PORÓWNANIE ZASTOSOWANIA KATALIZATORA ŻELAZOWO-CHROMOWEGO W C-ALKILACJI FENOLU I REAKCJACH KONDENSACJI N-BUTANOLU. MOŻLIWOŚĆ ZASTOSOWANIA NOŚNIKÓW WĘGLOWYCH

COMPARATIVE USE OF IRON-CHROMIUM CATALYST IN C- ALKYLATION OF PHENOL AND CONDENSATION REACTIONS OF N-BUTANOL. THE APPLICABILITY OF CARBON SUPPORTS

Roman Klimkiewicz - Instytut Niskich Temperatur i Badań Strukturalnych PAN, Wrocław, Institute of Low Temperature and Structure Research, PAS, Wrocław
Stefan Szarlik - Instytut Chemii Przemysłowej, Warszawa, Industrial Chemistry Research Institute, Warsaw

Skonfrontowano wydajności katalizatorów żelazowo-chromowych w alkilacji fenolu i w dwucząsteczkowej kondensacji n-butanolu w zależności od zawartości żelaza. W obu przypadkach wyższą wydajność pożądanych produktów uzyskano w procesach z katalizatorem o niższej zawartości tlenku żelaza (III). Materiały o zbliżonym składzie są także katalizatorami wysokotemperaturowej konwersji tlenku węgla parą wodną, w tym katalizatorami z zastosowaniem nośników węglowych.

Słowa kluczowe: *katalizator żelazowo-chromowy, nośniki węglowe, porównanie zastosowania*

The efficiency of iron-chromium catalysts in alkylation of phenol and in bimolecular condensation of n-butanol was compared depending on the iron content. In both cases, higher yields of the desired products were obtained in the process on the catalyst with a lower iron oxide (III) content. Materials with similar composition are also used as catalysts for high-temperature water-gas (CO) shift reaction, including catalysts on carbon supports.

Keywords: *iron-chromium catalyst, carbon supports, comparative use*

Catalytic supports are used to expand the surface area of a catalyst and usually they do not participate in the process of accelerating a reaction. In the case of non-oxidative chemical processes, carbonaceous materials can be used as catalyst supports. An example is the dehydrogenation of alcohols, therefore also bio-alcohols. The use of activated carbons obtained from lignite in such conditions gave a positive result [1]. Thus, efficient, ie. active and selective towards dehydrogenation and possible secondary reactions, metal oxide catalysts deposited on carbon supports predict high conversion yields.

Alkylation of phenol with primary alcohols is an industrially important reaction. C-methylation of phenol in the gas phase in the presence of a suitable catalyst is performed for obtaining ortho-cresol, 2,6-xylenol and many other alkylated phenols for further production of chemicals such as emulsifiers, plastics, dyes, flavoring agents, agrochemicals, pharmaceuticals, and especially non-ionic detergents and antioxidants in the plastics industry.

Various catalysts for gas-phase phenol alkylation have been reported in the literature. The first attempts at alkylation of phenol with methanol in the gas phase were carried out in the presence of a fixed bed catalysts consisting essentially of alumina. Unsatisfactory selectivity was the reason for the search for new solutions. In the search for a catalyst that will provide high selectivity and

yield of the alkylation reaction a number of solid catalysts was tested [2]. The best results in the methylation of phenol were obtained using catalysts based on iron oxide. Among them are mixed oxides - especially containing iron and chromium oxides [3, 4, 5]. Also the catalyst for high-temperature shift reaction [6] proved to be efficient in the alkylation [7-11].

A number of determinant factors with respect to results of alkylation were investigated [12, 13]. One of the research areas was the course of side reactions of methanol during the methylation. The accompanying transformations were analyzed, concerning formation of formaldehyde and it's consecutive Cannizzaro-like and Tishchenko-like reactions as well as CO elimination [14]. During the alkylation of phenol with primary alcohols higher than methanol simultaneous competitive reactions can occur. This is so because, as a result of dehydrogenation of primary alcohols, aldehydes and, consequently, esters are created (the Tishchenko reaction) while bimolecular condensation with CO elimination gives symmetrical ketones with 2n-1 carbon atoms [15].

