

Structure–Activity Relationship of Magnesium Tin Fluoride Catalysts (MSF) with Varying Sn Doping Levels in the Reduction of p-Nitrophenol (PNP) to p-Aminophenol (PAP)

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Abstract

The catalytic reduction of toxic p-nitrophenol (PNP) into industrially valuable p-aminophenol (PAP) requires efficient, non-noble metal catalysts to ensure sustainability and cost-effectiveness. In this study, Magnesium Tin Fluoride (MSF) catalysts were synthesized via a fluorolytic sol-gel method using magnesium methoxide and tin(II) chloride dihydrate as precursors to ensure high phase purity and minimize residual anion interference. The effects of varying Sn doping levels (0 to 0.150 mol) on the physicochemical properties were systematically investigated using XRD, FTIR, BET, and SEM-EDX. XRD analysis confirmed the retention of the tetragonal MgF_2 structure (JCPDS No. 70-2269), while subtle shifts in diffraction peaks indicated the successful incorporation of Sn^{4+} into the MgF_2 lattice. Nitrogen adsorption-desorption revealed that Sn doping significantly enhanced the specific surface area, peaking at 36.096 m^2/g for the MS4F sample (0.10 mol Sn), compared to only 10.391 m^2/g for the undoped MS0F. Catalytic testing showed that MS4F achieved an optimal PNP conversion of 98.55% and a PAP yield of 72.46%. The enhanced performance is attributed to the synergistic effect of increased surface area and optimized Brønsted acidity provided by hydroxyl groups, which facilitate electron transfer during the reduction process. However, excessive doping (MS5F) led to particle agglomeration and a subsequent decline in catalytic efficiency. This study establishes a clear structure–activity relationship, demonstrating that precise control of Sn concentration is vital for tailoring the structural integrity and reactivity of fluoride-based catalysts.

Keywords: Magnesium Tin Fluoride, Sol-gel synthesis, P-nitrophenol reduction, Sn doping, Structure–activity relationship

Introduction

Nitrophenols are a class of aromatic organic compounds widely utilized in various industrial applications, including dyes, pesticides, herbicides, and insecticides [1]. Among their isomeric forms 2-nitrophenol, 3-nitrophenol, and 4-nitrophenol (p-nitrophenol, PNP), the para-isomer exhibits high chemical stability and considerable toxicity, posing severe environmental and health risks [2]. Due to its highwater solubility and poor biodegradability, PNP

persists in aquatic environments, leading to long-term contamination. It is known to cause damage to vital organs such as the eyes, kidneys, and circulatory system [3] and is listed as a priority pollutant by the U.S. Environmental Protection Agency (EPA).

Conventional methods for the degradation of PNP, such as advanced oxidation, photodegradation, and biological treatments, often suffer from long reaction times, low conversion efficiencies, and complex

operational requirements [4]. Alternatively, catalytic reduction of PNP to p-aminophenol (PAP) has emerged as an efficient and sustainable approach, offering a valuable product with wide industrial applications. PAP serves as a precursor in the synthesis of pharmaceuticals, particularly paracetamol (acetaminophen), as well as in hair dyes, corrosion inhibitors, and resins [5].

The reduction of PNP is typically performed using sodium borohydride (NaBH_4) as a reducing agent, but the reaction requires an efficient catalyst to facilitate electron transfer between BH_4^- and PNP [6]. Noble metal catalysts such as Pt, Pd, Ag, and Au show excellent catalytic activity but are limited by high cost and scarcity. Consequently, recent studies have shifted toward developing non-noble metal catalysts, which are cost-effective and environmentally friendly.

Magnesium fluoride (MgF_2) has attracted attention as a bifunctional catalyst providing both Lewis and Brønsted acid sites, along with superior thermal and chemical stability [7,8]. However, its relatively low Lewis's acidity often limits its catalytic performance in redox reactions. To overcome this limitation, doping with metals such as tin (Sn) can effectively modify surface acidity and electronic structure, enhancing catalytic activity [9,10]. Sn-doped systems exhibit improved electron transfer efficiency, structural stability, and hydrogen activation capability [11].

The synthesis of Magnesium Tin Fluoride (MSF) catalyst has been effectively achieved via the sol-gel method. The selection of magnesium methoxide as the alkoxide precursor, achieved through the reaction of magnesium turning and methanol, reflects a strategic choice to ensure purity and minimize the presence of residual anions that may affect catalyst stability. Traditionally, alternative magnesium sources such as magnesium nitrate, magnesium chloride, and magnesium carbonate have shown potential, but their associated anions, such as NO_3^- , Cl^- , and CO_3^{2-} , can introduce undesirable acidity and cause colloidal instability.

The sol-gel method is particularly advantageous due to its ability to form homogeneous materials at relatively low temperatures while maintaining a high degree of purity, as highlighted by [12]. This process is characterized by the initial sol phase transitioning to a gel, resulting in the formation of a porous network. This

transition allows control over the physical and chemical properties of the resulting material.

Furthermore, the synthesis incorporates a crucial aging process to improve the integrity of the gel network by promoting cross-linking of polymer chains, thereby establishing a more robust structural framework [13]. By integrating tin (Sn) doping through this sol-gel approach, a more uniform dopant dispersion is expected, ultimately tailoring the structural characteristics and enhancing the catalytic efficiency of the MSF system.

Furthermore, the selection of the Sn doping amount (varying from 0 to 0.150 mol) is crucial in tailoring the structural properties of the catalyst. Changes in the characteristics of the final product due to differences in dopant concentration can lead to variations in catalytic activity and efficiency, thus encouraging the exploration of optimal doping conditions to improve performance [14].

In this study, tin-doped magnesium fluoride catalysts were synthesized via a sol-gel method to investigate the effect of Sn incorporation on their physicochemical properties and catalytic performance in the reduction of p-nitrophenol to p-aminophenol. The influence of varying Sn contents on catalyst characteristics and activity was systematically evaluated, aiming to develop an efficient and sustainable fluoride-based catalyst for environmental applications.

Materials and methods

Materials

All chemical reagents used in this research were of analytical grade and utilized without further purification. Magnesium turnings (99.98% purity) were purchased from Sigma-Aldrich, while tin(II) chloride dihydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, 98%) was supplied by Merck. The fluorinating agent, aqueous hydrogen fluoride (HF 40%), and the solvent, methanol (CH_3OH , 99.9%), were both obtained from Merck. Aquabides (Otsuka) was used throughout the synthesis and testing processes.

For the catalytic reduction experiments, p-nitrophenol ($\text{C}_6\text{H}_5\text{NO}_3$, 99%) was sourced from Aldrich, and sodium borohydride (NaBH_4 , 99.9%) was provided by Merck as the reducing agent. High-purity p-aminophenol ($\text{C}_6\text{H}_7\text{NO}$, 98%, Merck) served as the reference standard for analytical quantification. Characterization reagents included pyridine (99.5%, Merck) for surface acidity measurements and potassium

bromide (KBr) for FTIR sample preparation. Additionally, sodium nitroprusside and sodium carbonate (Merck) were employed to prepare the alkaline nitroferricyanide reagent required for the spectrophotometric detection of p-aminophenol.

Catalyst synthesis

Magnesium Tin Fluoride (MSF) catalysts were synthesized via a fluorolytic sol-gel method, modified from the procedure reported by [15]. The sol-gel approach was preferred due to its low-temperature processing, cost-effectiveness, and ability to produce highly pure and homogeneous materials [16,17]. The synthesis was performed with varying tin concentrations (0; 0.025; 0.050; 0.075; 0.100; and 0.150 mol), denoted as samples MS0F to MS5F, respectively.

The process began with the pre-treatment of magnesium turnings, which were heated at 100 °C to ensure dryness and remove surface impurities. The pre-heated magnesium was then reacted with methanol in a three-necked flask under reflux at 65 °C for 12 h to produce a pure magnesium methoxide emulsion. To incorporate the dopant, a specific amount of tin(II) chloride dihydrate was dissolved in methanol and added to the magnesium methoxide mixture while stirring continuously to ensure uniform dispersion of the Sn ions.

The fluorination step was conducted by adding 40% aqueous hydrogen fluoride (HF) dropwise into the metal-alkoxide mixture within a polyethylene vessel while stirring with a magnetic stirrer until a sol was formed. The sol was then stirred at a constant speed in a closed container for 3 h to facilitate the transition into a hydrogel. This hydrogel underwent an aging process at room temperature until a stable and robust gel structure was achieved through polymer cross-linking.

