

Preparation of Solid Superacid SO_4^{2-}/ZrO_2 and SO_4^{2-}/ZrO_2 -M_xO_y (M=Ce, Co, Mn, and Zn) and Its Application in Toluene Nitration

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ABSTRACT: The nitration reaction of aromatic compounds is one of the extensively studied chemical reactions that result in the manufacturing of various industrial products applied in pharmaceuticals, dyes, perfumes, and explosives. A series of modified sulfated zirconia (SZ) catalysts $SO_4^{2-}/ZrO_2-M_xO_y$ (M=Ce, Co, Mn, Zn, and M/SZ) doped with different metal elements by a coprecipitation method were investigated in the toluene nitration reaction. Various characterization techniques (X-ray diffraction, Brunauer–Emmett–Teller, thermogravimetric analysis, X-ray photoelectron spectroscopy, and temperature-programmed desorption of ammonia) indicated that doping metal elements in SZ led to excellent catalytic properties, increasing the specific surface area of the catalyst and facilitating the formation of a stable tetragonal zirconia phase. Doping zinc and cobalt in SZ enhanced the acidity of the catalyst and formed stronger acidic sites, promoting the generation of nitronium ions and providing more active sites for the toluene nitration reaction. Additionally, it reduced the loss of sulfate ions in the catalytic system that helped in improving the stability of the catalyst. Under the same conditions, the catalytic activity of toluene nitration reaction demonstrated the following order: Zn/SZ > Ce/SZ > Co/SZ > Mn/SZ > SZ, with the zinc-doped SZ catalyst exhibiting the best catalytic performance, achieving a toluene conversion rate of 78.58% and a para/ortho nitrotoluene ratio of 0.67.

1. INTRODUCTION

The nitration reaction of aromatic compounds as one of the extensively studied chemical reactions embraces a significant position in organic chemistry for synthesizing various industrial products and finds wide applications in pharmaceuticals,¹ dyes,² perfumes,³ and explosives.⁴

Methyl nitrobenzene, as an exuberant material, is a substantial intermediate in the military chemical industry and can be used for the synthesis of toluene amine and nitrobenzaldehyde.⁵ Its derivative, dinitrotoluene (DNT), is a pivotal intermediate for the preparation of trinitrotoluene explosives and is also a major raw material for toluene diisocyanate. Among them, 3,4-dinitrotoluene is mainly used to produce vitamin B_2 and herbicides, while 2,4-dinitrotoluene and 2,6-dinitrotoluene witness spacious industrial applications. Toluene nitration is an accustomed electrophilic substitution reaction. Hughes et al.⁶ conducted in-depth research on the

nitration process and insinuated that the dissociation of nitric acid during the nitration of aromatic hydrocarbons promotes the formation of NO^{2+} ions, which are the active intermediates in nitration. Henceforth, numerous studies have confirmed the existence of the nitronium ion.⁷ The presence of a catalyst facilitates the dissociation of nitric acid, shifting the equilibrium toward the formation of NO^{2+8} that reacts with the benzene ring to produce nitrotoluene. The basic mechanism is shown in the following equation

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$$HNO_3 + H^+ \rightleftharpoons H_2NO_3^+ \rightleftharpoons NO_2^+ + H_2O \tag{1}$$

$$ArH + NO_2^+ \rightleftharpoons Ar^+(H)NO_2 \rightleftharpoons ArNO_2 + H^+$$
(2)

The industrial production of nitrotoluene still relies on the technology of mixed nitration with nitric acid and sulfuric acid,⁹ giving the major products as ortho, meta, and para isomers along with the small amount of DNT, where paranitrotoluene usually occupies a steep requisition in the market.¹⁰ However, the mixed acid technology has problems such as poor selectivity, equipment corrosion, overnitration, and environmental unfriendliness.¹¹ Since then, solid acid catalysts owing to their high selectivity,^{12–15} recyclability,^{16–18} and noncorrosiveness¹⁹ have been recently demonstrated as the potential alternatives for sulfuric acid in the nitration reaction, giving the efficient, economical, and environmentally friendly nitration. Various solid acid catalysts including zeolites, $^{20-22}$ modified clays, $^{23-25}$ resins, $^{26-28}$ composite oxides, $^{29-31}$ heteropolyacids, $^{32-34}$ and $SO_4^{\ 2^-}/M_xO_y^{\ 35-37}$ have been widely adopted in the nitration of toluene. Where, the SO_4^{2-}/M_xO_y genre of solid superacid catalysts exhibits high conversion rates and selectivity for the liquid-phase nitration of toluene. The SO_4^{2-}/M_xO_y type of solid superacid catalysts possesses both appropriate Lewis and Brønsted acid sites, which originate from the surface sulfates of the catalyst. In modified sulfated zirconia (SZ) catalysts, the addition of other metals can alter their crystal structure, acid strength, and stability to enhance their activity. However, the influence of different metals on the modification of SZ and their role in the nitration of toluene are still not clear.

