

ISSN Print: 2664-6781
 ISSN Online: 2664-679X
 IJACR 2025; 7(1): 207-210
www.chemistryjournals.net
 Received: 22-11-2024
 Accepted: 27-12-2024

Sunil Yadav
 Department of Advanced
 Materials Research,
 Thiruvalluvar National
 Institute of Technology,
 Salem, Tamil Nadu, India

Dinesh Pandey
 Department of Advanced
 Materials Research,
 Thiruvalluvar National
 Institute of Technology,
 Salem, Tamil Nadu, India

Anita Joshi
 Department of Advanced
 Materials Research,
 Thiruvalluvar National
 Institute of Technology,
 Salem, Tamil Nadu, India

Kamini Hegde
 Department of Chemical and
 Materials Engineering, Dr.
 Bhimrao Ambedkar College of
 Applied Chemistry, Agra,
 Uttar Pradesh, India

Corresponding Author:
Sunil Yadav
 Department of Advanced
 Materials Research,
 Thiruvalluvar National
 Institute of Technology,
 Salem, Tamil Nadu, India

Sol-gel synthesis of mesoporous alumina with tunable pore size for catalyst support

Sunil Yadav, Dinesh Pandey, Anita Joshi and Kamini Hegde

DOI: <https://www.doi.org/10.33545/26646781.2025.v7.i1c.370>

Abstract

Roughly 60% of heterogeneous catalytic processes in the petrochemical sector rely on alumina-based supports, yet precise control over pore architecture during synthesis remains a practical bottleneck. This research reports a sol-gel route to mesoporous alumina using aluminum isopropoxide as precursor and nitric acid as peptizing agent, with systematic variation of the acid-to-aluminum molar ratio (0.05-0.25) and calcination temperature (450-750°C). Nitrogen adsorption-desorption isotherms revealed that surface areas ranged from 187.3 to 378.2 m²/g, with the highest value obtained at a HNO₃/Al ratio of 0.15 and a calcination temperature of 650°C. Pore diameters were tunable between 3.1 and 14.8 nm depending on synthesis conditions. X-ray diffraction confirmed γ -alumina as the dominant phase at 550-650°C, transitioning to θ -alumina above 700°C. Scanning electron microscopy showed a granular morphology with interconnected pore networks. The optimized material was tested as a support for palladium nanoparticles in a model hydrogenation reaction, achieving 94.7% conversion of cyclohexene at 60°C. These results establish a straightforward protocol for tailoring alumina porosity to specific catalytic demands.

Keywords: Sol-gel synthesis, mesoporous alumina, pore size tuning, catalyst support, nitrogen adsorption, calcination, gamma-alumina, palladium hydrogenation, surface area

Introduction

Global consumption of alumina-based catalyst supports exceeded 4.2 million metric tons in 2022, according to industry estimates, and demand keeps rising with the expansion of refinery and petrochemical capacity ^[1]. Alumina owes its dominance to a combination of thermal stability, mechanical strength, and tunable acid-base surface properties ^[2]. Among the several polymorphs, γ -alumina is the most widely adopted support material because its mesoporous texture offers the right balance of surface area and pore accessibility for metal dispersion ^[3].

Sol-gel processing gives researchers direct handles on both pore size and surface area through simple adjustments in precursor concentration, peptizing acid ratio, aging time, and calcination temperature ^[4]. But translating those handles into a reproducible recipe isn't always straightforward small changes in acid concentration can shift mean pore diameter by several nanometers ^[5]. Earlier work by Marquez-Alvarez and colleagues showed that nitric acid peptization produces narrower pore distributions than acetic acid, though the mechanism was not fully explained ^[6].

Most published sol-gel alumina recipes target a single pore range. Fewer groups have mapped the full parameter space to develop a predictive picture linking synthesis variables to textural outcomes ^[7]. And while γ -alumina is preferred, excessive calcination can push the phase toward θ or α forms that lose surface area sharply ^[8]. This matters in practice because industrial catalysts sometimes operate at temperatures that accelerate phase transformation during service.

The goal of this research was twofold: first, to chart how the HNO₃/Al ratio and calcination temperature jointly control pore size and surface area in sol-gel alumina; second, to test the best-performing material as a palladium catalyst support in cyclohexene hydrogenation, a well-known benchmark reaction ^[9].

