

# Carbon-supported Mg-Al oxide systems for aqueous ethanol conversion into 1-butanol

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## Introduction

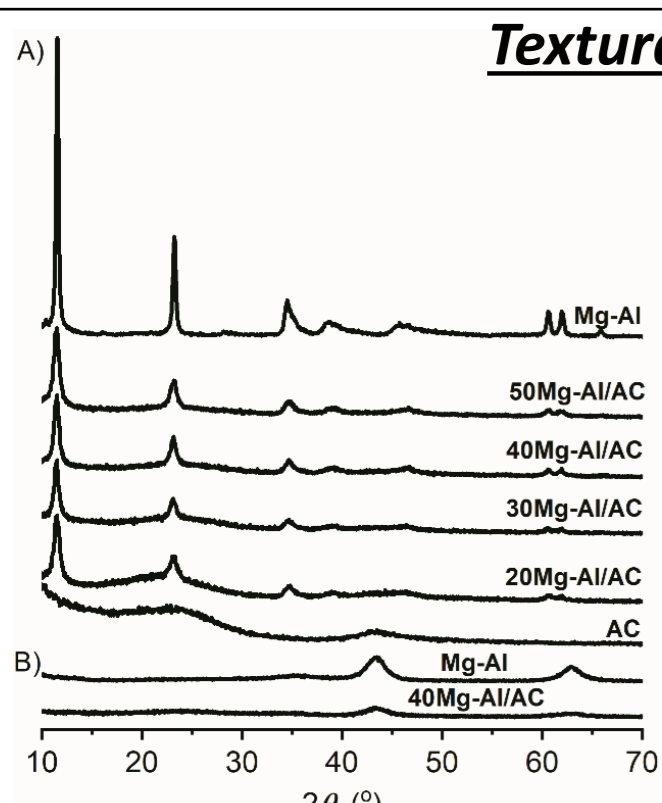
In relation to the reduction of world oil reserves, the development of catalysts for the production of industrially important substances using raw materials of non-petroleum origin like non-food biomass is one of the promising research areas. Much attention is paid to the processes of converting aqueous ethanol obtained from biomass processing into value-added organic products, namely 1-butanol. It is generally accepted to be a sequence of several different reactions starting from dehydrogenation of alcohol, followed by aldol condensation, dehydration and finally hydrogenation of the unsaturated aldehyde. Various catalysts are investigated for this purpose, including individual and doped oxides like MgO, Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, hydrotalcite-derived Mg-Al mixed oxides, Ca-hydroxyapatites, metals (Cu, Ni) deposited on various supports. The acid-base properties of these materials, and especially the balance between acidity and basicity, determine their activity in the key steps of the process, namely ethanol dehydrogenation and aldol condensation. *The present work is devoted to an investigation of catalytic properties of the hybrid catalysts containing hydrotalcite-derived Mg-Al oxides and activated carbon during ethanol condensation into 1-butanol in a flow mode. The effect of activated carbon as a carrier and the content of Mg-Al oxide phase on acid-base characteristics and catalytic properties of the hybrid catalysts are considered.*

## Methods

For catalyst preparation, coconut charcoal (RWAP 1208, fraction <0.1 mm, designated as AC) and hydrotalcite-derived Mg-Al mixed oxides (fraction <0.1 mm, designated as Mg-Al) were used. Mg-Al hydrotalcite was synthesized by co-precipitation method under conditions of high supersaturation (pH 10–12), filtered out, dried (393 K, 6 h) and calcined (873 K, 5 h) to obtain Mg-Al mixed oxides with Mg/Al molar ratio of 2. The preparation of Mg-Al/AC samples was performed by mixing the components in the presence of distilled water (wet mixing) followed by a treatment in an ultrasonic bath and drying (373 K, 6 h). The calcination of the powders was performed in argon flow at 773 K (1 h). The obtained samples contained 20, 30, 40 and 50 wt. % of the Mg-Al mixed oxides (the rest was activated carbon), designated as 20(30, 40, 50) Mg-Al/AC and characterized by X-ray diffraction, scanning and transmission electron microscopy, low-temperature nitrogen ad(des)orption, Fourier transform infrared, X-ray photoelectron and nuclear magnetic resonance spectroscopies, and temperature-programmed desorption of NH<sub>3</sub>, CO<sub>2</sub>, and H<sub>2</sub>O.

