https://doi.org/10.18321/cpc442

One-stage synthesis of 1,1-diethoxyethane from ethanol using copper-containing catalysts

M.M. Mambetova[1,3]*, K. Dossumov[1,2], G.E. Ergaziyeva[1,2], M.M. Anissova[2], B.B. Baizhomartov[1]

[1]al-Farabi Kazakh National University, Center of Physical Chemical Methods of Research and Analysis, 96 Tole bi str., Almaty, Kazakhstan
[2]Institute of Combustion Problems, 172 Bogenbay batyr str., Almaty, Kazakhstan
[3]Kazakh national women's teacher training university, 114 Gogol str., Almaty, Kazakhstan

ABSTRACT

The conversion of ethanol on low-percentage copper-containing catalysts at temperatures of 300 °C and 350 °C was studied. γ-Al_2O_3, SiO_2 and HZSM-5 were studied as the carrier of the active phase. It is shown that the main direction of ethanol conversion on low-percentage copper-containing catalysts is its dehydrogenation and subsequent conversion of the resulting products into 1,1-diethoxyethane. Among the studied catalysts (1 wt.% CuO/Al_2O_3, 1 wt.% CuO/SiO_2 and 1 wt.% CuO/ HZSM-5 the most active in the production of 1,1-diethoxyethane was 1 wt.% CuO/Al_2O_3, modification of it with cerium oxide led to an increase in its activity in the formation of 1,1-diethoxyethane, at the reaction temperature of 350 °C, the yield of the target product was 27 vol.%. The results showed that the modification of CuO/Al_2O_3 leads to an increase in the catalytic activity of the sample.

Keywords: 1,1-diethoxyethane, ethanol, catalyst, carrier, the method of preparation.

1. Introduction

Due to the growing demand for energy and concerns about climate change around the world, it is very important to use renewable biomass and its derivatives for the production of chemicals and fuels, which today mainly depend on fossil resources. One such example is bioethanol. It is widely available due to the fermentation of biomass and, in particular, cellulose residues [1,2], and has become a universal raw material for the synthesis of a wide range of chemicals with high added value: acetaldehyde [3], ethyl acetate [4], ethylene oxide [5], 1-butanol [6], isobutene [7] and 1,1-diethoxyethane [8-10].

1,1-Diethoxyethane (DEE), also called diethyl acetal, is an important chemical intermediate. It is used as a precursor in the synthesis of pharmaceuticals and perfumes [11], as well as polyacetal resins and alkylvinyl ethers[12]. It can also be used as an oxygenated additive of diesel fuel [13]. The possibility of synthesizing diethoxyethane based on renewable raw materials-ethanol, which has wide resources, determines the topical of this direction.

DEE is mainly formed by the interaction of acetaldehyde with ethanol.Carboxylic acids are used as catalysts [11, 14]. The disadvantages of this method are associated with the direct use of acetaldehyde, since it is toxic when stored for a long time, and it easily turns into a paraldehyde.

In order to avoid the direct use of acetaldehyde as a starting material and to increase the efficiency of the DEE synthesis, recent efforts have focused on the single-stage oxidation of ethanol in DEE, including the oxidation dehydrogenation of ethanol into acetaldehyde and its subsequent acetalisation with ethanol.

This paper presents the results of direct production of 1,1-diethoxyethane from ethanol using low-percentage catalysts based on copper oxide. The influence of the nature of the carrier on the activity of the copper catalyst in the conversion of ethanol is shown.

*Ответственный автор
E-mail: mambetova_manshuk@list.ru(М. Мамбетова)

2. Experimental part

Thermoconversion of ethanol was studied in a laboratory installation of the flow type (Fig. 1). Direct production of 1,1-dietoxyethane (DEE) from ethanol was carried out by passing a vapor-like ethanol through a reactor (2) with a heterogeneous solid catalyst (3) based on copper.

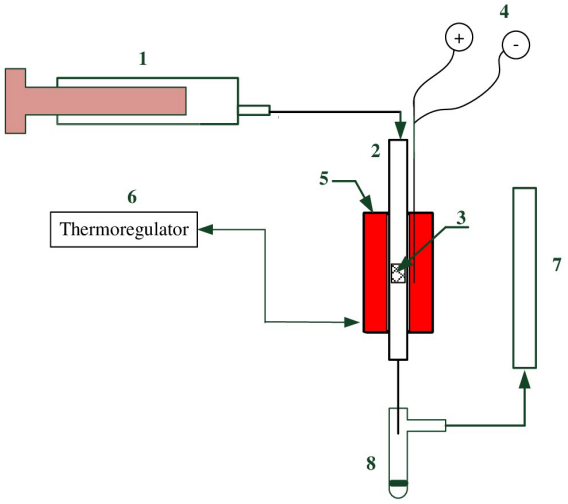

Fig. 1. Flow-through catalytic plant: 1 – ethanol dispenser, 2 – reactor, 3 – catalyst, 4 – reactor thermocouple, 5 – furnace, 6 – thermoregulator, 7 – rheometer; 8 – collection of liquid fractions.