Thus, catalysts for alkylation of hydroxyarenes with primary alcohols are characterized by similar properties as catalysts for the purposeful transformation of these alcohols to higher molecular products. There are examples of successful application of such

alkylation catalysts in the role of selective and efficient ketonization catalysts [16] as well as vice versa, i.e. the use of catalysts for bimolecular condensation of alcohols as effective catalysts for alkylation of hydroxyarenes with primary alcohols [17].

Catalysts comprising mixtures of oxides of iron, chromium, antimony, vanadium and silicon, as described in the patent PL 105922 [3], are very effective in the alkylation of phenol. Change in the composition of the catalyst obviously influence the alkylation results, but it turned out that an increase in amounts of iron oxide did not improve the yield [9].

It is therefore appropriate to confront these findings with the results of a primary alcohol transformations in the absence of phenol on these kind of catalysts. Furthermore, our intention was to verify the applicability of these materials as catalysts for primary alcohols dehydrogenation with consecutive bimolecular condensation reactions, including the influence of their content, thus the surface properties, on these results.

Justification of studies of catalytic transformation of alcohols is also an increasing interest in the synthesis gas chemistry, and hence, also in one of the potential directions of its use - obtaining oxygenates. Synthesis gas, also produced from non-petrochemical raw materials, including coal [18], is used as feedstock for a number of chemical syntheses such as Fischer - Tropsch process, whereby it is possible to obtain organic oxygenates [19] , especially alcohols [20], which may be starting materials for deeper transformations.

In contrast to ketonization of secondary alcohols and dehydrogenation of primary alcohols to aldehydes, the subsequent ketonization of primary alcohols is not a frequent topic of publications. Depending on reaction conditions, the bulk transformations scheme is shown in different ways [21]. Apart from aldehydes and ketones, esters can also be products (Tishchenko reaction). A related reaction, much more often reported, is ketonization carboxylic of acids. Thus, the raw material for ketonization may be alcohols, aldehydes, esters and carboxylic acids. Implementation of this process allows to obtain a series of oxygenates, in that, when using mixtures of primary alcohols or other combination of said raw materials, to obtain unsymmetrical ketones [16, 22]. This process allows the use of wastes containing those components or mixtures thereof [23, 24].

EXPERIMENTAL PART

Catalysts

In order to check the impact of changes in the composition, two variants of the iron-chromium catalyst („Fe1" and „Fe2") were used: the catalyst „Fe1" with a Fe_2O_3 content of 77 wt.% and the catalyst „Fe2" with a Fe_2O_3 content of 86 wt.%. The other ingredients are Cr_2O_3 (7 - 16%), CrO_3 and CuO. X-ray powder diffraction (X'Pert Pro PANalitycal) was used to characterize the resulting powders before and after catalytic tests.

Experimental conditions of the catalytic tests

Catalytic transformation of bio n-butanol (Jiangsu Lianhai Biological Technology Co., Ltd., 99,9%) was chosen as the test reaction. The experiments were performed in a quartz continuous-downflow reactor at atmospheric pressure. The reactor was placed in a Thermolyne F21100 vertical pipe furnace. The fixed bed contained 3 cm³ of a catalyst of 0.6−1.2 mm granulation. The substrate was fed in a continuous manner, starting from 200 °C, with the use of a Medipan 610-2 dosing pump at a flow

ratio from 3 up to 12 cm³ of liquid/h. No carrier gas was used. The products of the reaction collected in the temperature range of 200−400°C were analyzed with the use of a INCO N-505 gas chromatograph.

DISCUSSION OF RESULTS

Conversion, selectivity and yield dependences on temperature (Tables 1 and 2)

Both catalysts exhibit high activity towards dehydrogenation, high selectivity to consecutive ketonization, therefore high yield of dipropyl ketone (heptanone-4). At higher temperatures there is a slowdown in conversion growth or even its apparent decrease due to secondary hydrogenation of aldehyde. In comparison to other ketonization catalysts previously tested under the experimental conditions, on the „Fe1" and „Fe2" catalysts comparable yields were obtained in the temperature range up to several dozen degrees lower.

When comparing the „Fe1" and „Fe2" catalysts between each other, the results of temperature dependence indicate that the catalyst „Fe1" is more active and also more selective towards ketones. As a result, significantly higher ketone yields are obtained on „Fe1".