Following the aging stage, the solvent was removed via vacuum drying at 70 °C until a dry solid xerogel was obtained. The resulting xerogel was finely ground into a homogeneous powder and subsequently calcined at 375 °C for 5 h in a muffle furnace to eliminate residual methoxy groups, enhance the fluoride crystal structure, and stabilize the catalytic sites.

Characterization techniques

The physicochemical properties of the synthesized MSF catalysts were systematically investigated using the following instrumental techniques.

X-Ray Diffraction (XRD)

The crystalline structure and phase purity were analyzed using a Philips PW1140/90 diffractometer. The powder samples were finely ground and placed in a standard sample holder. Measurements were performed using CuK α radiation ($\lambda = 1.54 \text{ \AA}$) with a scanning range of $2\theta = 20^\circ$ to 80° . The resulting diffractograms were matched against the JCPDS database (specifically PDF No. 70-2269 for MgF $_2$). The average crystallite size was calculated using the Scherrer equation based on the full width at half maximum (FWHM) of the most intense peaks.

Fourier-Transform Infrared Spectroscopy (FTIR)

Functional groups and chemical bonds were identified using a Shimadzu 8400S FTIR spectrophotometer. Pellets were prepared by mixing 1.5 mg of catalyst with 0.5 g of spectroscopic-grade KBr followed by compression in a hand pellet press. The spectra were recorded in the wavenumber range of 4,000 - 400 cm $^{-1}$.

Surface area and porosity analysis

The specific surface area, pore volume, and pore diameter were determined via nitrogen adsorption-desorption isotherms using a Micromeritics Gemini VII Surface Area and Porosity Analyzer. Prior to analysis, samples underwent a degassing process at 125 °C for 3 h under a nitrogen flow of 30 cm 3 /min. The specific surface area was calculated using the Brunauer-Emmett-Teller (BET) method, while the pore size distribution was analyzed using the Barrett-Joyner-Halenda (BJH) method.

Surface acidity measurement (Pyridine Adsorption-FTIR)

The type and relative amount of acid sites (Lewis and Brønsted) were determined using the pyridine adsorption-FTIR method. 20 mg of catalyst was placed in a glass tube, stabilized with glass wool, and pre-heated at 150 °C for 1 h under N $_2$ flow. Subsequently,

50 μL of pyridine was added dropwise. The sample was then heated at 150 $^{\circ}\text{C}$ for an additional 3 h under N_2 to remove physisorbed pyridine. FTIR scans were performed in the range of 2,000 - 1,250 to identify characteristic peaks at approximately 1,450 cm^{-1} (Lewis) and 1,540 cm^{-1} (Brønsted).

Morphology and elemental mapping (FESEM-EDX)

Surface morphology and elemental distribution were observed using a Hitachi FlexSEM 100 Field Emission Scanning Electron Microscope equipped with Energy Dispersive X-Ray Spectroscopy (EDX). Samples were coated with carbon tape and analyzed at an acceleration voltage of 15 kV with a magnification of 5,000x.

UV-Vis spectroscopy

The concentration of reactants and products during catalytic testing was monitored using a Genesys 10S UV-Vis spectrophotometer. Quantitative analysis was conducted based on calibration curves at specific maximum wavelengths: 317 nm for p-nitrophenol (PNP), 410 nm for p-nitrophenolate (PNP^-), and 710 nm for p-aminophenol (PAP) after reaction with the alkaline nitroferricyanide reagent.

Catalytic activity testing

The catalytic performance of the synthesized Magnesium Tin Fluoride (MSF) was evaluated through the reduction of p-nitrophenol (PNP) to p-aminophenol (PAP) using sodium borohydride (NaBH_4) as the reducing agent. Prior to the activity tests, the calcined MSF catalysts were activated by heating at 100 $^{\circ}\text{C}$ for 60 min to ensure the availability of active sites on the catalyst surface.

The experimental procedure was conducted by mixing a 50 ppm PNP solution with 20 mg of in a beaker. Subsequently, 10 mg of the MSF catalyst was added to the mixture. The reaction was carried out at room temperature under constant stirring for 1 h to facilitate optimal electron transfer. Control experiments were also performed without the catalyst and without the reducing agent to verify the synergistic necessity of both components in overcoming the kinetic barrier of the reaction.

Upon completion of the reaction, the filtrate was separated and analyzed using a UV-Vis spectrophotometer (Genesys 10S). Quantitative and qualitative analyses were performed based on calibration curves at specific maximum wavelengths: 317 nm to monitor the residual p-nitrophenol (PNP), 410 nm to detect the p-nitrophenolate (PNP^-) intermediate, and 710 nm to quantify the formation of p-aminophenol (PAP).

For the accurate detection of PAP, the filtrate was first reacted with an alkaline nitroferricyanide reagent (prepared by dissolving 0.1 g sodium nitroprusside and 0.1 g sodium carbonate in 10 mL of methanol, 50% (v/v)) to produce a stable blue-green color prior to absorbance measurement.

The catalytic efficiency was calculated using the following equations.

$$\text{Conversion (\%)} = \frac{\text{initial mol of PNP} - \text{residual mol of PNP}}{\text{initial mol of PNP}} \times 100\% \quad (1)$$

$$\text{Yield (\%)} = \frac{\text{mol of product formed}}{\text{initial mol of reactant}} \times 100\% \quad (2)$$

$$\text{Selectivity (\%)} = \frac{\text{mol of specific product formed}}{\text{mol of converted reactant}} \times 100\% \quad (3)$$

Results and discussion

Catalyst characterization

XRD Analysis

The diffractogram of the synthesized Magnesium Tin Fluoride (MSF) catalyst provides crucial insights into its crystallographic structure and phase purity. As shown in the diffraction pattern (**Figure 1**), the sample matches the standard MgF_2 pattern from the JCPDS database (PDF No. 70-2269), which displays major diffraction peaks at approximately $2\theta = 27.229^{\circ}$, 40.43° , and 53.489° . This is consistent with previous studies, such as those reported by [18], which also identified similar peak positions in the synthesized MgF_2 catalyst, confirming the reliability of the synthesized material and the methodology used. No diffraction peaks attributable to crystalline SnO_2 (JCPDS No. 77-0452; characteristic peaks at $2\theta = 26.6^{\circ}$, 33.8° , and 51.56°) were detected in any doped sample, confirming the

formation of a single-phase MgF_2 solid solution rather than a physical mixture or phase-separated system.

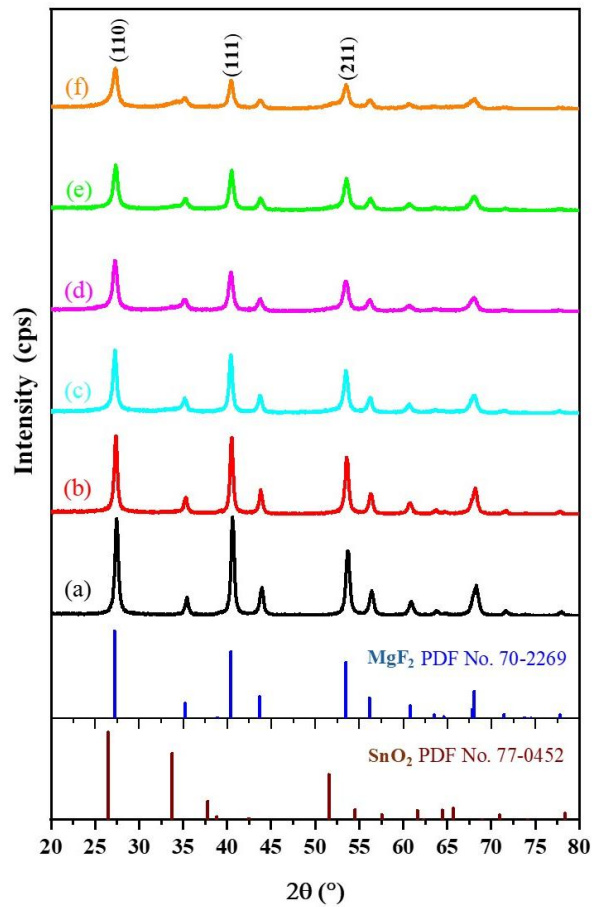


Figure 1 XRD patterns of MSF with reference sticks (a) MS0F; (b) MS1F; (c) MS2F; (d) MS3F; (e) MS4F; (f) MS5F. All peaks match tetragonal MgF_2 , while systematic peak shifts confirm Sn incorporation and changes in lattice structure.