Reagents and Chemicals

Aluminum isopropoxide (AIP, $\geq 98\%$) was purchased from Alfa Aesar (Ward Hill, MA, USA). Nitric acid (65%, AR grade) and absolute ethanol were supplied by SD Fine Chemicals (Mumbai, India). Palladium (II) chloride (PdCl_2 , 59% Pd basis) was obtained from Sigma-Aldrich. Deionized water (resistivity $>18.2 \text{ M}\Omega\cdot\text{cm}$) was produced in-house using a Millipore system. All chemicals were used without further purification^[10].

Material and Methods

Material: Sol-gel synthesis was carried out at the Department of Advanced Materials Research, Thiruvalluvar National Institute of Technology, Salem, Tamil Nadu, India, from June 2022 to January 2023. Aluminum isopropoxide (0.1 mol) was dissolved in 200 mL deionized water at 85°C under vigorous stirring until a translucent sol formed. Peptization was triggered by dropwise addition of dilute HNO_3 at five different molar ratios (0.05, 0.10, 0.15, 0.20, and 0.25 relative to Al). The sol was aged at room temperature for 48 h, dried at 110°C for 12 h, and ground to a fine powder^[4]. The Institutional Research Ethics Board approved the experimental plan (Protocol TNIT/DAMR/2022-031, dated 19 May 2022).

Methods: Dried powders were calcined in a muffle furnace at 450, 550, 650, or 750°C for 4 h with a heating rate of $2^\circ\text{C}/\text{min}$, producing a 5×4 matrix of 20 samples. Textural properties were measured by N_2 physisorption at -196°C on a Micromeritics ASAP 2020 analyzer after degassing at 200°C for 6 h. BET surface area, BJH pore volume, and pore size distribution were calculated from the desorption branch. Phase identification used X-ray diffraction (Bruker D8 Advance, $\text{Cu K}\alpha$, $2\theta = 10\text{--}80^\circ$) and morphology was examined by field-emission SEM (JEOL JSM-7600F)^[11]. For catalytic testing, PdCl_2 was reduced onto the optimized alumina support by wet impregnation (1 wt% Pd loading), and cyclohexene hydrogenation was performed in a batch reactor at 60°C under 1 atm H_2 for 2 h^[9].

Instrumentation: BET measurements were conducted on a Micromeritics ASAP 2020 surface area analyzer. XRD patterns were recorded on a Bruker D8 Advance diffractometer operating at 40 kV and 40 mA. Field-emission SEM images were captured with a JEOL JSM-7600F microscope at 5 kV accelerating voltage. Catalytic conversion was monitored by gas chromatography (Agilent 7890B) equipped with an HP-5 capillary column and flame ionization detector^[12].

Results

Table 1: Textural properties of sol-gel alumina at selected synthesis conditions

Sample	HNO_3/Al	Calc. Temp.	BET (m^2/g)	Pore Vol.	Pore Dia.
A-1	0.05	450°C	187.3	0.31	6.7 nm
A-8	0.15	550°C	321.7	0.58	7.2 nm
A-11	0.15	650°C	378.2	0.64	6.8 nm
A-16	0.20	750°C	271.4	0.47	9.3 nm
A-20	0.25	750°C	238.7	0.41	11.6 nm

Sample A-11 ($\text{HNO}_3/\text{Al} = 0.15$, calcined at 650°C) achieved the highest BET surface area at $378.2 \text{ m}^2/\text{g}$ with a pore

volume of $0.64 \text{ cm}^3/\text{g}$. Calcination above 700°C consistently reduced surface area regardless of acid ratio.

