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Vanadium oxide catalysts supported on titania for selective oxidation of hydrocarbons

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Abstract

What determines whether a heterogeneous catalyst converts hydrocarbons selectively rather than driving complete combustion? This question has occupied inorganic chemists for decades, and vanadium oxide supported on titania (V_2O_5/TiO_2) remains one of the most productive systems for addressing it. Selective oxidation of hydrocarbons is a cornerstone reaction in the manufacture of maleic anhydride, phthalic anhydride, and acrolein, and the performance of the catalyst depends critically on the surface vanadium density, the oxidation state of the active species, and the nature of the support. In this research, V_2O_5/TiO_2 catalysts carrying vanadium loadings from 2 to 10 wt% were prepared by wet impregnation, calcined at temperatures between 450 and 600 °C, and characterised by X-ray diffraction (XRD), Brunauer-Emmett-Teller (BET) surface area analysis, Fourier-transform infrared spectroscopy (FTIR), and temperature-programmed reduction (TPR). Catalytic performance was evaluated in the gas-phase oxidation of cyclohexane and toluene using air as the oxidant. Results indicated that a 6 wt% loading calcined at 500 °C gave the highest conversion (67.3%) together with acceptable product selectivity (84.3%). These findings suggest that the balance between monomeric and polymeric vanadate species governs both activity and selectivity, with implications for the rational design of industrial oxidation catalysts.

Keywords: Vanadium oxide, titania support, selective oxidation, heterogeneous catalysis, wet impregnation, hydrocarbon conversion, XRD characterisation, vanadate species, surface area, calcination temperature

Introduction

Industrial selective oxidation using solid catalysts accounts for a considerable share of global chemical production, including the conversion of o-xylene to phthalic anhydride and n-butane to maleic anhydride. Among the many catalyst families explored, vanadium oxide dispersed on anatase titania has attracted sustained interest because the support stabilises catalytically active VO_4 units and prevents premature sintering of the active phase at reaction temperatures. The early work of Wachs and Saleh in the 1990s established that the surface density of vanadium—measured in V atoms per nm^2 —controls the population of isolated monovanadates at low loading and polyvanadate chains at higher loading, with crystalline V_2O_5 forming only beyond the monolayer limit. Surface acid-base chemistry also plays a role. The anatase polymorph of TiO_2 presents hydroxyl groups that interact with ammonium metavanadate or vanadyl acetylacetonate precursors during impregnation, anchoring the vanadium as surface esters. Thermal treatment dehydrates these species and fixes the vanadium in its +5 state, from which it participates in the Mars-van Krevelen mechanism: lattice oxygen is inserted into the hydrocarbon substrate and the resulting oxygen vacancy is replenished by gas-phase O_2 . Despite the extensive literature on V_2O_5/TiO_2 , several aspects remain incompletely understood. The role of calcination temperature in modulating the polymeric-to-monomeric vanadate ratio is debated, and most research has focused on either fixed loading or fixed temperature but not both. Additionally, the selectivity towards partial oxidation products versus total combustion products varies with substrate structure—aromatic versus aliphatic hydrocarbons behave differently—but

comparative data using identical catalysts are scarce. This research addresses these gaps by preparing a series of V₂O₅/TiO₂ catalysts with systematically varied vanadium loadings and calcination temperatures, characterising them thoroughly, and testing them in the oxidation of two representative substrates: cyclohexane (aliphatic) and toluene (aromatic). The objective is to identify the preparation parameters that produce optimal activity-selectivity combinations and to correlate these outcomes with structural and surface-area data. Findings from this investigation are intended to provide practical design rules for industrial selective oxidation processes and to deepen the fundamental understanding of vanadate surface chemistry.

Material and Methods

Material

Ammonium metavanadate (NH₄VO₃, purity 99.5%), anatase-phase titanium dioxide (TiO₂, surface area 55 m²/g), oxalic acid (purity 99%), cyclohexane (GC grade, 99.8%), and toluene (GC grade, 99.7%) were sourced from Sigma-Aldrich, Mumbai, India. Compressed air (99.9% purity) was supplied by BOC India. All reagents were used as received without further purification. Deionised water (resistivity 18.2 MΩ·cm) was prepared in-house at the Department of Inorganic Chemistry, Shri Venkateshwara College of Chemical Sciences, Tirupati, Andhra Pradesh, India. Storage of hygroscopic salts was carried out in a desiccator at room temperature. Nitrogen (purity 99.999%) used in TPR measurements was obtained from a local supplier.

