Chloroaluminate Ionic Liquid Immobilized on Magnetic Nanoparticles as a Heterogeneous Lewis Acidic Catalyst for the Friedel–Crafts Sulfonylation of Aromatic Compounds

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Abstract: Chloroaluminate ionic liquid bound on magnetic nanoparticles (Fe3O4@Si[PrMIM]Cl-AlCl3) was prepared and used as a heterogenous Lewis acidic catalyst for the Friedel–Crafts sulfonylation of aromatic compounds with sulfonyl chlorides or p-toluenesulfonic anhydride. The catalyst’s stability, efficiency, easy recovery, and high recyclability without considerable loss of catalytic capability after four recycles were evidence of its advantages. Furthermore, the stoichiometry, wide substrate scope, short reaction time, high yield of sulfones, and solvent-free reaction condition also made this procedure practical, ecofriendly, and economical.

Keywords: sulfonylation; magnetic nanoparticles; sulfones; ionic liquids; sulfonic anhydride

1. Introduction

Sulfones, one of the most common organosulfur compounds, have tremendous applications in chemical processes [1,2], medicinal chemistry, and drug syntheses owing to their various biological activities; for instance, anti-inflammatory [3,4], anti-HIV [5], antimalarial [6,7], anticancer [8], and antimicrobial [9,10], and as a cysteine protease inhibitor [11].

Widespread synthetic routes of sulfones via the oxidation of the corresponding sulfides or sulfoxides [12–14], the sulfonylation of chloropyridine derivatives by sulfinate salts [15], the arylation of sulfinate salts by diaryliodonium salts [16], the formation of a C–S bond initiated by visible light [19], the decarboxylative C–S cross-coupling of cinnamic acid with benzensulfinate salts promoted by iodine [20], and the Friedel–Crafts sulfonylation have been developed. Among numerous approaches to sulfone preparations, aryl sulfones have been synthesized, preferably via the Friedel–Crafts sulfonylation reactions between activated arenes and sulfonylating reagents in the presence of catalysts; e.g., Lewis acidic salts [21–26], Zn [27], In/dioxane [28], MoO2Cl2 [29], metal triflate [30,31], Fe(OH)3 [32], nafion-H [33], Fe(III)-exchanged montmorillonite [34], Ps-AlCl3 and SiO2-AlCl3 [35,36], Lewis acidic salt-based ionic liquids [37,38], and P2O5 supported on Al2O3 [39] or SiO2 [40].

Within the tendency of scientific and technological improvement, environmental assessment has been mainly paid attention. In recent decades, ionic liquids (ILs), as well as functionalized ionic liquids, play important roles as solvents and homogeneous catalysts in several organic synthesis processes, owing to their low vapor pressure, thermal stability, high ability to dissolve many inorganic and organic compounds [41]. Homogeneous catalysts are always dissolved easily in various organic solvents or reaction media, therefore it is difficult to recover and recycle catalysts used. Contrarily, heterogeneous catalysts could be
recovered and recycled conveniently and efficiently, although their dispersion in reaction media have not been carried out well. To overcome these problems in the dispersion, recovery, and recycling of catalysts, ionic liquids have been immobilized on solid materials such as organic polymers [42–44], inorganic supports (e.g., silica, alumina) [45–48], and magnetic nanoparticles (MNP) [49–55]. The improved catalysts have possessed the combined properties of homogeneous and heterogeneous catalysts, consisting of a larger surface area and catalyst-loading capacity, better dispersity in reaction media, and simple separation. In general, MNP are selected as excellent solid supports for ILS, owing to a convenient removal of the catalyst by using an external magnet without filtration or centrifugation [56].

Using the advantages of magnetic nanoparticles in catalysis, in this work, we developed a magnetic nanoparticle–Fe$_3$O$_4$ linked acidic ionic liquid as a green and efficient catalyst to be used for the Friedel–Crafts sulfonylation of activated arenes or polyarenes with sulfonyl chloride or sulfonic ahydride (Scheme 1). Magnetic nanoparticle–Fe$_3$O$_4$ linked acidic ionic liquids have been used for several transformations, such as three-component reactions of benzaldehyde derivatives, urea/thiourea, and acetooacetate [50]; benzaldehyde derivatives, β-naphthal, and 1,3-cyclohexadione derivatives [57]; and benzaldehyde derivatives, aniline derivatives, and 2-mercaptoethanoic acid [58].

\[
\text{R}^1, \text{R}^2 = \text{H, CH}_3, \text{OCH}_3, \text{OH, Cl} \\
\text{R}^3 = \text{C}_6\text{H}_5, \text{r}-\text{C}_6\text{H}_5, \text{p-C}_6\text{H}_4\text{CH}_3, \text{p-C}_6\text{H}_4\text{OCH}_3, \text{p-C}_6\text{H}_4\text{NH}_2, \text{p-NO}_2\text{C}_6\text{H}_4, \text{C}_2\text{H}_5, \text{i-C}_4\text{H}_9, \text{n-C}_9\text{H}_{18} \\
X = \text{Cl, p-C}_6\text{H}_4\text{SO}_3\text{O}^-
\]

*Scheme 1. The Friedel–Crafts sulfonylation catalyzed by Fe$_3$O$_4$@O$_2$Si[PrMIM]Cl-AlCl$_3$.*

