

**Supercritical Fluid assisted Modification combined with the Resynthesis as Effective Tool to
Enhance Long-term Performance of SmCoO₃ catalyst
for Dry Reforming of Methane to Syngas**

Andrey V. Gavrikov^{a*}, Alexey S. Loktev^{a,c}, Andrey B. Ilyukhin^a, Igor E. Mukhin^b,
Mikhail A. Bykov^d, Konstantin I. Maslakov^d, Anton M. Vorobei^a, Olga O. Parenago^a,
Alexey A. Sadovnikov^{a,c}, Alexey G. Dedov^{a,c}

*^aKurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Moscow,
Russian Federation,*

^bNational University of Oil and Gas «Gubkin University», Moscow, Russian Federation,

^cA.V. Topchiev Institute of Petrochemical Synthesis, RAS, Moscow, Russian Federation,

^dDepartment of Chemistry, Lomonosov Moscow State University, Moscow, Russian Federation

Dry reforming of methane to Syngas (DRM) is of increasing significance concerning, first, the production of raw for commercial organic/petrochemical syntheses and for hydrogen energetic, and, second, the utilization of two most harmful greenhouse gases. Herein, new SmCoO₃-based DRM catalysts derived from heterometallic precursor and operating without preliminary reduction are reported. For the first time, the effect of supercritical fluids-assisted modification of the SmCoO₃-derived catalysts combined with the restoration of spent catalysts to SmCoO₃ onto its long-term performance was studied. Namely, the modification of heterometallic precursor by supercritical antisolvent precipitation (SAS) allows one to considerably decrease coke formation upon the exploitation of the derived SmCoO₃ sample. Moreover, the re-oxidation of corresponding spent catalysts followed by pre-heating under N₂ affords catalysts which stably provide Syngas yields of 88-95% for at least 41 h at 900 °C. The achieved yields are among the highest ones currently reported for DRM catalysts derived from both LnMO₃

perovskites and related oxides. The origins of such good performance are discussed. Given the simplicity and availability of all applied methods and chemicals, this result opens prospects for the exploiting SAS in the design of efficient DRM catalysts.

* Corresponding author. E-mail address:

gavrikov@igic.ras.ru;

penguin1990@yandex.ru

Keywords: Dry reforming of methane; Syngas; CO₂ utilization; Heterogeneous catalysts; Lanthanide cobaltites; SmCoO₃; Heterometallic precursors; Supercritical antisolvent precipitation; Solid-phase thermolysis

*Synthesis of [Co(phen)₃][Sm(NO₃)₅(H₂O)]·2MeCN (**SmCo**) precursor for SmCoO₃*

To prepare **SmCo**, 2.29 g (5.15mmol) of Sm(NO₃)₃·6H₂O was added to the solution of 1 g (5.15 mmol) of Co(NO₃)₂·6H₂O and 3.05 g (15.4 mmol) of phen·H₂O in 50 ml of hot (80 °C) MeCN. Precipitation of product started in a minute after the dissolution of Sm(NO₃)₃·6H₂O. After cooling the reaction mixture to room temperature and its exposition for 6 h, 4.2 g (70 %) of single phase (Fig.S1) **SmCo** was formed as large dark-olive crystals.

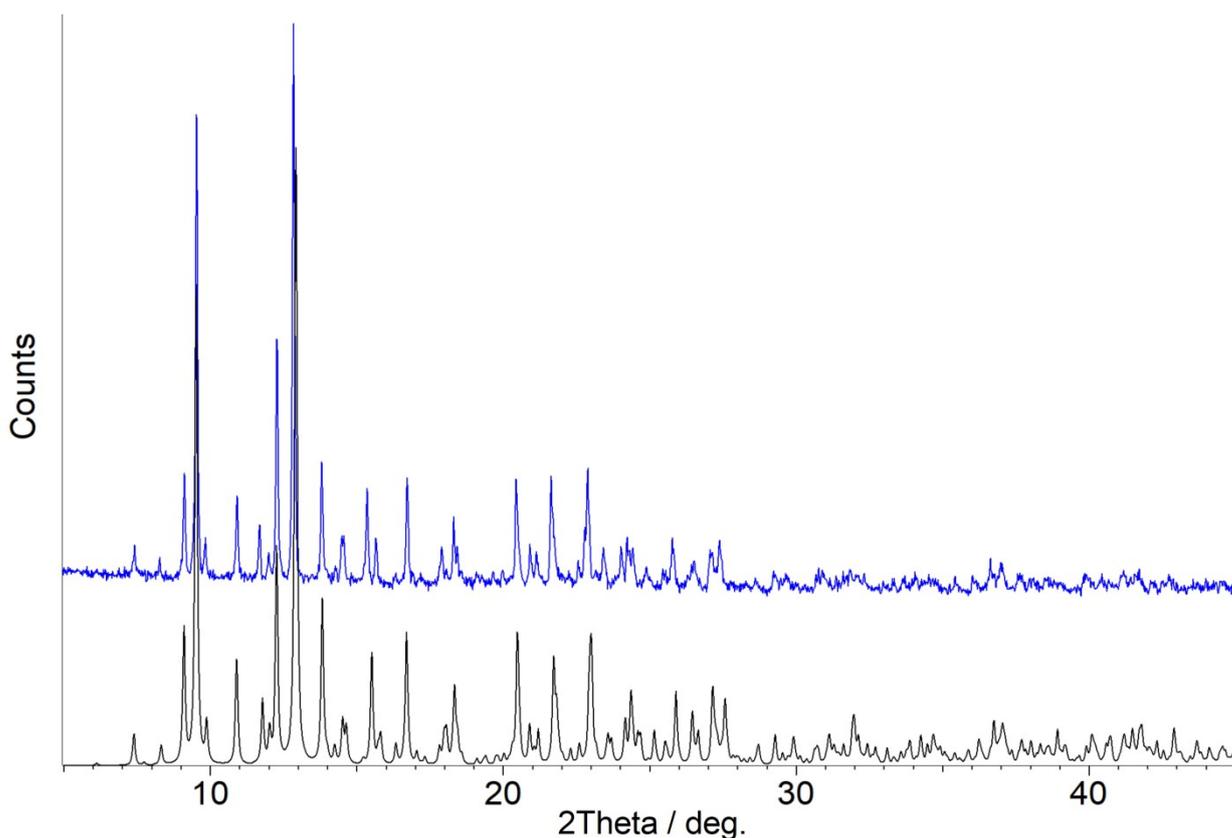


Fig. S1. Powder XRD pattern of **SmCo** (blue curve) in comparison with the calculated pattern for the [Co(phen)₃][Sm(NO₃)₅(H₂O)]·2MeCN precursor (this pattern can be extracted from CCDC 2099934) studied in [50] (black curve).