In this study, mixed oxide materials have been utilized in preparing a SZ solid acid catalyst SO_4^{2-}/ZrO_2 for toluene nitration. A series of modified SZ catalysts SO_4^{2-}/ZrO_2 - M_xO_y (M=Ce, Co, Mn, Zn, and M/SZ) doped with different metal elements by coprecipitation and impregnation methods was prepared and characterized by X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET) surface area analysis, thermogravimetric analysis (TGA), Fourier transform infrared (FT-IR), X-ray photoelectron spectroscopy (XPS), and temperature-programmed desorption of ammonia (NH₃-TPD) techniques. The experimental results revealed that under the same conditions, the zinc-doped SZ catalyst exhibited the best catalytic performance, achieving a 78.58% toluene conversion rate and a *para/ortho* nitrotoluene ratio of 0.67.

2. EXPERIMENTAL SECTION

2.1. Materials. Toluene (98%, Sinopharm Chemical Reagent Co., Ltd.), nitric acid (68%, Sinopharm Chemical Reagent Co., Ltd.), ammonia (ADAMAS-BETA), sulfuric acid (98%, Sinopharm Chemical Reagent Co., Ltd.), zirconium(III) oxide octahydrate (ZrOCl₂·8H₂O), cerium(III) nitrate hexahydrate [Ce(NO₃)₃·6H₂O, 98%, Sinopharm Chemical Reagent Co., Ltd.], cobalt(II) nitrate hexahydrate [Co(NO₃)₂·6H₂O, 98%, Sinopharm Chemical Reagent Co., Ltd.], manganese(II) nitrate tetrahydrate [Mn(NO₃)₂·4H₂O, 98%, ADAMAS-BETA], and zinc nitrate hexahydrate [Zn(NO₃)₂·6H₂O, 98%, Sinopharm Chemical Reagent Co., Ltd.] were used in this study.

2.2. Synthesis of the Catalysts. The SZ-type catalyst was prepared using a direct precipitation method by directly adding it to the solution for precipitation. The M/SZ (M = Ce, Co, Mn, and Zn) catalysts were prepared using a coprecipitation

method, where the metal nitrate was mixed in a certain proportion first, and the precipitant was added to the mixed solution for precipitation. 32.225 g of zirconium oxychloride or a mixture of different metal ion nitrates and zirconium oxychloride (with a molar ratio of metal ion to zirconium ion of 1:10) was dissolved in 250 mL of deionized water to prepare a 0.4 mol/L zirconium oxychloride solution. A concentrated ammonia solution was added to the vigorously stirred zirconium oxychloride solution drop by drop until the pH of the solution reached around 10, followed by continuous stirring for another 30 min. After aging at room temperature for 12 h, the precipitate was repeatedly washed with deionized water until the filtrate became neutral and free of Cl⁻¹ (confirmed by the absence of white precipitate upon addition of AgNO₃ solution), to avoid the influence of ammonium and chloride ions on the nitration reaction. The obtained precipitate was dried at 110 °C for 24 h and then pulverized into a powder with a particle size of 100 mesh. The powder was soaked in a 0.5 mol/L sulfuric acid solution for 6 h and then calcined at 600 °C for 3 h in a muffle furnace to obtain the SZ catalyst and M/SZ catalysts. Prior to use, the catalyst powders were molded and sieved, with samples in the size range of 20-40 mesh used for catalytic evaluation.

2.3. Catalyst Characterization. The catalysts were subjected to powder XRD analysis using an 18KW/D/ max2550VB/PC X-ray diffractometer equipped with a Cu target and an automated variable slit system.