The comparison of selectivity to butyraldehyde refers only to non-converted aldehyde into ester and ketone. This selectivity is higher on the „Fe1" catalyst, whereas the yield of butyraldehyde is higher at lower temperatures on the more active „Fe1" catalyst, and at higher temperatures on the less selective to ketone „Fe 2" catalyst. Slight selectivity to butyl butyrate and the yield of this ester are similar on both catalysts.

Conversion, selectivity and yield dependence on load (contact time) (Table 3)

It can be assumed that the differences between catalysts „Fe1" and „Fe2" at load of 1.0 h−1 are not very large (Tables 1 and 2). Raising the temperature about 20 - 40 degrees brings the results values obtained over the „Fe2"catalyst closer to those obtained for the „Fe1"catalyst. Next change of control parameters, namely contact time (load), much more differentiates the compared catalysts. The „Fe1" catalyst is much more resistant to changes in this parameter. The „Fe2" catalyst significantly loses its activity after the load increase (contact time reduction). Conversion values on both catalysts at 400°C and 1h⁻¹ are similar, and at 4h⁻¹ the conversion on „Fe2" is already lower by half.

With the increase in load, decrease in selectivity to the ketone occurs on both catalysts, wherein the differences in selectivity values (higher on „Fe1") are maintained up to 3h-1. Lower conversion and ketone selectivity values at shorter contact times cause decrease in dipropyl ketone yield values. This reduction is much greater in the case of the catalyst „Fe2". Moreover, increasing the catalyst load causes growth of the selectivity to unconverted aldehyde, more pronounced for „Fe2". Because trends in conversion value changes and trends in selectivity value changes are opposite, this is the cause of similar minor changes in the butyraldehyde yield values.

On both catalysts, increase in load results, despite lower conversion values, in increase in the yield of butyl butyrate. This is due to growth of selectivity to ester at the expense of ketone. These changes may occur either as a result of the intermediate position of the ester in the transformation scheme: n-alcohol → aldehyde → ester → ketone, then too short contact time does not allow for complete conversion ester → ketone (analogously

to aldehyde), or, when the ester is a product formed in parallel with the ketone, then the short contact time does not favor the secondary thermal decomposition of the ester to aldehyde. This is so called reverse - Tishchenko, or retro - Tishchenko reaction: ester → aldehyde.

The color of the liquid products obtained using the „Fe2"

catalyst is significantly darker than that obtained with the "Fe1" catalyst, which additionally confirms a greater share of secondary reactions.

As has already been observed [16, 17], materials that catalyze dehydrogenation and subsequent bimolecular condensation reactions of primary alcohols are characterized by

Tab. 1. Results of conversion of n-butanol on „Fe1"catalyst as a function of temperature at LHSV 1.0 h⁻¹
Tab. 1. Wyniki konwersji n-butanolu na katalizatorze „Fe1" w funkcji temperatury przy LHSV 1,0 h⁻¹

temp.	conversion	selectivity [%]						yield [%]					
[°C]	[%]	butyraldehyde	heptanone–4	butyl butyrate	butene	di-n-butyl ether	others	butyraldehyde	heptanone–4	butyl butyrate	butene	di-n-butyl ether	others
200	4	100	-	-	-	-	-	4	-	-	-	-	-
220	5	100	-	-	-	-	-	5	-	-	-	-	-
240	7	98	-	-	-	-	2	7	-	-	-	-	traces
260	10	98	-	-	-	-	2	10	-	-	-	-	traces
280	16	96	-	-	-	-	4	15	-	-	-	-	1
300	26	92	-	2	-	-	6	24	-	traces	-	-	2
320	37	73	11	11	-	-	5	27	4	4	-	-	2
340	50	50	26	16	2	-	6	25	13	8	1	-	3
360	81	17	64	9	4	-	6	14	52	7	3	-	5
380	93	9	72	2	6	3	8	8	67	2	6	3	7
400	89	7	71	-	8	7	8	6	63	-	7	6	7

