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SUPPLEMENTARY MATERIAL

Low-temperature catalytic decarboxylation of formic and acetic acid over Ru/TiO₂ catalyst: Prospects for continuous production of energy-rich gaseous mixtures

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S1. Detailed experimental section

S1.1. Catalyst preparation

The 3 wt. % Ru/TiO₂ catalyst was prepared as described by Pintar et al. (A. Pintar, J. Batista, T. Tišler, *Appl. Catal. B* 2008, 84, 30–41), i.e. by incipient impregnation of TiO₂ P25 extrudates (Degussa-Hüls, 1×2.5 mm, S_{BET}=47.3 m²/g) with an aqueous solution of RuCl₃ × H₂O (Acros Organics). Decomposition of ruthenium precursors and thermal stabilization of the catalyst was performed in a quartz tube by heating for 1 h at 300 °C in pure hydrogen (Linde, 5.0) with a flow of 250 mL/min.

S1.2. Characterization techniques

N₂ physisorption measurements were conducted at -196 °C (Micromeritics, TriStar II 3020 apparatus). Prior to measurements, samples were degassed in dry N₂ stream for 1 h at 90 °C, followed by 4 h at 180 °C using the Micromeritics SmartPrep Degasser.

The catalyst support as well as the as-synthesized and reduced catalysts were analyzed in powdered form by XRD technique (PANalytical X'pert PRO diffractometer, CuKα1 radiation, λ=0.15406 nm, 2θ between 20 and 80°, 0.034° increment measured for 100 s at each step). Average scattering domain size was estimated using Scherrer's equation. The required parameters for this calculation were obtained by fitting the measured X-ray line spectra with the Pearson type VII function in Origin 8.1 software. Distribution of TiO₂ polymorphs was

calculated as described by Spurr and Meyers (Quantitative Analysis of Anatase-Rutile Mixtures with an X-Ray Diffractometer, Anal. Chem. 29 (1957) 760-762).

Amounts of carbon deposited on the spent catalyst surface were determined using a CHNS elemental analyzer (Perkin Elmer, model 2400 Series II).

The possibility of catalyst regeneration was examined by means of temperature programmed oxidation (TPO) performed in a simultaneous thermal analyzer (Perkin Elmer, model STA 6000). To eliminate the contribution of sample moisture, the specimens were dried *in-situ* for 1 h at 105 °C in N₂ (60 mL/min). Subsequently, the gas stream was switched to air (60 mL/min) and TPO was performed in the 105–900 °C temperature range with 10 °C/min heating ramp.

Spent catalyst samples were analyzed using DRIFTS technique (FTIR apparatus by Perkin Elmer, model Frontier, equipped with DiffusIR diffuse reflection accessory by PIKE Technologies) to elucidate the organic nature of the carbon deposits. A LN₂ cooled MCT detector was used for data acquisition. The spectra were collected in the range between 450-4000 cm⁻¹, with 64 acquisitions per scan and 2 cm⁻¹ spectral resolution. KBr was used to collect the background prior to sample analysis.

Surface morphology of the prepared materials was characterized by means of a scanning electron microscope (Carl Zeiss, model SUPRA 35 VP).