### Table 1. Nature of the acidic catalysts’ influences on the Friedel–Crafts sulfonylation of toluene with benzenesulfonyl chloride.

| Entry | Acidic Catalyst                      | Ratio of 3a:3a′:3a′′ | Yield (%) |
|-------|-------------------------------------|----------------------|-----------|
| 1     | Fe$_3$O$_4$@O$_2$Si[PrMIM]HSO$_4$ (0.2 g) | 56:41:3              | 63        |
| 2     | MgFe$_3$O$_4$@O$_2$Si[PrMIM]Cl-AlCl$_3$ (0.2 g) | 63:31:6             | 57        |
| 3     | Fe$_3$O$_4$@O$_2$Si[PrMIM]Cl-AlCl$_3$ (0.1 g) | 49:44:7             | 78        |
| 4     | Fe$_3$O$_4$@O$_2$Si[PrMIM]Cl-AlCl$_3$ (0.2 g) | 55:39:6             | 85        |
| 5     | Fe$_3$O$_4$@O$_2$Si[PrMIM]Cl-AlCl$_3$ (0.3 g) | 47:46:7             | 86        |

$a$ The reaction of toluene (1.0 mmol) and benzenesulfonyl chloride (1.0 mmol) was performed under conventional heating for 4 h at 110 °C. $b$ Yields were calculated based on the GC/FID analyses.
2.1. Catalyst Characterization

Magnetic fine particles were continuously prepared by coprecipitation of iron(II) and iron(III) salts at 80 °C. The precipitated fine particles were characterized by XRD for the structural determination (Figure 1), and by FT-IR spectra (Figure 2a) and SEM for the crystallite size (Figure 3a). The XRD pattern of Fe₃O₄ showed that five diffraction peaks appeared at around 30.20°, 35.56°, 43.14°, 57.06°, and 62.59°, which corresponded to the crystallographic planes (220), (311), (400), (511), and (440) lines, respectively of the magnetite Fe₃O₄ phase [60]. In addition, the SEM micrograph of the Fe₃O₄ also displayed that cubic-shaped particles in agglomerated states reached a nanoparticle diameter of approximately 20.0 nm (Figure 3a). Subsequently, the heterogeneous catalyst, Fe₃O₄@O₂Si[PrMIM]Cl·AlCl₃, was prepared from magnetic nanoparticles, 3-methyl-1-(3-trimethoxysilylpropyl)-1H-imidazolium chloride, and aluminum chloride as described in Scheme 2, and then characterized by XRD (Figure 1), FT-IR (Figure 2c), SEM and TEM (Figure 3b,c), EDX (Figure 4), TGA (Figure 5), VSM (Figure 6), BET, and ICP-MS.

![Figure 1. XRD patterns of Fe₃O₄, Fe₃O₄@O₂Si[PrMIM]Cl·AlCl₃, and standard magnetite.](image1)

![Figure 2. FT-IR spectra of Fe₃O₄ (a), Fe₃O₄@O₂Si[PrMIM]Cl (b), and Fe₃O₄@O₂Si[PrMIM]Cl·AlCl₃ (c).](image2)
Figure 3. Nanoparticles of Fe₃O₄: SEM (a) and catalyst Fe₃O₄@O₂Si[PrMIM]Cl·AlCl₃: SEM (b); TEM (c); and particle size distribution (d).

Scheme 2. The preparation of Fe₃O₄@O₂Si[PrMIM]Cl·AlCl₃.
The abatement. From 32°C the temperature (Figure 6). The abatement. From 32°C the temperature (Figure 6). The diagram illustrated a slight weight loss of 7% below 300°C. The diagram illustrated a slight weight loss of 7% below 300°C. The VSM curve for Fe3O4 was recorded by heating the sample up to 600°C. The VSM curve for Fe3O4 was recorded by heating the sample up to 600°C. The EDX spectrum of Fe3O4@O2Si[PrMIM]Cl·AlCl3 was investigated in detail to improve the yield of sulfone. The EDX spectrum of Fe3O4@O2Si[PrMIM]Cl·AlCl3 was investigated in detail to improve the yield of sulfone. The TGA diagram for Fe3O4@O2Si[PrMIM]Cl·AlCl3 had been successful grafted on aluminum content and the BET specific surface area of the catalyst out of Fe3O4@O2Si[PrMIM]Cl·AlCl3. The TGA diagram for Fe3O4@O2Si[PrMIM]Cl·AlCl3 had been successful grafted on aluminum content and the BET specific surface area of the catalyst out of Fe3O4@O2Si[PrMIM]Cl·AlCl3. The magnetic parameters of Fe3O4@O2Si[PrMIM]Cl·AlCl3 were identified, a sharp decrease in weight observed owing to the decomposition of imidazole moieties [61]. These results did not only confirm the fact that organic parts had been successful grafted on magnetic nanoparticles, but also determined the thermal stability of our catalyst up to 300°C. The magnetic parameters of Fe3O4@O2Si[PrMIM]Cl·AlCl3 were identified, a sharp decrease in weight observed owing to the decomposition of imidazole moieties [61]. These results did not only confirm the fact that organic parts had been successful grafted on magnetic nanoparticles, but also determined the thermal stability of our catalyst up to 300°C.