Rietveld refinement performed using the Rietica software package with reference data from ICSD No. 8121 confirmed that the undoped MS0F possesses a tetragonal structure with space group $P4_2/mnm$ (No. 136). The refinement converged with excellent agreement factors: $R_p = 5.77$, $R_{wp} = 4.27$, and $\text{GoF} (\chi^2)$

$= 0.2044$, all well within the accepted thresholds (R_p and $R_{wp} < 20\%$; $\text{GoF} < 4\%$), confirming the high quality of the structural model. The refined lattice parameters for MS0F are $a = b = 4.622 \text{ \AA}$, $c = 3.054 \text{ \AA}$, with a unit cell volume of $65.246 \text{ \AA}^3$, in excellent agreement with published MgF_2 standards.

Table 1 2θ positions, d-spacing values, relative crystallinity and average crystallite size of MSF catalysts.

Catalyst	2θ (110) (°)	2θ (111) (°)	2θ (211) (°)	$d(110)$ (Å)	$d(111)$ (Å)	$d(211)$ (Å)	Crystallinity (%)	Average Crystallite Size (nm)
MS0F	27.437	40.590	53.677	3.248	2.221	1.706	100	20.885
MS1F	27.339	40.479	53.562	3.259	2.227	1.709	81.88	22.170
MS2F	27.264	40.379	53.522	3.268	2.231	1.711	63.81	18.813
MS3F	27.272	40.395	53.537	3.267	2.231	1.710	47.77	14.983
MS4F	27.338	40.482	53.545	3.260	2.226	1.710	46.30	15.405
MS5F	27.314	40.436	53.564	3.262	2.229	1.709	37.10	12.590

Systematic peak shift analysis (**Table 1**) demonstrates a progressive shift in 2θ positions with increasing Sn content, accompanied by corresponding changes in d-spacing values (**Table 2**). The initial shift toward lower 2θ values (higher d-spacings) from MS0F to MS2F–MS3F, followed by a partial recovery, is consistent with the substitutional incorporation of Sn^{4+} (ionic radius: 0.69 Å) into Mg^{2+} (ionic radius: 0.72 Å) lattice sites. When Sn^{4+} replaces some of the Mg^{2+} ions in the crystal lattice, the interplane distance (d-spacing) changes, leading to the observed shift in the diffraction peaks [19]. This behavior is in line with findings from similar doping studies, where the addition of smaller

ions causes a subtle shift in the lattice parameters [20]. The Rietveld-refined lattice parameters in **Table 2** reveal a systematic increase in both a and c parameters and unit cell volume from MS0F to MS4F (65.246 Å³ to 65.676 Å³), confirming that Sn^{4+} substitution causes a net lattice expansion despite the smaller ionic radius attributable to charge compensation and Coulombic effects upon aliovalent substitution. At MS5F, both a (4.602 Å) and c (3.042 Å) decrease, and the unit cell volume drops to 64.420 Å³, indicating that the crystal lattice has reached the saturation capacity for dopant incorporation, with excess Sn^{4+} likely undergoing surface segregation or inducing structural distortion.

Table 2 Lattice parameters and unit cell volume from Rietveld refinement (Rietica software, ICSD No. 8121).

Catalyst	a = b (Å)	c (Å)	Volume (Å ³)
MS0F	4.622	3.054	65.246
MS1F	4.626	3.059	65.392
MS2F	4.627	3.056	65.432
MS3F	4.633	3.059	65.673
MS4F	4.635	3.057	65.676
MS5F	4.602	3.042	64.420

Furthermore, the decrease in peak intensity with increasing Sn content indicates a decrease in crystallinity and reduction in crystallite size from 20.885 nm (MS0F) to 12.590 nm (MS5F) (**Table 1**) indicating that the presence of Sn^{4+} disrupts the regular atomic arrangement in the MgF_2 lattice. This observation is supported by the literature, which shows that doping elements can introduce defects in the crystal structure, thereby decreasing the overall crystallinity as shown in the study by [21].

FTIR spectroscopy

Fourier Transform Infrared Spectroscopy (FTIR) analysis was performed on the synthesized Magnesium Tin Fluoride (MSF) catalyst, providing information on the chemical bonds and functional groups present in the material and shown in **Figure 2**. **Figure 2** shows characteristic peaks indicate the presence of various functional groups, including hydroxyl (–OH), metal fluoride (Mg-F), and possible tin-linked bonds,

confirming the successful synthesis of the MSF material [22,23].

The prominent peak observed at around 3,400 cm^{-1} can be attributed to the stretching vibration of the hydroxyl (–OH) group, likely caused by moisture adsorption during the synthesis process [22]. The presence of this hydroxyl group is significant, as it can act as a Brønsted acid site, which is essential for various catalytic reactions. The role of hydroxyl groups in enhancing acidity and catalytic performance has been well documented [24].

Furthermore, peaks located in the 600 - 700 cm^{-1} range indicate stretching vibrations associated with the Mg-F bond, which are characteristic of metal fluorides. The intensity of these peaks was observed to increase with the stoichiometric addition of Sn, supporting the idea that tin doping can alter the electronic environment around Mg and enhance the stability of the Mg-F framework.

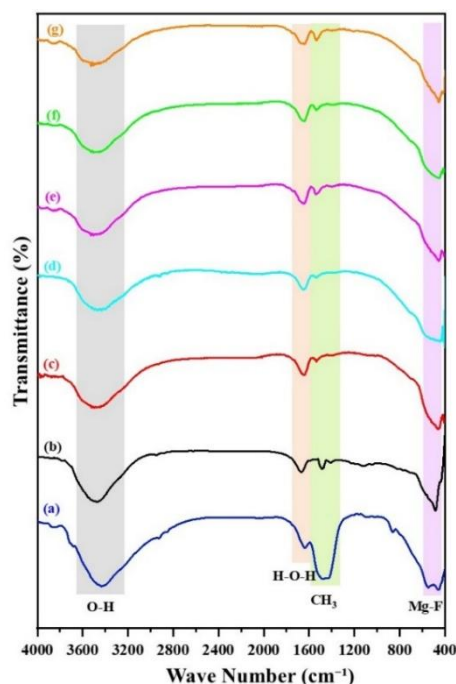


Figure 2 FTIR spectra of emulsion $\text{Mg}(\text{OCH}_3)_2$ and MS_xSn catalysts. (a) $\text{Mg}(\text{OCH}_3)_2$; (b) MS0F; (c) MS1F; (d) MS2F; (e) MS3F; (f) MS4F; (g) MS5F. The presence of $-\text{OH}$ and $\text{Mg}-\text{F}$ bands confirms fluoride formation, with spectral variations indicating modification of surface chemistry due to Sn doping.

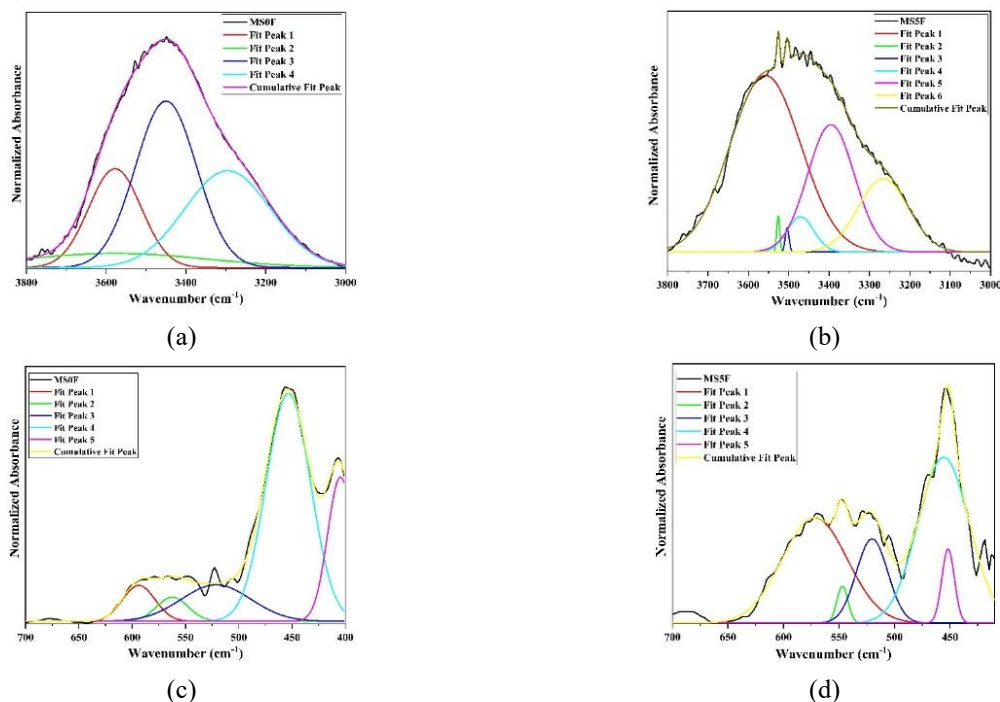


Figure 3 FTIR deconvolution analysis of MS0F and MS5F catalysts. (a, b) Deconvoluted hydroxyl stretching region ($3,000 - 3,800 \text{ cm}^{-1}$) and (c, d) Deconvolution of the metal–fluoride vibration region ($400 - 700 \text{ cm}^{-1}$).