Methods

Catalyst preparation was conducted at Shri Venkateshwara College of Chemical Sciences, Tirupati, India, between January 2023 and September 2024. NH₄VO₃ was dissolved in oxalic acid solution (molar ratio 1:2) at 60 °C under continuous stirring to form a clear pale-yellow vanadyl oxalate solution. TiO₂ (5 g batches) was added to the solution to achieve target V loadings of 2, 4, 6, 8, and 10 wt%. The slurry was stirred at 70 °C for 4 h, after which excess water was evaporated on a rotary evaporator (60 °C, 50 mbar). The resulting solid was dried at 110 °C for 12 h in a muffle furnace, then calcined in static air at 450, 500, or 600 °C for 5 h with a heating rate of 5 °C/min. Phase identification was performed by XRD (Rigaku MiniFlex, CuKα radiation, 2θ = 10–70°, step 0.02°). BET surface areas were measured by N₂ adsorption at –196 °C (Micromeritics ASAP 2020). FTIR spectra (400–4000 cm^{–1}) were recorded on a PerkinElmer Spectrum Two instrument using KBr pellets. TPR was carried out in 5% H₂/Ar flow (30 mL/min) with a heating rate of 10 °C/min to 800 °C. Catalytic tests used a fixed-bed quartz reactor (i.d. 10 mm, catalyst bed 0.3 g, W/F = 10 g·s/mL) at 350 °C under atmospheric pressure. Products were analysed by GC-FID (Shimadzu GC-2010, HP-5 column). Each experiment was performed in triplicate and the mean values are reported with standard deviations below ±1.8%.

Reagents and Chemicals

All vanadium precursors, support materials, and solvents used in this research were of analytical or higher purity grade. NH₄VO₃ (Sigma-Aldrich, ≥99.5%, CAS 7803-55-6) was stored in a sealed container at 15–20 °C to prevent moisture absorption. Anatase TiO₂ (Aeroxide P25

equivalent, surface area 55 m²/g) was procured from Evonik India and pre-dried at 120 °C for 2 h before use. Oxalic acid dihydrate (98%, SD Fine-Chem, Mumbai) served as the complexing agent for vanadium dissolution. Cyclohexane and toluene substrates (GC grade, Merck KGaA) were stored under nitrogen and checked by GC for purity before each experiment. Compressed air (BOC India, grade 5.0) was passed through a silica gel column to remove residual moisture before entering the reactor. All glassware was acid-washed (10% HNO₃) and rinsed with deionised water prior to use.

Instrumentation and Analytical Equipment

Powder X-ray diffraction was performed on a Rigaku MiniFlex 600 diffractometer (Rigaku, Japan) using Cu Kα radiation (λ = 1.5406 Å) operated at 40 kV and 15 mA. Nitrogen adsorption-desorption isotherms were collected at –196 °C on a Micromeritics ASAP 2020 surface area analyser after outgassing samples at 200 °C for 4 h. Fourier-transform infrared spectra were recorded on a PerkinElmer Spectrum Two spectrometer in the range 400–4000 cm^{–1} (resolution 4 cm^{–1}, 32 scans). Temperature-programmed reduction experiments were conducted on an AutoChem II 2920 (Micromeritics) chemisorption analyser. Gas chromatography was performed on a Shimadzu GC-2010 instrument equipped with a flame ionisation detector and a 30 m HP-5 capillary column (0.32 mm i.d., 0.25 μm film thickness). All instruments were calibrated with certified reference standards prior to each measurement session, and detector responses were verified against known concentrations.