## Results

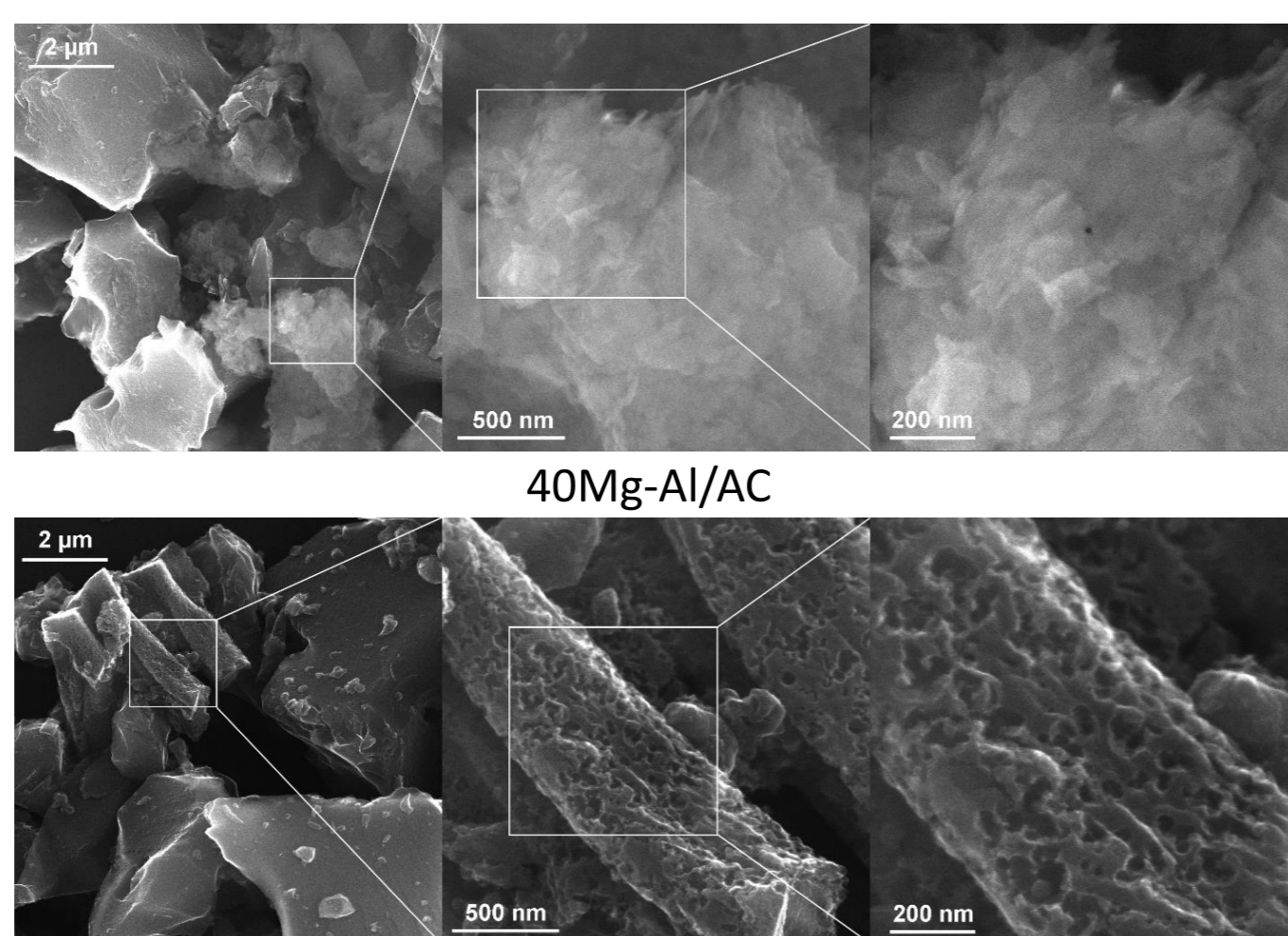
### Textural characteristics and local structure



**Fig. 1.** X-ray diffraction patterns of Mg-Al/AC samples, AC support and the Mg-Al active phase after drying (A) and calcination (B).