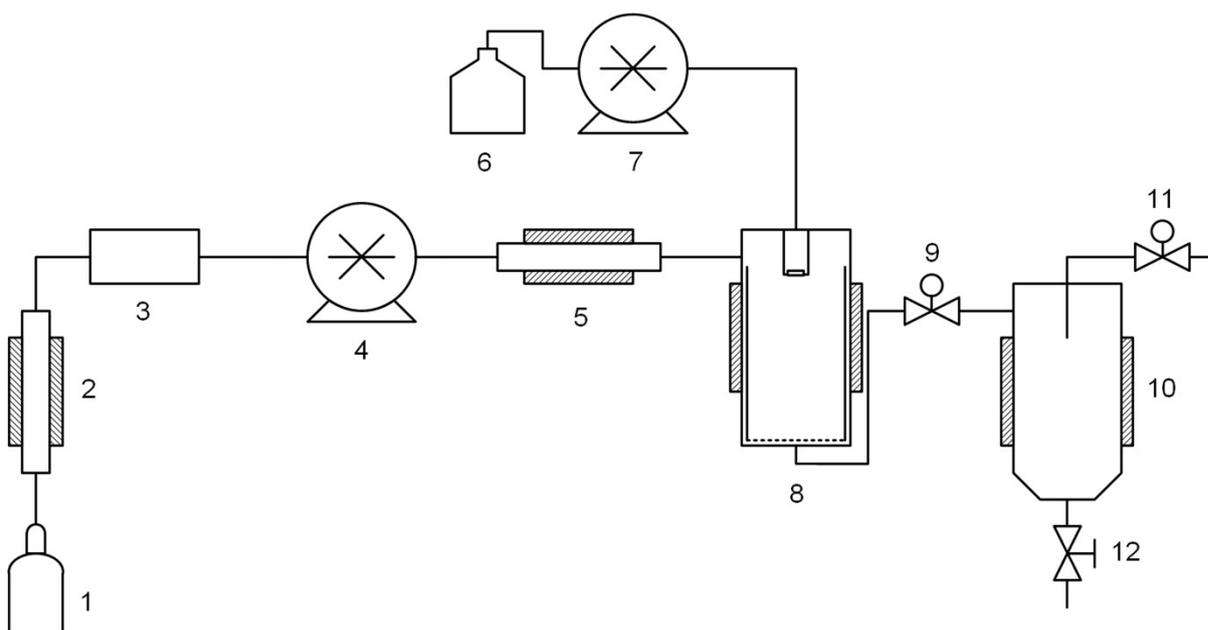


Fig. S2. Scheme of the setup for supercritical antisolvent precipitation: 1- CO₂ source; 2- cooling heat exchanger; 3 - Coriolis flowmeter; 4 - CO₂ pump; 5- heater; 6 - solution of precursor **1**; 7 - solution pump; 8- precipitation chamber, 9–automatic pressure regulator; 10 - cyclone separator; 11 - manual pressure regulator; 12 - drain valve.

The solution of **SmCo** (3 g) in methanol (250 ml) was introduced into the device, and pressure, temperature and rate of CO₂ flow were set to reach the operating values.

SAS micronization was performed at 40 °C and 150 bar with 50 g/min CO₂ flow and 1 ml/min solution flow. The diameter of spray nozzle was 200 μm. The liquid pump 7 was filled with methanol, 5 ml of which was sprayed at an operating rate into the precipitation vessel 8 to balance the composition of the fluid in the vessel. After that, the inlet line of the pump was moved into a container 6 with solution of **SmCo** which was further sprayed at the same rate. After spraying all solution of **SmCo**, an additional 15 ml of methanol was supplied to flush the solution supply line upstream of the spray nozzle. At the end of the spraying, the CO₂ flow was additionally maintained in the precipitation vessel 8 for 2 hours to flush out the residual methanol from the product. After ceasing the flow of CO₂, the pressure was gradually released to atmospheric *via* regulator 9. The resulting **SAS_SmCo** product was removed from the precipitation vessel 8 using a built-in basket. To remove residual methanol, the samples were additionally exposed at 80 °C for 1 h.