The temperature of the reactor is regulated by a thermostat (6). Ethanol was fed into the reactor using a dispenser (1). Determination of the concentration of the starting reagents and analysis of the reaction products were carried out on a chromatograph (GC-1000 LLC «Chromos» Russia).

Catalysts based on copper oxide were prepared by capillary impregnation of the carrier (γ-Al_2O_3, SiO_2, HZSM-5) in terms of moisture capacity with a solution of copper nitrate ($Cu(NO_3)_2 \cdot 5H_2O$). The catalysts were dried at 300 °C (2 h) and calcined at 500 °C within three hours.

3. Results and discussion

The results of studying the effect of the process temperature and the nature of the catalysts on the degree of conversion of ethanol into liquid and gaseous products are shown in Table. In non-catalytic experiments, the degree of ethanol conversion at temperatures of 300, 350 °C is no more than 5%. In the presence of catalysts, the degree of ethanol conversion increases sharply. The highest ethanol conversion (32%) occurs at a reaction temperature of 350 °C on a 1 wt.% CuO/SiO_2 catalyst. No significant influence of the nature of the catalysts on the degree of conversion was observed. However, the nature of the carrier influences the concentration of the obtained products of the reaction of thermal conversion of ethanol.

The highest concentration of reaction products is observed on a copper catalyst supported on aluminum oxide. All studied catalysts contain carbon oxides (CO, CO_2), hydrogen, methane, and ethylene present in the gaseous products of the ethanol conversion reaction.

The highest concentration of hydrogen (39.3 vol.%) is observed at a reaction temperature of 350 °C on a catalyst of 1 wt.% CuO/Al_2O_3. In the liquid products of the reaction of thermal conversion of ethanol on 1 wt.% CuO/ Al_2O_3 и 1 wt.% CuO/SiO_2 catalysts, 1,1-diethoxyethane, acetaldehyde and n-butanol in small amounts were mainly detected. On 1 wt.% CuO/HZSM-5 catalyst in liquid reaction products, in addition to 1,1-diethoxyethane, acetaldehyde, aromatic hydrocarbons (benzene, toluene) are formed in trace amounts, which are formed due to the oligomerization of ethylene [15].

The obtained results show that the increase in the degree of conversion of ethanol at 350 °C is mainly due to the formation of 1,1 diethoxyethane, acetaldehyde and hydrogen. The highest concentration of the target DEE product (20.9 vol.%) is observed at a reaction temperature of 300 °C on a catalyst of 1 wt.% CuO/Al_2O_3.

In order to increase the activity of 1 wt.% CuO/Al_2O_3 of the catalyst in the production of DEE, the influence of additives of lanthanum, nickel and cerium oxides has been studied. Which are used as modifying additives to increase the activity and stability of copper catalysts [16]. The content of additives was 0.5 wt.%. The modified catalysts were also studied in the thermal conversion of ethanol. The obtained results are presented in Fig. 2.

It can be seen from the figure that the addition of nickel and lanthanum oxides leads to a decrease in the activity of the catalyst at reaction temperatures of 300, 350 °C in comparison with 1 wt.% CuO/Al_2O_3 but the activity of the catalyst increases at 400 °C. Modification of 1 wt.% CuO/Al_2O_3 with cerium oxide leads to an increase in the yield of the target product DEE, the highest yield (27 vol.%) Is observed at a reaction temperature of 350 °C.