SI.3. Catalytic decarboxylation of FA and AA

Catalytic experiments were performed in an automated computer-controlled multiphase reactor system (PID Eng&Tech, model Microactivity Reference). Prior to catalytic runs, the as prepared catalyst was reduced in a quartz fixed-bed reactor (I.D.=10 mm) for 1 h at 300 °C and pure hydrogen (Linde, 5.0) flow of 250 mL/min. The obtained material was cooled to RT and then loaded ($m_{\text{cat}}=3$ g) into a pressure resistant tubular reactor with I.D.=9 mm (Autoclave Engineers, Hastelloy C-276 stainless steel), where it was supported by a metal frit ($d_{\text{pore}}=2$ μm) and a layer of glass wool ($m=50$ mg) to avoid downstream contamination of the system by catalyst fine particles. For the purpose of process control, temperature was measured with a corrosion resistant PTFE-clad K-type thermocouple, placed in the middle of the catalyst bed. The reactor was operated in a co-current down-flow trickle-bed mode. Before use, liquids were degassed at 50 °C for 30 minutes in an ultrasound bath (Cole Palmer, model 08895-46) and subsequently purged with pure Ar in order to maintain oxygen-free conditions. The catalyst bed was then soaked with ultrapure water and primed with the feed, both steps lasting 60 minutes. Employed feed concentration ranges were selected to illustrate typical wastewater content of carboxylic acids. Feed stream consisting of aqueous solutions of either formic (FA) or acetic acid (AA) ($c_{\text{acid}}=2$ to 20 g/L, $\Phi_{\text{vol,L}}=0.5$ mL/min) was flown over the catalyst particles by means of a positive alternative displacement pump (Gilson, model 307). The catalyst bed was soaked with ultrapure water and primed with the feed, both steps lasting 60 minutes. Nitrogen gas (Linde, 5.0) was fed through an electronic mass flow controller (Bronkhorst, model EL FLOW) and maintained at 10 bar partial pressure ($\Phi_{\text{N}_2}=50$ NmL/min)

to ensure a three phase reaction system. The gaseous and liquid components of the exiting stream were separated in a high-pressure G/L separator equipped with a Peltier cell operating at 15 °C and 1 mL liquid volume. At these conditions, the solubility of CO₂ in water within the separator was in the 10–30 mmol/L range, and was accounted for using the computer code provided by Diamond and Akinfiev (Solubility of CO₂ in water from –1.5 to 100 °C and from 0.1 to 100 MPa: evaluation of literature data and thermodynamic modelling, *Fluid Phase Equilib.* 208 (2003) 265-290). Solubilities of CH₄, H₂ and CO were negligible and therefore not considered (<2 mmol/L in water corresponding to <0.1 vol. % of the gas phase) (D.A. Wiesenburg, N.L. Guinasso, Equilibrium solubilities of methane, carbon monoxide, and hydrogen in water and sea water, *J. Chem. Eng. Data* 24 (1979) 356-360). Discharged gas stream was analyzed by gas chromatography (Agilent, model 7890A; Agilent 19095p-QO3 P-PLOT/Q and Agilent 19095p-MS0 HP-MOLSIEVE columns; TCD detector) to allow for online gas composition analysis of CH₄, CO₂, CO and H₂. Liquid effluent was collected by an autosampler and subsequently analyzed for total organic carbon (TOC) content (Teledyne Tekmar, model Torch) and carboxylic acid concentration by using HPLC (Agilent, model 1260 Infinity; Phenomenex 00G-4252-E0 Luna 5μ C18 column; DAD detector (λ=220 nm)). Blank tests confirmed negligible contribution of the reactor tube and TiO₂ support to conversion of carboxylic acids and decrease of TOC values.

Reactant conversion and selectivity for product formation were calculated as presented in equations (S1) and (S2), respectively.

$$X = \frac{(\phi_{feed} \times t_r) - \int_0^{t_r} (\phi_{effluent} \times dt_r)}{(\phi_{feed} \times t_r)} * 100\% \quad (S1)$$

$$S = \frac{\int_0^{t_r} (\phi_{product} \times dt_r)}{(\phi_{feed} \times t_r) - \int_0^{t_r} (\phi_{effluent} \times dt_r)} \quad (S2)$$