Tab. 2. Results of conversion of n-butanol on „Fe2"catalyst as a function of temperature at LHSV 1.0 h⁻¹
Tab. 2. Wyniki konwersji n-butanolu na katalizatorze „Fe2" w funkcji temperatury przy LHSV 1,0 h⁻¹

temp.	conversion	selectivity [%]						yield [%]					
[°C]	[%]	butyraldehyde	heptanone–4	butyl butyrate	butene	di-n-butyl ether	others	butyraldehyde	heptanone–4	butyl butyrate	butene	di-n-butyl ether	others
200	2	100	-	-	-	-	-	2	-	-	-	-	-
220	3	98	-	-	-	-	2	3	-	-	-	-	traces
240	4	96	-	-	-	-	4	4	-	-	-	-	traces
260	7	96	-	-	-	-	4	7	-	-	-	-	traces
280	12	94	-	-	-	-	6	11	-	-	-	-	1
300	19	90	-	4	-	-	6	17	-	1	-	-	1
320	29	76	5	13	-	-	6	22	1	4	-	-	2
340	42	58	14	18	2	-	8	24	6	8	1	-	3
360	68	32	42	9	4	5	8	22	29	6	3	3	5
380	83	17	56	1	6	10	10	14	46	1	5	8	8
400	91	11	58	-	10	8	13	10	53	-	9	7	12

Tab. 3. Results of conversion of n-butanol as a function of contact time (load of the catalyst bed) at 400ºC
Tab. 3. Wyniki konwersji n-butanolu w funkcji czasu kontaktu (obciążenie złoża katalizatora) w 400ºC

catalyst	LHSV	conversion	selectivity [%]						yield [%]					
			butyraldehyde	heptanone-4	butyl butyrate	butene	di-n-butyl ether	others	butyraldehyde	heptanone-4	butyl butyrate	butene	di-n-butyl ether	others
	[h⁻¹]	[%]												
„Fe1"	1	89	7	71	-	7	7	8	6	63	-	7	6	7
	2	91	9	66	4	5	8	8	8	60	4	5	7	7
	3	82	15	59	10	5	6	5	12	48	8	4	5	4
	4	61	27	49	16	3	3	2	16	30	10	2	2	1
"Fe2"	1	91	11	58	-	10	8	13	10	53	-	9	7	12
	2	82	17	55	3	9	6	10	14	45	2	7	5	8
	3	64	24	46	10	6	6	8	15	29	6	4	4	5
	4	33	37	21	24	5	6	7	12	7	8	2	2	2

specific properties that coincide with the features of catalysts for alkylation of hydroxyarenes with alcohols. Catalysts „Fe1" and „Fe2" for the methylation of phenol also proved to be very good catalysts for the transformation of n-butanol. The differences in selectivity and yield of the desired products suggest that changes in the composition of the catalyst „Fe2" with

respect to catalyst „Fe1" worsened its properties in relation to the ketonization reaction. This observation is consistent with the analogous comparison of the activity of such differentiated catalysts during alkylation reaction [9]. Both materials were not destroyed during the catalytic tests in the high-temperature regime under reducing conditions and in the presence of oxygen
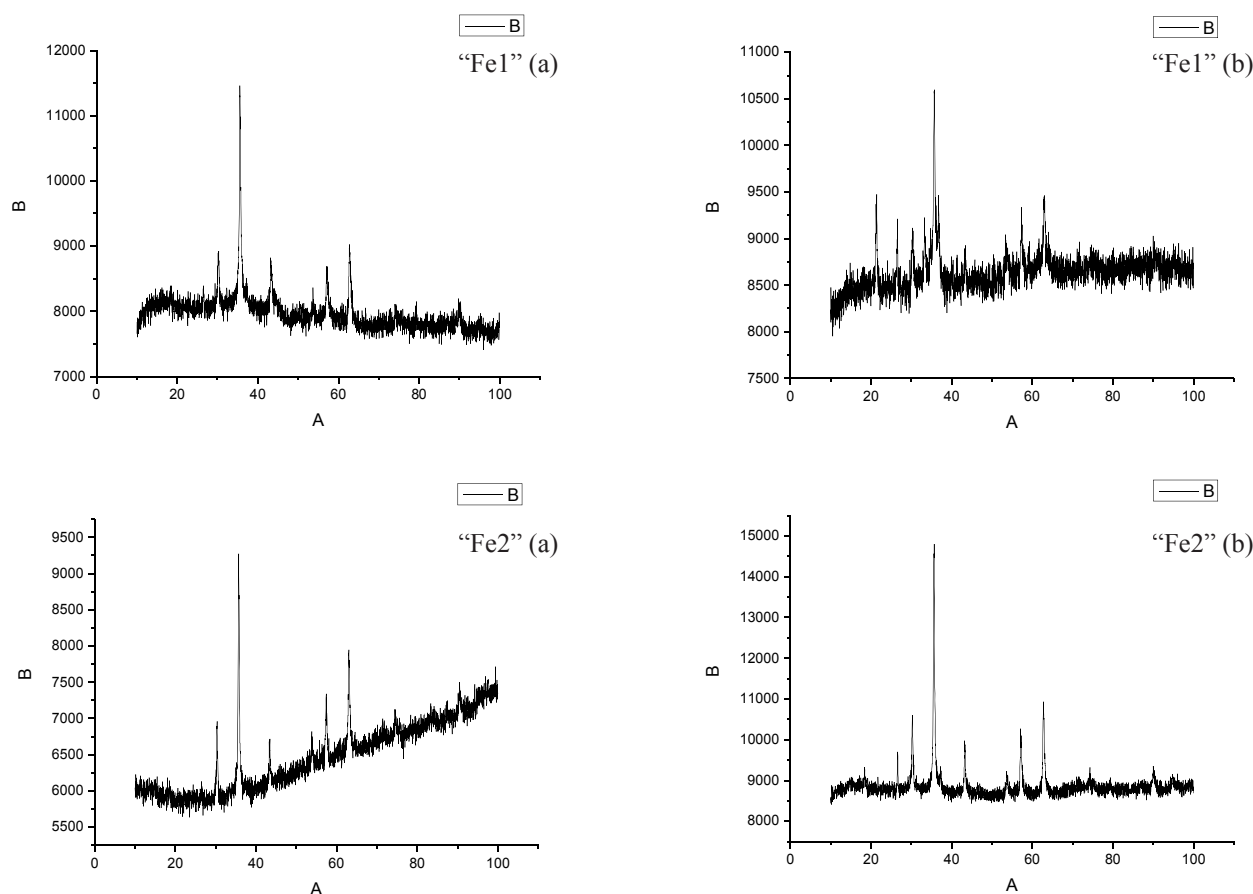