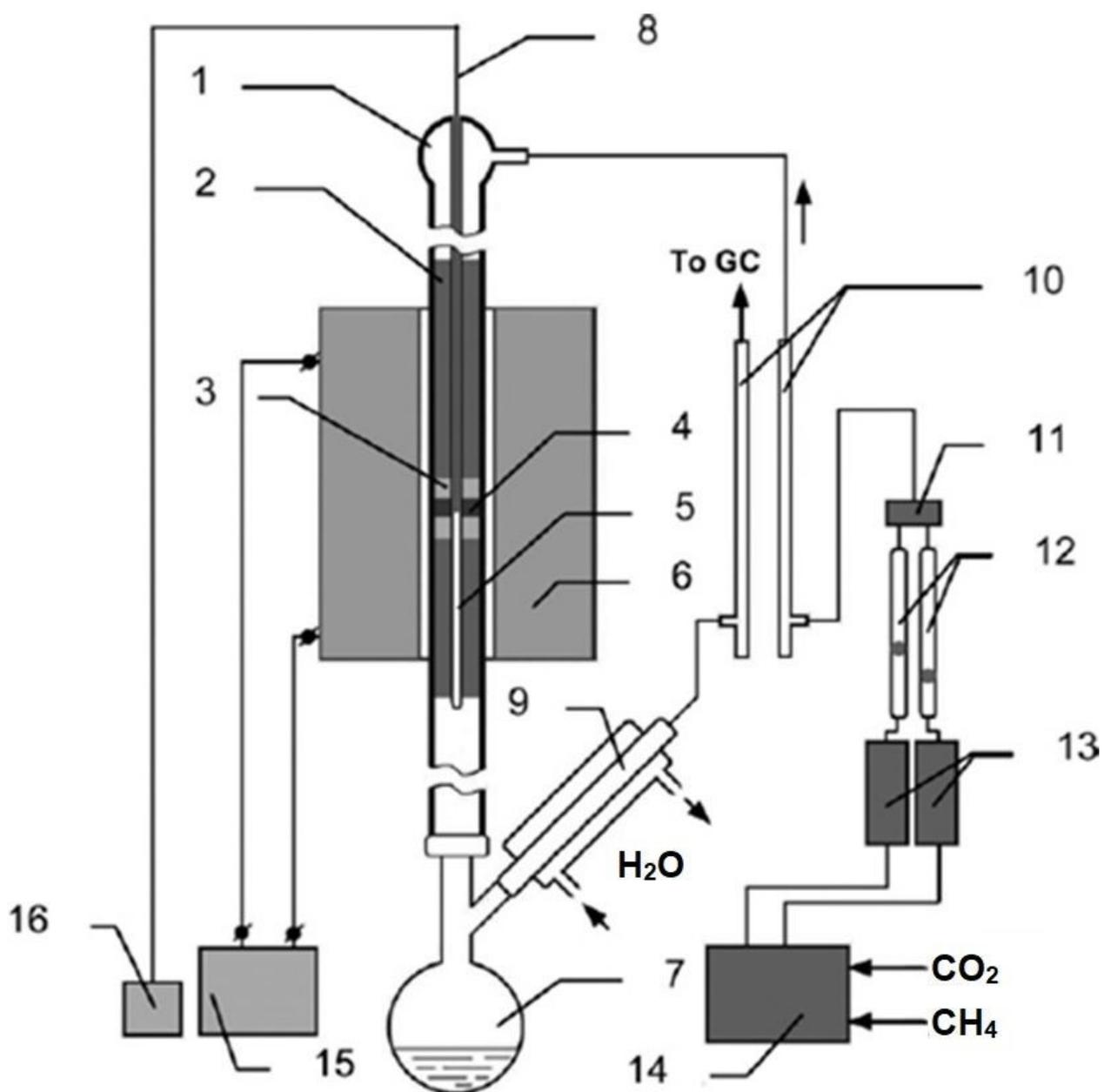


Fig. S3. Single-pass plug-flow setup. (1) Quartz reactor, (2) quartz-glass insert, (3) quartz wool, (4) catalyst, (5) internal pocket for thermocouple, (6) electric furnace, (7) condensate receiver (round-bottom flask), (8) thermocouple, (9) water cooler, (10) flow meters, (11) gas mixer, (12) ball-in-tube flow meters, (13) adsorbent, (14) gas flows shaper, (15) furnace controller, (16) temperature indicator.

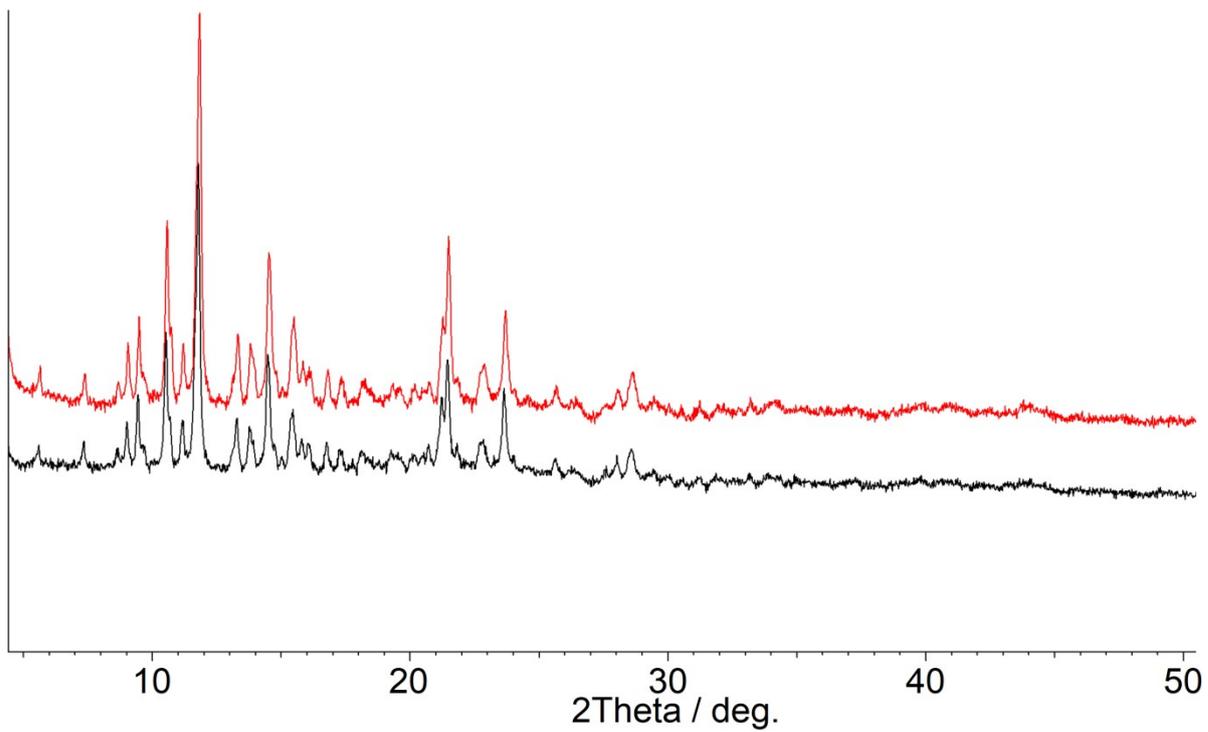


Fig. S4. Powder XRD pattern of **SAS_SmCo** (red curve) and similarly prepared sample studied in [50] (black curve).

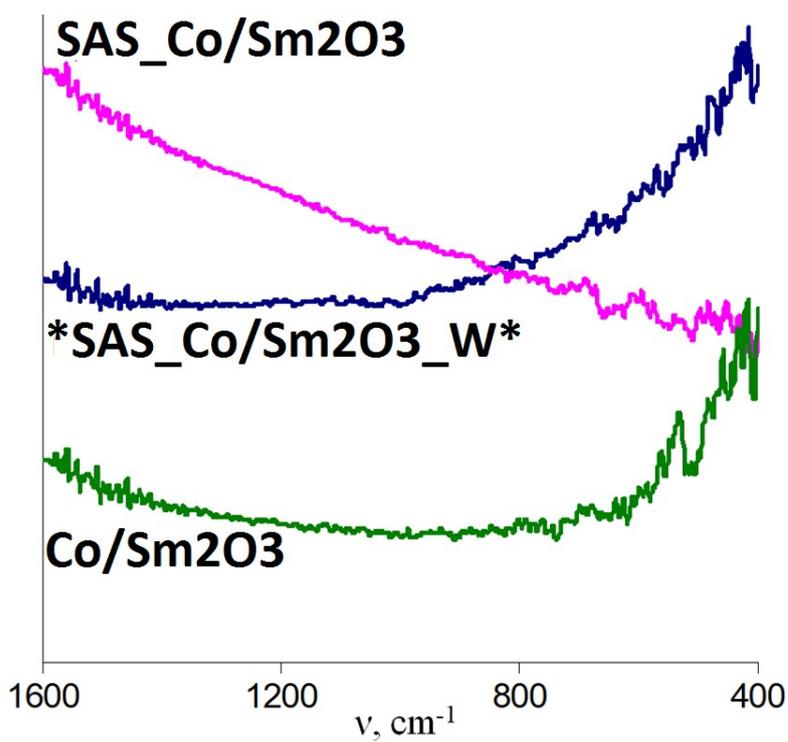


Fig. S5. IR spectra of spent catalysts after DRM process.