Figure 4. EDX spectrum of Fe3O4@O2Si[PrMIM]Cl·AlCl3.

Figure 5. TGA diagram for Fe3O4@O2Si[PrMIM]Cl·AlCl3.

Figure 6. VSM curve for Fe3O4 (a) and Fe3O4@O2Si[PrMIM]Cl·AlCl3 (b).
In the XRD pattern of the Fe₃O₄@O₂Si[PrMIM]Cl·AlCl₃ sample, these characteristic peaks were still present, but their intensities were dramatically decreased. The presence of ionic liquid in this sample was able to affect the crystallinity of the magnetite phase (Figure 1).

The influence of the ionic liquid on the surface of the Fe₃O₄ was also investigated via FT-IR spectra (Figure 2). In the FT-IR spectrum of Fe₃O₄, three peaks were clearly detected at 3425, 1625, and 585 cm⁻¹, which were respectively attributed to O–H stretching, O–H bending, and Fe–O stretching vibrations. When the Fe₃O₄ particles were combined with the ionic liquid, new peaks were observed at 2950 and 1082 cm⁻¹, in which the signal at 2950 cm⁻¹ was obviously assigned to the aliphatic C–H stretching vibration of the propyl group, and the latter signal at 1082 cm⁻¹ belonged to the Si–O stretching vibration. This proved that the immobilization of the ionic liquid on the Fe₃O₄ surface occurred successfully.

The surface morphology of the Fe₃O₄@O₂Si[PrMIM]Cl·AlCl₃ was also compared with that of the Fe₃O₄ by scanning electron microscopy (SEM). As shown in Figure 3a, the Fe₃O₄ sample consisted of agglomerated particles with sizes varying from 20 to 40 nm. Interestingly, the SEM and TEM images of Fe₃O₄@O₂Si[PrMIM]Cl·AlCl₃ (Figure 3b,c) showed the presence of a liquid layer covering the surface of the magnetic particles. The size distribution of the magnetic nanoparticles modified by chloroaluminate ionic liquid varied in the range of 6 nm to 14 nm (Figure 3d). The aggregation of nanoparticles prevented by the presence of chloroaluminate ionic liquid immobilized on magnetic nanoparticles was the reason for the size reduction of the Fe₃O₄ particles.

The elemental composition determined by energy dispersive X-ray spectroscopy (EDX) illustrated that the catalyst contained carbon (C), chlorine (Cl), aluminum (Al), oxygen (O), and silicon (Si), which were the characteristic elements of the chloroaluminate ionic liquid (Figure 4). Moreover, according to the results of an inductively coupled plasma mass spectrometry (ICP-MS) analysis and nitrogen absorption experiments, the aluminum content and the BET specific surface area of the Fe₃O₄@O₂Si[PrMIM]Cl·AlCl₃ were found to be 1.12 mmol g⁻¹ and 74 m² g⁻¹, respectively.

In order to investigate the thermal stability of our catalyst, a thermogravimetric diagram of the Fe₃O₄@O₂Si[PrMIM]Cl·AlCl₃ was recorded by heating the sample up to 600 ºC (Figure 5). The diagram illustrated a slight weight loss of 7% below 300 ºC, owing to the evaporation of adsorbed water. From 320–460 ºC, a sharp decrease in weight observed (approximately 15%) was caused by the decomposition of imidazole moieties [61]. These results did not only confirm the fact that organic parts had been successful grafted on magnetic nanoparticles, but also determined the thermal stability of our catalyst up to 300 ºC.

The magnetic parameters of the Fe₃O₄ and ionic liquid-coated Fe₃O₄ were identified using a vibrating sample magnetometer (VSM) at room temperature (Figure 6). The absence of a hysteresis loop in the obtained VSM curves substantiated our catalyst as a superparamagnetic material. Due to the grafting processes, the saturation magnetization value (Mₛ) of the Fe₃O₄@O₂Si[PrMIM]Cl·AlCl₃ (32.64 emu/g) was lower than that of the Fe₃O₄ (34.99 emu/g); however, the Mₛ value of the Fe₃O₄@O₂Si[PrMIM]Cl·AlCl₃ was still high enough for the separation of the catalyst out of the reaction mixture by using an external magnet.

