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Synthesis of dimethyl carbonate from methanol and CO_2 on the SnO_2/Al_2O_3-based catalyst

Alexander A. Greish, Elena D. Finashina, Olga P. Tkachenko, Elena V. Shuvalova and Leonid M. Kustov

Catalyst characterization

DRIFT

DRIFT spectra were recorded using a Nicolet Protégé-460 spectrometer equipped with a diffuse reflectance attachment, in the wavenumber interval of 400-6000 cm^{-1}, with resolution of 4 cm^{-1}. The measurements were carried out at room temperature. The catalyst sample was placed in the quartz ampoule with a CaF window. To improve the signal/noise ratio the spectra were recorded after 500 scans. To remove gases and water adsorbed the catalyst sample was pre-evacuated at 400^{o}C for 2 h. The processing of spectra was performed by using the OMNIC software.

XPS

XP spectra were measured by a modified ES-2403 spectrometer equipped with a PHOIBOS 100 MCD analyzer, using Al Kα excitation (1486.6 eV, 10 kV * 20 mA). The spectrometer was calibrated by binding energy of Au $4f_{7/2}$ level = 84.0 eV and Ni $2p_{3/2}$ = 852.7 eV.

Catalyst samples were allowed to outgas before the analysis (ca. 3 x 10^{-6} Pa) and they were sufficiently stable during the examination. All spectra were registered at ambient temperature. Survey spectra were collected between 20 and 1400 eV with a 0.5 eV step. Detailed spectra were recorded for the regions of C 1s, O 1s, Al 2p, Sn 3d, Cl 2p, F 1s, K 2p, Zn 2p, Cu 2p and Cu L_3VV Auger electrons with a step of 0.05 eV. Data acquisition was realized by the SpecsLab2 software and analysis was performed by the CasaXPS software.

The binding energy of XPS peaks (with accuracy ± 0.1 eV) was corrected with account of sample charging by referencing to the C 1s peak at 285.0 eV (external standard) and Al 2p peak at 74.2 eV (internal standards). The surface atomic elemental ratios (with accuracy ± 10%) were evaluated from line intensity ratios using the Scofield interaction cross sections together with an empirically derived function describing the energy dependence of the analyzer transmittance of the instrument used.

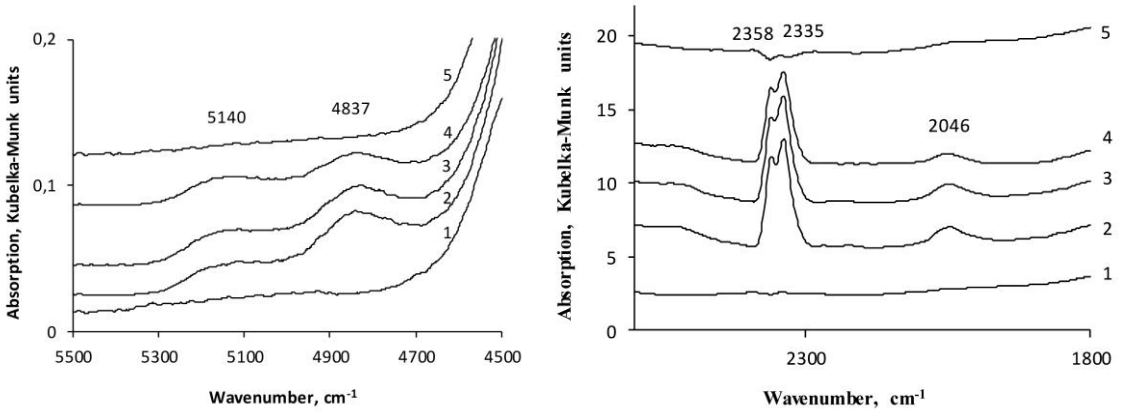
XRD

The phase composition of the catalysts was examined by X-ray diffraction analysis. XRD patterns were recorded using a DRON-2 diffractometer with Ni-filtered Cu Kα radiation (λ =

0.1542 nm) in a step scanning mode, with a step of 0.02° and a counting time of 0.6 s per step in the range of 2Θ = 20°–80°. Identification of the phases was performed by comparison of the position and intensity of the peaks with the data from the files of the International Center for Diffraction Data.