The specific surface area and pore volume of the catalysts were determined using a surface area and porosity analyzer (ASAP 2020-M). Prior to analysis, the samples were subjected to a 2 h degassing treatment at 150 °C. The analysis was conducted using nitrogen gas as the adsorbate at liquid nitrogen temperature (77 K). The BET and Barrett–Joyner–Halenda methods were used to estimate the specific surface area and pore volume of the samples based on the N₂ adsorption isotherm.

The decomposition of sulfate species in the catalyst was characterized using TGA (TGA-8000). The chemical bonding forms in the catalyst were determined using an INVENIO S + Hyperion 3000 infrared spectrometer at room temperature. FT-IR spectra were recorded in the range of 400–4000 cm⁻¹ with a resolution of 0.4 cm⁻¹. XPS of the samples was performed using the Thermo Scientific K-Alpha spectrometer. The peak of C 1s was calibrated with a binding energy of 284.6 eV for all measurements.

The acidity of the catalyst was determined using the AutoChem1 II 2920 NH₃-TPD technique. The sample was placed in a reaction tube and subjected to a drying pretreatment by ramping up the temperature from room temperature to 500 °C at a rate of 10 °C/min under a flow of helium (He) for 1 h. The sample was then cooled to 50 °C and exposed to a saturated 10% NH₃/He mixture for 1 h. Switch to a He flow for 1 h to remove weakly adsorbed NH₃ on the surface. Finally, the temperature was ramped up to 700 °C at a rate of 10 °C/min under a He atmosphere to desorb the adsorbed species, and the released gases were detected.

2.4. Catalytic Test. Under atmospheric pressure, SZ and M/SZ (M=Ce, Co, Mn, and Zn) catalysts were used for liquid-phase nitration of toluene. According to a certain ratio of nitric acid to toluene, a certain amount of toluene was placed in a three-necked flask that was interconnected with a thermometer and a condenser reflux system, while nitric acid was placed in a constant-pressure dropping funnel. The setup

was connected to a thermometer and a condenser reflux system. The mixture was stirred and heated until the toluene reached a certain temperature. Then, a certain mass of the catalyst was added to the three-necked flask, followed by the slow dropwise addition of nitric acid at a controlled rate. After the completion of the addition, the reaction temperature was maintained constant while stirring for a certain period of time.

After the reaction, the mixture was filtered using a Büchner funnel, and the filtrate was transferred to a separating funnel for layer separation, where the orange organic phase was collected and subsequently washed with 5% NaHCO₃ solution and deionized water to achieve a pH close to neutral. The product was then dried by filtration using anhydrous calcium chloride and weighed, and a sample was taken for analysis using gas chromatography.

3. RESULTS AND DISCUSSION

3.1. Characterization Results. Figure 1 shows the XRD patterns of SZ and M/SZ (M=Ce, Co, Mn, and Zn) catalyst



Figure 1. XRD patterns of SZ and M/SZ catalysts.

samples. All samples doped with metal ions exhibited characteristic diffraction peaks corresponding to zirconium oxide. The characteristic peaks at 30.1, 34.9, 50.2, 59.7, and 62.6° correspond to crystal planes of (111), (200), (220), (311), and (222), respectively, which are consistent with the tetragonal phase of zirconium sulfate oxide. No diffraction peaks corresponding to the doped metal oxides were observed, indicating that the doped metal was uniformly distributed in the lattice or on the sample surfaces. The lattice spacing and particle size of the tetragonal phase of zirconium oxide are smaller compared to the monoclinic phase. Additionally, the tetragonal phase of zirconium oxide tends to be more stable with decreasing particle size due to the influence of surface energy.³⁸ In the SZ catalyst, both tetragonal and monoclinic phases are present, while in the M/SZ catalyst, no obvious monoclinic phase is observed. This suggests that the presence of transition-metal oxides slows down the transformation of zirconium oxide from a metastable phase to the monoclinic phase,³⁸ making the tetragonal phase of zirconium oxide more stable.