To gain a deeper understanding of the surface functional groups and structural distribution, Gaussian deconvolution was applied to the broad FTIR absorption bands (**Figure 3**). In the hydroxyl stretching region ($3,000 - 3,800 \text{ cm}^{-1}$), the broad envelope was resolved

into individual components representing various surface hydroxyl environments. For the undoped MgF_2 (MS0F), deconvolution revealed four individual components with a primary peak at $3,449.97 \text{ cm}^{-1}$ ($R^2 = 0.99926$). As Sn doping levels increased, the distribution became

more complex; the MS5F sample exhibited six resolved peaks, indicating a higher variety of hydroxyl environments induced by the dopant. This increased area of specific resolved peaks provides semi-quantitative evidence for a higher density of Brønsted acid sites (BAS), which are crucial for the final protonation step of the p-nitrophenolate intermediate into p-aminophenol (PAP).

In the fingerprint region ($400 - 700 \text{ cm}^{-1}$), deconvolution was used to analyze the structural integrity of the metal-fluoride framework. The overlapping bands were resolved into five distinct fit peaks for both MS0F and MS5F. A characteristic shift in the peak centers (x_c) was observed following Sn incorporation; notably, the dominant stretching component shifted from 453.48 cm^{-1} in MS0F to 455.71 cm^{-1} in MS5F. These spectroscopic shifts confirm that Sn^{4+} ions ($0.69 \text{ \AA}$) have successfully substituted Mg^{2+} ($0.72 \text{ \AA}$) within the lattice, causing local electronic perturbations. This structural 'disorder' identified through deconvolution aligns with the XRD results and confirms the formation of a single-phase Magnesium Tin Fluoride structure, which enhances catalytic efficiency by providing a more reactive and accessible surface.

Surface area and porosity

The Brunauer-Emmett-Teller (BET) method is a widely used technique for determining the surface area and porosity of materials, which are critical factors influencing the catalytic performance of metal-based catalysts. The BET analysis of the synthesized Magnesium Tin Fluoride (MSF) catalysts reveals significant insights into the effects of Sn doping on the surface characteristics and pore structure of the materials.

The BET analysis revealed specific surface areas ranging from 10.391 to $36.096 \text{ m}^2/\text{g}$ across different Sn doping levels. Analysis shows that the MSF catalyst exhibits a significant increase in specific surface area with increasing Sn doping levels, peaking at an optimal concentration of 0.10 mole of Sn. The highest observed BET surface area is $36.096 \text{ m}^2/\text{g}$, which is in line with previous literature findings showing that higher metal loading can facilitate the formation of more active surface sites [25]. The correlation between increased surface area and enhanced catalytic activity is well documented, with larger surface areas allowing better reactant accessibility to active sites.

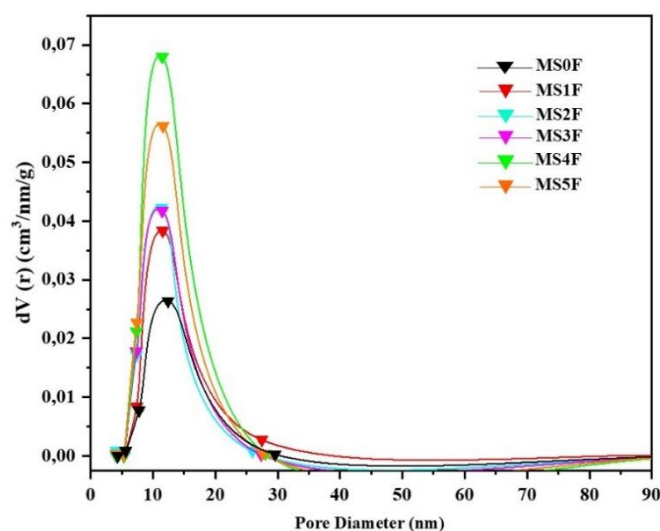


Figure 4 Pore size distribution of MSF catalysts derived from BJH analysis. All samples exhibit mesoporosity, with more uniform pores at optimal Sn doping and slight pore blockage at higher concentrations.

It is well known that the surface area of a catalyst influences its reactivity. In the case of MSF, the increased surface area due to Sn doping can enhance the mass transfer rate, thereby improving the overall

catalytic reaction efficiency [26]. The additional porosity also allows for better accommodation of reactants and products within the structure, further promoting catalytic switching.

Pore size distribution (PSD) analysis using the Barrett-Joyner-Halenda (BJH) method showed that the MSF samples predominantly exhibited mesoporous characteristics (**Figure 4**). The average pore diameter shifted with changes in Sn concentration, indicating that doping affects not only the quantity but also the morphology of pores within the catalyst. The highest pore volume of 0.225 cm³/g observed in MS4F, highlighting the importance of surface characteristics in catalytic efficiency [27]. However, as Sn doping levels exceed the optimal threshold (MS5F), a structural breakdown is observed. The pore volume decreases to 0.199 cm³/g, following the trend of reduced specific surface area (21.134 m²/g). This reduction is attributed to heavy particle agglomeration caused by excessive Sn

species, which partially blocks the mesoporous channels and covers active surface sites. Unlike MS4F, which maintains an ideal pore structure for reactant diffusion, the MS5F catalyst's structural integrity is compromised, leading to a significant drop in PAP yield and selectivity.

The narrowing of pore size at higher Sn doping levels may indicate agglomeration or the formation of dense clusters, which can hinder active site accessibility and potentially lead to decreased catalytic performance. This is supported by research showing that optimal pore dimensions are critical for catalytic efficiency; pores that are too large or too small can limit the transport of reactants and products [28].

Table 3 BET surface area, pore volume, and pore diameter.

Catalyst	S _{BET} (m ² /g)	Average pore diameter (nm)	Pore volume (cm ³ /g)
MS0F	10.391	12.408	0.098
MS1F	19.892	11.554	0.156
MS2F	17.395	11.408	0.150
MS3F	24.341	11.478	0.145
MS4F	36.096	11.485	0.225
MS5F	21.134	11.609	0.199

Surface acidity analysis (Pyridine-FTIR)

The surface acidity of the MSF catalysts was qualitatively and semi-quantitatively evaluated using pyridine-adsorption FTIR spectroscopy. The resulting spectra (**Figure 5**) reveal three characteristic bands at approximately 1,450, 1,490, and 1,540 cm⁻¹. The band at 1,450 cm⁻¹ is attributed to the coordination of pyridine with Lewis acid sites (LAS) [29], while the band at 1,540 cm⁻¹ indicates the formation of pyridinium ions on Brønsted acid sites (BAS) [30]. The intermediate band at 1,490 cm⁻¹ represents the combined interaction of pyridine with both types of acid sites [31].

Integration of the peak areas (**Table 4**) demonstrates a clear correlation between Sn-doping and surface acidity. For the undoped catalyst (MS0F), the total acidity is relatively low at 0.198 units. Upon the incorporation of Sn⁴⁺ ions, the acidity progressively increases, reaching a maximum of 0.557 units for the MS4F sample (0.10 mol Sn). This enhancement in LAS is primarily due to the substitution of Mg²⁺ by Sn⁴⁺ in the MgF₂ lattice, which creates structural defects and increases the surface electrophilicity, making the active sites more capable of accepting electron pairs from the reactants.

