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Kinetics of N_2O decomposition over bulk and supported $LaCoO_3$ perovskites

Petr V. Zemlianskii, Alexander L. Kustov, Gennady I. Kapustin, Nikolay A. Davshan, Konstantin B. Kalmykov, Vladimir V. Chernyshev and Leonid M. Kustov

Content

S1. Experimental

Materials

For the synthesis of bulk and supported $LaCoO_3$ the following chemicals were used as received. $La(NO_3)_3 \cdot 6H_2O$, $Co(NO_3)_2 \cdot 6H_2O$ and glycine ($C_2H_5NO_2$) (99+%) were obtained from Acros Organics. Commercial tetragonal ZrO_2 doped with La_2O_3 (10% La_2O_3, 90 % ZrO_2, 124 m^2/g) was obtained from Saint-Gobain and further referred to as ZrO_2-La.

Instrumentals

The PXRD measurements were performed using an Empyrean (PANalytical) diffractometer equipped with a linear position-sensitive X'Celerator detector. Ni-filtered CuKα radiation was employed. Standard Bragg-Brentano (reflection) geometry was used.

TEM studies of the materials were performed using a JEM-2100 JEOL transmission electron microscope (Tokyo, Japan).

For the SEM measurements, a LEO EVO 50 XVP (Karl Zeiss, Germany) electron microscope equipped with the energy dispersion analyzer INCA - energy 450 (Oxford Instruments, England) was used.

Specific surface area measurements were carried out by the nitrogen adsorption-desorption technique using a «ASAP 2020 Plus» unit («Micrometrics») at 77 K according to ISO 9277-2010.

UV-Vis diffuse reflectance spectra were collected with a spectrophotometer Shimadzu UV-3600 Plus equipped with the integrating sphere ISR-603 at room temperature. The range of wavelengths was 200–800 nm. Barium sulfate was used as a diluent.

Catalytic test

The N_2O decomposition process was carried out using a lab unit consisting of a quartz flow reactor with the diameter of 4 mm placed in a furnace. The products were analyzed by the use of gas chromatography (Crystall-5000). For all the experiments, 100% N_2O was applied, the gas space velocity was 3000 h^{-1}. The size of the catalyst grains was 0.1 – 0.14 mm. The catalyst loading was 0.1 g. The total gas flow rate was 300 ml/h. The catalyst bed was heated steadily with the registration of products at the outlet of the reactor in parallel.

The N_2O conversion was calculated considering the fact that the decomposition reaction proceeds with a change in the number of moles:

$$\alpha_{vis.} = \frac{C_0 - C_i}{C_0} \quad (S1)$$

$$\alpha_{real} = \frac{2\alpha_{vis.}}{(3 - \alpha_{vis.})} \quad (S2)$$

$\alpha_{vis.}$ is an apparent conversion of N_2O. C_0 and C_i are the inlet and outlet concentrations of N_2O. α_{real} is a real conversion of N_2O.

The specific activity was determined according to the following equation:

$$P = \frac{Q_0 \cdot \alpha_{real}}{22.4 \cdot m \cdot A_{BET}} \quad (S3)$$

P is the activity. Q_0 is the total gas flow equaled 300 ml/h, m is the catalyst loading equaled 0.1 g, A_{BET} is the specific surface area, m^2/g.

S2. Characterization of samples

Textural properties

The pore size distribution of all the samples synthesized is presented in Figure S1.