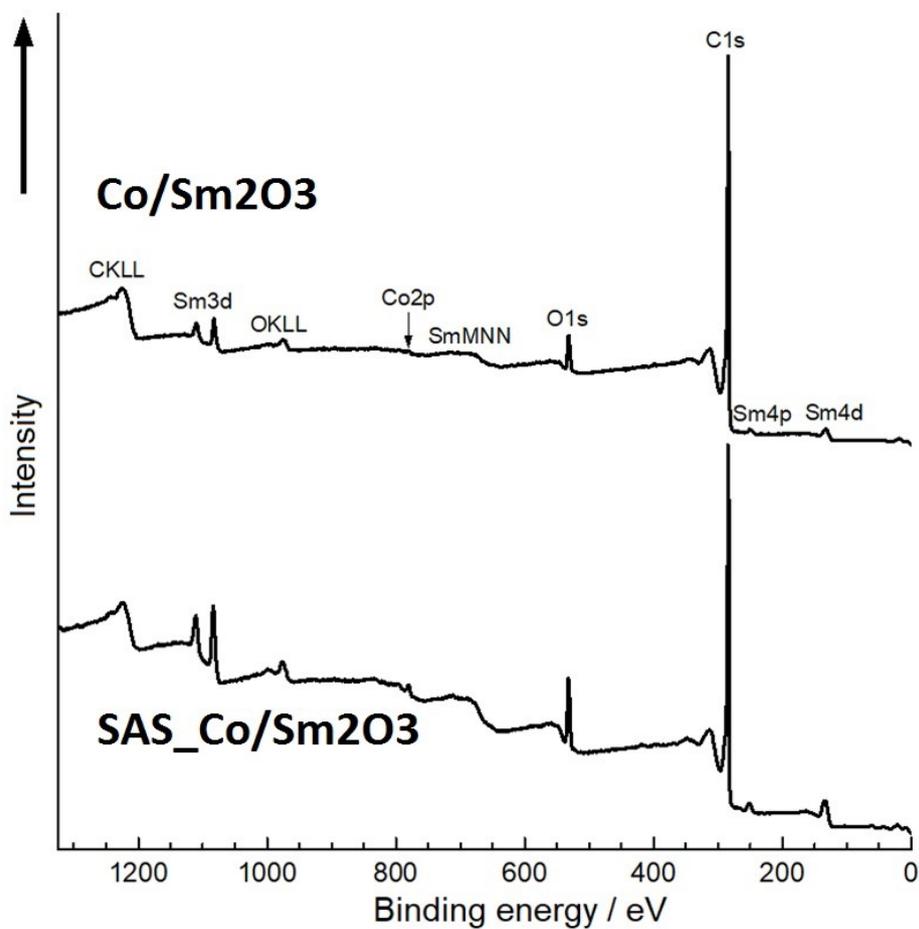


Fig. S6. Survey XPS spectra of $\text{Co/Sm}_2\text{O}_3$ and $\text{SAS_Co/Sm}_2\text{O}_3$ spent catalysts.

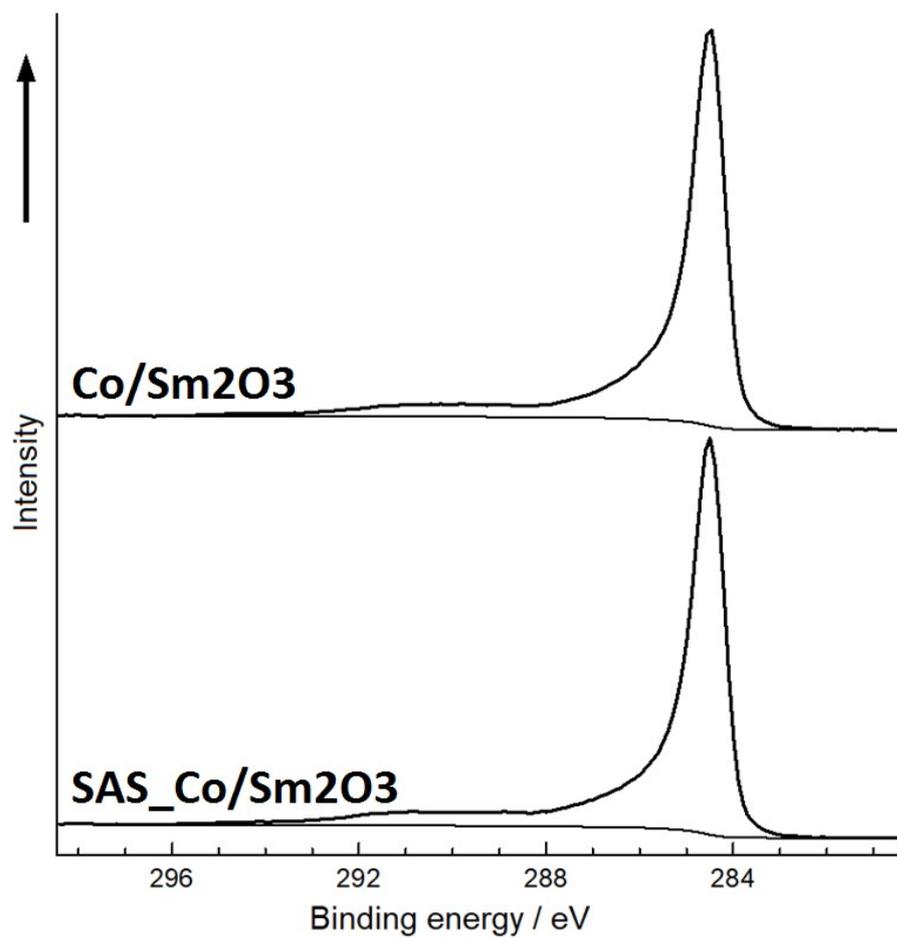


Fig. S7. C1s XPS spectra of **Co/Sm2O3** and **SAS_Co/Sm2O3** spent catalysts.