ϕ_{feed} – molar flow rate (mol/h) of reactant in feed

$\phi_{effluent}$ – molar flow rate (mol/h) of reactant in liquid-phase effluent

$\phi_{product}$ – molar flow rate (mol/h) of product in exhaust

t_r – test run duration in h

S2. Supplementary results

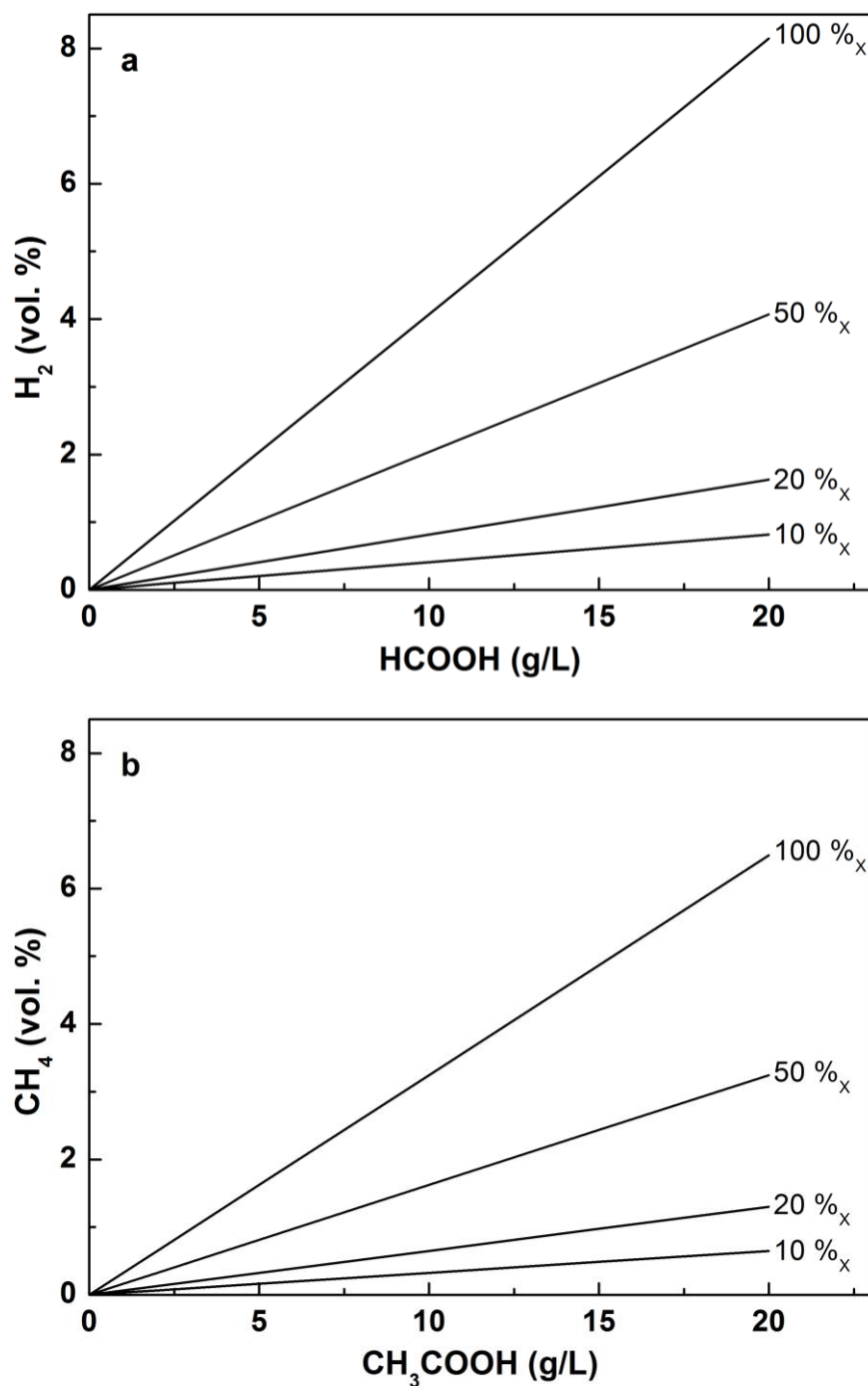


Fig. S1: Theoretical composition of outlet gas stream based on AA and FA decarboxylation stoichiometry assuming 100 % selectivity for decarboxylation and indicated conversions (x) of (a) FA and (b) AA at $\Phi_G=50$ NmL/min, $\Phi_L=0.5$ mL/min).