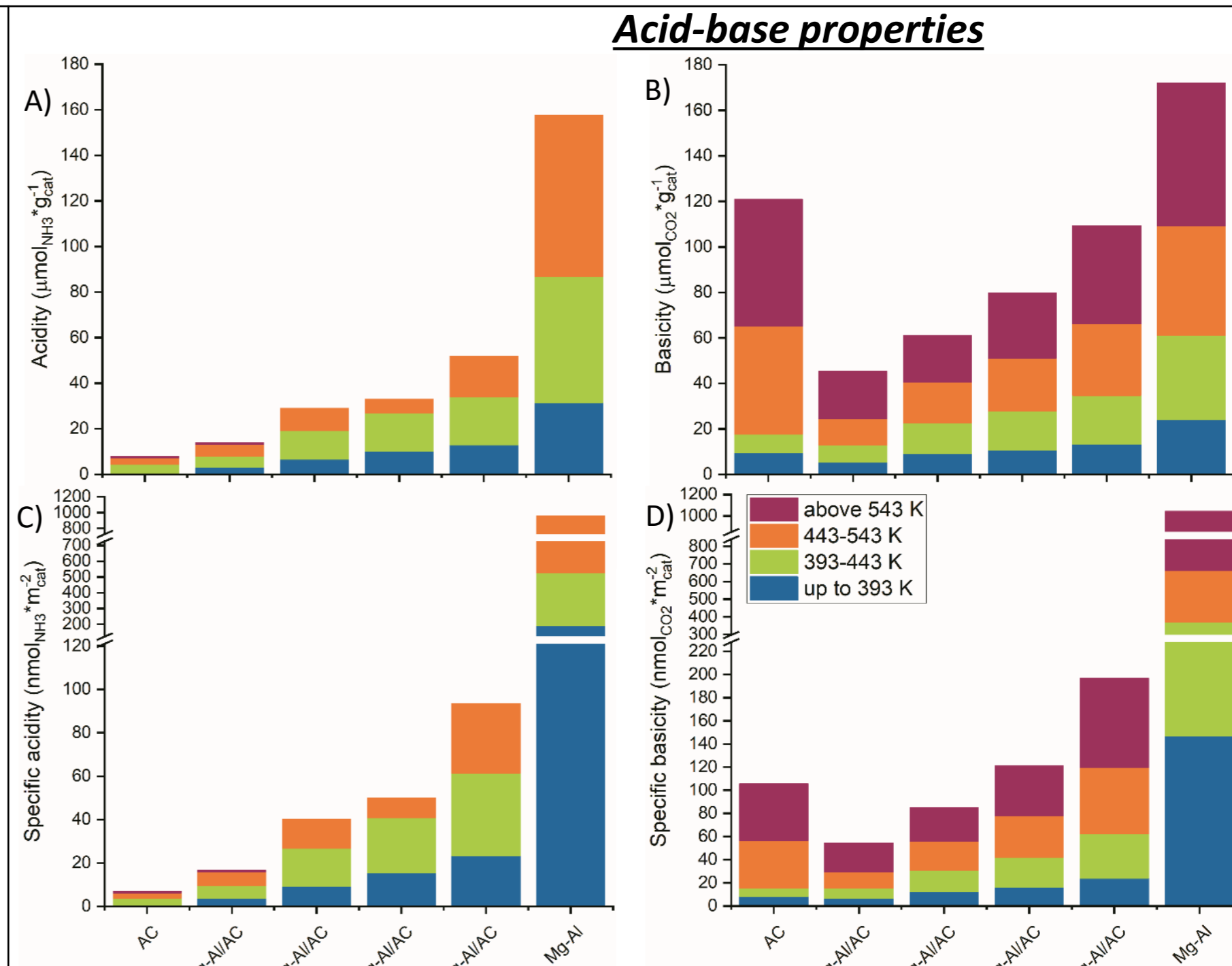
The micrographs of 40Mg-Al/AC after calcination and the AC support are shown in Fig. 2. The aggregates of activated carbon have different shape and sizes. Herewith, the mesopores of 35–75 nm are detected for the AC support. The surface morphology of AC is retained in 40Mg-Al/AC sample. Wherein, there are separate aggregates of the Mg-Al active phase showing a well-developed platelet structure typical of layered materials.

