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Gas-phase oxidative carbonylation of methane to acetic acid over zeolites

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Zeolite catalysts used. In this study, we used commercial ZSM-5 zeolites (Zeolyst, USA) with different molar ratios (SiO_2/Al_2O_3): CBV 3024E (CBV-30, SiO_2/Al_2O_3 = 33), CBV 8014 (CBV-80, SiO_2/Al_2O_3 = 85), and CBV 30014G (CBV-300, SiO_2/Al_2O_3 = 307). To obtain the H-form of the zeolites (HCBV), all of the above-listed samples manufactured in ammonium form were calcined at 500 °C in air in a muffle furnace for 4 h.

Analysis of the elemental composition of the zeolites used. The elemental analysis of the zeolites was carried out by X-ray fluorescence (XRF) spectroscopy on an ARL™ PERFORM'X Sequential analyzer (USA). X-ray tube with a rhodium anode was used as a source of emission (running voltage was 30–60 kV).

Table S1 The elemental composition of the zeolites used.

Zeolite	Element content[a]/wt%							
	Si	Al	Na	K	Ca	Mg	Fe	Zr
CBV-30	44.18	2.90	0.019	0.0006	0.067	0.019	0.019	0.0003
CBV-80	45.68	1.17	0.018	0.0007	0.034	0.018	0.013	0.0002
CBV-300	46.38	0.31	0.011	0.0007	0.020	0.014	0.006	0.0002

a) Determined by XRF spectroscopy.

Determination of the adsorption properties of the zeolites used. The adsorption characteristics of the zeolites were determined by low-temperature nitrogen adsorption. The analysis was performed on a Micromeritics ASAP-2000 analyzer (USA). Previously, all the samples were evacuated to $4 \cdot 10^{-1}$ Pa at a temperature of 350 °C for 6 h. Nitrogen adsorption was carried out at 77 K. The specific surface area was calculated by the BET (Brunauer-Emmet-Teller) method at a relative partial pressure P/P_0 of 0.02. The total pore volume and micropore volume was evaluated by the BJH (Barrett-Joyner-Halenda) method at P/P_0 = 0.99 and by the Horvath-Kavazoe method at P/P_0 = 0.02, respectively.

Table S2 Specific surface area and pore volume of the zeolites used.

Zeolite	S_{BET}[a]/$m^2 \cdot g^{-1}$	S_{meso}/$m^2 \cdot g^{-1}$	V_{total}[c]/$cm^3 \cdot g^{-1}$	V_{micro}[b]/$cm^3 \cdot g^{-1}$	V_{meso}[d]/$cm^3 \cdot g^{-1}$
CBV-30	412	113	0.219	0.126	0.093
CBV-80	399	131	0.220	0.112	0.108
CBV-300	360	270	0.204	0.042	0.162

a) Determined by BET method at p/p_0 = 0.02; b) determined by Horvath-Kawazoe method at p/p_0 = 0.02; c) determined by BJH method at p/p_0 = 0.99; d) determined as $V_{total} - V_{micro}$.

Catalysts acidity measurements. The acidic properties of the catalysts were measured by the temperature-programmed desorption of ammonia (NH_3-TPD) using an USGA-101 apparatus (UNISIT, Russia) according to the following procedure.

Immediately prior to ammonia adsorption, the specimens were calcined at 500 °C in a helium flow (30 ml/min) for 2 h, and then cooled to 60 °C. The specimens were saturated with ammonia in a flow (ammonia/helium mixture) for 2 h. Loosely-bound physically adsorbed ammonia was removed at 100 °C in a helium flow (30 ml/min) for 0.5 h. Afterwards, the specimens were heated up to 800 °C in the temperature rise mode with a ramp rate of 10 °C/min in a helium flow (30 ml/min), and the ammonia desorption peaks were recorded. The analytical signal was detected on a TCD.

The density of Brønsted (BAS) and Lewis (LAS) acid sites was determined by Fourier-transform infrared spectroscopy of adsorbed pyridine (Py-FTIR) using a Nicolet is-10 FTIR spectrometer (Thermo Fischer Scientific, USA). Previously pressed specimens were placed in a vacuum system ($1.33 \cdot 10^{-3}$ Pa) with a transparent in situ cell at 450 °C for 2 h. Next, it was cooled to 60 °C and saturated with pyridine vapors in a flow (pyridine/helium mixture) (30 ml/min) for 0.5 h. Pyridine excess and physically adsorbed pyridine were evacuated at 200 °C for 0.5 h, and, in the temperature rise mode (ramp rate, 10 °C/min) up to 350 °C, the spectra were collected.