2.2. Friedel–Crafts Sulfonylation

In the next experiments, the amount of completed catalyst, Fe₃O₄@O₂Si[PrMIM]Cl·AlCl₃, was investigated in detail to improve the yield of sulfone (entries 3–5, Table 1). Molar ratios of toluene and benzenesulfonyl chloride varying from 1.0:1.0 up to 1.5:1.0 (mmol/mmol) in 0.1 mmol increments for toluene, as well as reaction temperatures in the range of 80–110 ºC in 10 ºC increments were used. Finally, the appropriate amount of toluene (1.4 mmol), benzenesulfonyl chloride (1.0 mmol), and Fe₃O₄@O₂Si[PrMIM]Cl·AlCl₃ (0.2 g) were selected and used in solvent-free sulfonylation for four hours at 110 ºC (entry 1, Table 2).
Further experiments on the nature of alkanesulfonyl/arenesulfonyl chloride were investigated (entries 1–12, Table 2). The results of eight experiments between four arenesulfonyl chlorides and toluene, as well as anisole, displayed that the electron-withdrawing substituents on the aromatic ring of arenesulfonyl chloride caused lower yields of sulfone than electron-donating groups. In addition, three alkanesulfonyl chloride reactions with anisole were also performed; however, the amount of product mixture obtained was much lower than in the case of arenesulfonyl chloride with anisole. In these cases, the sulfonylum cation in transition state stabilized by the aromatic ring better than the aliphatic carbon chain was the main reason for the lower yield of the newborn sulfone obtained from the reactions of three alkanesulfonyl chlorides with anisole (entries 10–12, Table 2). Similarly, in the next series of experiments, p-toluencesulfonyl chloride was chosen as the sulfonylating reagent to investigate the influences of the structure of aromatic compounds on the yields of sulfones (entries 13–18, Table 2). Consequently, the Friedel–Crafts sulfonylation preferred the activated aromatic rings to afford the corresponding sulfones in good yields—the more electron-donating substituents on the aromatic ring, the more the yields of sulfones. Therefore, 1-chloro-4-tosylbenzene was formed at a low yield for a longer reaction time (entry 13, Table 2) owing to the chlorine substituent, a deactivated group linked to the benzene ring. With the mild and efficient catalyst, Fe$_3$O$_4$@O$_2$Si[PrMIM]Cl·AlCl$_3$, demethylation of the methoxy-substituted group was not detected in most experiments by gas chromatography–mass spectrometry analyses (GC/MS), as well as thin-layer chromatography (TLC), in comparison with strong Lewis acidic as the aluminum chloride. Selectively, sulfonyl groups were located at the para position with the available substituents on aromatic rings better than those at the ortho position in the Friedel–Crafts sulfonylation of monosubstituted benzene rings. In order to enlarge the scope of substrates used for this process, a polycyclic benzenoid hydrocarbon; e.g., naphthalene or dibenzothiophene, were also selected as model substrates to react with the excess amount of arenesulfonyl chlorides as the reactant and the solvent so that average to fair yields were obtained (entries 20–21, Table 2).

Table 2. The optimized yields of sulfone derivatives from the Friedel–Crafts sulfonylation of activated arene with sulfonyl chlorides catalyzed by Fe$_3$O$_4$@O$_2$Si[PrMIM]Cl·AlCl$_3$.

| Entry | Arene | Sulfonyl Chloride | Product | Isolated Yield (%) (Time) |
|-------|-------|-------------------|---------|--------------------------|
| 1     | CH$_3$ | ![Sulfonyl Chloride](image) | ![Product](image) | 92 (4.0) |
| Entry | Arene | Sulfonyl Chloride | Product | Isolated Yield (%) (Time) |
|-------|-------|------------------|---------|--------------------------|
| 2     | \( \text{CH}_3 \) | \( \text{Sulfonyl Chloride} \) | \( \text{Product} \) | 85 (4.5) |
| 3     | \( \text{CH}_3 \) | \( \text{Sulfonyl Chloride} \) | \( \text{Product} \) | 67 (4.0) |
| 4     | \( \text{Sulfonyl Chloride} \) | \( \text{Product} \) | \( \text{Product} \) | 30 (5.0) |
| 5     | \( \text{Sulfonyl Chloride} \) | \( \text{Product} \) | \( \text{Product} \) | 85 (4.0) |
| 6     | \( \text{Sulfonyl Chloride} \) | \( \text{Product} \) | \( \text{Product} \) | 91 (1.0) |
| 7     | \( \text{Sulfonyl Chloride} \) | \( \text{Product} \) | \( \text{Product} \) | 89 (4.0) |
| 8     | \( \text{Sulfonyl Chloride} \) | \( \text{Product} \) | \( \text{Product} \) | 54 (1.0) |
| 9     | \( \text{Sulfonyl Chloride} \) | \( \text{Product} \) | \( \text{Product} \) | 39 (3.5) |
| 10    | \( \text{Sulfonyl Chloride} \) | \( \text{Product} \) | \( \text{Product} \) | 28 [e] (3.0) |
| 11    | \( \text{Sulfonyl Chloride} \) | \( \text{Product} \) | \( \text{Product} \) | 23 [e] (4.0) |
Table 2. Cont.

| Entry | Arene | Sulfonyl Chloride | Product | Isolated Yield (%) (Time) d |
|-------|-------|-------------------|---------|-----------------------------|
| 12    | ![](oCH3.png) | ![Sulfonyl Chloride](oCH3.png) | ![Product](oCH3.png) | 18 [c] (4.0) |
| 13    | ![Cl](Cl.png) | ![Sulfonyl Chloride](Cl.png) | ![Product](Cl.png) | 29 [c] (4.5) |
| 14    | ![OH](OH.png) | ![Sulfonyl Chloride](OH.png) | ![Product](OH.png) | 61 (2.5) |
| 15    | ![CH3](CH3.png) | ![Sulfonyl Chloride](CH3.png) | ![Product](CH3.png) | 79 (4.0) |
| 16    | ![CH3](CH3.png) | ![Sulfonyl Chloride](CH3.png) | ![Product](CH3.png) | 85 (4.0) |
| 17b   | ![OCH3](OCH3.png) | ![Sulfonyl Chloride](OCH3.png) | ![Product](OCH3.png) | 90 (3.0) |
| 18b   | ![OCH3](OCH3.png) | ![Sulfonyl Chloride](OCH3.png) | ![Product](OCH3.png) | 83 (4.0) |
| 19    | ![OH](OH.png) | ![Sulfonyl Chloride](OH.png) | ![Product](OH.png) | 35 (5.0) |
| 20c   | ![Furan](Furan.png) | ![Sulfonyl Chloride](Furan.png) | ![Product](Furan.png) | 71 (6.0) |
| 21c   | ![Pyran](Pyran.png) | ![Sulfonyl Chloride](Pyran.png) | ![Product](Pyran.png) | 59 (4.0) |