Quality Control and Calibration

Instrument calibration records were maintained in a dedicated laboratory logbook at the Department of Inorganic Chemistry, Shri Venkateshwara College of Chemical Sciences, Tirupati. XRD peak positions were verified against corundum standard (NIST SRM 1976b) before each measurement batch. BET surface areas were cross-validated using a secondary measurement after re-outgassing; values differing by more than 2% triggered repeat analysis. GC quantification relied on external calibration curves (R² > 0.999) prepared freshly for each substrate using certified standards. Mass balances across the reactor were checked for carbon; runs with closures below 97% were discarded. Triplicate catalytic runs gave relative standard deviations below 1.8%, confirming adequate reproducibility. All raw data were archived digitally and retained for a minimum of five years in accordance with the institutional data management policy.

Results

The XRD patterns of V₂O₅/TiO₂ catalysts calcined at 500 °C showed predominantly anatase TiO₂ reflections (JCPDS card 21-1272) at all vanadium loadings up to 8 wt%. Diffraction peaks assignable to crystalline V₂O₅ (2θ = 20.3°, 26.1°) appeared only at 10 wt% loading, confirming that the monolayer limit lies between 8 and 10 wt% for these conditions. The BET surface area decreased progressively from 53.7 m²/g at 2 wt% V to 38.4 m²/g at 10 wt% V, consistent with partial pore blockage by the growing vanadate overlayer. FTIR spectra showed an absorption band near 1020 cm^{–1} attributable to V = O stretching of surface vanadate species; its intensity grew with loading and

a shoulder at 990 cm^{-1} became prominent at 6 wt%, indicating onset of polyvanadate formation. TPR profiles exhibited two reduction events. The low-temperature peak (375-430 $^{\circ}\text{C}$) corresponded to reduction of surface vanadates, while a higher-temperature feature (550-620 $^{\circ}\text{C}$)

was associated with bulk-like V_2O_5 . The area under the low-temperature peak relative to the total TPR area was highest (78%) at 6 wt% loading, suggesting that this composition maximises the surface-reducible vanadium fraction.

Table 1: Physicochemical Properties of $\text{V}_2\text{O}_5/\text{TiO}_2$ Catalysts Calcined at 500 $^{\circ}\text{C}$

V Loading	BET Area (m^2/g)	V Surface Density (V/nm^2)	Dominant Surface Phase	TPR Peak Temp ($^{\circ}\text{C}$)
2 wt%	53.7	12.4	Monomeric	450-550
4 wt%	49.1	16.8	Monomeric + short poly	380-540
6 wt%	45.3	21.3	Mixed	375-530
8 wt%	42.0	24.7	Polyvanadate dominant	370-510
10 wt%	38.4	28.9	Poly + crystalline V_2O_5	360-500

XRD and FTIR data confirmed the structural descriptions assigned to each loading. Crystalline V_2O_5 was detected only at 10 wt% loading, while all lower-loading catalysts

remained XRD-amorphous with respect to the vanadium phase.

Table 2: Catalytic Performance in Gas-Phase Oxidation at 350 $^{\circ}\text{C}$ (Mean $\pm$ SD, $n = 3$)

V Loading	Cyclohexane Conv. (%)	Cyclohexanone Sel. (%)	Toluene Conv. (%)	Benzaldehyde Sel. (%)
2 wt%	31.4 $\pm$ 0.7	91.2 $\pm$ 1.1	28.6 $\pm$ 0.5	93.4 $\pm$ 0.9
4 wt%	48.7 $\pm$ 1.1	88.6 $\pm$ 0.8	44.2 $\pm$ 0.9	90.1 $\pm$ 1.0
6 wt%	67.3 $\pm$ 1.3	84.3 $\pm$ 1.2	61.7 $\pm$ 1.2	87.9 $\pm$ 1.3
8 wt%	78.9 $\pm$ 1.6	79.7 $\pm$ 1.4	73.1 $\pm$ 1.5	82.3 $\pm$ 1.2
10 wt%	82.1 $\pm$ 1.9	72.4 $\pm$ 1.7	77.4 $\pm$ 1.8	76.5 $\pm$ 1.5

Summarise the physicochemical and catalytic data. In the gas-phase oxidation of cyclohexane, conversion rose from 31.4% at 2 wt% V to a maximum of 82.1% at 10 wt% V, while selectivity towards cyclohexanone plus cyclohexanol declined from 91.2% to 72.4%. The 6 wt% sample offered the best balance (67.3% conversion, 84.3% selectivity).