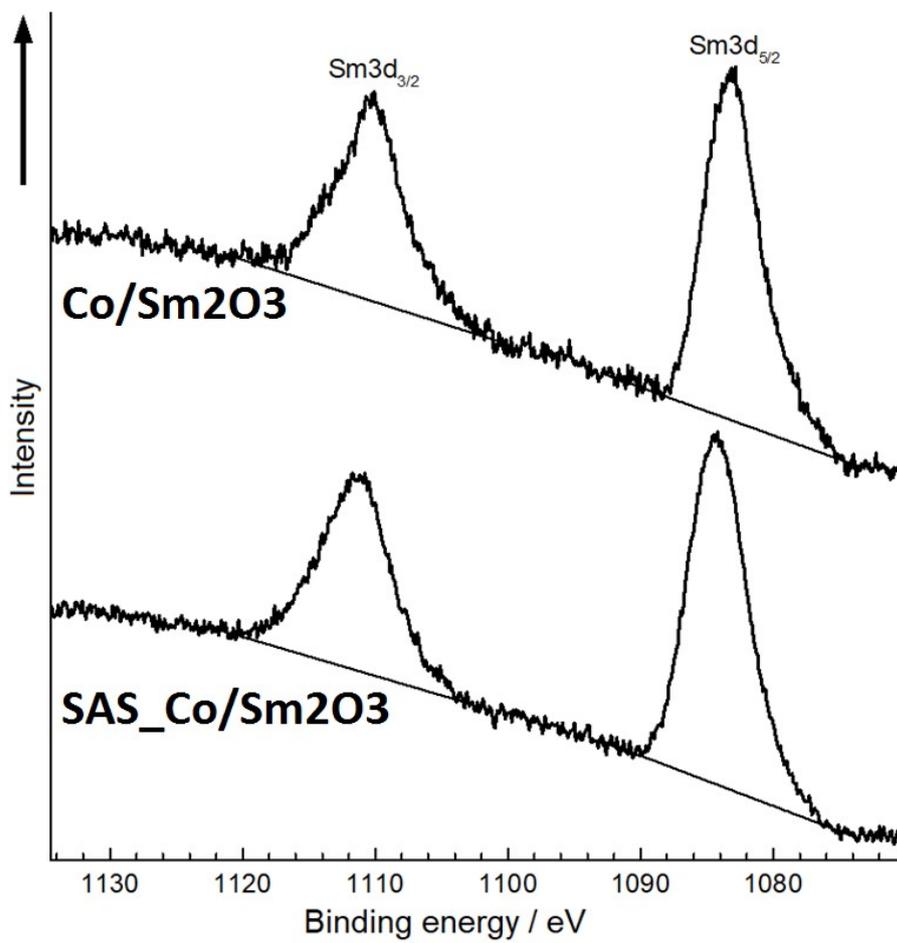


Fig. S8. Sm3d XPS spectra of **Co/Sm₂O₃** and **SAS_Co/Sm₂O₃** spent catalysts.

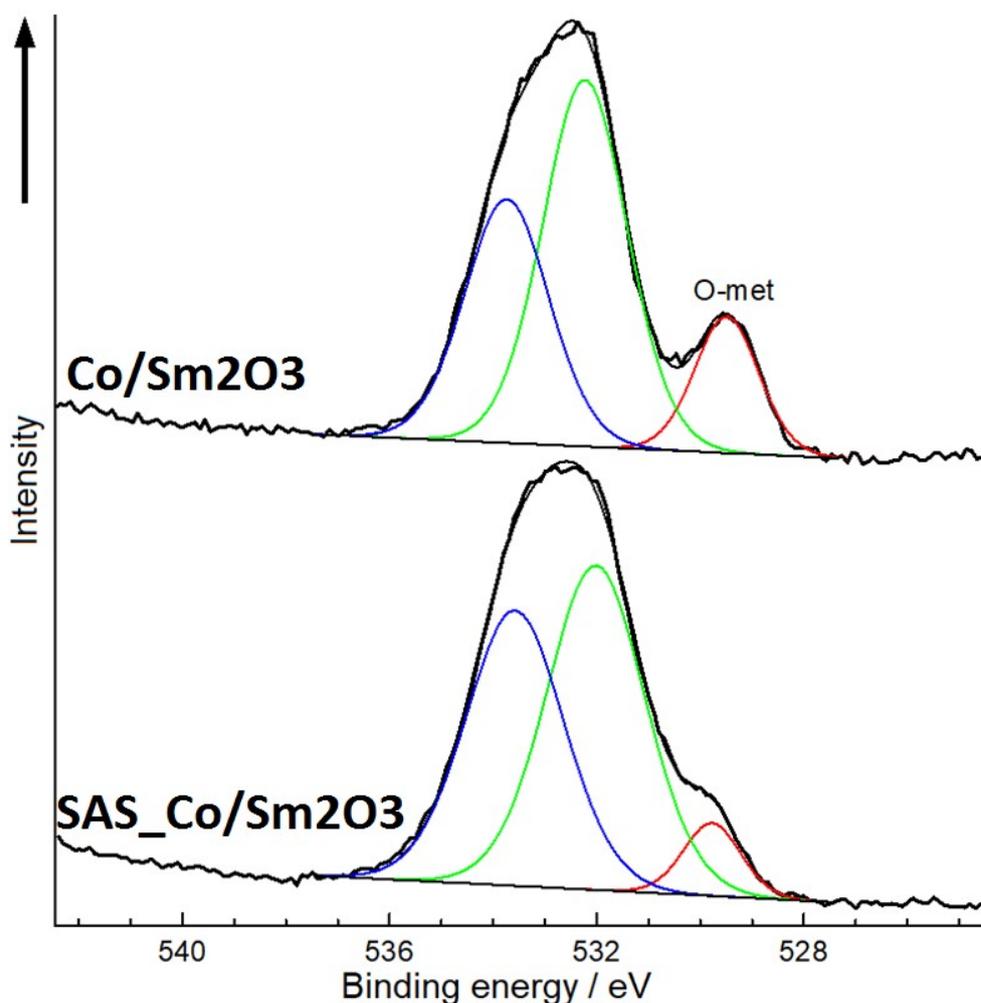


Fig. S9. O1s XPS spectra of **Co/Sm₂O₃** and **SAS_Co/Sm₂O₃** spent catalysts.

Table S1. Content of different Co species (at. %) on the surface of spent catalysts determined from the fitting of Co2pXPS spectra with synthetic components. Co2p_{3/2} binding energies (eV) of components are shown in parenthesis.

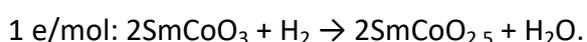
Sample	Co ⁰	Co ²⁺	Co ³⁺
SAS_Co/Sm₂O₃	0 (777.9)	40 (781.9)	60 (779.9)
Co/Sm₂O₃	5 (777.9)	28 (781.7)	67 (780.0)

Table S2. Results of blank experiments.

T, °C	X CH ₄ , %	X CO ₂ , %	Products yield, %			
			C ₂ H ₄	CO	H ₂	Coke
700	5	6	0	0	1	5
800	4	3	0	0	1	3
900	5	8	0	0	1	6
900	5	6	0,5	0	1	6

Temperature-programmed reduction of SAS_SmCoO3 sample

Initially, H₂-TPR profile was recorded in 50-850 °C range (Fig. S10a). Near 160 °C, drastic decrease in the background intensity was observed, which can be explained by the H₂O desorption from the pores of the sample. Above 700 °C, notable increase of the baseline occurs due to H₂ adsorption by the resulting material. Thus, representative temperature range of 200-700 °C was further analyzed (Fig. S10b). In this range, two distinct and intensive peaks at 400 °C and 528 °C are observed. These peaks agree well with the literature data for H₂-TPR of SmCoO₃ [1-4]. The peak at 400 °C is associated with the process of single-electron reduction of Co³⁺ to Co²⁺ within SmCoO₃ structure:



The second peak at 528 °C indicates triply-electron reduction of perovskite phase to Co/Sm₂O₃ composite:

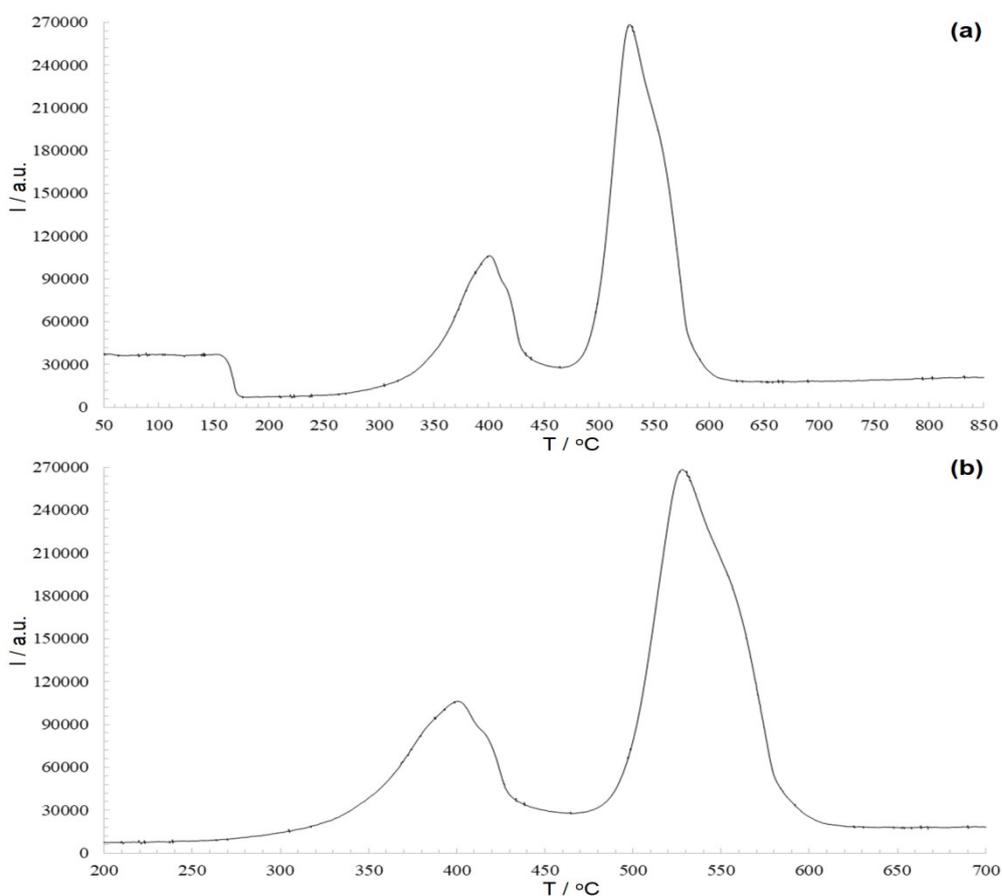
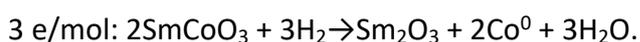


Fig S10. H₂-TPR profile of SAS_SmCoO₃ sample in 50-850 (a) and 200-700 °C (b) range.

1. O.U. Osazuwa, H.D. Setiabudi, R.A. Rasid, C.K. Cheng, *J. Nat. Gas Sci. Eng.*, 2017, **37**, 435-448. <https://doi.org/10.1016/j.jngse.2016.11.060>;
2. O.U. Osazuwa, C.K. Cheng, *J. Clean. Prod.*, 2017, **148**, 202-211. <https://doi.org/10.1016/j.jclepro.2017.01.177>;
3. O.U. Osazuwa, C.K. Cheng, *Malaysian J. Catal.*, 2017, **2**, 12-17. <https://mjcat.utm.my/index.php/MalJCatal/article/view/23>;
4. R. Lago, G. Bini, M.A. Peña, J.L.G. Fierro, *J. Catal.*, 1997, **167**, 198-209. <https://doi.org/10.1006/jcat.1997.1580>.

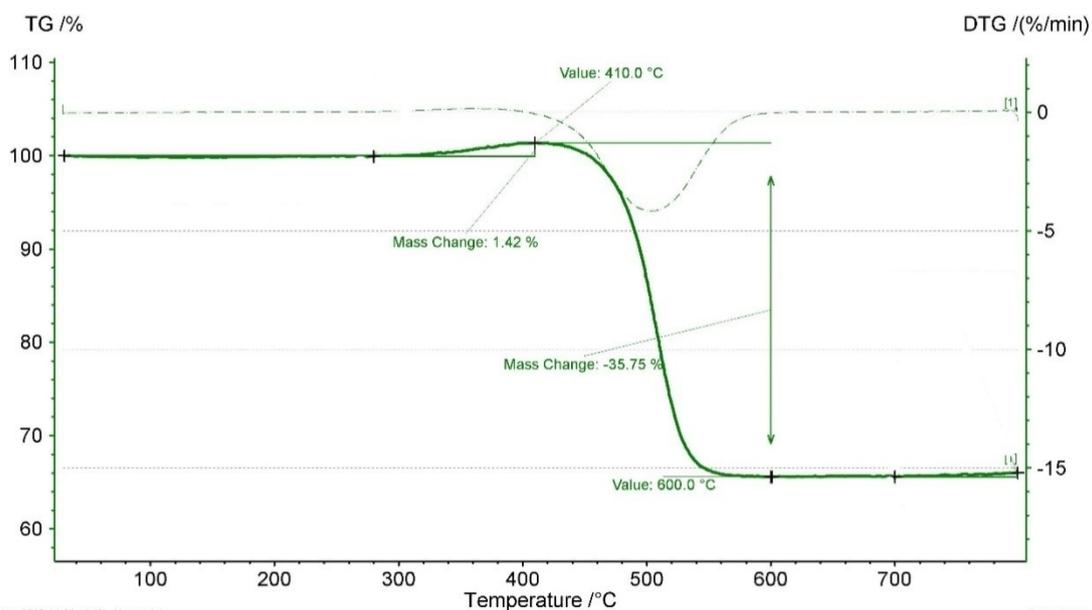


Fig S11. TG (solid line) and DTA (dashed line) of *SAS_Co/Sm2O3_W* sample.