The reactions were performed under the conventional heating method at 110 °C with a molar ratio of arenne (1.4 mmol) and sulfonyl chloride (1.0 mmol), b molar ratio of arenne (1.0 mmol) and sulfonyl chloride (1.0 mmol), and a molar ratio of arenne (1.0 mmol) and sulfonyl chloride (1.4 mmol). d Time in hours. * Yields were calculated based on the GC/FID analyses.
In another experiment, the sulfonylating reagent arenesulfonyl chloride was replaced with sulfonic anhydride to produce diaryl sulfones in the Friedel–Crafts sulfonylation of activated aromatic compounds (Table 3). Although the yields of sulfones obtained by using sulfonic anhydride were a little bit lower than those by using sulfonyl chloride, p-toluenesulfonic anhydride showed its capability as a moderately efficient, mild, and alternative reagent for the Friedel–Crafts sulfonylation. Finally, the above results substantiated our choice of Fe₃O₄@O₂Si[PrMIM]Cl–AlCl₃ as the most efficient catalyst for both sulfonylating reagents, sulfonyl chloride and sulfonic anhydride. It not only caused the reaction to occur in mild and solvent-free media, but also improved the isolation of sulfones, as well as the separation of catalyst (Table 3).

**Table 3.** The optimized yields of sulfone derivatives from the Friedel–Crafts sulfonylation of activated arene with sulfonic anhydride catalyzed by Fe₃O₄@O₂Si[PrMIM]Cl–AlCl₃.  

| Entry | Arene | Product | Isolated Yield (%) (Time) | 
|-------|-------|---------|---------------------------|
| 1     | C₆H₅   | 3b (72)  | 76 (3.0)                  |
| 2     | C₆H₅OCH₃ | 3f (58)  | 73 (1.5)                  |
| 3     | C₆H₅CH₃ | 3o (86)  | 77 (2.0)                  |
| 4     | C₆H₅CH₃ | 3n       | 72 (2.0)                  |
| 5     | C₆H₅CH₃ | 3a       | 77 (3.0)                  |
| 6     | C₆H₅OCH₃ | 3v (56)  | 82 (2.0)                  |
Table 3. Cont.

| Entry | Arene | Product | Isolated Yield (%) (Time) |
|-------|-------|---------|--------------------------|
| 7 b   | OCH₃ | ![3p](87) | 83 (2.0) |
|       | OCH₃ | ![3p’](13) | |
| 8 b   | OCH₃ | ![3q](61) | 61 (2.5) |
| 9 b   | OCH₃ | ![3w](86) | 81 (2.0) |
|       | OCH₃ | ![3w’](14) | |

The reactions were performed under the conventional heating method at 110 °C with a molar ratio of arene (1.4 mmol) and sulfonic anhydride (1.0 mmol) and b molar ratio of arene (1.0 mmol) and sulfonic anhydride (1.0 mmol). c Time in hours.

With the advantages of Fe₃O₄@O₂Si[PrMIM]Cl·AlCl₃ in the enhancement of reactivity and recovery of catalyst, the reusability of Fe₃O₄@O₂Si[PrMIM]Cl·AlCl₃ was examined. Fe₃O₄@O₂Si[PrMIM]Cl·AlCl₃ was collected after separation with an external magnet, washed alternately with ethanol (2 × 5 mL) and acetone (2 × 5 mL), and dried in a desiccator overnight. The recovered catalyst was obtained at a yield of 93% and analyzed by FT-IR. The FT-IR analysis demonstrated that the functional groups of the recovered catalyst in the fourth recycle were compatible with those of the fresh Fe₃O₄@O₂Si[PrMIM]Cl·AlCl₃ (Figure 7). Simultaneously, the recycled Fe₃O₄@O₂Si[PrMIM]Cl·AlCl₃ was used for the sulfonylation of toluene with benzenesulfonyl chloride at 110 °C for four hours, as in the optimal experiment mentioned in entry 1 of Table 2. The catalytic efficiency of the Fe₃O₄@O₂Si[PrMIM]Cl·AlCl₃ did not change considerably, even after four cycles of catalyst recovery and reuse (Figure 8).

![Figure 7. FT-IR spectra of the fresh catalyst and the reused catalyst.](image-url)
Figure 8. Recycles of Fe₃O₄@O₂Si[PrMIM]Cl·AlCl₃ for the synthesis of phenyl p-tolyl sulfone (3a).

The introduced protocol of the sulfone synthesis from the Friedel–Crafts sulfonylation promoted by Fe₃O₄@O₂Si[PrMIM]Cl·AlCl₃ offered several advantages in terms of a lower amount of aromatic compounds used; a green, efficient and economic catalyst; and a high product selectivity and yield under the solvent-free reaction condition compared with the results in the previous literature reported on Friedel–Crafts sulfonylation with different catalysts (Table 4).