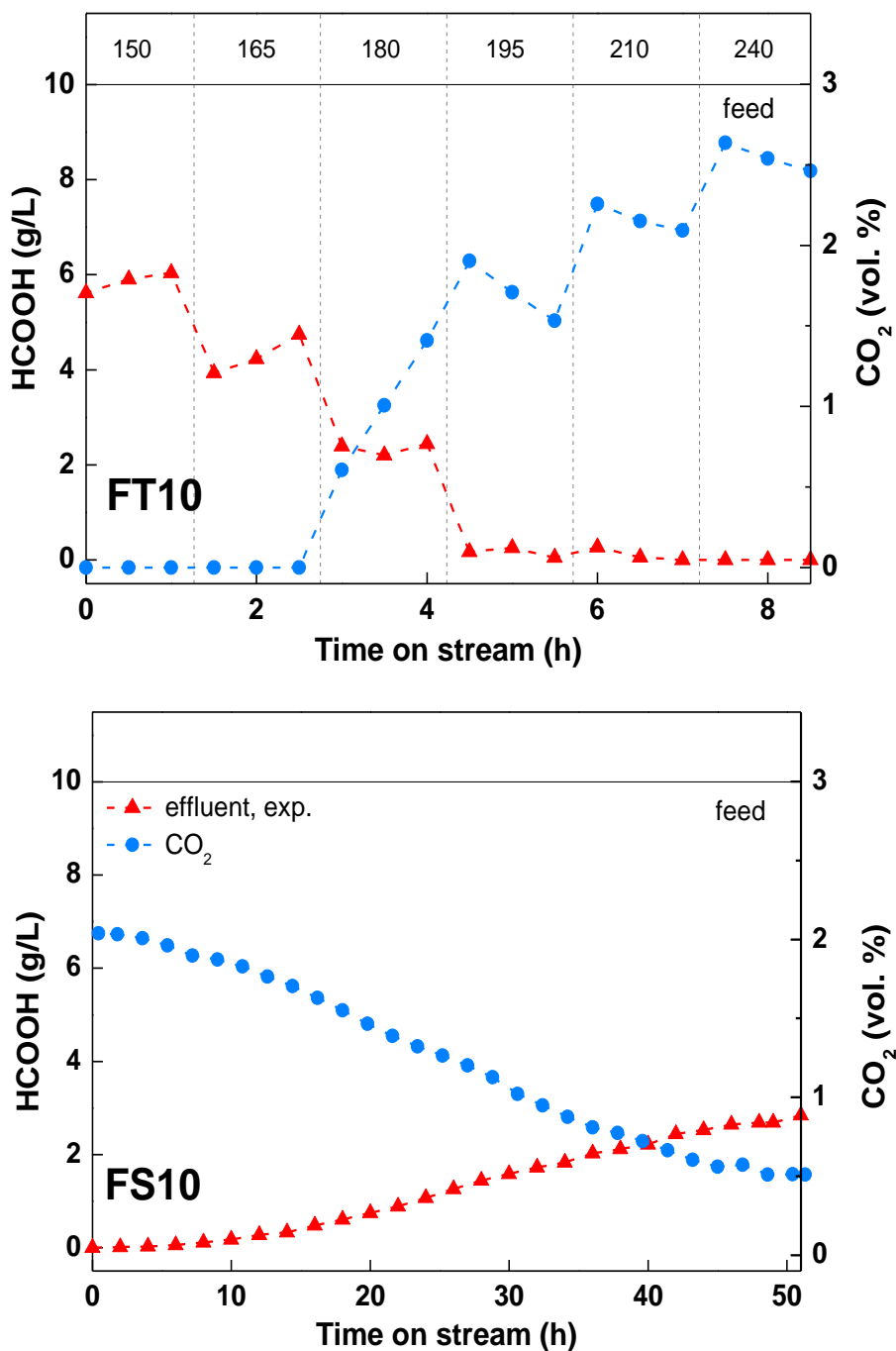


Fig. S2: Conversion of FA at feed concentration of 10 g/L at (FT10) $T_r=150\text{--}240\text{ }^\circ\text{C}$ and (FS10) $T_r=180\text{ }^\circ\text{C}$. Outlet gas phase composition is also shown.