Fig. 1. X-ray diffraction patterns of the "Fe1" and "Fe2" iron-chromium catalysts before (a) and after (b) catalytic tests
Rys. 1. Dyfraktogramy rentgenowskie katalizatorów żelazowo-chromowych „Fe1" i „Fe2" przed (a) i po (b) testach katalitycznych

containing compounds (Fig. 1). These observations encourage the consideration of the option of supporting these oxide systems on carbonaceous materials [25]. A positive example of such carbonaceous supports for this type of catalysts is the iron catalyst for high-temperature water-gas (CO) shift reaction deposited on the carbon support [26].

References/Literatura

[1]   Klimkiewicz R., *Katalityczne właściwości węgli aktywnych otrzymanych z węgla brunatnego.* Górnictwo Odkrywkowe 51/1 2010

[2]   Niu L., Li Z., Jiang F., Zhou M., Wang Z., Xiao G., *Preparation, characterization and use of K_2O, Al_2O_3 and SiO_2 modified iron oxide as catalyst for the vapor phase synthesis of 2,3,6-trimethylphenol from m-cresol and methanol.* React. Kinet. Mech. Cat. 112 2014

[3]   Biały J., Penczek I., Kopytowska N., Wrzyszcz J., Kulak S., *Sposób wytwarzania dwu- i/lub jednoortometylowej pochodnej fenolu.* Polish Patent 105922 1978

[4]   Ito M., *Method for alkylation of phenols, and catalyst therefor.* Patent EP 0419045 A1 1990

[5]   Szarlik S., Łysik P., Górska A., Krakowiak J., Wielgosz Z., Stasiński J., *Sposób wytwarzania 2,6-dimetylofenolu,* Polish Patent 227248 2015

[6]   Śpiewak Z., Gołębiowski A., Kruk J., Stołecki K., Baran P., *Katalizator TZC-3/1 do wysokotemperaturowej konwersji tlenku węgla.* Przem. Chem. 86/5 2007

[7]   Żukowski W., Berkowicz G., Baron J., Kandefer S., Jamanek D., Szarlik S., Wielgosz Z., Zielecka M., S*elective phenol methylation to 2,6-dimethylphenol in a fluidized bed of iron-chromium mixed oxide catalyst with o–cresol circulation.* Chem. Cent. J. 8:51 2014