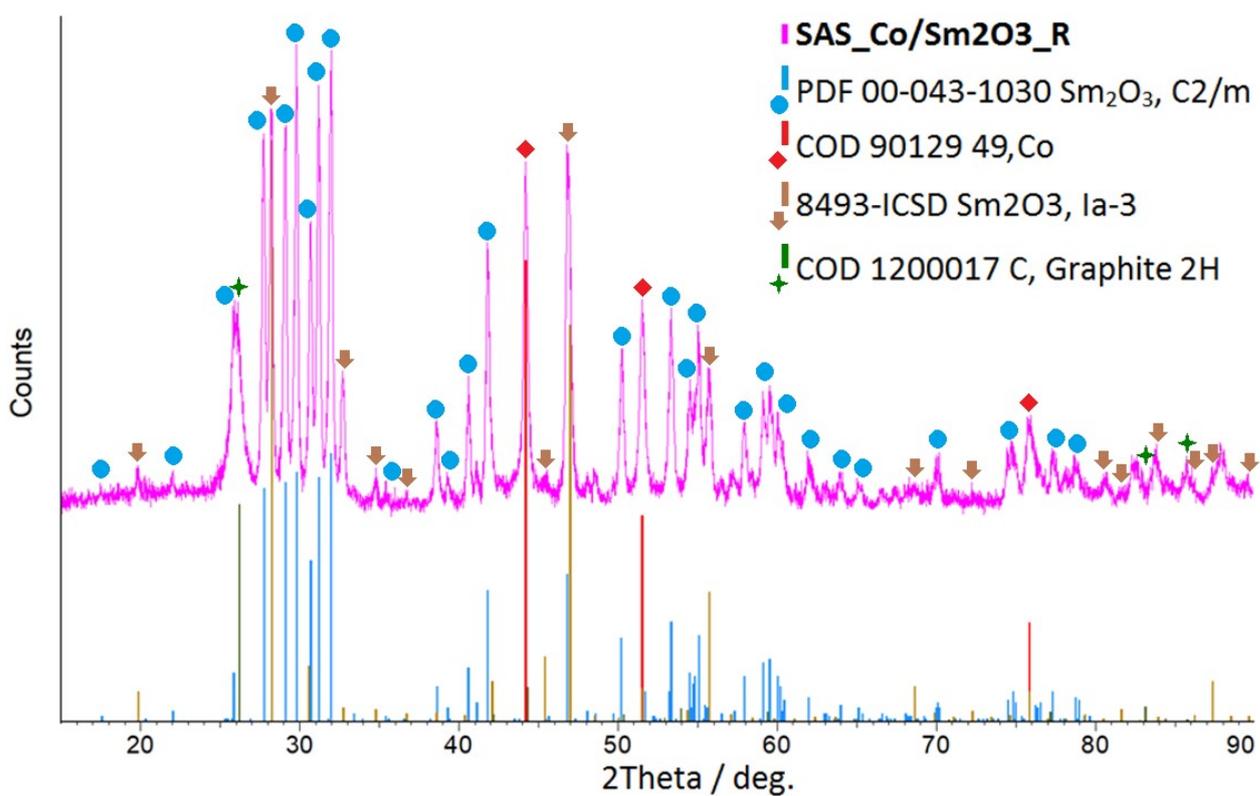


Fig S12. Powder XRD pattern of SAS_Co/Sm2O3_R sample.

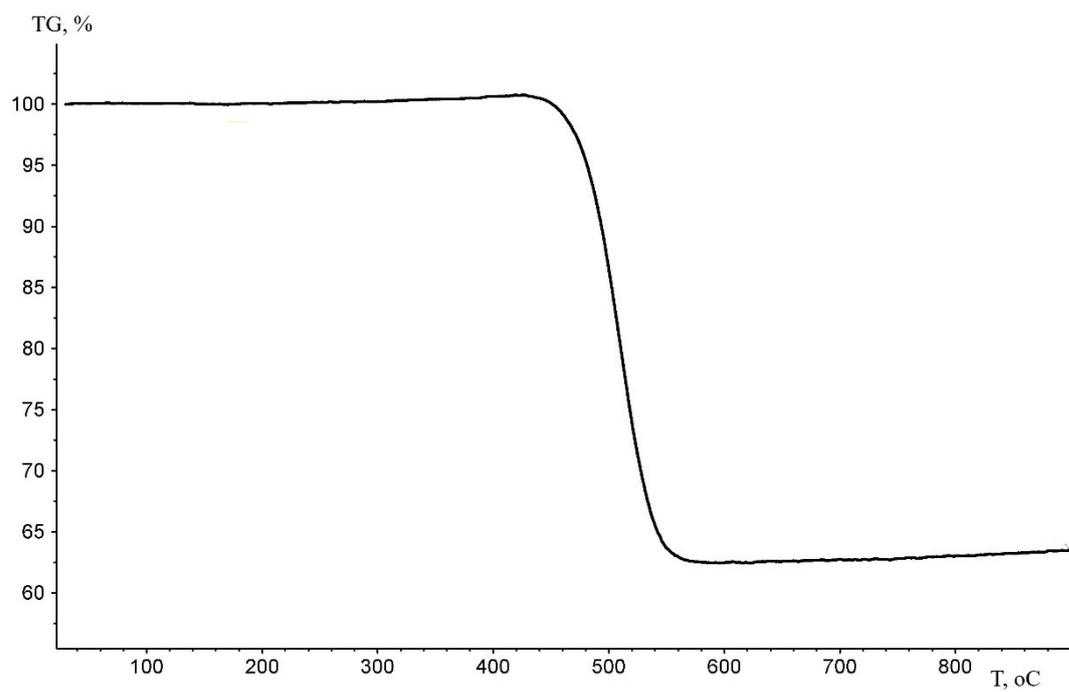


Fig S13. TG curve of SAS_Co/Sm₂O₃_R sample.

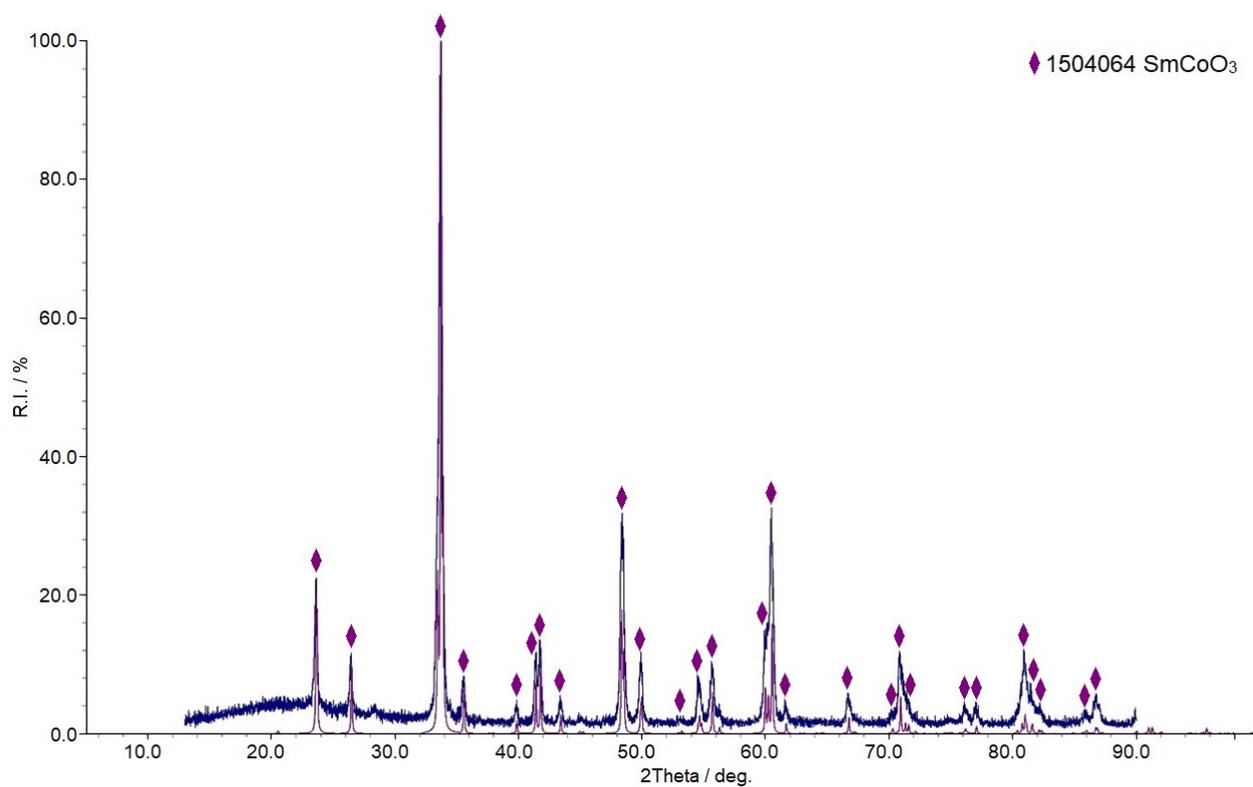


Fig. S14. Powder XRD pattern of SAS_Co/Sm₂O₃ sample after its annealing at 800 °C for 2 h.