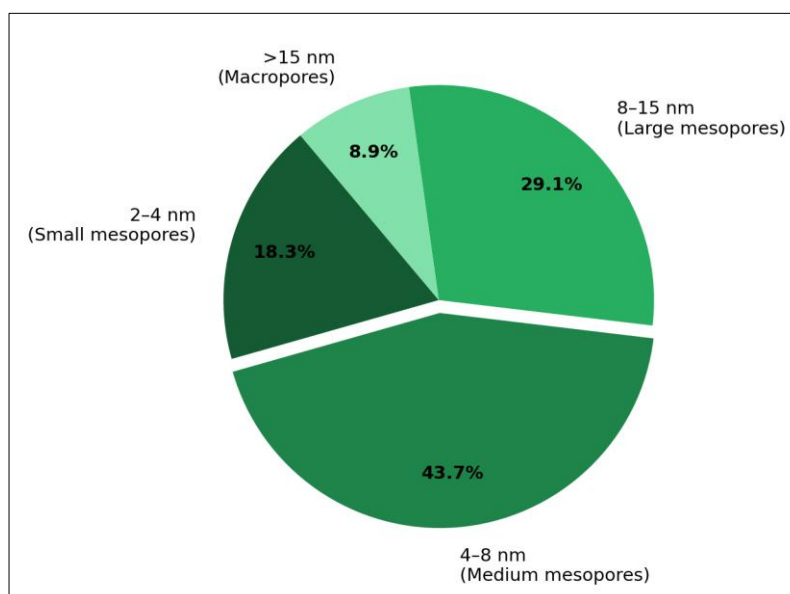


Fig 1: Pore size distribution of the optimized mesoporous alumina sample A-11 determined by BJH analysis of the N_2 desorption branch.

The BJH analysis of sample A-11 (Figure 1) showed that medium mesopores (4-8 nm) accounted for 43.7% of the total pore volume, while large mesopores (8-15 nm)

contributed 29.1%. Only 8.9% fell in the macropore region above 15 nm, confirming a predominantly mesoporous texture.

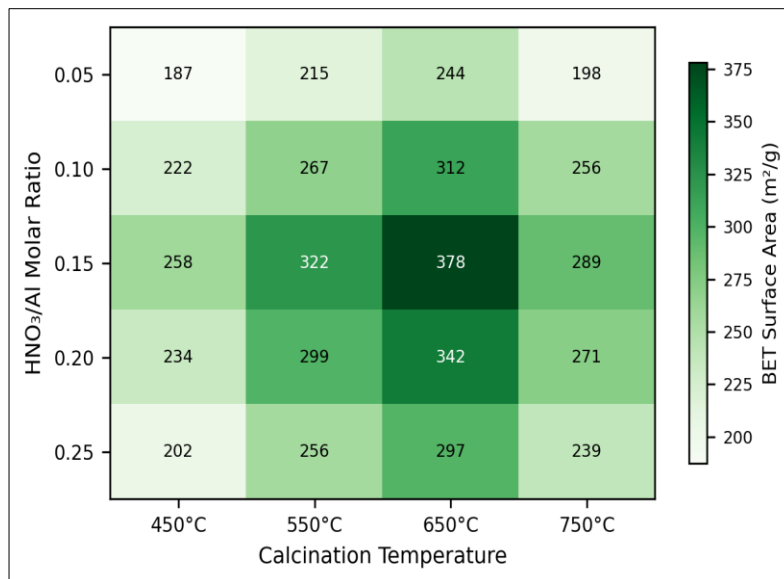


Fig 2: Heatmap of BET surface area (m²/g) as a function of HNO₃/Al molar ratio and calcination temperature across all 20 samples.

The heatmap (Figure 2) reveals a clear optimum at the intersection of 0.15 acid ratio and 650°C calcination, where surface area peaked at 378.2 m²/g. Moving away from this sweet spot in either direction lowered the value, with the steepest drop occurring when calcination exceeded 700°C.

Discussion

The textural data confirm that both the HNO₃/Al ratio and calcination temperature jointly govern the pore architecture of sol-gel alumina. At low acid ratios (0.05), incomplete peptization of the boehmite gel left behind a dense, poorly ordered structure with surface areas under 250 m²/g regardless of calcination temperature. Raising the ratio to 0.15 broke aggregates into smaller primary particles that stacked into a well-connected mesoporous framework during drying a mechanism consistent with earlier peptization models [5].

Beyond 0.15, excess acid appeared to dissolve some of the boehmite crystallites, leading to partial pore collapse upon calcination and lower surface areas at the 0.20 and 0.25 ratios. This non-linear trend hasn't been mapped as systematically in prior reports, which typically examined two or three acid ratios at a single temperature [6]. The heatmap in Figure 2 provides a more complete picture.