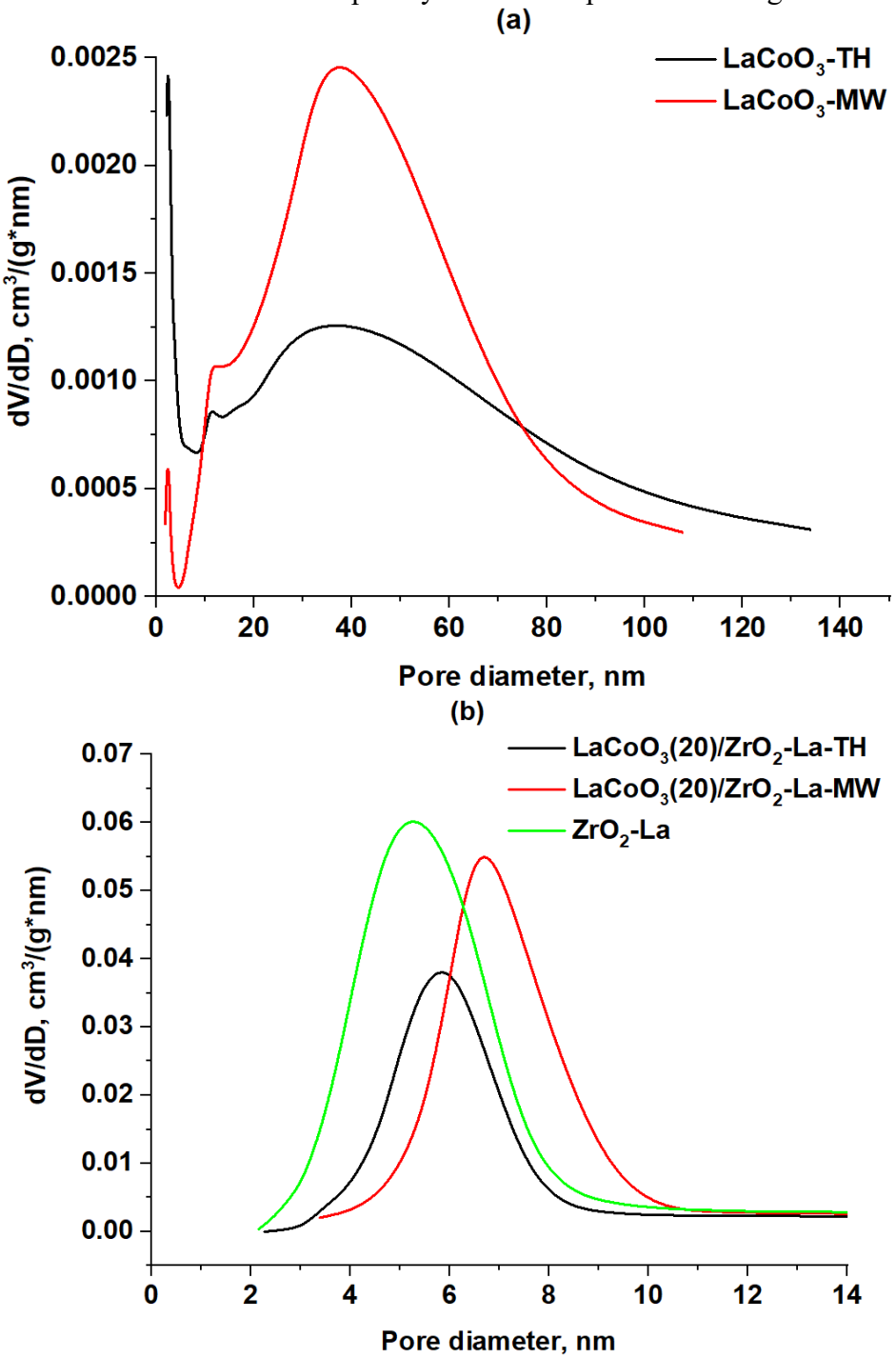

Figure S1 Pore size distribution of all the samples synthesized in this work: bulk $LaCoO_3$ – (a) and supported $LaCoO_3$ – (b)

SEM and TEM

The $LaCoO_3$-TH and $LaCoO_3$-MW TEM photos are presented in Figure S2.

