

Supplementary Information

The relevance of the Lewis acid sites on one-pot gas phase reaction of levulinic acid into ethyl valerate using CoSBA-xAl bifunctional catalysts

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1) N₂ adsorption-desorption isothermal and pore distribution of calcined CoSBA-xAl samples

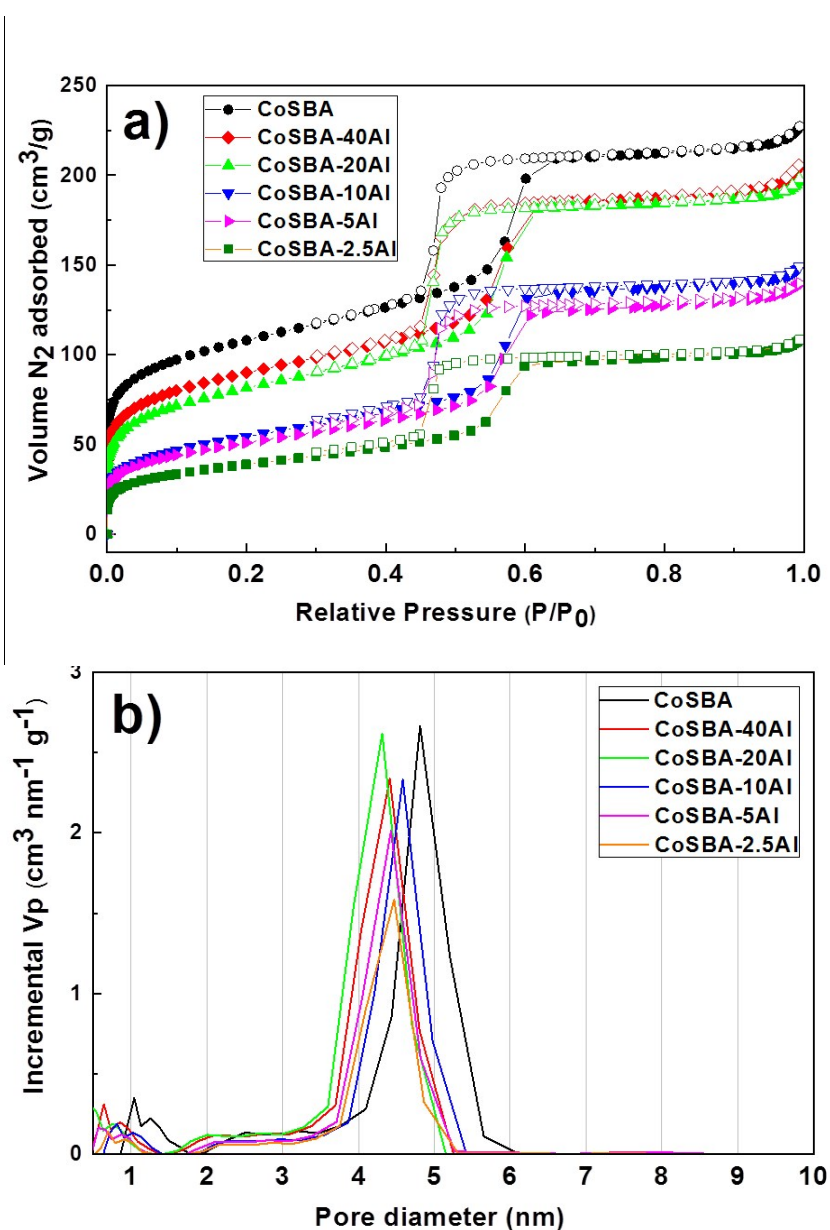


Figure S1. Textural properties of CoSBA-xAl bifunctional catalysts. a) N₂ adsorption-desorption isotherms and b) Pore size distribution.

2) Small-angle XRD patterns of the SBA, SBA-2.5Al and CoSBA-2.5Al samples

The small-angle powder XRD patterns of calcined aluminum-free SBA-15 (SBA), the support with the highest aluminum content (SBA-2.5Al) and this support incorporating the cobalt (CoSBA-2.5Al) are shown in Fig. 2S. All samples exhibit three well-resolved diffraction peaks at 2θ values at around 1.08, 2.06, and 2.74, indexed to the (100), (110) and (200) reflections of the hexagonal space group $p6mm$ ¹. It suggests the preservation of the SBA-15 structure after the incorporation of Al and Co species. The decrease in the intensity of diffraction peaks for the latter sample can be attributed to the decline in the difference between the channel walls of the matrices. The shift in the reflections of SBA-2.5Al and CoSBA-2.5Al samples towards slightly higher 2θ angles is due to the oxide monolayer coating the inner walls of SBA-15.²