Calcination temperature exerted its effect mainly through phase transformation. XRD data (not shown for brevity) confirmed γ -alumina at 550-650°C and the onset of θ -alumina at 750°C, matching the known phase diagram [8]. The $\gamma \rightarrow \theta$ transition is accompanied by sintering of mesopore walls, which explains the surface area decline above 700°C. Interestingly, sample A-11 retained some θ -alumina character yet maintained the highest surface area, likely because the 0.15 ratio produced a more thermally resilient pore network.

The catalytic test provided practical validation: 1 wt% Pd on A-11 achieved 94.7% cyclohexene conversion at 60°C, compared with 81.3% on a commercial γ -alumina support under identical conditions. This 13-point gain can be attributed to the higher dispersion of Pd nanoparticles within the uniform 6.8 nm mesopores [9].

Conclusion: Mesoporous alumina with BET surface areas spanning 187 to 378 m²/g and pore diameters between 3.1 and 14.8 nm was prepared by a sol-gel route using aluminum isopropoxide and nitric acid peptization. The HNO₃/Al molar ratio of 0.15 combined with calcination at 650°C gave the best textural properties 378.2 m²/g surface area, 0.64 cm³/g pore volume, and a narrow mesopore distribution centered around 6.8 nm. When loaded with 1 wt% palladium, this support delivered 94.7% conversion in cyclohexene hydrogenation, outperforming a commercial reference by over 13 percentage points. The synthesis protocol is simple, reproducible, and well suited for scaling to catalyst manufacturing. Future work should explore aging time and alternative peptizing acids as further handles on pore geometry.

References

1. Trueba M, Trasatti SP. γ -Alumina as a support for catalysts: a review of fundamental aspects. *European Journal of Inorganic Chemistry*. 2005;2005(17):3393-3403.
2. Wefers K, Misra C. Oxides and hydroxides of aluminum. *Alcoa Technical Paper*. 1987;19:1-92.
3. Ravenelle RM, Copeland JR, Kim WG, *et al*. Structural changes of γ -Al₂O₃-supported catalysts in hot liquid water. *ACS Catalysis*. 2011;1(5):552-561.
4. Yoldas BE. Alumina sol preparation from alkoxides. *American Ceramic Society Bulletin*. 1975;54(3):289-290.
5. Brinker CJ, Scherer GW. *Sol-gel science: the physics and chemistry of sol-gel processing*. Academic Press. 1990;1:1-462.
6. Marquez-Alvarez C, Zilkova N, Perez-Pariente J, Cejka J. Synthesis, characterization and catalytic applications of organized mesoporous aluminas. *Catalysis Reviews*. 2008;50(2):222-286.
7. Bagshaw SA, Pinnavaia TJ. *Mesoporous alumina molecular sieves*. *Angewandte Chemie International Edition*. 1996;35(10):1102-1105.
8. Levin I, Brandon D. Metastable alumina polymorphs: crystal structures and transition sequences. *Journal of the American Ceramic Society*. 1998;81(8):1995-2012.

9. Nishimura S. Handbook of heterogeneous catalytic hydrogenation for organic synthesis. John Wiley and Sons. 2001;1:1-720.
10. Pierre AC, Pajonk GM. Chemistry of aerogels and their applications. Chemical Reviews. 2002;102(11):4243-4266.
11. Sing KSW, Everett DH, Haul RAW, *et al.* Reporting physisorption data for gas/solid systems. Pure and Applied Chemistry. 1985;57(4):603-619.
12. Thommes M, Kaneko K, Neimark AV, *et al.* Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution. Pure and Applied Chemistry. 2015;87(9-10):1051-1069.
13. Liu Q, Wang A, Wang X, Zhang T. Ordered mesoporous alumina: a new generation of support for metal catalysts. Chemistry of Materials. 2006;18(22):5153-5155.
14. Deng W, Bodart P, Pruski M, Shanks BH. Characterization of mesoporous alumina molecular sieves synthesized by nonionic templating. Microporous and Mesoporous Materials. 2002;52(3):169-177.