

Supporting Information

New Insights into the Composition and Catalytic Performance of VO_x-Ga/γ-Al₂O₃ for the Oxidative Dehydrogenation of Propane to Propene

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Experimental Section

Materials

Support material, γ-Al₂O₃ (S_{BET}= 268 m²/g; 99.9 %) was used as received from Alfa Aesar, Ammonium metavanadate (NH₄VO₃; 99.9 %), Gallium nitrate (Ga (NO₃)₃ xH₂O; 99.9 %) and Oxalic acid (C₂H₂O₄; 98 %) were purchased from Sigma-Aldrich.

Catalyst preparation

The catalysts were prepared by an incipient wetness impregnation method. First, the amount of support (5.4 g); commercial γ-Al₂O₃ was suspended in 30 ml of distilled water, and the solution was sonicated for 45 min to get uniform dispersion. To this, the desired amount of ammonium metavanadate (0.96 g) and gallium nitrate (0.66 g) was dissolved in an aqueous oxalic acid solution was added dropwise. After impregnation, the mixture was stirred at 80 °C for 3 h. The resulting material was dried at 120 °C overnight, followed by calcination at 560 °C at static air for 4 h with a 2 °C min⁻¹ ramping rate and denoted as VGA-2. A series of catalysts were prepared with different ratios of VO_x and Ga supported γ-Al₂O₃, represented in Table 1.

Catalyst characterization

Powder X-ray diffraction patterns were collected on PANalytical Xpert pro dual goniometer fitted with a Cu K α source ($\lambda = 1.5406 \text{ \AA}$) and K α -ray radiation at a voltage of 40 kV and 30 mA current with step size 0.008 using a flat holder Bragg-Brentano geometry. The Nitrogen adsorption-desorption isotherms were measured by Quantachrome Autosorb IQ (USA) at 77 K after pre-treating at 300 °C under He atmosphere for 6 h. The specific surface areas of the catalysts were determined by Brunauer-Emmett-Teller (BET) analysis. The morphology of the catalysts was analyzed by SEM using JEOL-JSM-5200 systems. HR-TEM and HAADF-STEM were performed using an FEI Technai TF-30 instrument operating at 300 kV. Samples were suspended using isopropyl alcohol and deposited on carbon-coated copper grids. The acidic nature of the catalysts was executed by NH₃-TPD using the Micromeritics Autochem-2920 instrument (USA). Before the NH₃ adsorption, the samples were pre-treated at 300 °C under He atmosphere (20 mL.min⁻¹) for 1 h. After that, the sample was cooled to 50 °C, and the analysis was performed by adsorbing 10 % NH₃ in He. Later NH₃ desorption was monitored while heating the sample from 50-800 °C at a 5 °C min⁻¹ ramping rate. The data was recorded by a thermal conductivity detector (TCD). Raman spectra were recorded using a Horiba JY LabRAMHR800 Raman spectrometer coupled with a microscope in reflectance mode with a 632.8 nm excitation laser source and spectral resolution of 0.3 cm⁻¹. H₂-TPR experiments were examined using Micromeritics Autochem-2920 (USA) instrument, where 50 mg sample was loaded in a quartz tube, and the sample was oxidized at 250 °C using 10 % O₂ in helium to make the material fully oxidized and pre-treated at 300 °C for 60 min under Ar flow. Then, the furnace temperature was reduced to 50 °C, and H₂-TPR analysis was started from 50-900 °C with a heating rate of 5 °C min⁻¹ using 5 % H₂/Ar (30 mL/min⁻¹). A thermal conductivity detector recorded the H₂ consumption. X-ray photoelectron spectroscopy (XPS) was carried out on a ThermoKalpha+ spectrometer using monochromated Al K α radiation with energy 1486.6 eV. The thermal stability of the catalysts was confirmed by using TGA (Mettler Toledo TGA/SDTA851e) by heating under airflow. Diffuse reflectance spectra (DRS) of all powder samples for the present study were evaluated with a Shimadzu UV-vis-NIR spectrophotometer (Model UV-3600 plus). Reflectance data were converted to absorbance data via Kubelka-Munk transformation. BaSO₄ powder was used as the reference sample. The in-situ DRIFTS spectra were collected using a Thermo Scientific Nicolet, iS50 spectrometer equipped with an MCT detector (cooled by liquid N₂) at a resolution of 4 cm⁻¹ and 200 scans. Before adsorption, the catalysts were pre-treated at 300 °C with N₂ 50 mL/min⁻¹ for 1 h. Afterward, the sample was cooled to ambient temperature, and background spectra were collected. Eventually, propane was introduced into the reaction chamber, and spectra were collected at 30 °C. Further, the cell temperature was increased to 350 °C at a ramping rate of 5 °C min⁻¹, and spectra were collected under (C₃H₈/O₂/Ar) for all the samples. The catalyst surface acid site type was determined by FTIR (Thermo Scientific Nicolet, iS50 spectrometer) by utilizing pyridine as a probe molecule. Prior to analysis, the catalyst was preheated under nitrogen flow at 250 °C for 2 h. The samples were further cooled down to 100 °C after pretreatment. Finally, the pyridine stream was introduced into the samples (100-200 °C), and FTIR spectra were collected in absorbance mode. The precise coordination nature of the