Figure 2a-e shows the scanning electron microscopy (SEM) images of SZ, Co/SZ, Ce/SZ, Zn/SZ, and Mn/SZ catalysts,

respectively. From Figure 2a, it can be seen that there are many irregular particles on the surface of SZ without introducing other metals. From Figure 2b,e, it can be observed that the introduction of CoO and MnO₂ leads to the decrease in size and an increase in the density of irregular particles on the catalyst surface. Figure 2d shows that the introduction of ZnO leads to an increase in the particle size on the catalyst surface, which may be due to the delayed crystallization process caused by the introduction of zinc oxide. Figure 2c demonstrates that the introduction of CeO₂ reduces the number of irregular particles on the catalyst surface, which may be attributed to CeO₂ hindering the bonding of each ZrO₂ unit. Overall, the introduction of metal oxides does not alter the original morphology of the catalyst. ZrO₂ particles are well-dispersed without aggregation. Figure 2f shows the energy-dispersive spectroscopy (EDS) images of Ce/SZ, Co/SZ, Zn/SZ, and Mn/SZ catalysts, demonstrating that the different metal oxide particles are evenly distributed on the surface of ZrO₂.

The N₂ adsorption-desorption isotherms and pore size distribution of SZ and M/SZ (M=Ce, Co, Mn, and Zn) catalysts are shown in Figure 3, elaborating that all samples exhibit typical type-IV N₂ adsorption isotherms;³⁹ all catalysts exhibited an H_2 hysteresis loop. The presence of a H_2 hysteresis loop and a clear hysteresis loop in the adsorption curve at a P/P_0 greater than 3.6 nm is consistent with the reported presence of a mesoporous structure and larger pore size in the catalysts.⁴⁰ The pore size distribution of all catalyst samples is uniform, concentrated at 5-10 nm. The BET specific surface area, average pore size, and pore volume of the catalysts are shown in Table 1. It can be observed that the catalysts doped with metal ions have a smaller BET specific surface area compared to the SO₄²⁻/ZrO₂ catalyst. However, their average pore size and pore volume are larger than the SO_4^{2-}/ZrO_2 catalyst, illustrating the changes in internal pore shape and structure or the aggregation of sulfate species on the catalyst surface.⁴¹

TGA was conducted on the catalysts before and after the reaction to assess their thermal stability and sulfate group content, as shown in Figure 4. It can be seen in Figure 4a that all catalysts exhibited two weight-loss stages. The first weight loss occurred at around 80 °C, which can be attributed to the desorption of free water in the large voids on the catalyst surface or particle layers. The second weight loss occurred between 600 and 800 °C caused by the decomposition of sulfate groups on the catalyst. Figure 4b reveals that the catalysts after the reaction exhibited continuous weight loss in the range of 80-600 °C, indicating the decomposition of adsorbed free water and high-boiling organic substances on the catalyst surface. This suggests that the catalyst can be regenerated through high-temperature calcination. According to the mass change in the range of 600-800 °C, it can be concluded that the used Zn/SZ experienced the highest mass loss, indicating the highest sulfate loading and better stability, as it is less prone to loss during the reaction.

Figure 5a shows the infrared spectra of SZ and M/SZ catalysts. When the catalysts are exposed to air, they inevitably adsorb water molecules. The stretching vibration of hydroxyl groups in water molecules causes a broad peak at 3400 cm⁻¹, while the deformation vibration of hydroxyl groups results in a peak at 1625 cm⁻¹.⁴² The peaks at 500–800 cm⁻¹ correspond to the stretching vibration frequencies of metal–oxygen (M–O) bonds in metal oxides. The broad peaks at 1074, 1136, and 1244 cm⁻¹ are attributed to the stretching vibration of S–O



Figure 2. SEM images of catalysts: (a) SZ, (b) Co/SZ, (c) Ce/SZ, (d) Zn/SZ, and (e) Mn/SZ; EDS images of catalysts: (f) Co/SZ, Ce/SZ, Mn/SZ, and Zn/SZ.



Figure 3. (a) N_2 adsorption-desorption isotherms and (b) pore width distributions of catalysts.

Table	1.	Specific	Surface	Area	and	Pore	Structure	of
Cataly	sts							

n²/g)	(nm)	(cm^3/g)
6.39	4.37	0.140
8.70	3.82	0.059
7.83	9.28	0.156
0.08	6.00	0.115
6.31	6.04	0.153
6.39 8.70 7.83 0.08 6.31	4.37 3.82 9.28 6.00 6.04	0.140 0.059 0.156 0.115 0.153

bonds, the symmetric stretching vibration of O–S–O bonds, and the asymmetric stretching vibration of O=S=O bonds in sulfate groups, indicating the presence of sulfate species in the catalyst. The chelating bidentate complex formed between SO_4^{2-} and Zr^{4+} ions can alter the electronic environment around the metal ions, facilitating the formation of strong Lewis acid sites on the surface of sulfate-modified metal oxides,³⁶ thereby enhancing the catalytic activity.