The diffraction pattern of AC (Fig. 1) possesses two wide peaks at 24° and 43° pointing on the amorphous nature of the material. The diffractogram of the dried Mg-Al sample demonstrates the typical features of a hydrotalcite compound. The intensity of those peaks decreases progressively according to the reduction in the Mg-Al content of the samples. In parallel, two small and wide peaks at 2θ = 24° and 43° appear with an increase the AC content in the samples. The crystalline structure of hydrotalcite collapses after calcination leading to the formation of Mg-Al mixed oxides.



**Fig. 2.** Scanning electron microscopy images of the calcined 40Mg-Al/AC sample and AC support.

### Acid-base properties



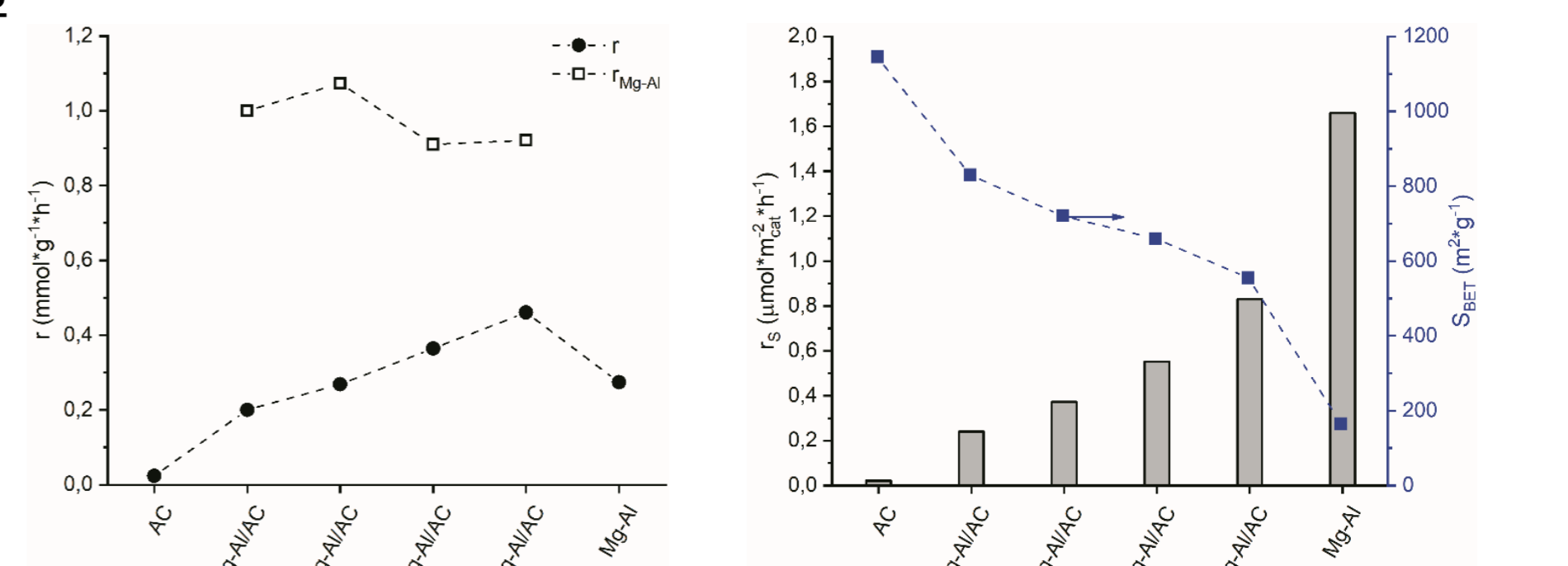
**Fig. 3.** The values of acidity (A) and basicity (B), and corresponding specific values (C, D) of Mg-Al/AC system depending on the content of Mg-Al active phase.

Acid-base properties of the Mg-Al/AC samples were studied by one-pass temperature-programmed desorption of NH<sub>3</sub> and CO<sub>2</sub> with mass-spectral control. Based on the data obtained (Fig. 3), on the surface of Mg-Al/AC hybrid catalysts, there are acid and basic sites of various strength. The number and strength of acid and basic sites are determined by the Mg-Al content in the composition and rise with an increase in the content of the Mg-Al phase. It can be suggested that basic sites of AC support are partially overlapped/blocked by the Mg-Al active phase.