gallium species found on the catalysts was analyzed by gathering ^{71}Ga MAS NMR (magic-angle spinning NMR) data using Bruker NEO Avance III 500 MHz Spectrometer.

Catalytic Testing

The catalytic activity of ODHP was performed in a fixed bed continuous flow reactor using molecular oxygen as an oxidant. The temperature was controlled by a two-zone furnace connected with an 8 mm internal diameter and 480 mm length Inconel reactor tube. The catalyst bed temperature was measured by a K-type thermocouple, and $\text{C}_3\text{H}_8/\text{O}_2/\text{Ar}$ gas feed was controlled by Brooks make mass flow controllers (5890E series). The calcined catalysts were sieved to 1.2 to 1.7 mm grain size; 0.5 g of the catalyst was loaded at the centre of the tube by using glass wool. The ODHP reaction was carried out from 325-500 °C with different GHSV and various catalyst compositions. The products were analyzed by Thermo Fisher Trace 1110 gas chromatography coupled with TCD and FID. The hydrocarbons were separated by the Alumina plot column (Restek), and other permanent gases were analyzed by Porapak Q and Molecular sieve columns.

Figures

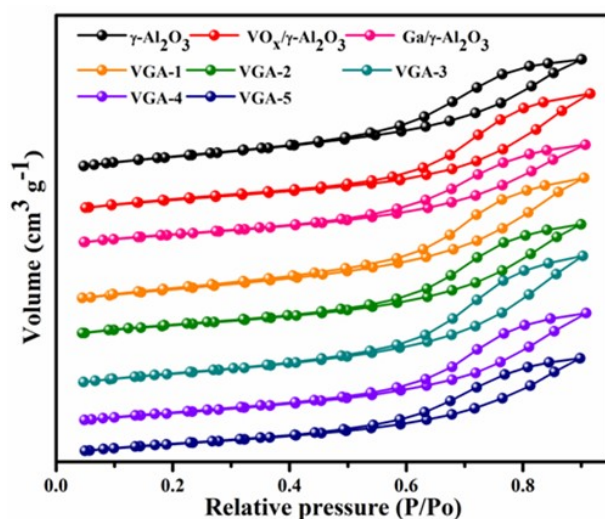


Figure S1. N_2 -sorption isotherms of the synthesized catalysts.

NH_3 -TPD examined the surface acidity of the V-Ga oxide catalysts, and the results are listed in Table 1. All the catalysts exhibit two TPD peaks, one below 300 °C and another at 400 °C temperature (Fig. S2). These two peaks are assigned to acid sites with weak and medium strength, respectively.^[1] The TPD analysis probed that moderate acidity increases the activity of ODHP, whereas strong acid sites decrease the catalytic activity and activate the propene.^[2,3] The nature of the acidic sites in the catalyst was identified by Py-FTIR, and the results are depicted in Fig. S3. The bands at 1450 and 1615 cm^{-1} appeared for all the catalysts, corresponding to the coordinately bonded pyridine adsorbed on the Lewis acid sites of the catalyst.^[4] However, the Lewis acid strength was increased noticeably upon loading the V and

Ga oxide. The two less-intense bands observed at 1507 and 1540 cm^{-1} are assigned to pyridine molecule protonated at Brønsted acidic sites.^[5] On the other hand, the absorbance band at 1489 cm^{-1} originates from pyridine associated with both Brønsted and Lewis acidic sites.^[6]

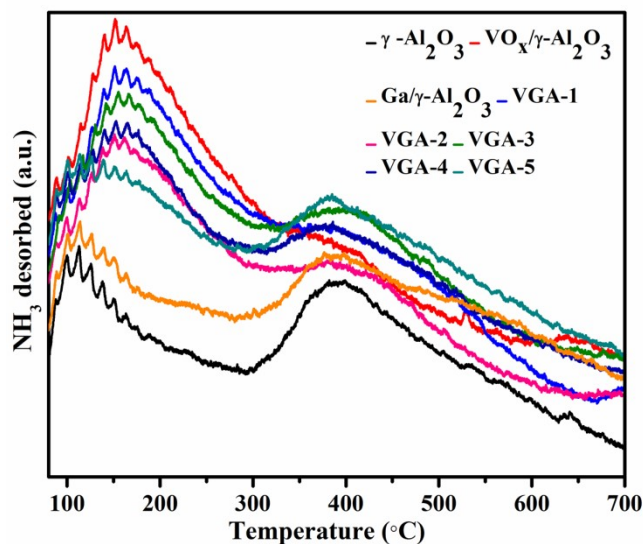


Figure S2. NH_3 -TPD profiles of the calcined catalysts.