Figure 5b shows the comparison of NH_3 -TPD curves for five catalysts. The NH_3 -TPD curve is divided into three regions based on temperature: weak region (<200 °C), moderate region (200-450 °C), and strong region (>450 °C).⁴³ From the figure, it can be observed that all five catalysts simultaneously show the existence of weak, medium, and strong acid sites, indicating a wide distribution of acid sites and a typical steamed bread peak.⁴⁴ Based on the desorption peak area of NH_3 , it can be seen that doping with zinc and cobalt increases the weak and strong acid sites compared to the SZ catalyst. Doping with cerium increases the medium acid sites while decreasing the strong acid sites. Doping with manganese leads to a reduction in both weak and strong acid sites. These results indicate that doping metals in SZ has an impact on the

100

95

90

85

80

Weight(%)

80



200

400





Figure 5. FT-IR and NH₃-TPD of SZ and M/SZ catalysts.

acid sites, and the surface acidity of the prepared catalysts follows the order of Zn/SZ > Co/SZ > SZ > Ce/SZ > Mn/SZ.

XPS analysis was conducted to investigate the chemical states of elements in the catalyst, and the spectra are shown in Figure 6. In the Ce 3d region, the spectrum can be divided into eight energy bands.⁴⁵ The sub-bands labeled as v' and u' belong to Ce³⁺, while the sub-bands labeled as v, v", v"", u, u", u^{*m*} belong to Ce⁴⁺. According to previous reports, the existence of Ce³⁺ can cause an imbalance in surface charge, increase oxygen vacancies and unsaturated chemical bonds, and generate more surface adsorbed oxygen,^{46,47} thereby promoting catalytic performance. In the Co 2p spectrum, at 781.25, 796.24, 784.78, and 799.77 eV, the peaks can be deconvoluted into Co^{3+} and Co^{2+} spin doublets. A higher Co^{3+}/Co^{2+} ratio is more favorable for the adsorption and dissociation of carbon and hydrogen bonds.⁴⁸ In the Mn 2p region, the signals at binding energies of 641.1 and 653.4 eV are attributed to Mn⁴⁺ and Mn³⁺, respectively. The former can be resolved into two peak components at 640.5 eV (Mn^{3+}) and 642.1 eV (Mn^{4+}) ,

while the later can be resolved into two peak components at 651.7 eV (Mn^{3+}) and 653.3 eV (Mn^{4+}). The Mn^{3+} sites may originate from weak Mn-O bonds. Concerning the Zn 2p region, signals at 1021.9 and 1045.1 eV were detected for Zn^{2+} ions.

600

Temperature(°C)

800

1000

1200

Figure 6b displays the spectra of Zr 3d over the prepared catalysts, and the 3d orbitals of each spectrum split into two characteristic peaks with a binding energy difference of 2.4 eV, which can be attributed to Zr^{4+} . It can be observed that in the catalyst doped with metal, the energy bands of Zr $3d_{3/2}$ and Zr $3d_{5/2}$ exhibit a slight shift toward lower energy, indicating that the doping metal helps stabilize the tetragonal phase of zirconia and suppress the formation of monoclinic zirconia.⁴⁹ The S 2p spectra exhibited a single peak at 168.8 eV in Figure 6c, which was consistent with S⁶⁺ species and belonged to the sulfate species.⁵⁰ The O 1 s spectra of SZ and M/SZ catalysts are shown in Figure 6d, fitted by two peaks. The lower binding energy at 529.9 eV corresponds to lattice oxygen (referred to as O_{latt}), while the higher binding energy at 531.6 eV

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Figure 6. XPS spectra of (a) M (M=Ce, Co, Mn, and Zn), (b) Zr 3d, (c) S 2p, and (d) O 1s spectra of SZ and M/SZ catalysts.

corresponds to surface adsorbed oxygen (referred to as O_{ads}).⁵¹ Doping different metals can alter the relative content of O_{latt} and O_{ads} in the catalyst.⁵² The maximum O_{ads}/O_{latt} ratio for $SO_4^{2^2}/ZrO_2$ –ZnO is 0.72, indicating that the catalyst has the highest number of oxygen vacancies. In conjunction with experimental results, the quantity of surface adsorbed oxygen plays a promoting role in the nitration of toluene.