TG-DTA

Thermal analysis was performed by TG-DTA method using a Derivatograph-C instrument (MOM Company). The catalyst sample (18 mg) was placed in the platinum crucible and heated in air from 20 to 700°C at a heating rate of 10°C/min. Alumina was used as a reference in the DTA measurements



a b

Figure S1 DRIFT spectra of the adsorbed MeOH/CO_2 mixture on SnO_2(Cu,Zn,K)/Al_2O_3 in the regions of (a) 4500-5500 cm^{-1} and (b) 1800-2400 cm^{-1}: 1, after evacuation of the sample at 20°C for 4 h;. 2, in 10 min after introduction of the CO_2/MeOH mixture at 20°C; 3, in 1 h after; 4, after heating of the sample at 100°C for 30 min; 5, after evacuation of the sample at 20°C for 30 min.

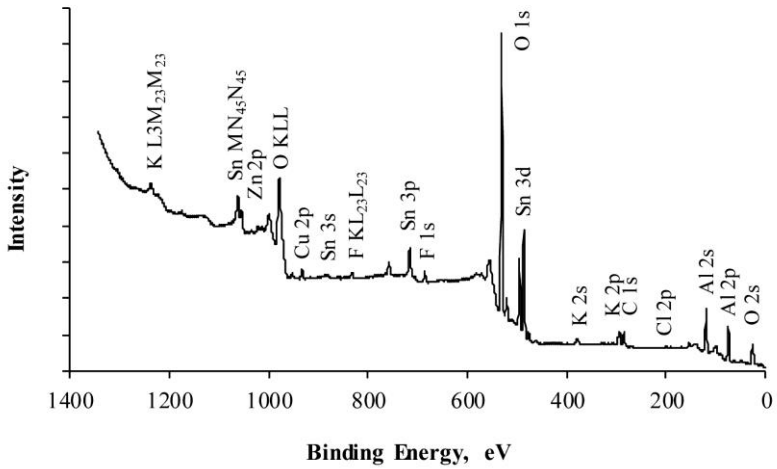


Figure S2 Panoramic XPS spectrum of the sample SnO_2(Cu,Zn,K)/Al_2O_3.

Table S1 XPS data of the sample $SnO_2(Cu,Zn,K)/Al_2O_3$.

Binding Energy, eV							Cu L_3VV Kinetic Energy, eV	Cu Auger param., eV	Cu state
Sn $3d_{5/2}$	O 1s	Cl 2p	Zn $2p_{3/2}$	K $2p_{3/2}$	F 1s	Cu $2p_{3/2}$			
486.9	531.2	199.0	1022.4	293.8	686.0	932.4	914.4	1850.2	Cu^+
						933.5	917.8	1847.9	Cu^{2+}

Surface atomic ratio					
Sn/Al	Cl/Al	Zn/Al	K/Al	F/Al	Cu/Al
0.134	0.031	0.007	0.055	0.043	0.008

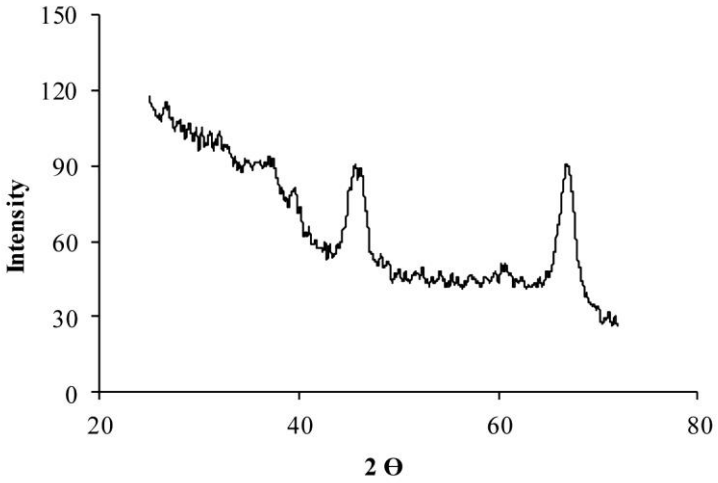


Figure S3 The XRD pattern of the sample $SnO_2(Cu,Zn,K)/Al_2O_3$.