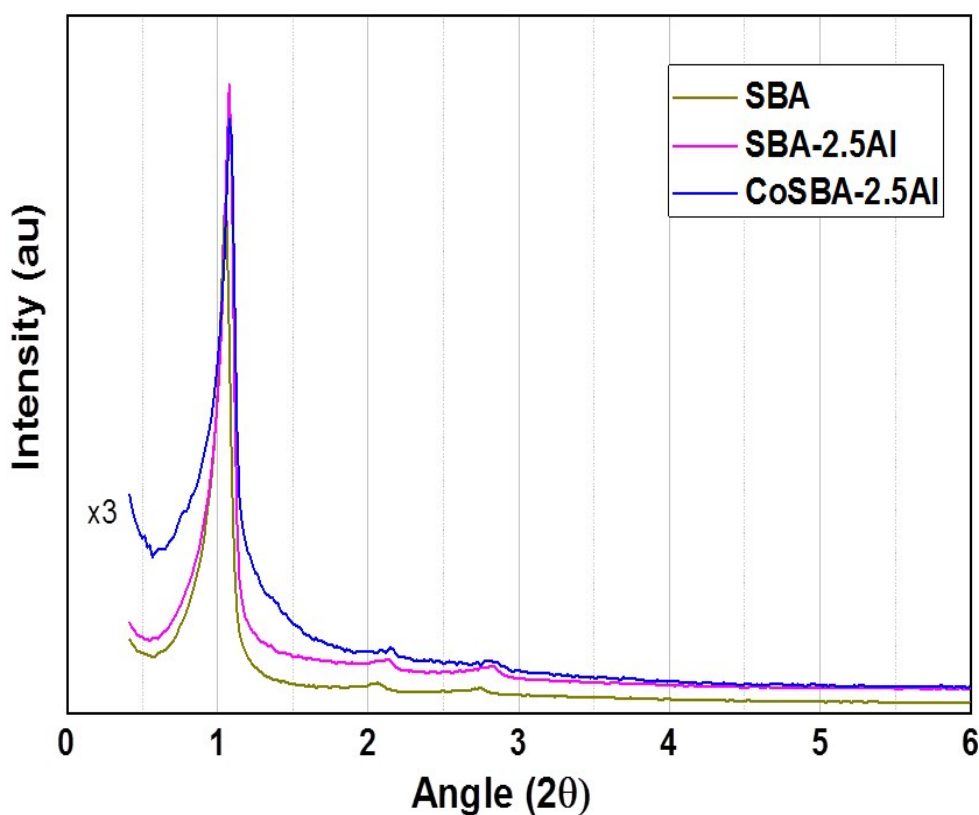


Figure S2. Small angle XRD for SBA, SBA-2.5Al and CoSBA-2.5Al samples

3) XRD patterns of the calcined CoSBA-xAl samples

Powder X-ray diffraction (XRD) patterns were recorded in the 10–90° 2 θ range in the scan mode (0.04°, 500 s accumulation) using an X'Pert Pro PANalytical diffractometer with Cu K $\alpha_{1,2}$ ($\lambda = 0.15418$ nm) radiation. The calcined sample diffractograms are shown in Figure S3, where for simplicity three diffraction patterns of the series have been displayed. Several diffraction peaks are observed, the most intense at 2 $\theta = 31.2$, 36.9, 59.2, and 63.2, which are associated with the Co $_3$ O $_4$ spinel (1, JCPDS 00-001-1152) formed during the calcination in air.

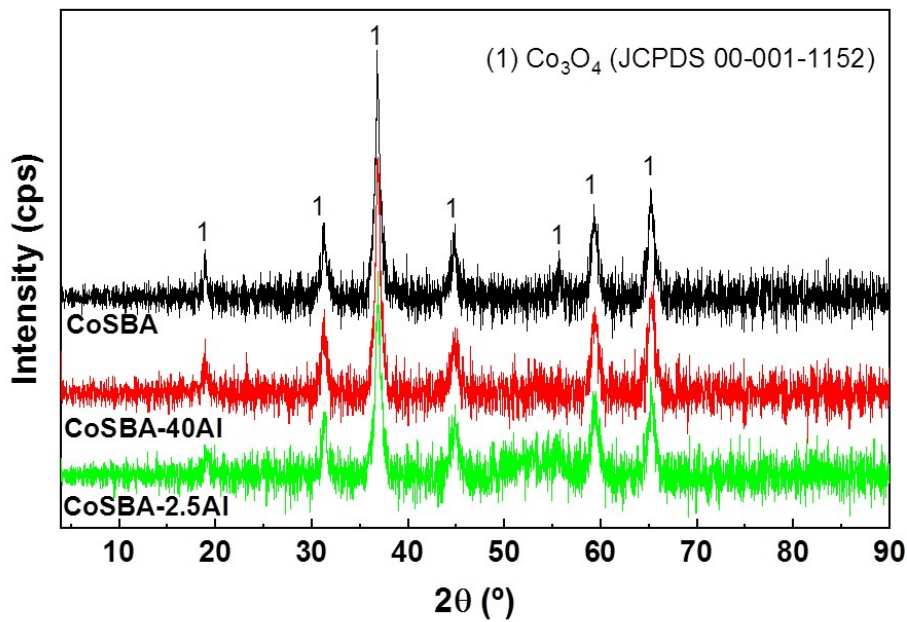


Figure S3. XRD patterns of calcined CoSBA-xAl samples

4) DRIFS spectra after CD₃CN adsorption of the SBA-10Al acid support and reduced CoSBA-10Al catalyst