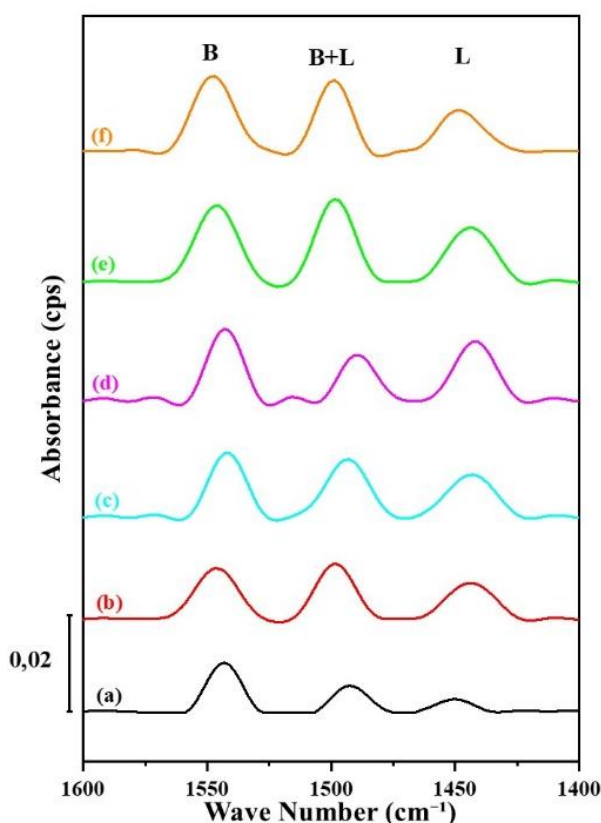


Figure 5 FTIR spectra of catalyst after pyridine adsorption (a) MS0F; (b) MS1F; (c) MS2F; (d) MS3F; (e) MS4F; (f) MS5F. Pyridine-FTIR spectra of MSF catalysts showing bands of Lewis ($\sim 1,450\text{ cm}^{-1}$) and Brønsted ($\sim 1,540\text{ cm}^{-1}$) acid sites. Increasing intensity with Sn doping indicates enhanced surface acidity.

Table 4 The results of the integration area under the peak to determine the Lewis and Brønsted acidity of the MSF catalyst.

Catalyst	Acid site (Unit area)		Amount of Brønsted & Lewis acid areas
	Brønsted	Lewis	
MS0F	0.158	0.040	0.198
MS1F	0.209	0.162	0.371
MS2F	0.222	0.191	0.413
MS3F	0.233	0.225	0.478
MS4F	0.312	0.245	0.557
MS5F	0.301	0.175	0.476

The significance of these findings lies in the structure–activity relationship observed during the catalytic tests. The increased concentration of BAS in the MS4F sample plays a pivotal role in the final stage of the reaction mechanism, specifically facilitating the protonation of the p-nitrophenolate (PNP[−]) intermediate into the target p-aminophenol (PAP) product.

Meanwhile, the LAS facilitate the initial adsorption of the nitroaromatic substrate onto the catalyst surface.

However, a decline in acidity to 0.476 units was observed for the MS5F sample. This overdoping effect suggests that excessive Sn concentration leads to the agglomeration of Sn species or the blocking of active sites, which inhibits pyridine interaction and subsequently reduces the overall catalytic efficiency

[32]. Thus, precise control of the Sn dopant level is essential for optimizing the synergistic interaction between Lewis and Brønsted sites required for efficient PNP reduction.

Morphological studies

SEM images (**Figure 6**) show a marked change in particle morphology with increasing Sn doping levels.

The undoped MSF catalyst exhibited relatively uniform, spherical particles, while samples with higher Sn concentrations exhibited an aggregated structure with irregular particle shapes. This observation aligns with previous studies showing that metal doping tends to alter particle shape and size due to complex interactions between the metal and the host matrix [19].

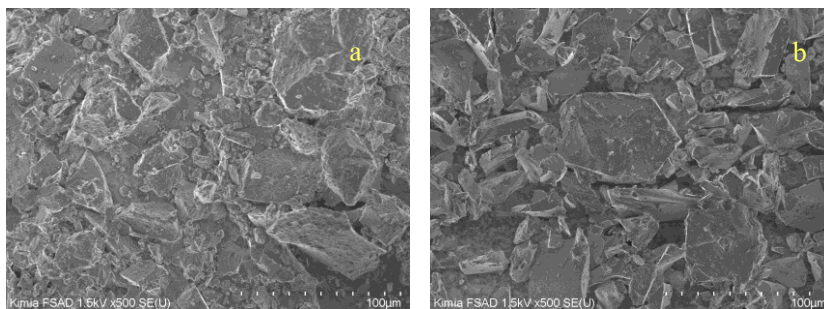


Figure 6 Surface Morphology of catalysts (a) MS0F and (b)MS4F. Sn doping produces finer particles and rougher surfaces, indicating improved dispersion and increased availability of active sites.

The particle size distribution analyzed from SEM images shows a trend where optimal Sn doping (approximately 0.10 mol) results in finer and more consistent particle sizes. This confirms the findings of

[20], who emphasized that controlled doping levels can improve catalyst particle uniformity, thus generating more active sites for catalytic processes.

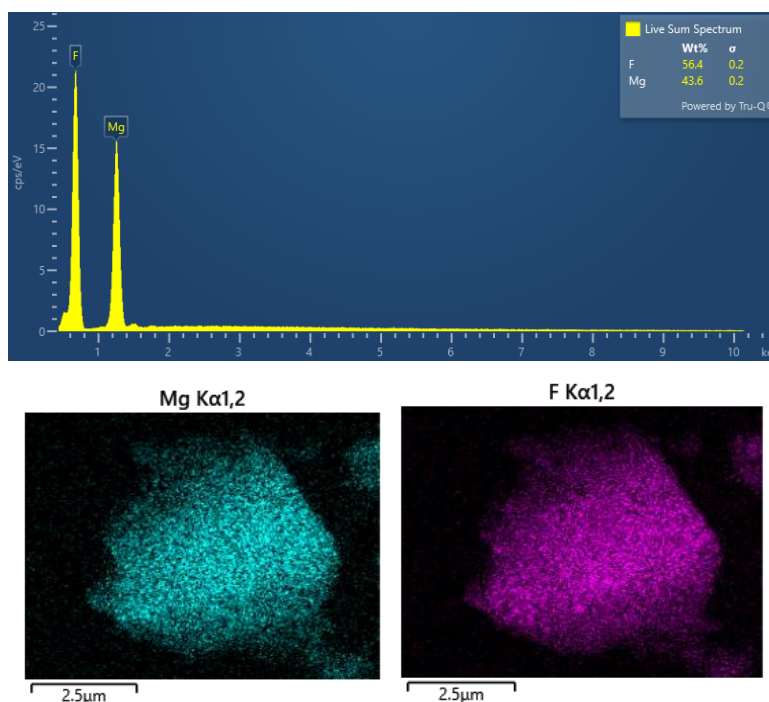


Figure 7 EDX spectrum of MS0F confirming the presence of Mg and F elements without detectable impurities, indicating high phase purity.