3.2. Catalyst Activity. *3.2.1. Effect of Various Catalysts.* The outcomes of the nitration reaction of toluene using different catalysts are shown in Table 2. Zirconium oxide catalysts doped with various metal elements have improved the conversion rate of toluene. Among them, the zinc-doped zirconium oxide catalyst exhibits excellent performance in terms of the conversion rate of toluene. Based on the characterization data, the main reason is the introduction of zinc oxide, which increases the stability of the tetragonal phase of SZ, increases the pore diameter and pore volume, and facilitates the nitration reaction of toluene. It also enhances the stability of sulfate ions in the catalyst, reducing the loss of sulfate ions during the reaction process and promoting continuous reaction. The doping of metal elements enhances the acidity of the catalyst. However, due to the reaction taking

Table 2. Effect of Various Catalysts on Toluene Nitration^a

catalyst	se nit	electivity rotoluene	of /%	p/o	conversion of toluene/%
	ortho	meta	para		
SZ	58.27	4.06	33.41	0.57	71.54
Ce/SZ	54.73	5.09	35.37	0.64	78.53
Co/SZ	54.77	5.46	36.53	0.66	77.32
Mn/SZ	54.42	4.89	35.15	0.64	72.63
Zn/SZ	55.04	5.31	36.89	0.67	78.58
^a Condition	ns: reacta	nt mola	ratio (H	INO ₂ /to	oluene) = 2.5:1; catalyst

dosage = 1 g; reaction time = 2 h; reaction temperature = $60 \degree C$.

place in an ambient air environment, the strong acidity of the catalyst can easily lead to the oxidation of toluene, resulting in the formation of byproducts such as benzaldehyde. Therefore, when using metal-doped zirconium oxide catalysts for the nitration of toluene, the content of byproducts increases.

3.2.2. Effect of Reaction Temperature. The effect of reaction temperature on nitration of toluene was studied by performing the reaction at five different temperatures, using SZ as the catalyst and keeping all other parameters constant. It can

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be observed from Table 3 that the conversion rate of toluene increases with the increase of reaction temperature, reaching its

Table 3. Effect of Reaction Temperature on Toluene Nitration^a

reaction temperature/°C	se niti	electivity rotoluene	of e/%	p/o	conversion of toluene/%
	ortho	meta	para		
30	60.69	4.56	34.75	0.57	31.75
40	58.87	4.91	36.22	0.62	44.77
50	56.09	5.13	35.45	0.63	55.31
60	58.27	4.06	33.41	0.57	71.54
70	52.59	8.59	31.27	0.59	55.87
^a Conditions, react	ant mol	nr ratio	(HNO)	(toluona)	-25.1, catalue

Conditions: reactant molar ratio (HNO₃/toluene) = 2.5:1; catalyst dosage = 1 g; reaction times = 2 h.

maximum value (71.54%) at 60 °C. With further increase in reaction temperature, the conversion rate of toluene decreases. As the temperature increases, the ratio of p/o nitrotoluene increases, indicating that increasing the temperature helps in the formation of nitrotoluene.

3.2.3. Effect of Reaction Time. The effect of reaction time on nitration toluene was studied in the range of 0.5 to 3 h, using SZ as the catalyst and keeping all other parameters constant. In Table 4, as the reaction time increases, the

Table 4. Effect of Reaction Time on Toluene Nitration^a

reaction time/min	eaction selectivity of me/min nitrotoluene/%				conversion of toluene/%
	ortho	meta	para		
30	62.25	4.08	33.67	0.54	50.87
45	59.29	4.04	33.64	0.57	44.17
60	59.13	4.23	33.53	0.57	51.41
90	57.97	4.21	33.39	0.58	49.45
120	58.27	4.06	33.41	0.57	71.54
180	48.76	5.49	20.54	0.42	49.45
^a Conditions: re	actant m	olar rati	o (HNO	₃ /toluene	e) = 2.5:1; catalysts

dosage = 1 g; reaction temperature = $60 \degree C$.

conversion rate of toluene increases. When the reaction time is 2 h, the conversion rate reaches its highest value of 71.54%. However, with further increase in reaction time, the conversion rate of toluene decreases. There is not much change in the proportion of nitrotoluene and *ortho*-nitrotoluene, indicating that the reaction time has little effect on the formation of nitrotoluene isomers.