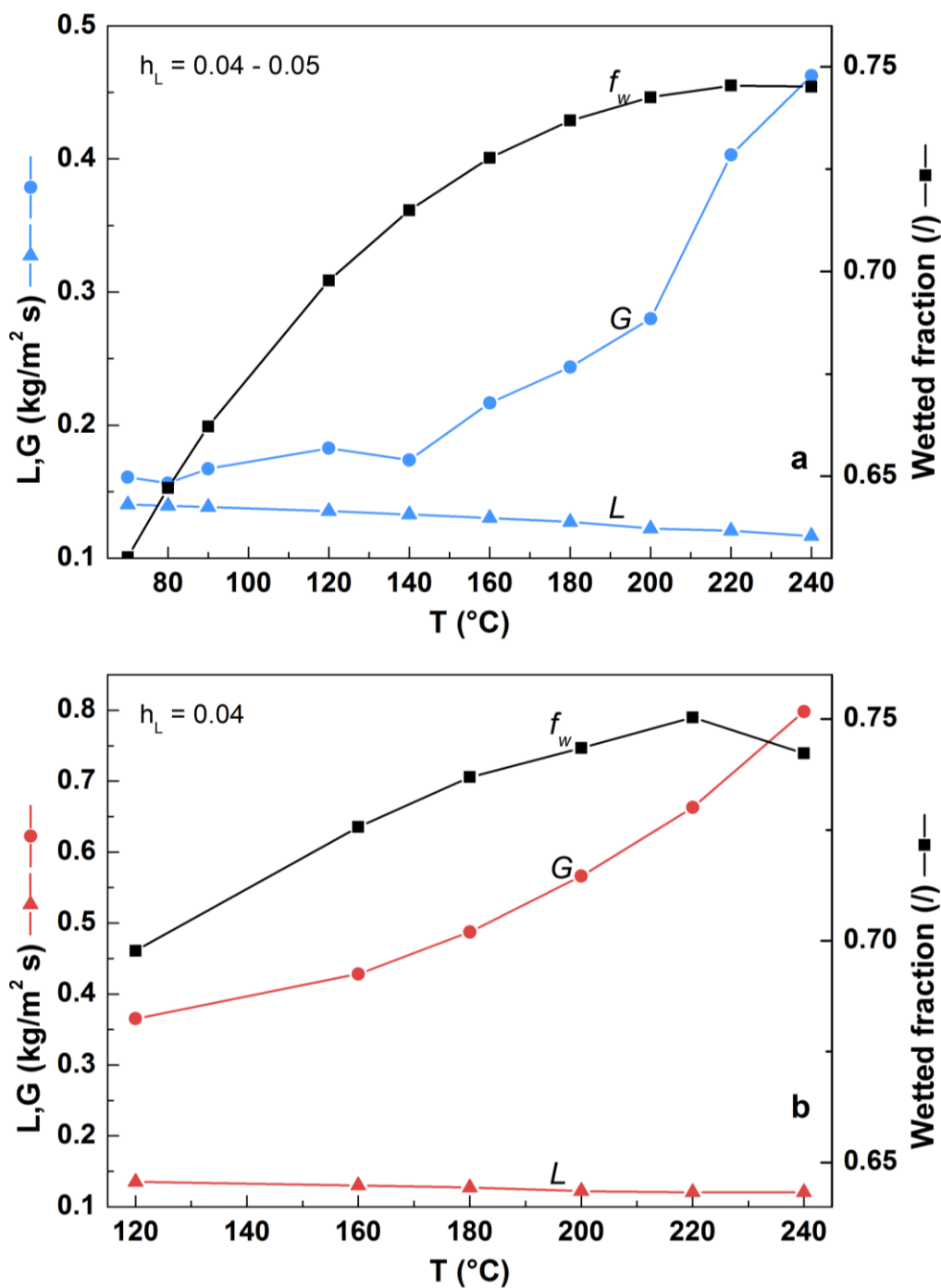


Fig. S3: Trickle-bed hydrodynamic parameters (f_w – wetted fraction, G – gas mass velocity, L – liquid mass velocity, h_L – liquid holdup) at the employed reaction conditions and Ru/TiO₂ catalyst with (a) FA and (b) AA feed (estimated accordingly to the procedure described in A. Pintar, G. Berčić, M. Besson, P. Gallezot, *Appl. Catal. B* 2004, 47, 143–152).