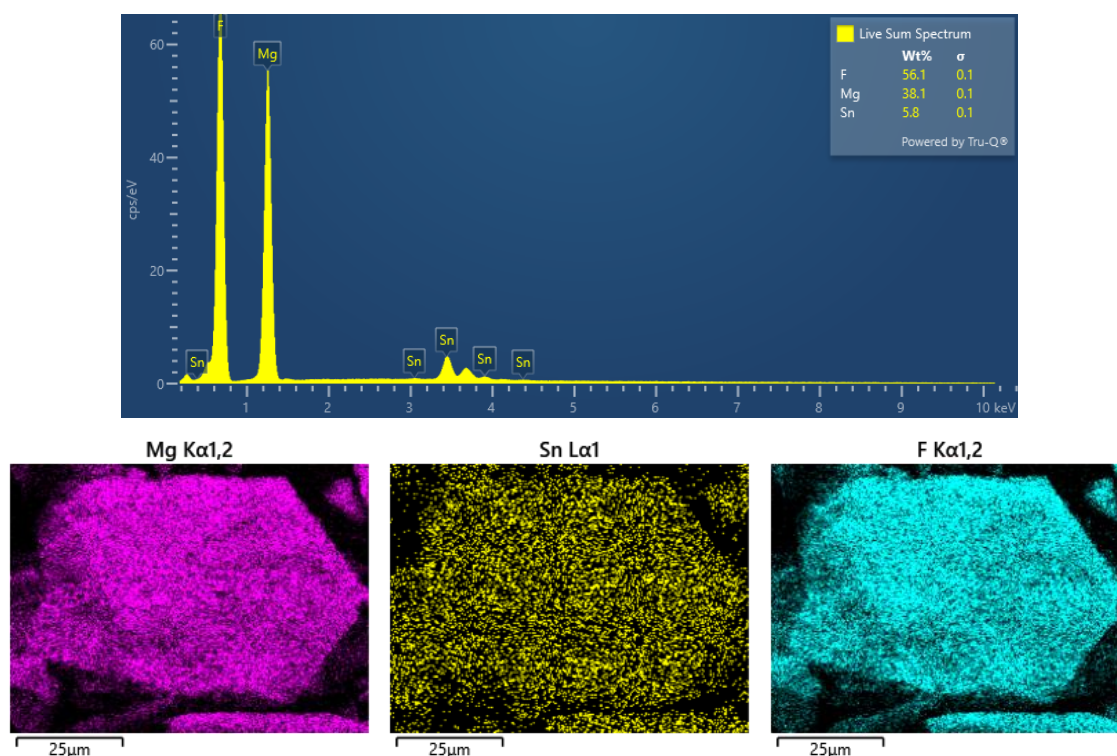


Figure 8 EDX spectrum of MS4F confirming the presence of Mg, F, and Sn, demonstrating successful and uniform Sn incorporation.

However, excessive Sn doping resulted in particle agglomeration, resulting in larger agglomerates with reduced surface area. This clumping can hinder the accessibility of reactants to the catalytic site, which has been documented to negatively impact catalytic activity and selectivity [33]. This finding is significant, as it demonstrates that while doping can improve certain characteristics, there is an optimal threshold beyond which negative effects can occur.

In addition to dimensional changes, SEM analysis revealed variations in surface roughness at different doping levels. The presence of rough surfaces has been associated with increased catalytic activity, as increased roughness can facilitate reactant adsorption and enhance mass transfer during reactions [34]. The rougher surfaces observed in highly doped samples may help explain the increased competitive reaction rate, despite the presence of significant agglomeration.

Catalytic performance

This study extensively investigated the catalytic activity of magnesium tin fluoride (MSF) in the selective reduction of p-nitrophenol (PNP) to p-aminophenol (PAP) using sodium borohydride (NaBH_4) as a reducing agent. This study revealed important insights into how various physicochemical properties of catalysts directly affect their catalytic performance, confirming previous findings in the literature [35].

The results (**Figure 9**) showed a significant influence of catalyst characteristics such as crystallinity, surface area, and pore volume on the PNP conversion rate and PAP yield. Specifically, the MS4F catalyst, with an optimal Sn doping of 0.10 mol, demonstrated the highest performance, achieving a PNP conversion of 98.55% and a PAP yield of 72.46%. This performance correlation corroborates the assertion by [36] regarding the enhancement of catalytic activity through careful tuning of metal doping.

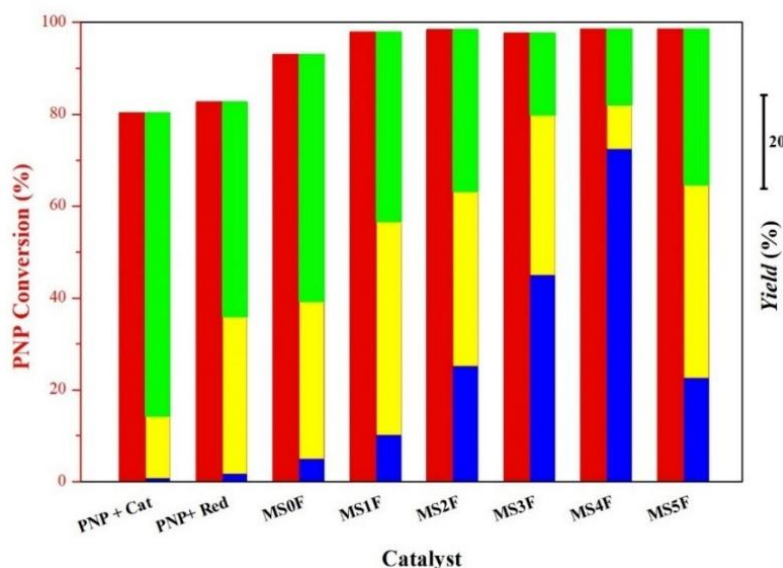


Figure 9 Catalytic performance of MSF catalysts with varying Sn-doping levels for the reduction of p-nitrophenol (PNP) to p-aminophenol (PAP). (Red: PNP Conversion; Blue: PAP Yield; Yellow: PNP⁻ Yield; Green: Others Yield). Reaction conditions: 50 ppm PNP, 20 mg, 10 mg catalyst, 1 h reaction time.

Figure 9 illustrates the synergistic effect between the MSF catalyst and the reducing agent. The control experiments (PNP + Catalyst and PNP + Red) show negligible PAP yields (< 2%), confirming that neither the catalyst nor the reducing agent alone can overcome the kinetic barrier of electron transfer.

As Sn doping levels increase from MS0F to MS4F, a significant rise in PAP yield (from 4.99% to 72.46%) is observed. This correlates with the increased specific surface area and optimized Brønsted acidity found in MS4F, which facilitates the protonation of the intermediate. The reduction in the yellow bar (Yield of PNP⁻) for MS4F (9.51%) indicates high catalytic efficiency in completing the reduction pathway. However, MS5F shows a sharp decline in performance due to overdoping, which leads to particle agglomeration and blockage of active sites, as evidenced by the increase in intermediates and side products.

The reduction process begins with the deprotonation of the hydroxyl group on PNP, producing the intermediate p-nitrophenolate (PNP⁻). The subsequent adsorption of PNP⁻ and hydride ions from NaBH₄ onto the catalyst surface facilitates the electron transfer necessary for the reduction reaction [37]. This multi-step mechanism demonstrates the crucial role of the catalyst in enhancing electron transfer, as described in a previous report. Without a catalyst, the reduction

success is significantly lower, as evidenced by the minimal PAP yields when the reaction was carried out without a catalyst or reducing agent (0.77% and 1.74%, respectively).

In this context, the synergy between the catalyst and NaBH₄ emerged as a crucial factor for the successful reduction of PNP. The effective transfer facilitated by MSF catalysts enhances the conversion rate, while the inherent stability of the fluoride framework, achieved through controlled aging and high-temperature calcination at 375 °C, provides a robust foundation for consistent catalytic performance. Furthermore, the catalyst demonstrated excellent physical stability throughout the process and was easily recovered from the reaction mixture via simple filtration, indicating its potential for reuse. Detailed multi-cycle reusability tests and post-reaction characterization are scheduled for a follow-up study to further validate its long-term durability.

This study emphasizes the importance of Sn doping on the catalytic properties of MSF. Gradual Sn addition significantly improves catalytic performance while achieving optimal acidity and surface properties, as reflected in the increase in PAP yield from only 4.99% using an undoped catalyst (MS0F) to a maximum of 72.46% with MS4F. The increase in Brønsted acidity directly correlates with increased conversion efficiency

through protonation of the p-nitrophenolate (PNP^-) intermediate to PAP. However, these findings also highlight critical concerns regarding overdoping. The observed decrease in catalytic activity and PAP yield at higher Sn ratios (MS5F) underscores the delicate balance required in catalyst design. Excess Sn

compromises the structure and availability of active sites on the catalyst. This is in line with existing literature showing that optimal doping levels are crucial for maintaining structural integrity and catalytic efficiency [36,38].