3.2.4. Effect of the Nitric-Acid-to-Toluene Ratio. The outcomes of the toluene nitration at different concentrations of nitric acid are shown in Table 5, using SZ as the catalyst and keeping all other parameters constant. It can be observed that with an increase in the amount of nitric acid, the conversion rate of toluene increases. When the molar ratio of nitric acid to toluene is 2.5, the yield of nitrotoluene reaches 71.54%. This is because when the amount of nitric acid is low, a significant amount of water is generated during toluene nitration, diluting the concentration of the nitric acid solution, hindering the generation of nitronium ions, and resulting in a lower conversion rate of toluene. Therefore, the optimal reactant ratio is determined to be n(nitric acid)/n(toluene) = 2.5.

3.2.5. Effect of Catalyst Dosage. The outcomes of the nitration of toluene using the zirconium oxide catalyst with

Table 5. Effect of Reactant Molar Ratio on Toluene Nitration $\!\!\!\!\!\!^a$

<i>n</i> (nitric acid)/ <i>n</i> (toluene)	yield of	f nitrotol	uene/%	p/o	conversion of toluene/%				
	ortho	meta	para						
1.0	50.80	4.92	31.73	0.62	31.45				
1.5	53.96	5.11	33.89	0.63	42.79				
2.0	58.27	4.06	33.41	0.57	64.02				
2.5	55.32	5.42	35.00	0.63	71.54				
3.0	55.43	5.34	35.62	0.64	67.01				
^a Conditions: catalyst dosage = 1 g; reaction temperature = 60 °C; reaction time = 2 h									

sulfuric acid at different catalyst dosages are shown in Table 6, using SZ as the catalyst and keeping all other parameters

able 0. Effect of Catalyst Dosage of Toluelle Millation	Гable	6.	Effect	of	Catalyst	Dosage	on	Toluene	Nitration
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0	losage of catalyst/g	yield of	f nitrotol	uene/%	p/o	conversion of toluene/%
		ortho	meta	para		
	0	62.55	5.11	32.33	0.52	60.93
	0.5	59.77	5.38	34.85	0.58	62.31
	1.0	55.32	5.42	35.00	0.63	71.54
	1.5	55.45	5.28	34.91	0.63	70.48
	2.0	61.38	4.87	29.86	0.48	68.96
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^{*a*}Conditions: reactant molar ratio (HNO₃/toluene) = 2.5:1; reaction time = 2 h; reaction temperature = 60 °C.

constant. The results demonstrate that the conversion rate of toluene exhibits a noteworthy increment with an increase in the dosage of the SZ catalyst when the dosage is less than 1 g.

This is because when the catalyst dosage is low, there are fewer active sites, resulting in fewer active intermediates, namely, nitronium ions. As a result, the reaction rate is slow. Increasing the catalyst dosage at this point enhances the nitration reaction rate and promotes the progress of the reaction. However, when the catalyst dosage exceeds 1 g, as its dosage continues to increase, the yield of nitrotoluene decreases. This suggests that the catalyst in the reaction has reached a state of saturation at this point. From the perspective of maximizing catalyst efficiency, the optimal catalyst dosage is chosen to be 1 g. At this dosage, the conversion of toluene is 71.54%.

4. CONCLUSIONS

A series of SZ and metal-loaded M/SZ (M=Ce, Co, Mn, and Zn) solid superacid catalysts were prepared using impregnation and coprecipitation methods. Under solvent-free conditions, the catalytic activity was ranked as follows: Zn/SZ > Ce/SZ > Co/SZ > Mn/SZ > SZ, indicating that the doping of metals in SZ promotes toluene nitration. Characterization of the catalysts revealed that the presence of doped metals transformed the crystalline form of zirconia from the monoclinic phase to a more stable tetragonal phase. Additionally, it increased the surface area of the catalyst and altered the pore structure, providing favorable conditions for the conversion of toluene to nitrotoluene. Furthermore, the SZ catalyst doped with zinc exhibited higher oxygen adsorption on its surface compared to other catalysts. The formation of chelating bidentate complexes between SO₄^{2–} and Zr⁴⁺ was more stable,

resulting in the presence of more weak and strong acid sites. Moreover, SO_4^{2-} was less prone to loss during the reaction, leading to excellent performance in toluene nitration.

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Notes

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