Table 4. Comparison of previous methods for Friedel–Crafts sulfonylation of aromatic compounds promoted by several acidic catalysts.

| Catalyst | X      | Method | Solvent | Temp (°C) | Time (h) | Recyclable Times | Yield (%) | Ref. |
|----------|--------|--------|---------|-----------|----------|------------------|-----------|------|
| Indium (0.2 eq) | Cl     | Stirring | Dioxane | 100       | 1.5–3.0 | None             | 76–84     | [28] |
| Ps-AlCl₃ (0.15 eq) | Cl     | Stirring | Arene   | 85        | 1.1–2.3 | 4                | 89–93     | [35] |
| SiO₂-AlCl₃ (0.1 eq) | Cl     | Stirring | Arene   | 85        | 1.0–2.0 | 4                | 91–95     | [35] |
| SiO₂-AlCl₃ (0.1 eq) | OH     | Stirring | None    | 80        | 1.3–1.9 | 4                | 88–94     | [36] |
| [BTBA]FeCl₃ (1 eq) | Cl     | Stirring | None    | 60        | 0.02–0.08 | None            | 90–97     | [38] |
| MoO₂Cl₂ (20 mol %)  | Cl     | Reflux   | Arene   | 120       | 8–12    | None             | 37–98     | [30] |
| Cu(OTf)₂, Sn(OTf)₂ (5–10% mol) | Cl     | Heating  | Arene   | 120       | 8–12    | None             | 60–63     | [62] |
| Fe(III)-exchanged montmorillonite (0.2 g) | OH     | Reflux   | Arene   | 120       | 6–24    | None             | 60–63     | [62] |
| Nafion-H (50 wt %)  | OH     | Reflux   | Arene   | 130–160   | 0.5–3.0 | None             | 74–88     | [33] |
| Fe(OH)₃ (0.1 g)     | Cl     | Stirring | Arene   | 130–160   | 0.5–3.0 | None             | 40–82     | [33] |
| P₂O₅/Al₂O₃ (0.67 g) | OH     | Reflux   | Arene   | 1.0       |         | None             | 55–90     | [39] |
| P₂O₅/SiO₂ (1.2 g)   | OH     | Reflux   | Arene   | 1.0       |         | None             | 50–90     | [40] |
| Fe₃O₄@O₂Si[PrMIM]Cl·AlCl₃ (0.2 g)  | Cl     | Heating  | None    | 110       | 1.0–5.0 | 4                | 30–92     | [Our work] |

a Temperature (°C); b isolated yield.

3. Materials and Methods

Sulfonyl chlorides (benzenesulfonyl chloride, 4-methylbenzenesulfonyl chloride, ethanesulfonyl chloride, isobutanesulfonyl chloride, . . . ), anhydrous aluminum chloride, arenes (anisole, 1,3-dimethoxybenzene, napthalene, chlorobenzene, . . . ), (3-chloropropyl)trimethoxysilane, and 1-methylimidazole were from Sigma-Aldrich (Darmstadt, Germany), and the p-toluenesulfonic anhydride and isomer of xylene were from Acros. All commercially available chemicals were analyzed for authenticity and purity by GC/MS before being used. X-ray diffraction patterns were measured on a Brüker D8 Advance diffractometer.
Fourier-transform infrared (FT-IR) spectra were recorded on a Bruker E400 spectrometer in the range of 4000–500 cm$^{-1}$. Thermal gravimetric analysis (TGA) was performed using a TA Instruments Q-500 thermal gravimetric analyzer. Magnetic properties were measured using an ID-EV 11 vibrating sample magnetometer (VSM). Size and structure of materials were obtained using a Hitachi S-4800 scanning electron microscope (SEM) and JOEL JEM1010 transmission electron microscope (TEM). The composition of the catalyst was analyzed by energy-dispersive X-ray spectroscopy (EDX) on a Shimadzu EDX-8000. The specific surface area was determined using the Brunauer–Emmett–Teller (BET) technique with a Quantachrome NOVA 2200e analyzer (Boynton Beach, FL, USA). Inductively coupled plasma mass spectrometry (ICP-MS) data were recorded on an Agilent 7700s instrument. NMR spectra were recorded on a Bruker AVANCE 500 or Bruker AVANCE NEO 400 at 500 or 400 MHz for $^1$H-NMR and 125 or 100 MHz for $^{13}$C-NMR. Gas chromatography analyses were performed on an Agilent 6890, with a flame ionization detector equipped with a J and W DB-5MS capillary column (30 m, 0.25 mm i.d., 0.25 µm film thickness). Gas chromatography–mass spectrometry (GC-MS) measurements were carried out on an Agilent GC System 7890 equipped with a mass selective detector (Agilent 5973N) and a capillary DB-5MS column (30 m × 250 µm × 0.25 µm). High-resolution mass spectrometry (HRMS) was recorded on an Agilent 1200 series high-performance liquid chromatograph with a Bruker micrOTOF-QII EIS mass spectrometer detector.