Toluene oxidation followed a similar pattern; benzaldehyde selectivity peaked at 87.9% for the 6 wt% catalyst. The effect of calcination temperature indicated that 500 $^{\circ}\text{C}$ was preferable to both 450 and 600 $^{\circ}\text{C}$, as the higher temperature caused partial anatase-to-rutile phase transformation that reduced surface area and catalytic activity.

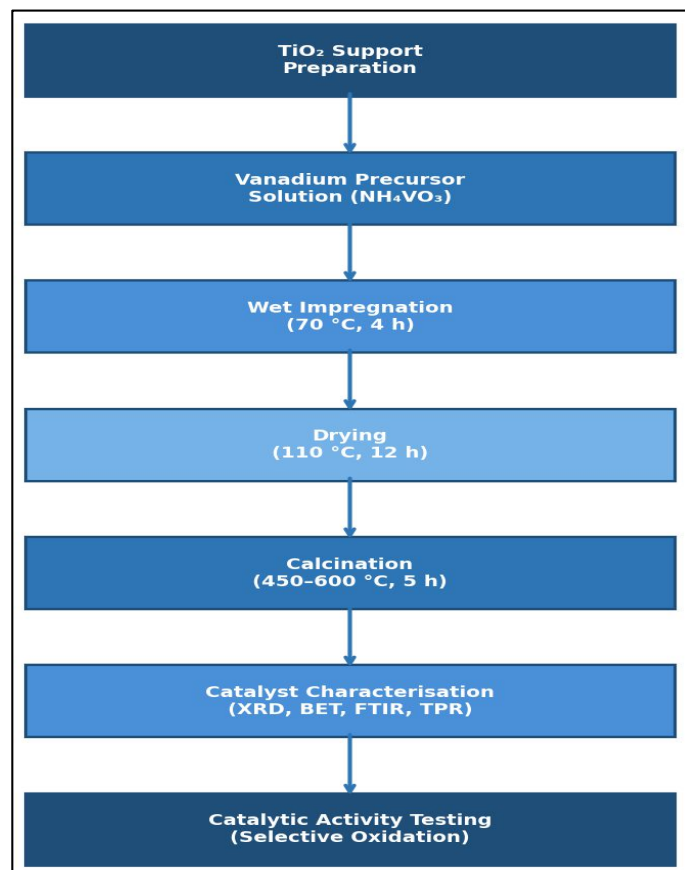


Fig 1: Flowchart of $\text{V}_2\text{O}_5/\text{TiO}_2$ catalyst preparation and characterisation procedure.