Table. Thermal conversion of ethanol in the presence of a copper catalyst deposited on various carriers

T, °C	Samples, 1 wt.% CuO on supports	XEth, %	Concentration of reaction products, vol.%							
			H_2	CO	CO_2	CH_4	C_2H_4	AA	DEE	n-Butanol
300	Without catalyst	0.5	-	-	traces	-	-	-	-	-
	HZSM-5	22.0	3.8	4.7	2.4	0.4	0.7	4.7	8.2	3.7
	SiO_2	28.7	13.0	3.0	0.4	0.6	3.0	1.5	1.0	0.8
	Al_2O_3	26.0	30.0	2.0	1.5	2.5	24.0	14.6	20.9	-
350	Without catalyst	5.0	-	-	2.0	-	-	-	-	-
	HZSM-5	29.1	12.4	7.7	1.7	2.7	11.2	9.5	4.8	2.2
	SiO_2	32.0	8.9	2.8	2.4	0.8	37.1	5.2	1.7	2.6
	Al_2O_3	31.3	39.3	2.7	0.7	0.1	0.5	15.4	18.6	4.5

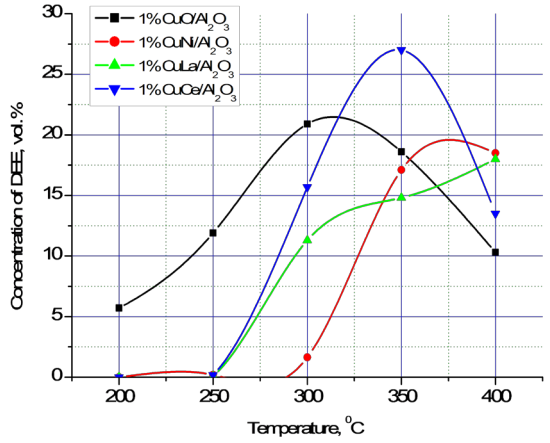

Fig. 2. Effect of the reaction temperature and the nature of modifying additives on the activity of 1 wt.% CuO in the thermal conversion of ethanol to DEE.

4. Conclusion

Thus, in thermal conversion of ethanol on low-percentage copper catalysts at reaction temperatures of 300, 350 °C, independent of the nature of the carrier, the main reaction is the dehydrogenation of ethanol to acetaldehyde and hydrogen, as well as the interaction of acetaldehyde with ethanol to formation of 1,1-diethoxyethane. The highest concentration of the target DEE product (27 vol.%) is observed on a catalyst of 1 wt.% CuO/Al_2O_3 modified with cerium oxide at a reaction temperature of 350 °C. It is expected that the study of the effect of reaction parameters on the activity of the developed catalysts in a wide range of technological modes and screening of catalysts in a complex of physico-chemical methods will reveal effective technological modes and the optimal composition of the catalyst for the one-stage synthesis of 1,1-diethoxyethane from ethanol.

Acknowledgment

This work is funded by the Science Committee of the Ministry of Education and Science of the Republic of Kazakhstan (Grant No. AP08855936).

References

[1]. Rass-Hansen J, Falsig H, Jorgensen B, Christensen CH (2007) Chemical Technology and Biotechnology 82:329-333. DOI:10.1002/jctb.1665
[2]. Bauer JC, Veith GM, Allard LF, Oyola Y, Overbury SH, Dai S (2012) ACS Catalys 2(12):2537-2546. DOI:10.1021/cs300551r
[3]. Gole JL, White MJ (2001) Journal of Catalysis 204:249-252. DOI:10.1006/jcat.2001.3335
[4]. Nielsen M, Junge H, Kammer A, Beller M (2012) Angewandte Chemie International Edition 51:5711-5713. DOI:10.1002/anie.201200625
[5]. Lippits MJ, Nieuwenhuys BE (2010) Catalysis Today 154:127-132. DOI:10.1016/j.cattod.2010.03.019
[6]. Ogo S, Onda A, Iwasa Y, Hara K, Fukuoka A, Yanagisawa K (2012) Journal of Catalysi 296:24-30. DOI:10.1016/j.jcat.2012.08.019
[7]. Sun J, Zhu K, Gao F, Wang C, Liu J, Peden CHF, Wang Y (2011) Journal of the American Chemical Society 133:11096-11099. DOI:10.1021/ja204235v
[8]. Liu H, Iglesia E (2005) Journal of Physical Chemistry 109:2155-2163. DOI:10.1021/jp0401980
[9]. Bueno AC, Gonçalves JA, Gusevskaya EV (2007) Applied Catalysis A: General 329:1-6. DOI:10.1016/j.apcata.2007.06.008
[10]. Thavornprasert KA, Menorval BdlGd, Capron M, Gornay J (2012) Biofuels 3:25-34. DOI:10.4155/bfs.11.144
[11]. Silva VMTM, Rodrigues AE (2005) AIChE Journal 51 (10):2752-2768. DOI:10.1002/aic.10531