[8]   Łysik P., Górska A., Szarlik S., *Gas-phase methylation of phenol over iron−chromium catalyst.* Ind. Eng. Chem. Res. 53 2014

[9]   Łysik P., Górska A., Szarlik S., *Synthesis of 2,6-dimethylphenol by alkylation of phenol with methanol in gas-phase over iron catalyst.* Przem. Chem. 92/5 2013

[10]   Baron J., Berkowicz G., Zukowski W., Kandefer S., Szarlik S., Zielecka M., Wielgosz Z., Jamanek D., *Synthesis of 2,6-dimethylphenol in a catalytic fluidized bed of industrial iron-chromium catalyst.* Przem. Chem. 92/5 2013

[11]   Berkowicz G., Zukowski W., Baron J., *Effect of temperature on o-cresol methylation in a fluidized bed of commercial iron-chromium catalyst TZC-3/1.* Pol. J. Chem. Technol. 15/3 2013

[12]   Grabowska H., Klimkiewicz R., Tylus W., Godowski P.J., *A search for reason for deactivation of alkylation iron catalyst.* Appl. Catal. A, Gen. 240/1-2 2003

[13]   Dmytrzyk J., Kotarba A., Grabowska H., Klimkiewicz R., *Changes in surface composition of Fe-Si-Cr-K oxide alkylation catalyst: the marked role of potassium ferrites.* Res. Chem. Intermed. 30/3 2004

[14]   Crocellà V., Cerrato G., Magnacca G., Morterra C., Cavani F., Maselli L., Passeri S., *Gas-phase phenol methylation over Mg/Me/O (Me = Al, Cr, Fe) catalysts: mechanistic implications due to different acid-base and dehydrogenating properties.* Dalton Trans. 39 2010

[15]   Klimkiewicz R., *Primary alcohols, aldehydes and ester transformations into ketones over oxide catalysts.* Pol. J. Environ. Stud. 17 2008

[16]   Grabowska H., Klimkiewicz R., Syper L., Wrzyszcz J., *The catalytic condensation of ω-phenyl-substituted alcohols in the presence of an iron oxide.* Res. Chem. Intermed. 26/4 2000

[17]   Klimkiewicz R., Grabowska H., Teterycz H., *Sn–Ce–Rh–O monophase system as a new type of ortho-selective catalyst for phenol alkylation.* Appl. Catal. A, Gen. 2461 2003

[18]   Rzepa S., Marek A., *Problemy usuwania zanieczyszczeń w technologii podziemnego zgazowania węgla brunatnego - badania, koncepcja rozwiązania.* Górnictwo Odkrywkowe 51/6 2010

[19]   Klimkiewicz R., *Możliwości pozyskiwania organicznych związków tlenowych w wyniku zgazowania węgla.* Górnictwo Odkrywkowe 55/1 2014

[20]   Kulawska M., *Synteza małocząsteczkowych alkoholi alifatycznych z gazu syntezowego.* Przem. Chem. 79/12 2000

[21]   Kumar R., Enjamuri N., Shah S., Sadeq Al-Fatesh A., Bravo-Suárez J.J., Chowdhury B., *Ketonization of oxygenated hydrocarbons on metal oxide based catalysts.* Catalysis Today, 2017, In Press, https://doi.org/10.1016/j.cattod.2017.09.044

[22]   Klimkiewicz R., Grabowska H., Syper L., *Metameric esters ketonization in the vapor phase over solid catalyst,* Res. Chem. Intermed. 29/1 2003

[23]   Gaertner C.A., Serrano-Ruiz J.C., Braden D.J., Dumesic J.A., *Ketonization reactions of carboxylic acids and esters over ceria-zirconia as biomass-upgrading processes,* Ind. Eng. Chem. Res. 49 2010

[24]   Klimkiewicz R., Morawski I., Trawczyński J., *Catalytic conversion of C12–C14 primary alcohols mixture into long-chain ketones,* Catal. Commun. 11 2010

[25]   Rzepa S., *Możliwości wykorzystania węgla brunatnego poza energetyką.* Górnictwo Odkrywkowe 45/6 2003

[26]   Jedynak A., Kowalczyk Z., Sentek J., Stołecki K., Pielaszek J., *Osadzony na węglu żelazowy katalizator wysokotemperaturowej konwersji tlenku węgla parą wodną.* Przem. Chem. 9 2001