{-1}).

Entry	Catalyst	T[°C]	C$_4$OH[a]	Selectivity [%]											
				1-C$_4$"	c-2-C$_4$"	t-2-C$_4$"	i-C$_4$"	CH$_4$	C$_2$	C$_2$"	C$_3$	C$_3$"	n-C$_4$	i-C$_4$	≥C$_5$
1	I.	400	n	21,4	26,7	40,5	7,4	0,1	0,07	0,5	0,02	1,33	0,42	0,05	1,1
2	IV.	400	n	16,4	16,4	19,9	18,2	0,3	0,39	0,21	0,21	6,12	0,93	0,93	6,7
3	I.	474	n	15,9	16,3	22,8	27,4	0,7	0,48	0,18	0,18	7,01	0,89	0,89	3,2
4	IV.	472	n	12,1	12,9	18,3	31,1	0,9	1,90	0,37	0,37	9,60	2,01	2,01	6,1
5	I.	400	2	21,1	25,0	36,7	14,4	0,2	0,01	0,20	0,01	1,21	0,20	0,08	1,1
6	IV.	400	2	14,3	16,1	26,3	31,8	0,6	0,06	0,44	0,39	3,59	0,24	0,09	4,5
7	I.	471	2	16,6	16,5	23,3	30,2	0,4	0,17	0,83	0,08	6,52	0,53	0,94	3,4
8	IV.	471	2	10,8	15,3	23,5	33,3	0,8	0,08	0,66	0,67	7,61	0,31	0,91	6,8
9	I.	400	i	14,3	15,6	23,5	40,1	0,2	0,01	0,10	0,01	0,13	0,33	0,12	1,8
10	IV.	400	i	13,4	14,5	22,9	39,9	0,5	0,03	0,29	0,06	3,91	0,08	0,14	3,3
11	I.	470	i	12,9	13,4	18,4	39,8	0,5	0,16	0,52	0,11	5,98	0,25	1,64	5,4
12	IV.	472	i	10,3	14,5	21,7	38,7	0,9	0,05	0,36	0,06	5,83	0,16	0,16	6,9
13	I.	400	t	4,1	4,9	7,0	81,1	0,3	0,01	0,02	0,02	0,24	0,07	1,32	1,1
14	IV.	400	t	5,6	6,7	9,7	75,3	0,5	0,00	0,03	0,02	1,93	0,00	0,29	0,8
15	I.	470	t	12,9	13,9	15,2	41,6	0,8	0,07	0,06	0,6	5,36	0,11	1,35	5,5
16	IV.	470	t	13,5	15,0	22,4	33,4	0,8	0,04	0,30	0,05	6,60	0,32	1,39	6,0

Table 3. Dehydration of 1,4-butane diol over three different solid acidic catalysts

Catalyst	Reaction temperature of the dehydration (±2°C) [°C]	GHSW [g.cm-3.h-1] with 1,4-butanediol [%]	Conversion of the 1,4-butandiole [%]	Selektivity to tetrahydrofuran [%]
Cation exchanger resin in H-form	96	0,32	100	99,5-99,8
. (CHEROX 3300)	250	1,0	99,0	99,1-99,6
IV.	220	1,0	99,4-99,6	99,6-99,8

We are ready to reveal further concrete data needed for successful use in organochemical processes to interested parties in case of earnest interest.

References

[1] Berkman S., Marrtell J. C., Engloff G.: Catalysis Inorganic and Oganic. Book Department Reinhold Publishing Corporation (1940), Russian translation: Kataliz v neorganičeskoj i organičeskoj chimii. Gosudarstvennoe naučno-techničeskoe izdateľstvo neftjanoj i gorno-toplivnoj literatury, Moskva – Leningrad (1949).

[2] Cram D. J., Hammond G. S.: Organic Chemistry, Seconf Edit. McGraw-Hill Book Company, New York-SanFrancisco-Toronto-London (1964).

[3] [Mitsui Toatsu Chem. Inc.]: Jap. Pat. 57-188 535 (1981).

[4] Ejnochi Z., Jaromirska M., Dziedzic C.: Przem. Chemicz. 62 (7), 395 (1983).

[5] Zieboriak K., Ratajczak W., Kowalska H.: Polish Pat., 100 643 (1976) and 110 645 (1978)

[6] Macho V., Jureček Ľ., Morávek Š.: Ropa a uhlie 29, 504 (1987).

[7] Rohrer J. C., Sinfelt J. H..: J. Phys. Chem. 66, 2070 (1962).

[8] Pismann I. I., Ninalalov I. I., Dalin M. A.: Azerbajdž. Chim. Žur. 1965, No. 1, 69.

[9] Otromba M., Zaideľ V., Taniewski M.: Neftechimija 20, 659 (1980).

[10] Macho V., Jureček Ľ., Jurečeková E., Ivančaiová A., Hudec P.: Ropa uhlie 33 (7), 413 (1991).

[11] Macho V., Jurečekova E., Jureček Ľ., Komora L., Kupec P., Kavala M., Kezl P., Ecker A., Weinstabl H.: Austrian Patent 400 951 B (1995).

[12] Macho V., Jureček Ľ., Jurečeková E., Komora L., Kavala M.: SK Patent 280 789 (2000); Appl.: 27 07 1992.

[13] Macho V., Králik M., Jureček Ľ., Jurečeková E., Balážová J.: Appl. Catal. A.: General 203, 5 (2000).

[14] Macho V., Jureček Ľ., Komora L., Dérer T., Jurečeková E., Komorová E.: Registered Utility Models: SK 1726 (1997).

[15] Jureček Ľ., Macho V., Králik M., Kaszonyi A.: Chem. Prumysl 39/64 (5), 240 (1989).

[16] Macho V., Králik M., Jurečeková E., Hudec J., Jureček Ľ.: Appl. Catal. 214, 251 (2001).

[17] Narayanan S., Murphy K. V.: Appl. Catal. A.: General 213, 273 (2001).

[18] Zhuang Q., Miller J. M.: J. Appl. Catal. A.: General 209, L-1 (2001).