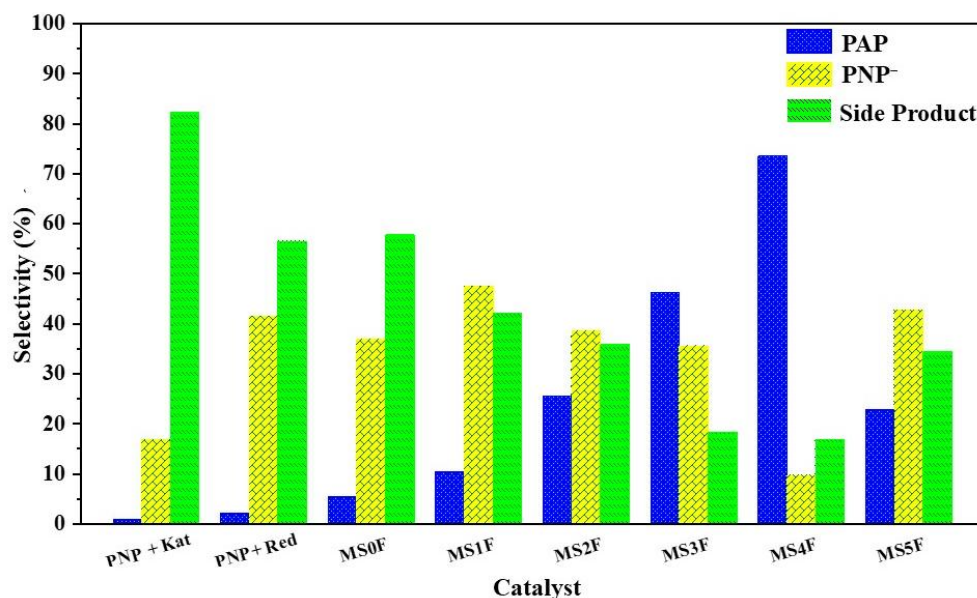


Figure 10 Product selectivity of p-aminophenol (PAP), p-nitrophenolate (PNP^-) intermediate, and other side products in the reduction of p-nitrophenol over MSF catalysts with varying Sn doping levels.

Selectivity analysis is a crucial parameter for evaluating the ability of Magnesium Tin Fluoride (MSF) catalysts to specifically direct the reduction of p-nitrophenol (PNP) toward the target product, p-aminophenol (PAP). According to the data in **Figure 10**, there is a significant increase in PAP selectivity as Sn doping levels rise, reaching an optimal point with the MS4F sample.

The MS4F catalyst (0.100 mol Sn) demonstrated the most superior performance, achieving the highest PAP selectivity of 73.53%. This indicates that at this specific composition, the catalyst possesses the most ideal balance of Lewis and Brønsted acid sites to facilitate complete electron transfer and protonation. In contrast, the undoped catalyst (MS0F) exhibited very low selectivity toward PAP, at only 5.36%, with the reaction product being dominated by side compounds (57.76%). This confirms that pure MgF_2 surfaces lack the specific directing capability required to efficiently form the amine group.

Interestingly, the selectivity toward the p-nitrophenolate (PNP^-) intermediate showed a downward trend as the catalysts became more active. PNP^- selectivity peaked at 47.44% for MS1F but dropped drastically to just 9.65% for MS4F. This sharp decrease in intermediate selectivity serves as strong evidence that the MS4F catalyst is highly efficient in driving the further transformation of PNP^- into PAP, thereby minimizing the accumulation of intermediate compounds within the reaction system.

Selectivity towards side products (others) was also sharply reduced in the optimal catalytic system. From a high of approximately 82.21% in the control tests (PNP + catalyst without reductor), this figure shrank to its lowest level of 16.82% for MS4F. These side products are suspected to be partial reduction compounds, such as p-nitrosophenol or p-hydroxylaminophenol, which typically form when electron transfer is incomplete. The success of MS4F in suppressing these side products suggests that its mesoporous structure and high density of active sites effectively stabilize intermediates and

guide the entire reaction pathway toward the target product.

Optimizing technical reaction conditions is vital for further minimizing side products and achieving higher selectivity toward p-aminophenol (PAP). While the use of NaBH_4 creates a basic environment necessary for the deprotonation of p-nitrophenol to the p-nitrophenolate (PNP^-) intermediate, the final reduction step requires an adequate supply of protons to facilitate the complete cleavage of the $\text{N}=\text{O}$ bond. In this system, the MSF catalyst acts as a solid acid, providing Brønsted acid sites that supply protons locally at the active surface. Future optimizations focusing on pH regulation could balance the hydride donor efficiency of NaBH_4 with proton availability at the catalyst surface. Additionally, increasing the stirring speed would enhance mass transfer rates, ensuring more effective contact between reactants and the mesoporous active sites, thereby preventing the accumulation of partial reduction intermediates such as p-nitrosophenol or p-hydroxylaminophenol.

However, **Figure 10** also illustrates the negative impact of overdoping in the MS5F sample (0.150 mol Sn). At this concentration, PAP selectivity plummeted back to 22.91%, while the selectivity for side products increased again to 34.38%. This phenomenon occurs because excessive Sn concentrations lead to particle

agglomeration that covers the surface-active sites, disrupting the specific interaction between the reactants and the catalyst's acid sites, which ultimately results in a loss of reaction control.

Correlation between catalytic results and catalyst characteristics (Structure–activity relationship)

The catalytic performance of Magnesium Tin Fluoride (MSF) in the reduction of p-nitrophenol (PNP) to p-aminophenol (PAP) is fundamentally governed by a synergistic structure–activity relationship involving surface chemistry and textural properties. A critical factor is the surface acidity, which significantly increases upon tin doping. The substitution of Mg^{2+} (0.72 Å) with the smaller Sn^{4+} (0.69 Å) creates structural defects and enhances Lewis acid sites (LAS), which are essential for the initial adsorption of the nitroaromatic substrate onto the catalyst surface. Simultaneously, the presence of surface hydroxyl groups ($-\text{OH}$) acting as Brønsted acid sites (BAS) facilitates the final reaction step, the protonation of the p-nitrophenolate (PNP^-) intermediate into the target PAP product. The MS4F catalyst (0.10 mol Sn) achieved the highest total acidity (0.557 units), directly correlating with its maximum PNP conversion of 98.55% (**Figure 11**) and PAP yield of 72.46% (**Figure 12**).

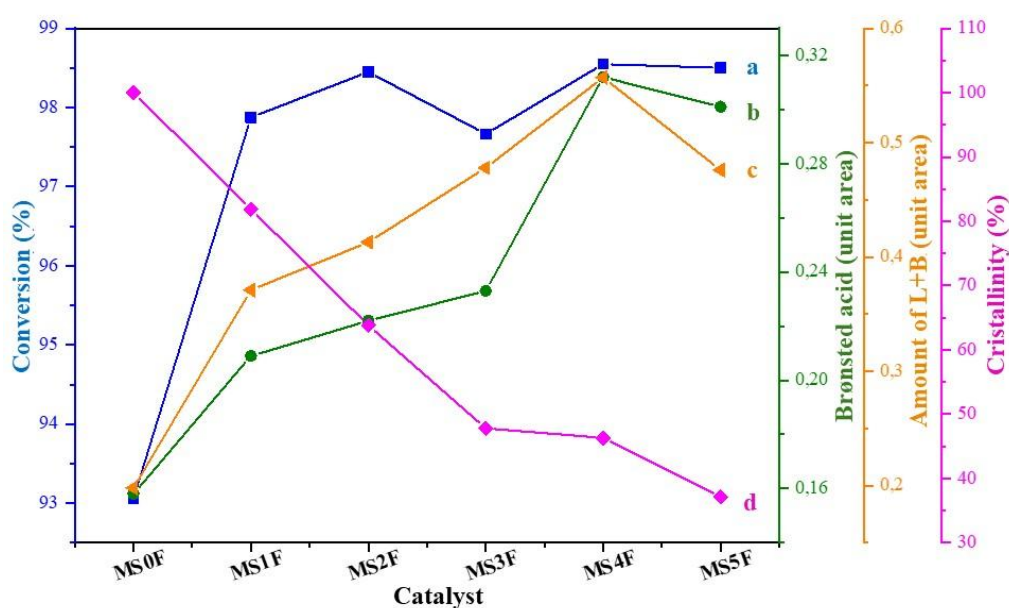


Figure 11 Correlation between p-nitrophenol (PNP) conversion (a) with Brønsted acid (b), Lewis and Brønsted acid number (c), and crystallinity (d).