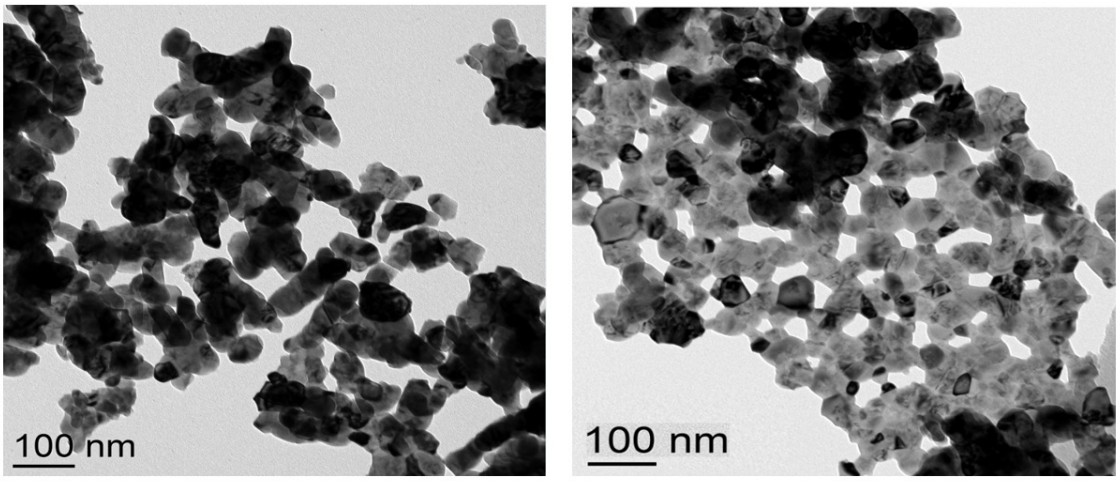

Figure S2 TEM photos of $LaCoO_3$-TH (a) and $LaCoO_3$-MW (b).

The SEM photos with Co element mapping are depicted in Figure S3.

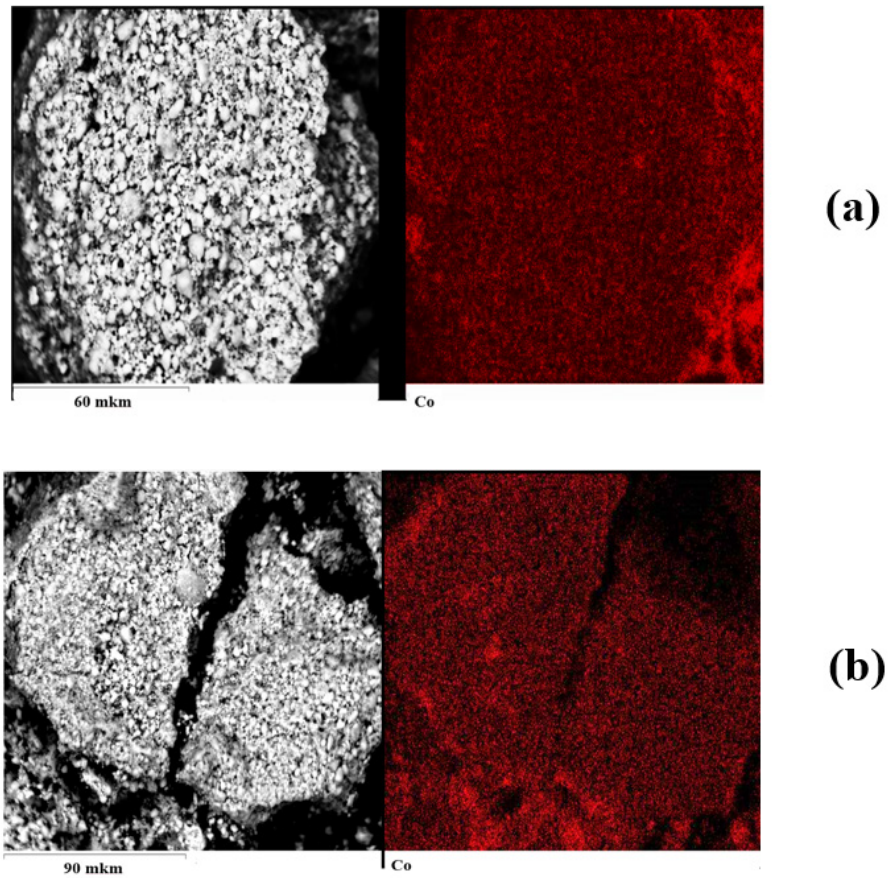

Figure S3 SEM photos and Co distribution over the ZrO_2 surface: $LaCoO_3$(20)/ZrO_2-La-TH (a); $LaCoO_3$(20)/ZrO_2-La-MW (b).