The density of BAS and LAS were estimated based on integrated intensity of the bands at 1545 and 1455 cm^{-1}, respectively, and calculated as follows from (1):

$$C = \frac{A}{\varepsilon} \cdot \frac{S}{m}, \quad (1)$$

where C is the acid sites density (mmol·g^{-1}), S is the wafer surface area, A is the integrated area of the bands at 1545 and 1455 cm^{-1}, m is the wafer weight (g), and ε is the molar extinction coefficient (1.67 and 2.22 cm·μmol^{-1}) assigned to BAS and LAS, respectively.

Catalytic experiments running. Testing the catalysts in the methane oxidative carbonylation was carried out under continuous feed of reactants in a flow fixed-bed catalytic reactor (inner diameter 16 mm). The reactor is made of a special-property alloy (Hastelloy C276), which is distinguished by excellent corrosion resistance to various aggressive media, including acids.

For the experiment, the catalyst (3 g) was mixed with quartz in an equal volume ratio and placed in the isothermal zone of the reactor. The acetic acid synthesis reaction was performed at 250–450 °C and 6.5 MPa. The feed gas flow was composed of 57 vol% of methane, 3 vol% of oxygen, 10 vol% of carbon monoxide, and 30 vol% of nitrogen/water. The feed of the mixture was varied in the range GHSV = 1250–40000 h^{-1}.

The gas mixture feed (except for water) was controlled by a F-232M-RAD-33-V gas flow controller (Bronkhorst, Netherlands). The gas products flow rate was measured using a DC-1C-M gas meter (Shinagawa, Japan). A high-pressure fluid-flow pump HPP 5001 (Czech Republic) was used to feed the required quantity of water to the reactor, wherein it was mixed with the gas flow to form a vapor-gas mixture. The reaction temperature was operated using a TRM-210 automatically-controlled regulator (OVEN, Russia), and the pressure in the system was maintained by a KPB1NOD412P200B0 mechanical back-pressure regulator (Swagelok, USA).

The gaseous and liquid reaction products were analyzed by a gas chromatography using a Chromatech-Crystall 5000 unit (Chromatech, Russia) provided with chromatographic columns. Gases (except for oxygen) were analyzed on a packed column with a SKT–4 activated carbon phase (1 m × 3 mm × 0.2-0.5 mm). Oxygen was determined on a packed column with NaX zeolite phase (3 m × 3 mm × 0.18–0.25 mm). A Poraplot Q open-tubular column (25 m x 0.53 mm x 10 microns) was used to analyze liquid products (oxygenates). Chromatographic run was

performed in the programmed temperature rise mode from 50 to 280 °C, with an argon (50 ml/min) being carrier gas. Gases and liquid components were identified on TCD and FID, respectively.

The chromatograms were obtained and processed using a "Chromatech Analytic" software application.

The catalyst efficiency was estimated by specific productivity (ρ), which was calculated according to the equation (2):

$$\rho = \frac{n_{product}}{m_{cat}}, \mu mol \cdot g_{cat}^{-1} \cdot h^{-1} \quad (2)$$

where $n_{product}$ and m_{cat} are product quantity ($\mu moles \cdot h^{-1}$), and catalyst charge (g), respectively.

Table S3 Carbon balance of the reaction.

Reaction conditions		Carbon of CH_4/ $mmol \cdot h^{-1}$	Carbon of CO/ $mmol \cdot h^{-1}$	Carbon of CO_2/ $mmol \cdot h^{-1}$	Carbon of methanol/ $mmol \cdot h^{-1}$	Carbon of acetone/ $mmol \cdot h^{-1}$	Carbon of acetic acid/ $mmol \cdot h^{-1}$	Carbon in total/ $mmol \cdot h^{-1}$
Before catalysis		152.05	26.72	–	–	–	–	178.77
After catalysis	Dry mixture, 350 °C	151.52	13.36	11.27	0.001	0.000	0.001	176.15
	Dry mixture, 450 °C	148.62	21.91	3.02	0.074	0.000	0.0002	174.62
	Wet mixture, 350 °C	150.87	11.86	13.43	0.075	0.000	0.014	176.25
	Wet mixture, 450 °C	147.46	24.10	2.80	0.415	0.003	0.196	174.97