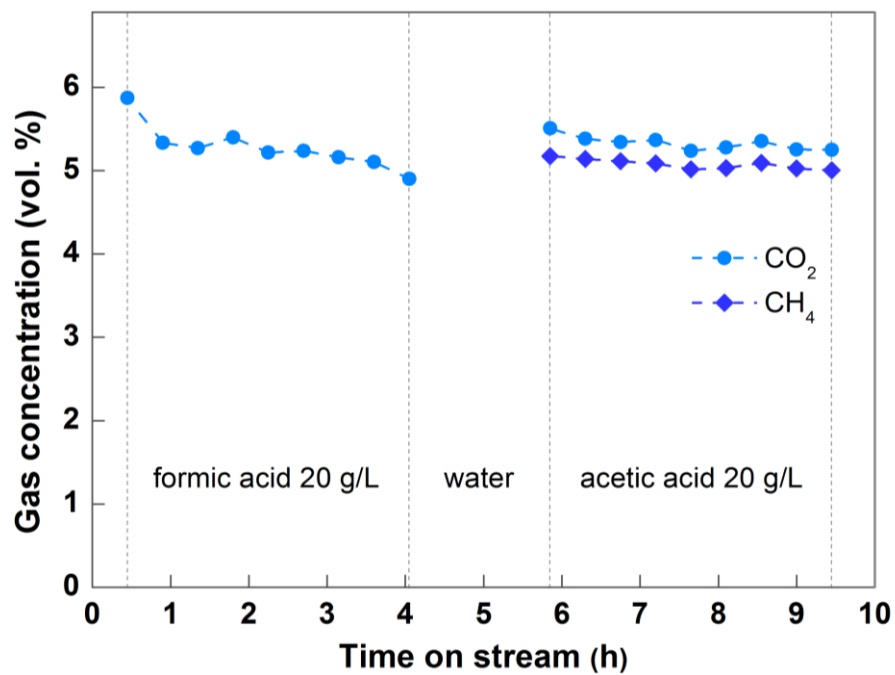


Fig. S4: Composition of gas produced from FA and AA at feed concentration of 20 g/L and $T_r=225$ °C.