DR-UV-Vis spectra

DR-UV-Vis spectra of all the samples as well as $(F(R)*hv)^2$-Photon energy curves are demonstrated in Figure S4.

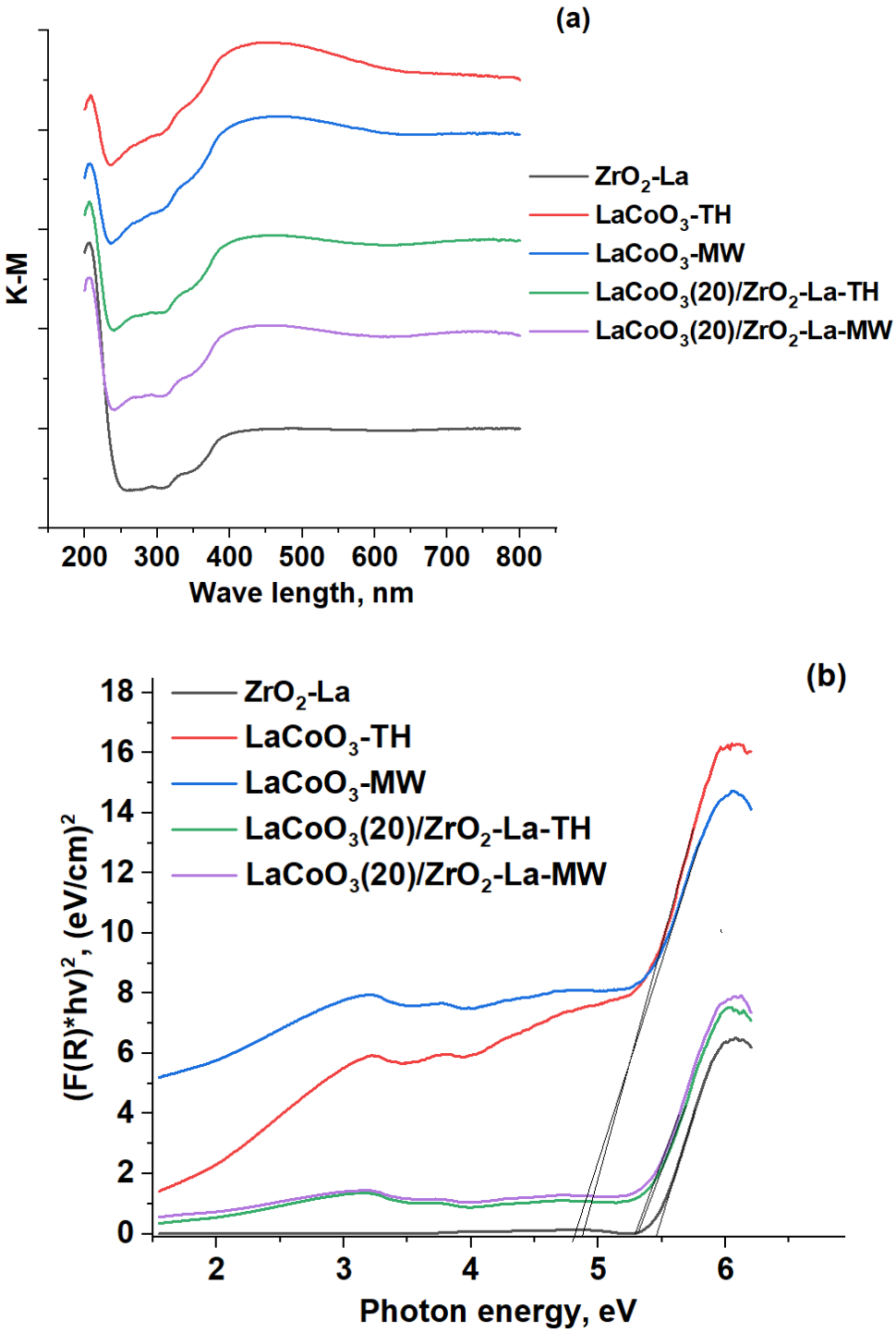

Figure S4 DR-UV-Vis spectra (a) and $(F(R)*hv)^2$-Photon energy curves (b) of all the samples synthesized and the support

S3. Results of the catalytic tests

Temperature curves of specific activities are presented in Figure S5.