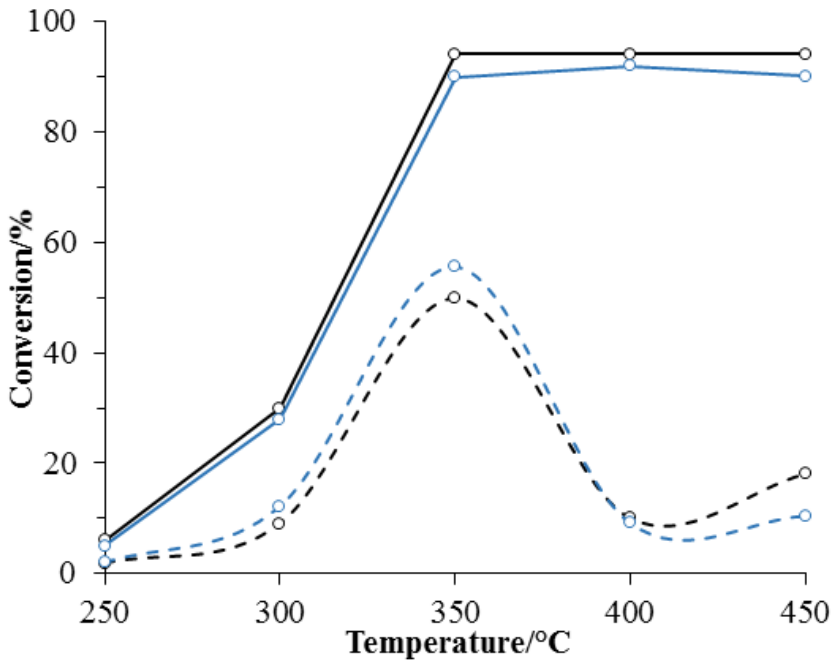

Figure S1 Dependence of oxygen (solid line) and carbon monooxide (dashed line) as a function of temperature for dry (57 vol% of CH_4, 3 vol% of O_2, 10 vol% of CO, and 30 vol% of N_2) (black line) and wet (57 vol% of CH_4, 3 vol% of O_2, 10 vol% of CO, and 30 vol% of H_2O) (blue line) mixtures (HCBV-30, P = 6.5 MPa, GHSV = 1250 h^{-1}).

The conversion profiles of oxygen (X_{O2}) and carbon monooxide (X_{CO}) and their values in both ways of running a process are quite close and differ by a few percent (Figure S1). X_{O2} in the case of a dry mixture feeding over the entire length of the studied temperatures is ahead of X_{O2} in the case of a wet mixture feeding. At the same time, already at 350 °C, X_{O2} reaches an almost exhaustive value, which after 350 °C barely change (94.1–94.2% for a dry mixture versus 90.0–92.0% for a wet mixture). As for carbon monoxide, the X_{CO} curve is extreme. When the temperature increases from 250 °C to 350 °C, X_{CO} increases from 1.8 to 50.0% on the dry mixture and from 2.0 to 55.6% on the wet mixture. The temperature increment to 400 °C reduces the X_{CO} to 10.0 and 9.1% in both cases, respectively. This nature of X_{CO} curve in the temperature range below 350 °C can be explained by a high proportion of the interaction of O_2 with CO to form CO_2, which can be seen from the symbiotic change in CO_2 and X_{CO} in the 250–350 °C region. The drop in X_{CO} above 350 °C is most likely due to the competitive activation of methane at elevated temperatures and its involvement in the oxidation process. There are several reasons for the higher X_{CO} values in the wet mixture compared to the dry mixture. First, due to

the formation of additional hydroxyl groups as a result of water adsorption on the catalyst surface, the activation energy of CO oxidation decreases.[S1] On the other hand, the presence of water vapor favors the water-gas shift reaction ($CO + H_2O \leftrightarrow CO_2 + H_2$), which takes place at temperatures mainly up to 350 °C. However, at elevated temperatures, excess water has a negative effect on CO conversion, that is observed at 450 °C. The reduced value of X_{CO} for the wet mixture (10.4% versus 18.0% for the dry mixture) is probably due to the occupation of the active catalyst surface and blocking acid sites by adsorbed water vapor molecules.[S2]

Table S4 Specific productivity for oxygenates at various temperatures (wet mixture: 57 vol% of CH_4, 3 vol% of O_2, 10 vol% of CO, and 30 vol% of H_2O; P = 6.5 MPa, GHSV = 1250 h^{-1}).

Specific productivity/μmol·g_{cat}^{-1}·h^{-1}			
T, °C	Methanol	Acetone	Acetic acid
HCBV-30			
250	7.3	0.0	0.3
300	19.1	0.0	2.0
350	24.9	0.0	2.3
400	273.2	0.3	11.7
450	138.4	0.4	32.6
Non-catalytic			
450	113.3	0.0	0.0

A non-catalytic experiment at 450 °C showed the absence of acetone and acetic acid in the oxidation products. The occurrence of acetic acid in the catalyzed experiments and its absence in the non-catalytic run, apparently, evidences the direct participation of the zeolite acid sites in the methane oxidative carbonylation.

References

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