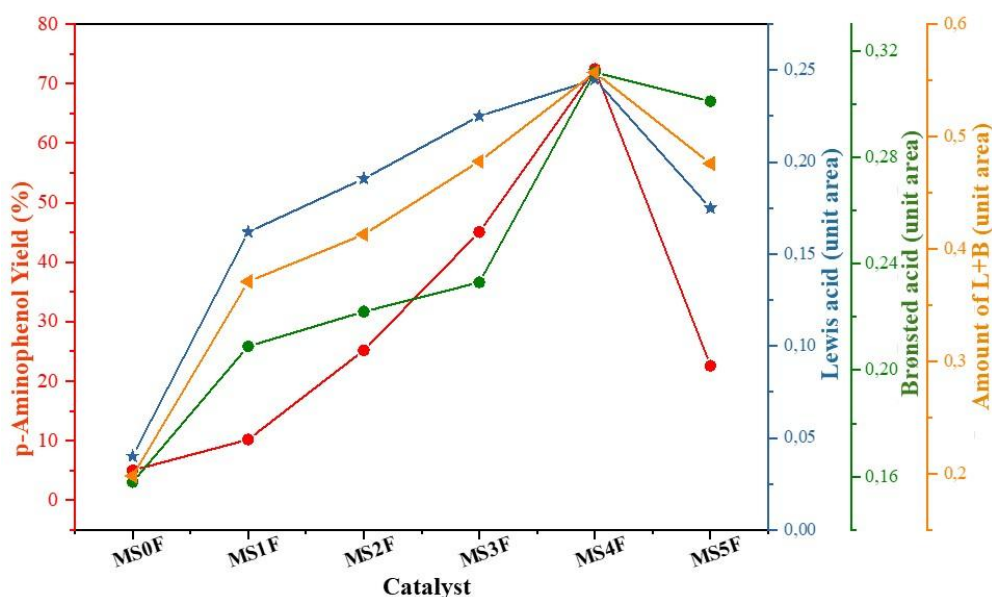


Figure 12 Relationship between PAP yield and catalyst acidity. Increased acidity enhances protonation steps, resulting in higher PAP formation.

Crystallinity and structural disorder also significantly influence catalytic reactivity (**Figure 11**). As Sn doping levels increase, the XRD peak intensities decrease, indicating a reduction in crystallinity and an increase in structural defects. While undoped MgF_2 (MS0F) is highly crystalline and regular, the semi-

crystalline nature of MS4F introduces more exposed active sites and lattice distortions that accelerate electron transfer kinetics. This structural “disorder” is strategically beneficial for higher conversion rates compared to the overly ordered structure of undoped magnesium fluoride.

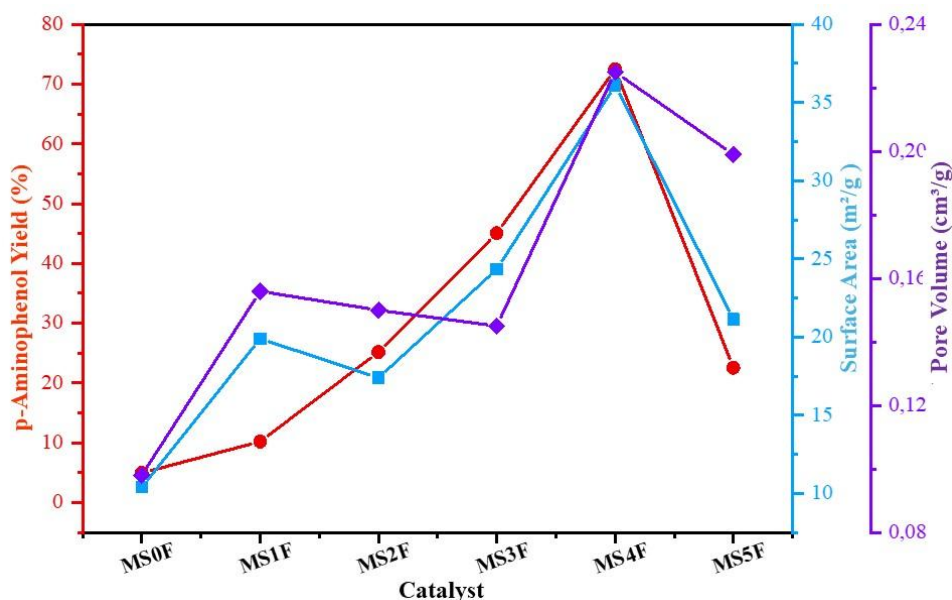


Figure 13 Correlation of PAP yield with surface area and pore volume. Improved textural properties enhance catalytic performance, with an optimum at intermediate Sn doping.

The textural characteristics, specifically surface area and pore volume (**Figure 13**), play a vital role in reactant accessibility to these active sites. Sn doping was

found to triple the specific surface area, increasing from 10.391 m²/g in the undoped MS0F to 36.096 m²/g in MS4F. This dramatic increase provides a higher density

of active sites for electron transfer between the BH_4^- donor and the PNP acceptor. Furthermore, the increase in pore volume, peaking at $0.225 \text{ cm}^3/\text{g}$ for MS4F, facilitates faster reactant diffusion and more effective contact within the mesoporous framework.

Catalytic selectivity is strongly influenced by the average pore diameter. Catalysts with larger pore sizes, such as MS0F (12.408 nm), demonstrate lower selectivity, resulting in a high yield of side products (53.75%). In contrast, the MS4F catalyst features a more optimal and narrower pore distribution (11.485 nm), which effectively guides the reaction toward the target PAP product and minimizes side products to only 16.58%. Higher concentrations of Lewis and Brønsted sites further stabilize intermediates, preventing the formation of undesired by-products such as nitroso or hydroxylamine compounds.

Finally, the study highlights the detrimental effects of overdoping observed in the MS5F sample (0.150 mol Sn). Excessive tin levels lead to particle agglomeration and a subsequent reduction in specific surface area and available acid sites. This structural breakdown causes a sharp decline in PAP yield—dropping from 72.46% in MS4F to only 22.56% in MS5F—as the reactant molecules can no longer efficiently access the blocked active sites. Thus, precise control of the Sn dopant level is the single most important factor in optimizing the structure–activity synergy of fluoride-based catalysts.

Conclusions

In this study, we successfully synthesized a Magnesium Tin Fluoride (MSF) catalyst via a sol-gel method, exploring the impact of varying tin (Sn) doping levels on its physicochemical properties and catalytic performance in the reduction of p-nitrophenol (PNP) to p-aminophenol (PAP). The XRD results confirmed the tetragonal structure of MgF_2 , with characteristic peaks matching those in the JCPDS database (PDF No. 70-2269), indicating successful synthesis. The optimal Sn doping level of 0.10 mol (MS4F) significantly improved the catalytic performance, achieving a PNP conversion of 98.55% and a PAP yield of 72.46%. These findings demonstrate the critical role of Sn metal doping in optimizing catalytic activity and highlight the delicate balance required in catalyst design: Excessive doping leads to agglomeration and decreased catalytic

effectiveness. The enhanced catalytic activity of the MSF catalyst illustrates the importance of tailoring the structural characteristics of fluoride-based materials to facilitate better electron transfer mechanisms during the reduction of nitro compounds. Our study supports a growing body of literature advocating the strategic incorporation of metals to enhance catalyst performance in environmentally friendly chemical processes.

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Declaration of Generative AI in Scientific Writing

During the preparation of this manuscript, the authors used Paperpal (by Editage) to refine the language, grammar, and academic tone of the text. This AI-assisted technology was employed solely to enhance readability and ensure the manuscript adheres to standard English academic writing conventions, particularly in addressing previous concerns regarding linguistic clarity. After using this tool, the authors reviewed and edited the generated suggestions as necessary and take full responsibility for the integrity and accuracy of the scientific content presented in the publication.

CRedit Author Statement

Amirul Hilmi: Conceptualization, Methodology, Investigation, Data curation, Formal analysis, Writing – original draft. **Riska Amelia Lawarti:** Conceptualization, Methodology, Investigation, Data curation, Formal analysis, Writing – original draft. **Mintang Mulyanto:** Conceptualization, Methodology, Investigation, Data curation, Formal analysis, Writing – original draft. **Harsasi Setyawati:** Formal analysis, Validation, Writing – review & editing. **Ika Fitri Ulfindrayani:** Formal analysis, Validation. **Doty Dewi Risanti:** Formal analysis, Resources (Characterization

support). **Affiah Rosyidah**: Formal analysis, Validation. **Irina Kris Murwani**: Conceptualization, Resources, Supervision, Funding acquisition, Project administration, Writing – review & editing.

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