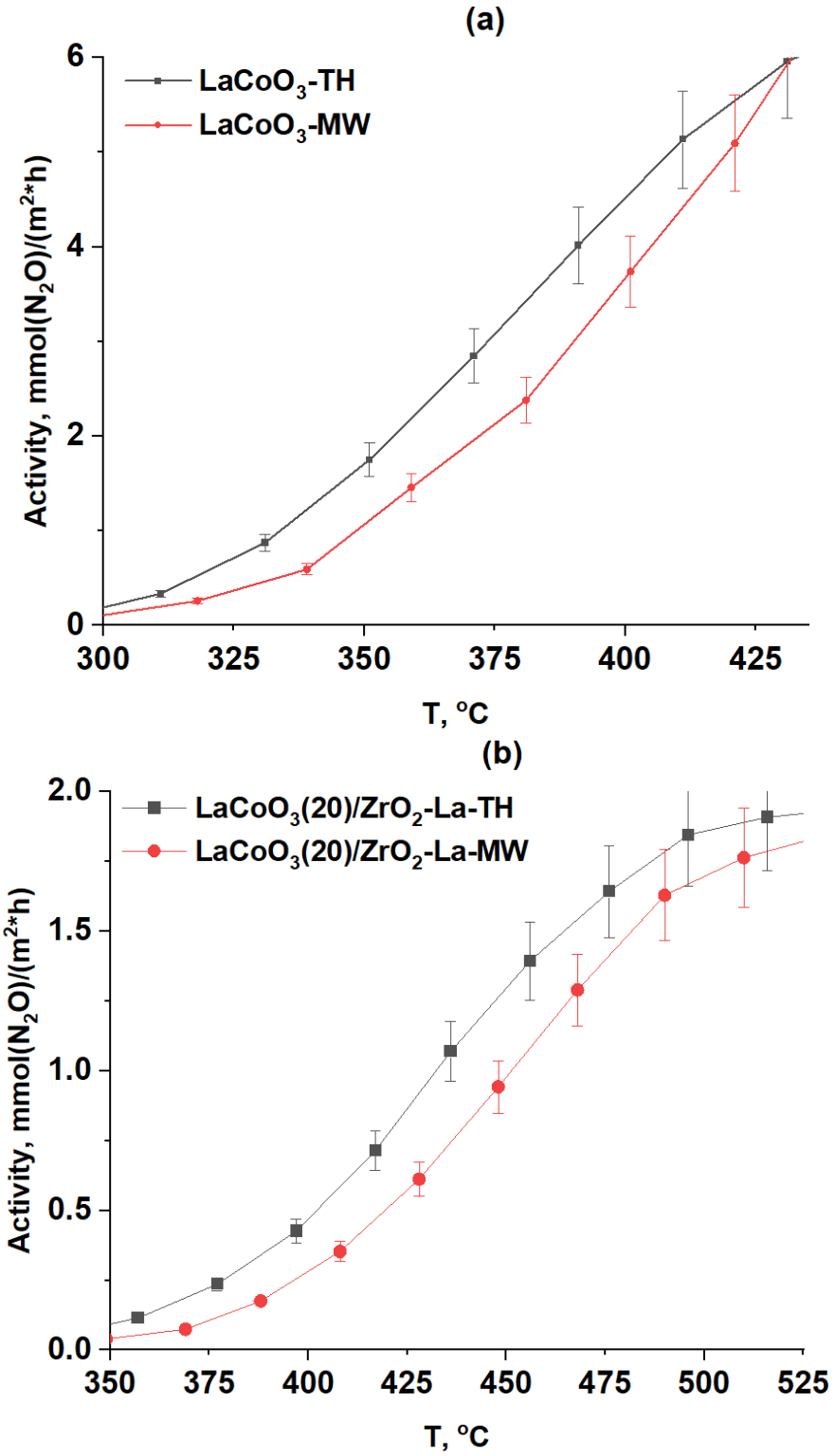

Figure S5 Temperature curves of specific activities: for the bulk samples – (a) and for the supported ones – (b)