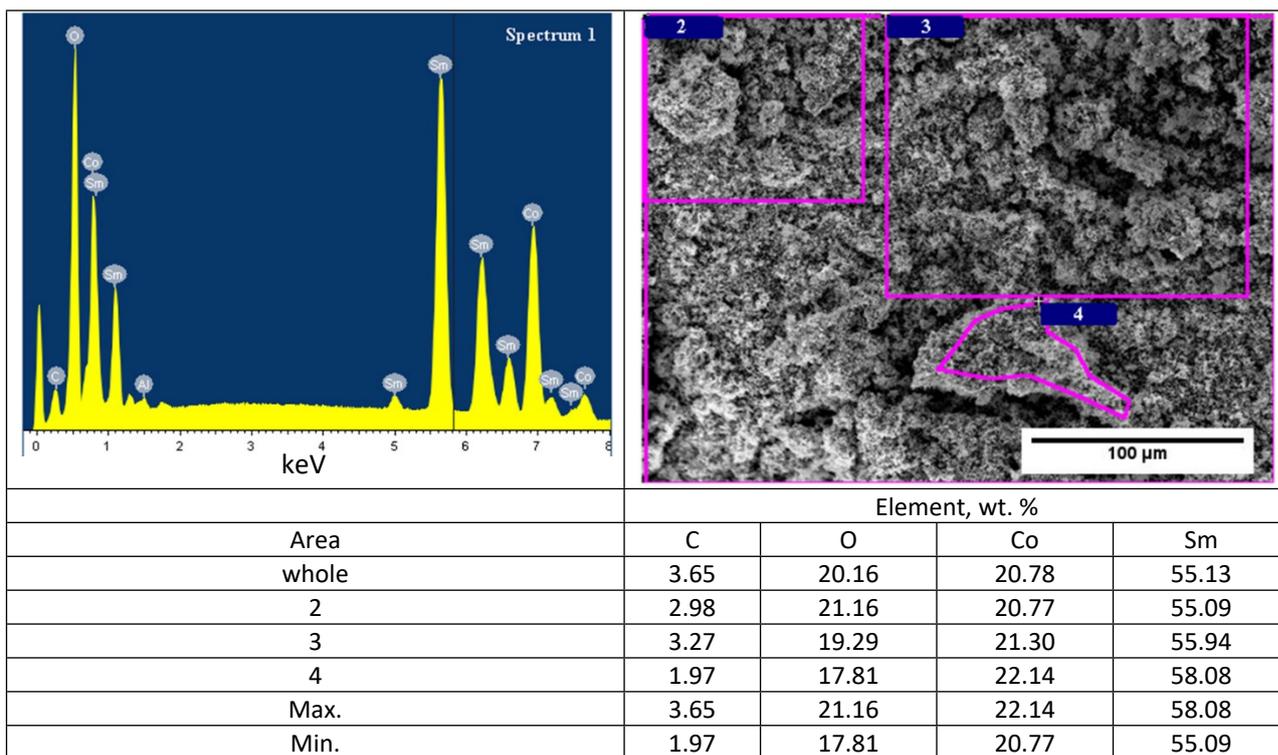


Fig. S15.EDX data of **SAS_Co/Sm₂O₃** sample after its annealing at 800 °C for 2 h.

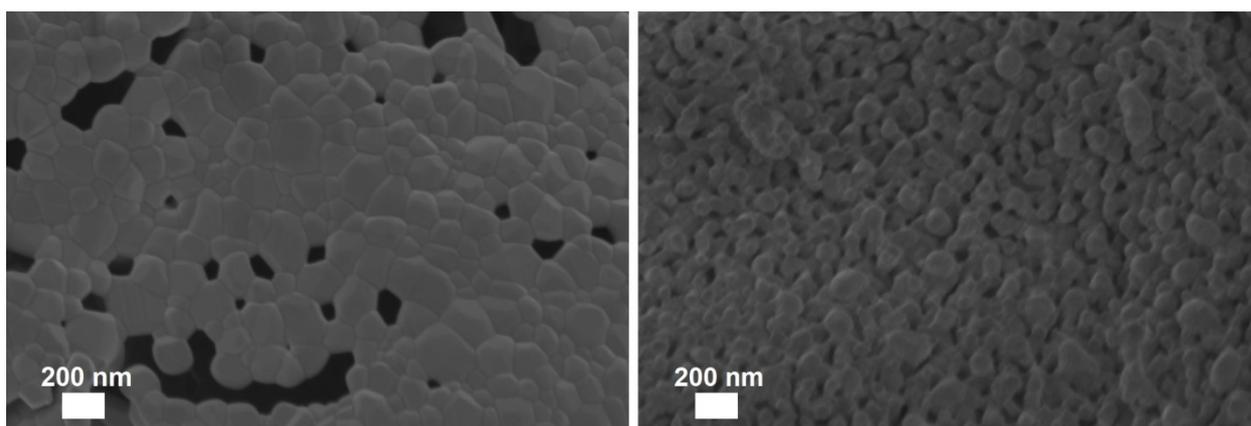


Fig. S16.SEM images (×100000) of ***SAS_Co/Sm₂O₃*** (left) and **SAS_SmCoO₃_R** (right) catalysts.

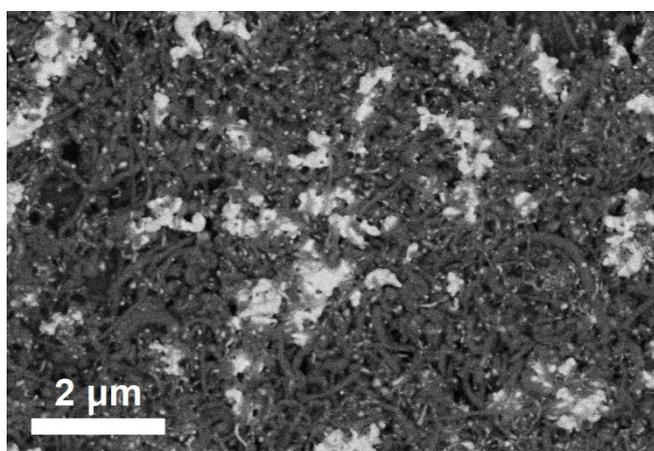


Fig. S17. SEM image (×30000) of **SAS_Co/Sm₂O₃_R** spent catalyst.