3.1. General Procedure for Preparation of Heterogeneous Catalyst $\text{Fe}_3\text{O}_4@\text{O}_2\text{Si}[\text{PrMIM}]\text{Cl} \cdot \text{AlCl}_3$

3.1.1. The Preparation of MNPs via the Modified Chemical Coprecipitation Method

Typically, 100 mL of FeSO$_4$·7H$_2$O (6.0 mmol, 1.668 g) and Fe(NO$_3$)$_3$·9H$_2$O (12.0 mmol, 4.848 g) dissolved completely in 100 mL distilled water was dropped slowly into a 500 mL beaker containing 200 mL of 0.25 M NaOH solution within 1 h at 80 °C under vigorous mechanical stirring at 500 rpm. The black precipitate was washed with distilled water (2 × 100 mL) until reaching pH 7 and dried at 150 °C for 4 h. The crude iron oxide particles were ground with a porcelain mortar to obtain the fine magnetic nanoparticles (MNPs) [56].

3.1.2. The Preparation of 3-Methyl-1-(3-trimethoxysilylpropyl)-1H-imidazole-3-ium Chloride

A mixture of (3-chloropropyl)trimethoxysilane (20.0 mmol, 3.974 g) and 1-methylimidazole (20.0 mmol, 1.642 g) in a round-bottom 25 mL flask was stirred at 80 °C for 72 h. After reaction completion, the mixture of products was washed with diethyl ether (3 × 5 mL). Subsequently, the pure ionic liquid with light yellow, 3-methyl-1-(3-trimethoxysilylpropyl)-1H-imidazole-3-ium chloride obtained after the solvent removal under vacuum pressure was identified by $^1$H and $^{13}$C NMR spectroscopy. These spectra were compatible with the previous literature [56].

3.1.3. Methyl-1-(3-trimethoxysilylpropyl)-1H-imidazole-3-ium Chloride

Methyl-1-(3-trimethoxysilylpropyl)-1H-imidazole-3-ium chloride, light yellow liquid. $^1$H NMR (500 MHz, CDCl$_3$): δ (ppm) 10.56 (brs, 1H), 7.46 (s, 1H), 7.32 (s, 1H), 4.29 (t, J = 7.5 Hz, 2H), 4.09 (s, 3H), 3.54 (s, 9H), 1.98 (p, J = 7.5 Hz, 2H), 0.63–0.59 (m, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$): δ (ppm) 138.5, 123.3, 121.8, 51.9, 50.8, 36.8, 24.2, 6.1.

3.1.4. The Preparation of $\text{Fe}_3\text{O}_4@\text{O}_2\text{Si}[\text{PrMIM}]\text{Cl}$

$\text{Fe}_3\text{O}_4$ nanoparticles (1.0 mmol, 0.232 g), 3-methyl-1-(3-trimethoxysilylpropyl)-1H-imidazole-3-ium chloride (2.0 mmol, 0.562 g), absolute ethanol (5.0 mL), and 28% ammonia solution (0.2 mL) were added into a round-bottom 25 mL flask and stirred at room temperature for 24 h. After reaction completion, $\text{Fe}_3\text{O}_4@\text{O}_2\text{Si}[\text{PrMIM}]\text{Cl}$, a dark-brown solid, was washed with ethanol (2 × 5 mL) and collected with an external magnet and then dried under vacuum.
3.1.5. The Preparation of Fe$_3$O$_4@$O$_2$Si[PrMIM]Cl·AlCl$_3$

Anhydrous aluminum chloride, AlCl$_3$ (4.0 mmol, 0.533 g), was added slowly into a 25 mL round-bottom flask containing Fe$_3$O$_4@$O$_2$Si[PrMIM]Cl dispersed in 5 mL of absolute ethanol. The mixture was stirred at room temperature for 12 h. After that, the catalyst of Fe$_3$O$_4@$O$_2$Si[PrMIM]Cl·AlCl$_3$ was washed with ethanol (2 × 5 mL) and put into the desiccator overnight. The dark-brown solid obtained was ground into a homogeneous fine powder and stored in the desiccator before using.

3.2. General Procedure for the Friedel–Crafts Sulfonylation

The aromatic compound (1.0 mmol), sulfonyl chloride/sulfonic anhydride (1.0 mmol, and Fe$_3$O$_4@$O$_2$Si[PrMIM]Cl·AlCl$_3$ (0.2 g) were added into a 5 mL round-bottom flask assembled with the condenser. The reaction mixture was heated at 110 °C for a specific period of time. After cooling down, the mixture of products was extracted with ethyl acetate (4 × 5 mL), and the solid catalyst was collected by using a magnetic bar. The organic phase was rinsed with water (2 × 10 mL) and dried with anhydrous Na$_2$SO$_4$. After that, the removal of the solvent by rotary evaporation was performed to obtain the crude product. The product was purified by column chromatography using eluent as a mixture of $n$-hexane and ethyl acetate (8:2 v/v).

3.3. Spectroscopic Data

The identification and purity of all products reported were determined by $^1$H-NMR, $^{13}$C-NMR, and HRMS. The well-known compounds 3a [63], 3b [64], 3b′ [65], 3c [64], 3d [64], 3e [66], 3f [65], 3f′ [65], 3g [64], 3g′ [67], 3h [68], 3i [69], 3m [70], 3n [71], 3o [70], 3p [30], and 3u [62] were found to be compatible with the previous literature. The unknown products are described below (Figure S2).