### Catalytic properties

**Table 1.** Indices of ethanol conversion over Mg-Al/AC hybrid catalysts (T = 548 K, LHSV = 0,14 L<sub>EtOH</sub>·L<sub>cat</sub><sup>-1</sup>·h<sup>-1</sup>).

Catalyst	TOS, h	X <sub>EtOH</sub> , %	Selectivity, %							Y <sub>AAV</sub> , %	Y <sub>BuOH</sub> , %	
			1-Butanol	Butenes	1-Butanal	1,3-Butadiene	Acetaldehyde	Ethylene +DEE	C <sub>5+</sub>			Others
AC	0.5	8	9	5	2	<0.5	78	<0.5	3	3	6	1
	1	8	9	3	3	<0.5	82	<0.5	1	2	7	1
	2	9	8	2	3	<0.5	84	<0.5	1	2	8	1
20Mg-Al/AC	0.5	16	69	6	1	1	10	<0.5	5	8	2	11
	1	13	60	7	1	1	14	<0.5	8	9	2	8
	2	9	47	7	2	1	26	1	9	7	2	4
30Mg-Al/AC	0.5	23	74	1	3	<0.5	10	2	6	4	2	17
	1	18	57	1	5	<0.5	20	2	9	6	4	10
	2	13	46	2	5	<0.5	29	2	10	6	4	6
40Mg-Al/AC	0.5	21	76	2	2	<0.5	6	3	6	5	1	16
	1	19	65	2	3	<0.5	13	2	10	5	2	12
	2	15	52	2	5	<0.5	23	2	10	6	3	8
50Mg-Al/AC	0.5	25	66	6	1	<0.5	3	7	11	6	1	16
	1	25	59	5	1	<0.5	4	6	15	10	1	15
	2	18	56	4	2	<0.5	11	9	13	5	2	10
Mg-Al	0.5	16	63	1	<0.5	2	3	15	10	6	<0.5	10
	1	13	63	1	<0.5	2	4	15	9	6	1	8
	2	8	61	<0.5	<0.5	3	8	17	6	5	1	5



**Fig. 4.** Initial formation rates of 1-butanol calculated per unit mass of Mg-Al/AC catalyst (r) and Mg-Al active phase in the composition (r<sub>Mg-Al</sub>), and per unit surface area of the catalyst (r<sub>s</sub>). The specific surface area (BET) of the catalysts are given.

Ethanol conversion over AC does not exceed 9 %, and the main product is acetaldehyde (Table 1). The main product over Mg-Al/AC catalysts is 1-butanol. The increase in ethanol conversion and selectivity towards 1-butanol over Mg-Al/AC samples compared to the AC support can be attributed to the formation of acid sites on the catalyst surface, namely the sites formed by Al<sup>3+</sup> cations in the [Al<sup>3+</sup>-O<sup>2-</sup>-Mg<sup>2+</sup>] structures. The formation rate of 1-butanol calculated per unit mass of the Mg-Al active phase in the catalyst (Fig. 4) is 3–4 times higher for Mg-Al/AC catalysts than for Mg-Al sample.

## Conclusions

Higher values of ethanol conversion and selectivity towards 1-butanol are achieved in the presence of Mg-Al/AC hybrid catalysts than over individual components, namely Mg-Al (hydrotalcite-derived) oxide system and activated carbon (coconut charcoal). This can be caused by a redistribution of the active sites of Mg-Al oxide phase over highly dispersed support and increasing their availability for reagents. The Mg-Al/AC catalysts showed higher stability of operation over time-on-stream [1], including in the conversion of aqueous ethanol, as compared to Mg-Al oxide system. The observed lifetime prolongation of Mg-Al/AC hybrid catalysts and higher water tolerance are suggested to be a result of a cooperative effect of the active oxide phase and activated carbon support.

## References

1. Larina O.V., Kyriienko P.I., Shcherban N.D., Yaremov P.S., Balakin D.Yu., Khalakhan I., Veltruská K., Soloviev S.O., Orlyk S.M. Carbon-Supported Mg–Al Oxide Hybrid Catalysts for Aqueous Ethanol Conversion into 1-Butanol in a Flow Reactor // Ind. Eng. Chem. Res. – 2021. – <https://doi.org/10.1021/acs.iecr.1c02153>.

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