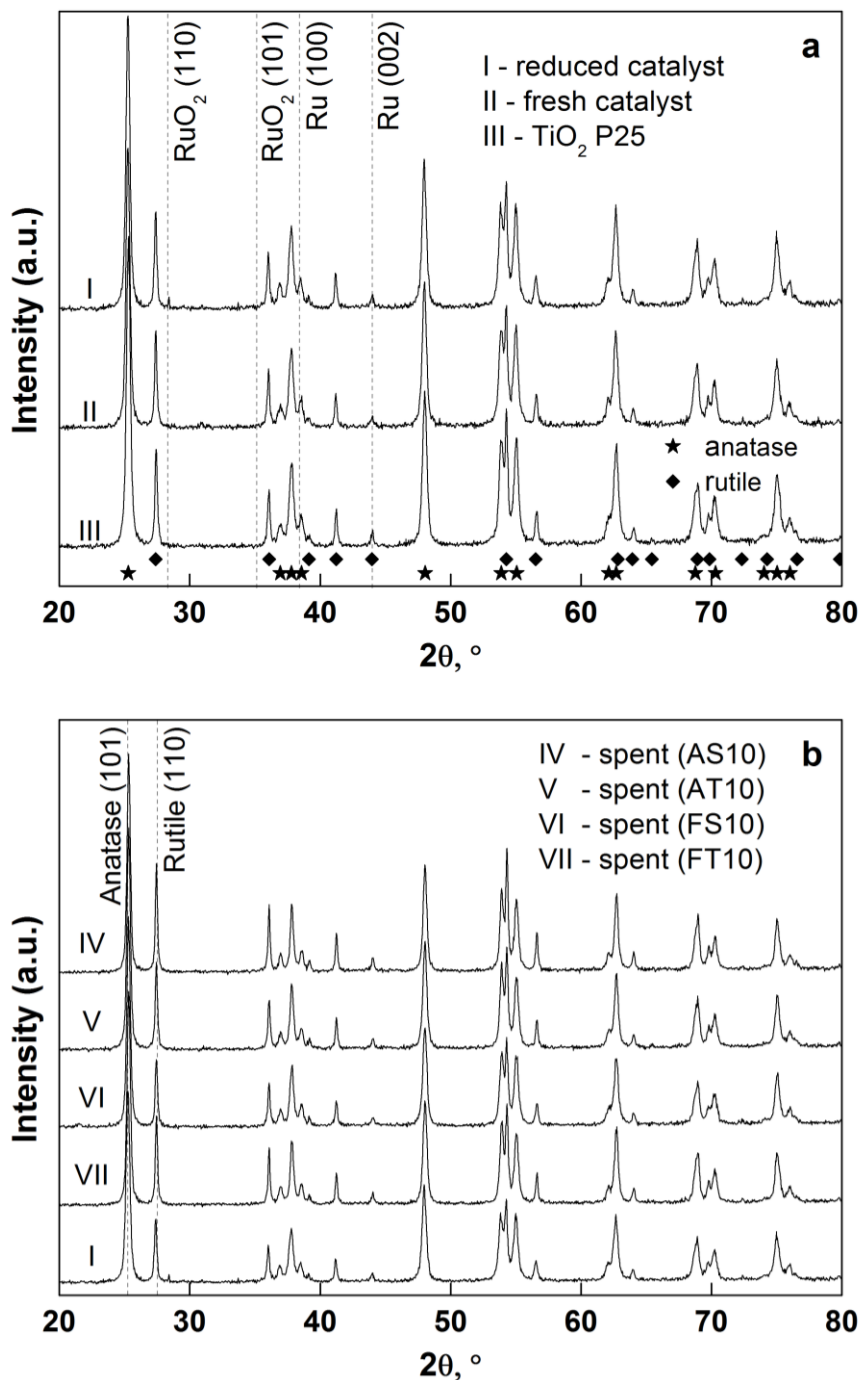


Fig. S5: XRD diffractograms of (a) TiO₂ support and 3% Ru/TiO₂ catalysts before and after thermal stabilization; (b) 3% Ru/TiO₂ catalysts before and after catalytic runs (annotated peak positions were obtained from the following PDF standards: hexagonal Ru (00-006-0663), tetragonal RuO₂ (00-021-1172), tetragonal TiO₂ – anatase (00-021-1272), tetragonal TiO₂ – rutile (01-089-0552)).