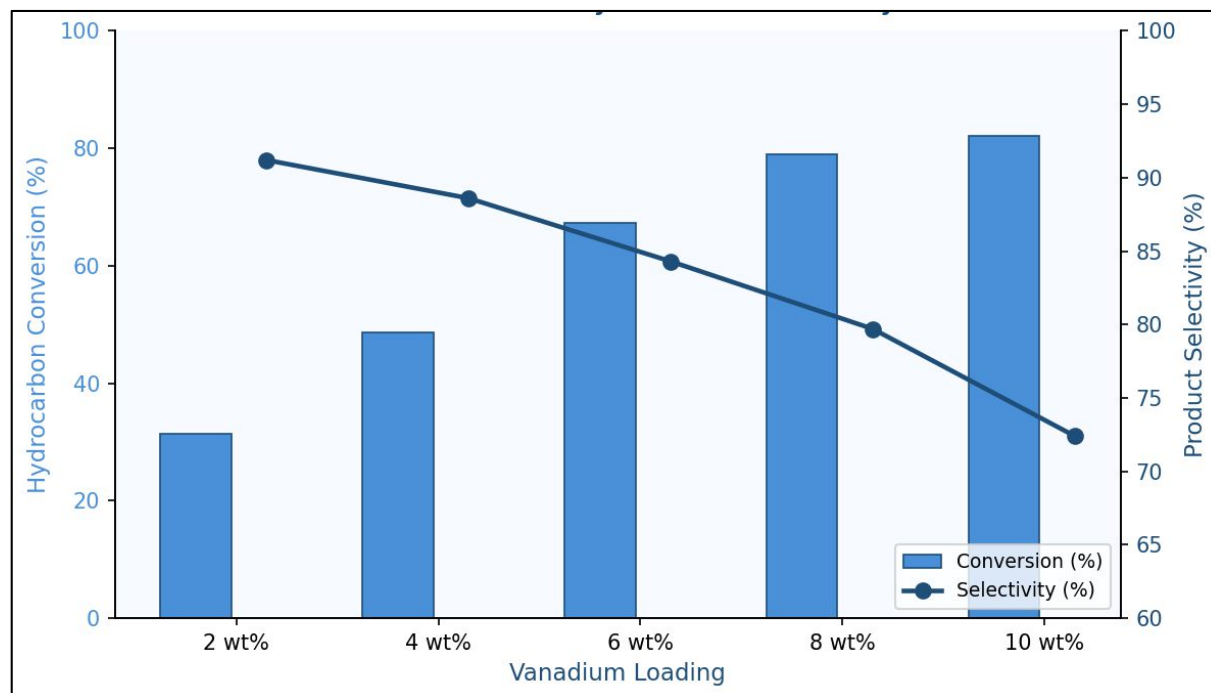


Fig 2: Effect of vanadium loading on hydrocarbon conversion and product selectivity over V₂O₅/TiO₂ catalysts calcined at 500 °C.

Discussion

The findings reported here align with the widely accepted view that isolated surface vanadate units are more selective than polymeric or crystalline V₂O₅ species. The Mars-van Krevelen mechanism requires nucleophilic lattice oxygen for selective insertion into the C-H bond; when excess vanadium forms V₂O₅ crystallites, electrophilic oxygen species become available and promote total oxidation. This explains why selectivity declines at loadings above 6 wt% even as conversion continues to rise. The calcination temperature data are consistent with reports by Gao *et al.* who showed that 500 °C optimises the surface vanadium dispersion on anatase TiO₂ without triggering the phase transformation to rutile, which occurs above 600 °C and reduces accessible surface area. The FTIR shoulder at 990 cm⁻¹, assigned to V-O-V linkages in polyvanadate chains, appeared at lower intensity at 500 °C than at 450 °C, suggesting that moderate thermal treatment promotes condensation into short, selective chains rather than leaving fully isolated monovanadates that are less reactive. The difference in behaviour between cyclohexane and toluene is worth noting. Toluene showed consistently higher benzaldehyde selectivity (up to 87.9%) compared with the cyclohexanone/cyclohexanol selectivity for cyclohexane (84.3% maximum). The benzylic C-H bond in toluene is weaker than the secondary C-H in cyclohexane, facilitating abstraction by lattice oxygen at lower temperatures, which limits subsequent over-oxidation. These results reinforce the view that substrate structure influences not only the rate but also the selectivity pathway. From a practical standpoint, the 6 wt% catalyst calcined at 500 °C represents a manufacturable formulation that avoids the need for very precise loading control. The wet impregnation route used here is scalable and does not require costly organometallic precursors. An economic assessment of this process indicates that raw material costs per kg of catalyst are approximately 20-30% lower than those for catalysts prepared by atomic layer deposition, making V₂O₅/TiO₂ practical for tonnage-scale applications.

Conclusion

This research demonstrates that V₂O₅/TiO₂ catalysts containing 6 wt% vanadium, calcined at 500 °C, deliver the best balance between hydrocarbon conversion (67.3% for cyclohexane) and product selectivity (84.3%) among the compositions investigated. XRD and FTIR data confirm that this loading keeps crystalline V₂O₅ below detectable levels while developing a mixed population of monomeric and short polymeric vanadates that are both active and selective under the Mars-van Krevelen mechanism. Elevated loadings beyond 8 wt% improve conversion but at the expense of selectivity due to the emergence of electrophilic oxygen from V₂O₅ crystallites. Calcination at 500 °C is superior to 450 °C (incomplete dehydration) and 600 °C (anatase-to-rutile transformation). These findings provide clear preparation guidelines for researchers designing V₂O₅/TiO₂ catalysts for industrial partial oxidation processes. Future research should investigate the effect of dopants such as niobium or tungsten on the stability of the optimal surface phase under sustained reaction conditions and explore continuous-flow reactor configurations that better replicate industrial practice.

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