[12]. Silva VMTM, Rodrigues AE (2001) Chemical Engineering and Science 56:1255-1263. DOI:10.1016/S0009-2509(00)00347-X
[13]. Nord KE, Haupt D (2005) Environmental Science and Technology 39:6260-6265. DOI:10.1021/es048085h
[14]. Silva VMTM, Rodrigues AE (2004) AIChE Journal 48:625-634. DOI:10.1002/aic.690480319
[15]. Beregovtsova NG, Sharipov VI, Baryshnikov SV, Grishechko LI, Vos'merikov AV, Kuznetcov BN (2014) Journal of Siberian Federal University 7:242-251.
[16]. De Waele J, Galvita VV, Poelman H, Gabrovska M, Nikolova D, Damyanova S, Thybaut JW (2019) Applied Catalysis A: General 591:117401. DOI:10.1016/j.apcata.2019.117401

Одностадийный синтез 1,1-диэтоксиэтана из этанола на медных катализаторах

М.М. Мамбетова[1,3]*, К. Досумов[1,2], Г.Е. Ергазиева[1,2], М.М. Анисова[2], Б.Б. Байжомартов[1]

[1]Казахский национальный университет имени Аль-Фараби, Центр физико-химических методов исследования и анализа, Алматы, Казахстан
[2]РГП НА ПХВ «Институт проблем горения», Алматы, Казахстан
[3]Казахский национальный женский педагогический университет, Алматы, Казахстан

Аннотация

Исследовано превращение этанола на низкопроцентных медьсодержащих катализаторах, при температурах 300 и 350 °С. В качестве носителя активной фазы исследованы: γ-Al_2O_3, SiO_2 и HZSM-5. Показано, что основным направлением конверсии этанола на низкопроцентных медьсодержащих катализаторах является его дегидрирование и последующее превращения образующихся продуктов в 1,1-диэтоксиэтан. Среди изученных катализаторов (1 мас.% CuO/Al_2O_3, 1 мас.% CuO/ SiO_2 и 1 мас.% CuO/HZSM-5) наиболее активным в получении 1,1-диэтоксиэтана оказался 1 мас.% CuO/Al_2O_3, модифицирование его оксидом церия привело к повышению его активности в образовании 1,1-диэтоксиэтана, при температуре реакции 350 °С выход целевого продукта составил 27 об.%. Результаты показали, что модифицирование Cu/Al_2O_3 приводит к повышению каталитической активности образца.

Ключевые слова: 1,1-диэтоксиэтан, этанол, катализатор, носитель, метод приготовления.

Этанолдан бірсатылы 1,1-диэтоксиэтан синтезін алуға арналған мыс құрамды катализаторлар

М.М. Мамбетова[1,3]*, К. Досумов[1,2], Г.Е. Ергазиева[1,2], М.М. Анисова[2], Б.Б. Байжомартов[1]

[1]әл-Фараби атындағы Қазақ ұлттық университеті, Физика-химиялық зерттеу және талдау әдістері орталығы, Алматы қ., Қазақстан
[2]РМК «Жану проблемалары институты» ШЖҚ, Алматы қ., Қазақстан
[3]Қазақ Ұлттық қыздар педагогикалық университеті, Алматы қ., Қазақстан

Аңдатпа

Этанолдың 300 және 350 °С температураларда төмен пайыздық мысқұрамды катализаторлардағы конверсиясы зерттелді. Белсенді фазаның тасымалдауышы ретінде γ-Al_2O_3, SiO_2 және HZSM-5 зерттелді. Этанолды конверсиялаудың негізгі бағыты ретінде төмен пайыздық мысқұрамды катализаторларда дегидрлеу және түзілетін өнімдердің кейіннен 1,1-диэтоксиэтанға айналуы болып табылатыны көрсетілген. Зерттелген катализаторлар арасында (1 мас.% CuO/Al_2O_3, 1 мас.% CuO/SiO_2 және 1 мас.% CuO/HZSM-5) 1,1-диэтоксиэтан алуда ең белсенді 1 мас.% CuO/Al_2O_3 болды, оның церий оксидімен модификациялануы 1,1-диэтоксиэтан түзілуі барысында белсенділігінің жоғарылауына әкелді, 350 °С реакция температурасында мақсатты өнімнің шығуы 27 көл.% құрады. Алынған нәтижелер CuO/Al_2O_3 катализаторын модификациялауда үлгінің каталитикалық белсенділігінің артатындығын көрсетті.

Кілт сөздер: 1,1-диэтоксиэтан, этанол, катализатор, тасымалдағыш, дайындалу әдісі.