Fig. S4A shows SBA-10Al spectra as an example of the band intensity evolution during the entire operation of CD₃CN adsorption and subsequent flushing with Ar at different temperatures and times. In addition to the two bands already assigned in the manuscript, a new band at lower frequencies 2266 cm⁻¹ was observed, whereas a CD₃CN flow was going through the sample that is associated with the physisorbed CD₃CN^{3,4}. After 5 minutes of flushing with a flow of Ar at room temperature this band disappears completely. The band assigned to adsorption on silanol groups (2272 cm⁻¹) rapidly decreases with the increase of the temperature and the flushing time. In contrast, the band associated with stronger acidity was maintained or even increases during the followed procedure.

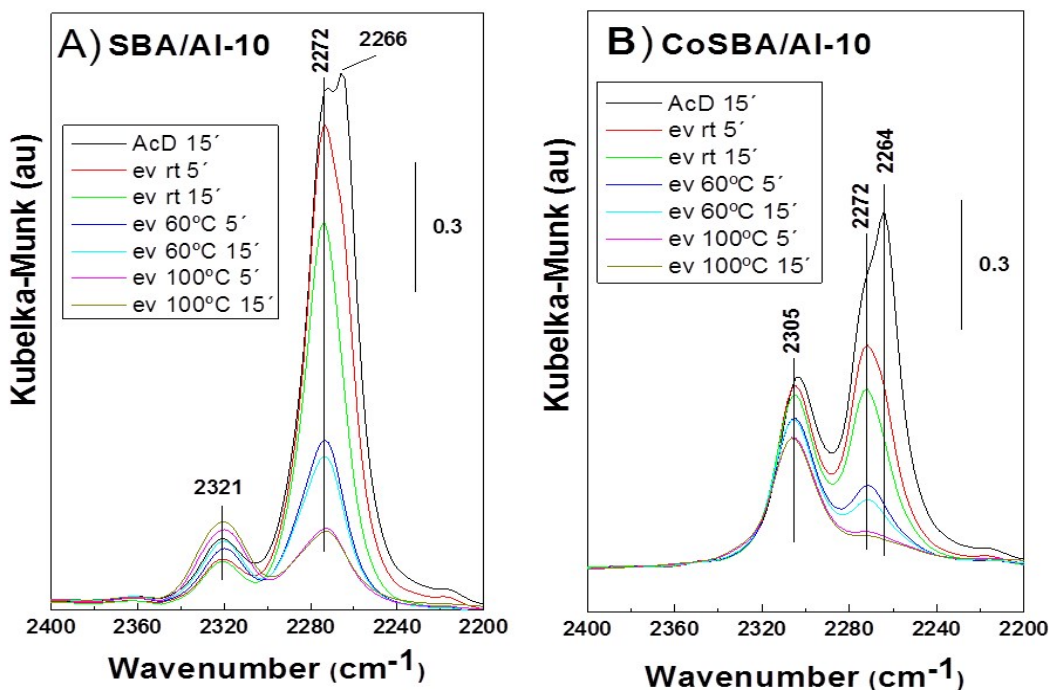


Figure S4. DRIFT spectra during the removal process of physisorbed AcD. A) SBA-10Al support and B) CoSBA-10Al catalysts

Parallel to the supports, Figure S4B shows the spectra obtained with CoSBA-10Al reduced catalyst where the band intensity evolution during the CD₃CN adsorption and subsequent flushing at different temperatures and times process is also collected. The intensity of the band associated with CD₃CN adsorbed on silanol groups (2272 cm⁻¹) is lower, whereas the band at 2305 cm⁻¹ is more intense than the band 2321 cm⁻¹ described previously on the support.

References

- 1 M. Gómez-Cazalilla, J. M. Mérida-Robles, A. Gurbani, E. Rodríguez-Castellón and A. Jiménez-López, *J. Solid State Chem.*, 2007, **180**, 1130–1140.
- 2 M. Kondeboina, S. S. Enumula, V. R. B. Gurram, R. R. Chada, D. R. Burri and S. R. R. Kamaraju, *J. Ind. Eng. Chem.*, 2018, **61**, 227–235.
- 3 R. Mariscal, M. López-Granados, J. L. G. Fierro, J. L. Sotelo, C. Martos and R. Van Grieken, *Langmuir*, 2000, **16**, 9460–9467.
- 4 D. Jamroz, J. Stangret and J. Lindgren, *J. Am. Chem. Soc.*, 1993, **115**, 6165–6168.