

Supporting Information

Selective Catalytic Oxidation of Lean-H₂S Gas Stream to Elemental Sulfur at Lower Temperature

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Figure S1

For the catalyst with the lowest V-content, the shift of this Raman signal could be due to the interaction of the CeO₂ with the sulfur while, for the sample with the highest V-content, the shifting phenomenon could be due to the interaction of the support with the incipient formation of the vanadium sulfide [1-2]. For the sample with the highest vanadium content (50 wt%), it is possible to see an intense Raman band at 138 cm⁻¹ that can be ascribed to the incipient transformation of the bulk V₂O₅ into VS₂ [2]. This hypothesis will be successively clarified considering also the results of the characterizations performed on the catalysts after the catalytic activity tests. This Raman band, which is rather broad, is only visible for the bulk V₂O₅ after the sulfuration.

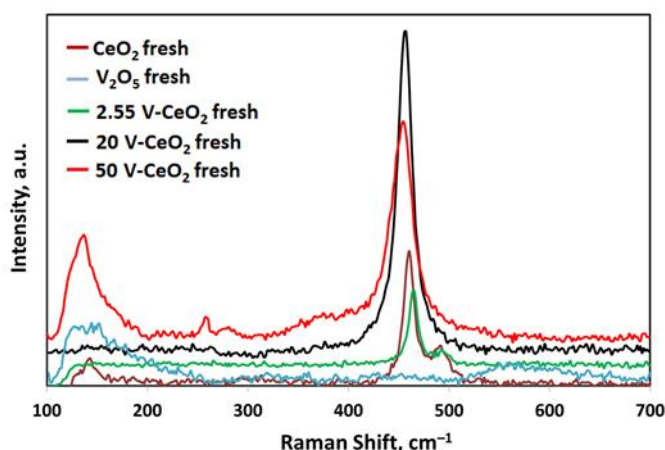


Figure S1. Raman spectra of CeO₂, V₂O₅ and 2.55, 20, 50 V-CeO₂ fresh catalysts.

Figure S2

Generally, this shift could be due to the increased number of oxygen vacancies of the cerium oxide after the impregnation with V-species and it could depend on the V-metal loading. The Raman mode at 460 cm^{-1} corresponding to symmetric Ce-O_8 vibrations, must be extremely sensitive to any disturbance in the symmetry of the oxygen sublattice, including changes in the oxygen stoichiometry of cerium dioxide caused by thermal treatment and/or dimensional defects [3]. A very dissimilar result was obtained for the 2.55 V- CeO_2 used catalyst. Indeed, for this sample, it is possible to observe Raman signals at 148, 216, 434 and 468 cm^{-1} ascribable to the sulfur whereas the band of CeO_2 is noticeable at 465 cm^{-1} (Figure S2 b) [1]. The signal at 216 cm^{-1} with a low intense band at 148 cm^{-1} could be attributed to S-S-S bending vibration, while the band at 468 cm^{-1} could be related to S-S stretching of polymeric sulfur species adsorbed at the multilayer level [4]. For the used 20 V- CeO_2 , Raman bands related to the sulfur at 148, 216, 243, 433, and 470 cm^{-1} are present [1]. The Raman spectra of the catalyst with the highest vanadium loading (Figure S2 d) are very different, where an additional Raman band at 138 cm^{-1} is observable, typical of vanadium sulfide in VS_2 form [2]. These results suggest that the sulfur deposition on the catalyst surface is favoured in samples at lower V-loading (2.55 V- CeO_2 and 20 V- CeO_2), while it is not observable in catalysts having high V-loading (50 V- CeO_2). The coverage of the support by the sulfur produced during the reaction is evidenced by the absence of the CeO_2 peaks on the 2.55 and 20 V- CeO_2 used catalysts. However, the disappearance of the CeO_2 Raman band on the 50 V- CeO_2 used sample is likely due to the further VS_2 segregation during the reaction that could have determined the coverage of the support.

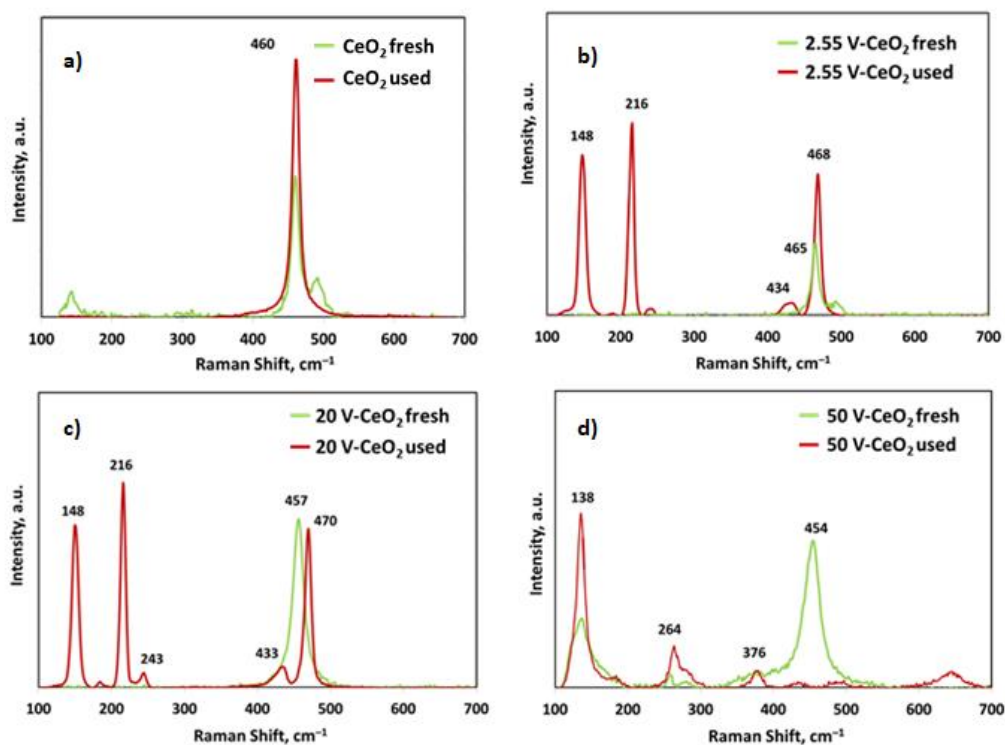


Figure S2. Raman spectra of fresh and used catalysts CeO_2 (a), 2.55 V- CeO_2 (b), 20 V- CeO_2 (c), 50 V- CeO_2 (d).

References

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