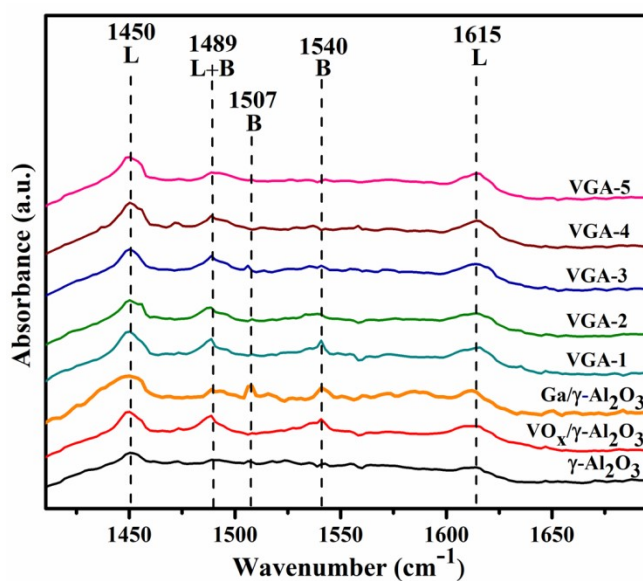


Figure S3. Pyr-FTIR spectra of the calcined catalysts.

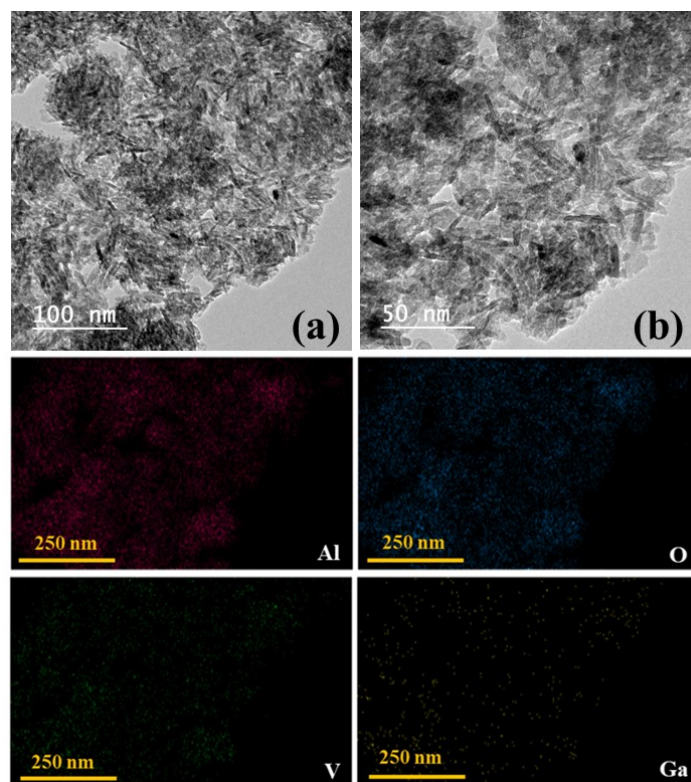


Figure S4. (a-b) HR-TEM and elemental mapping images of fresh VGA-2 catalyst.