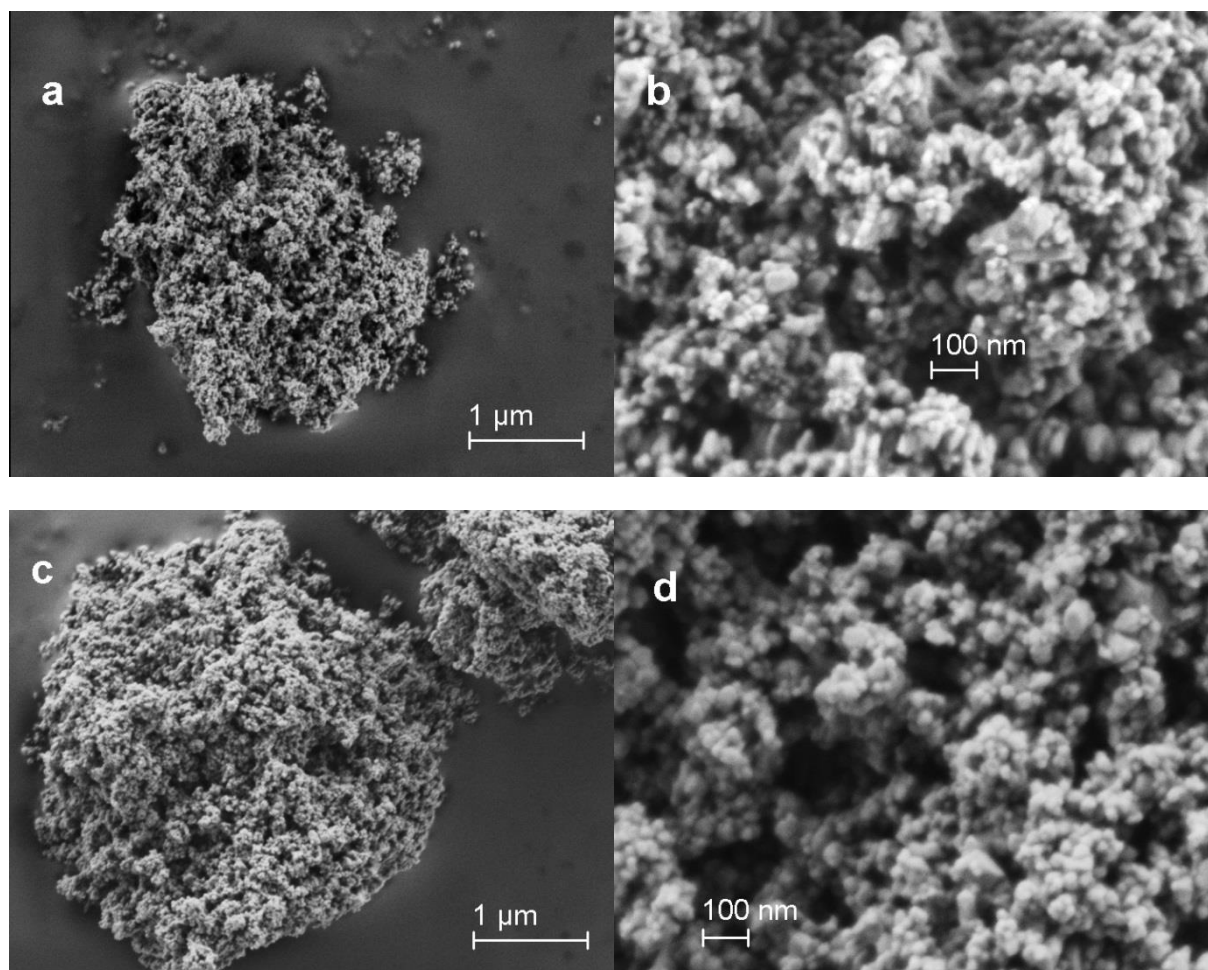


Fig. S6: SEM micrographs of the 3 wt. % Ru/TiO₂ catalyst (a, b) prior and (c, d) after use in the 70 h long AS10 test.

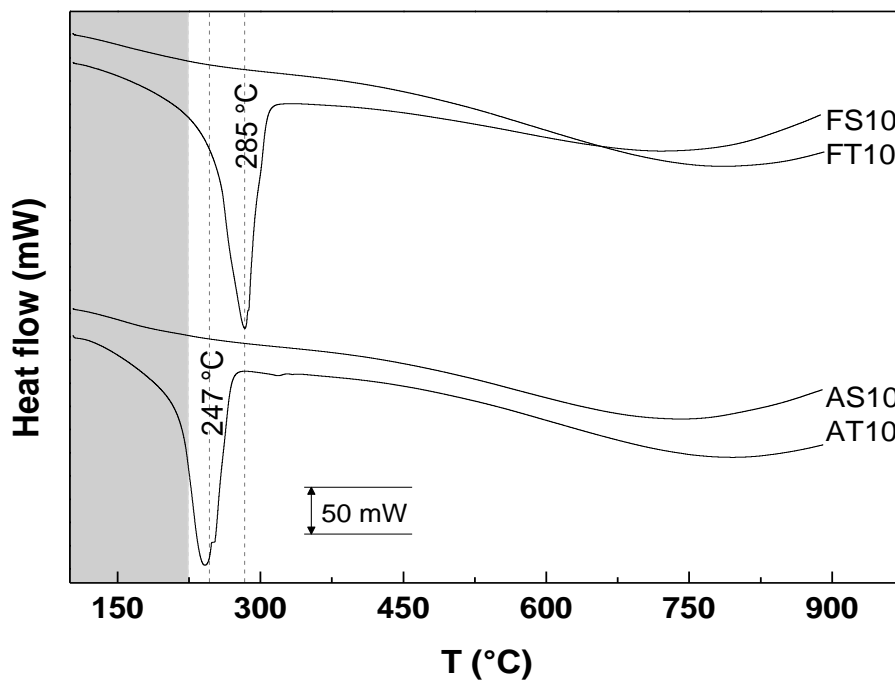


Fig. S7: Heat flow, measured by dynamic scanning calorimetry (DSC) during thermal desorption of carbonaceous deposits from spent 3% Ru/TiO₂ catalysts (negative peaks – endothermic process). Gray-shaded area – temperature range, covered during AA and FA decarboxylation experiments.