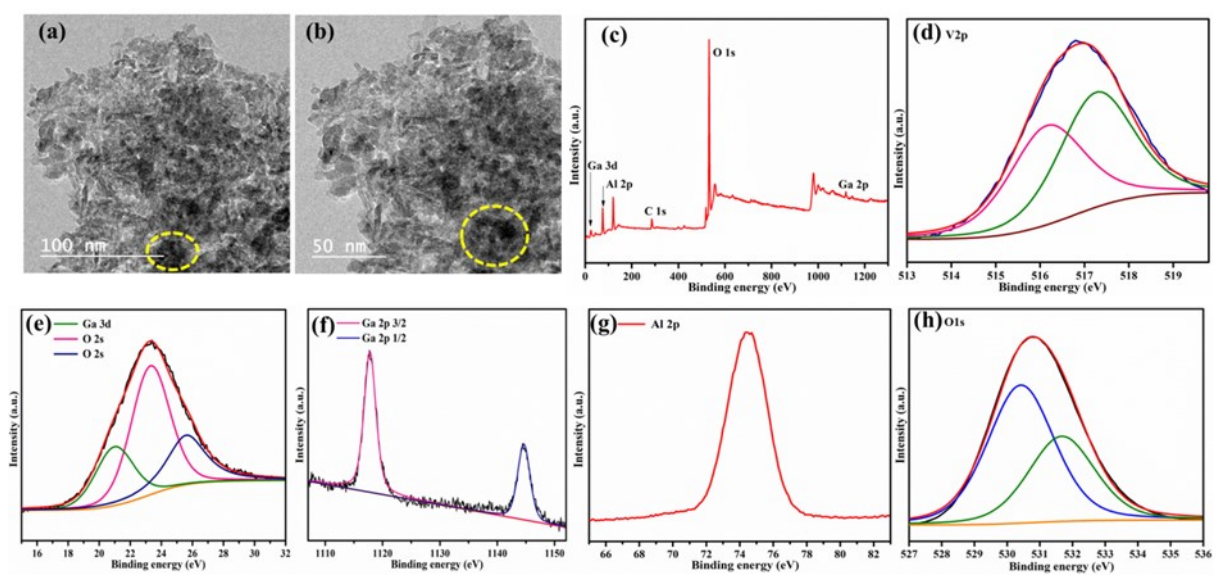


Figure S5. TEM and XPS spectra of spent VGA-2 catalyst (a-b) HRTEM images; (c) Full scan XPS, (d) V 2p, (e) Ga 3d, (f) Ga 2p, (g) Al 2p and (h) O 1s core level spectra.

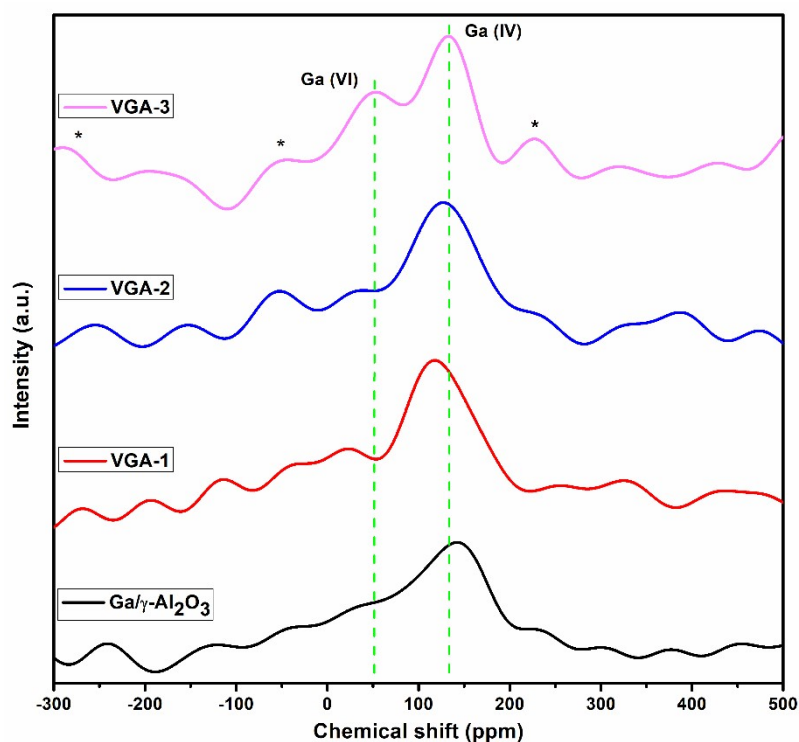


Figure S6. ^{71}Ga MAS NMR spectra of the calcined catalysts. Asterisks denote the spinning sidebands.

References

1. S. Rostom, H.I. de Lasa, *Ind. Eng. Chem. Res.* **2017**, 56, 45, 13109–13124.
2. T.S. Kharlamova, K.L. Timofeev, M.A. Salaev, V.A. Svetlichnyi, O.V. Vodyankina, *Appl. Catal., A*, **2020**, 598, 117574.
3. J.H. Carter, T. Bere, J.R. Pitchers, D.G. Hewes, B.D. Vandegehuchte, C.J. Kiely, S.H. Taylor, G.J. Hutchings, *Green Chem.*, **2021**, 23, 9747–9799.
4. A. Takagaki, J.C. Jung, S. Hayashi, *RSC Adv.*, **2014**, 4, 43785–43791.
5. M.M. Maronna, E.C. Kruissink, R.F. Parton, F. Soulimani, B.M. Weckhuysen, W.F. Hoelderich, *Phys. Chem. Chem. Phys.* **2016**, 18, 22636–22646.
6. P. Kandasamy, P. Gogoi, A.T. Venugopalan, T. Raja, *Catalysis Today* **2021**, 375, 145–154.