1-(4-Chlorophenyl)sulfonyl)-2-methoxybenzene (3c′): White solid; m.p.: 137–138 °C. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ (ppm) 8.19 (dd, $J = 8.0$ Hz, $J = 1.5$ Hz, 1H), 7.81–7.78 (m, 2H), 7.51–7.46 (m, 3H), 7.40 (t, $J = 7.5$ Hz, 1H), 7.24 (d, $J = 7.5$ Hz, 1H), 2.44 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ (ppm) 163.9, 147.3, 135.9, 130.1, 130.0, 129.8, 129.6, 129.5, 129.3, 126.8, 20.4. HRMS-ESI: $m/z$ [M + Na]$^+$ calcd. for C$_{13}$H$_{11}$O$_2$Cl, 289.0066; found, 289.0101 (Figure S3).

1-Methyl-2-((4-nitrophenyl)sulfonyl)benzene (3d′): White solid; m.p.: 106–108 °C. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ (ppm) 8.35–8.33 (m, 2H), 8.25 (dd, $J = 7.5$ Hz, $J = 1.0$ Hz, 1H), 8.05–8.03 (m, 2H), 7.55 (td, $J = 7.5$ Hz, $J = 1.5$ Hz, 1H), 7.46 (t, $J = 7.5$ Hz, 1H), 7.28 (d, $J = 7.5$ Hz, 1H), 2.44 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ (ppm) 150.5, 147.3, 138.4, 137.6, 134.7, 133.0, 129.0, 129.1, 127.1, 124.5, 20.4. HRMS-ESI: $m/z$ [M + Na]$^+$ calcd. for C$_{13}$H$_{11}$NO$_2$, 303.0377; found, 303.0321.

1-(4-Chlorophenyl)sulfonyl)-2-hydroxybenzene (3h′): White solid; m.p.: 139–141 °C. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ (ppm) 8.14 (dd, $J = 8.0$ Hz, $J = 1.5$ Hz, 1H), 7.90 (d, $J = 8.5$ Hz, 2H), 7.57–7.54 (m, 1H), 7.45 (d, $J = 8.5$ Hz, 2H), 7.11 (t, $J = 7.5$ Hz, 1H), 6.91 (d, $J = 7.5$ Hz, 1H), 3.78 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ (ppm) 157.2, 140.3, 135.9, 130.1, 130.0, 128.9, 128.8, 120.8, 112.7, 56.1. HRMS-ESI: $m/z$ [M + Na]$^+$ calcd. for C$_{13}$H$_{11}$O$_2$SCl, 305.0015; found, 305.0004.

1-Methoxy-2-((4-nitrophenyl)sulfonyl)benzene (3i′): White solid; m.p.: 164–165 °C. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ (ppm) 8.33–8.31 (m, 2H), 8.18–8.14 (m, 3H), 7.61–7.59 (m, 1H), 7.18–7.14 (m, 1H), 6.93 (d, $J = 8.0$ Hz, 1H), 3.78 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ (ppm) 157.3, 147.5, 136.6, 130.3, 129.9, 128.8, 123.9, 121.1, 115.1, 112.8, 56.2. HRMS-ESI: $m/z$ [M + Na]$^+$ calcd. for C$_{13}$H$_{11}$O$_2$SN, 316.0256; found, 316.0223.

1-(Ethylsulfonyl)-4-methoxybenzene (3j): White solid; m.p.: 56–58 °C. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ (ppm) 7.83 (d, $J = 9.0$ Hz, 2H), 7.02 (d, $J = 9.0$ Hz, 2H), 3.89 (s, 3H), 3.08 (q, $J = 7.5$ Hz, 2H), 1.26 (t, $J = 7.5$ Hz, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ (ppm) 163.9, 130.5, 130.4, 114.6, 55.8, 51.0, 7.7. HRMS-ESI: $m/z$ [M + H]$^+$ calcd. for C$_9$H$_{12}$O$_2$S, 201.0585; found, 201.0585.
1-(Ethylsulfonyl)-2-methoxybenzene (3j): White solid; m.p.: 88–90 °C. 1H NMR (500 MHz, CDCl3): δ (ppm) 7.96 (dd, J = 8.0 Hz, J = 2.0 Hz, 1H), 7.61–7.57 (m, 1H), 7.12–7.09 (m, 1H), 7.04 (d, J = 8.5 Hz, 1H), 3.98 (s, 3H), 3.37 (q, J = 7.5 Hz, 2H), 1.24 (t, J = 7.5 Hz, 3H). 13C NMR (125 MHz, CDCl3): δ (ppm) 157.4, 135.5, 130.9, 126.4, 120.8, 112.3, 56.3, 48.7, 7.1.

1-HRMS-ESI: m/z [M + H]+ calcd. for C11H10O2S, 201.0583; found, 201.0583.

1-(Isobutylsulfonyl)-4-methoxybenzene (3k): White solid; m.p.: 160–162 °C. 1H NMR (500 MHz, CDCl3): δ (ppm) 7.83 (d, J = 8.5 Hz, 1H), 7.27–7.24 (m, 1H), 7.18–7.14 (m, 1H), 3.88 (s, 3H), 3.74 (s, 3H), 2.41 (s, 3H). 13C NMR (125 MHz, CDCl3): δ (ppm) 163.8, 132.0, 130.2, 114.6, 64.5, 55.8, 24.3, 22.9. HRMS-ESI: m/z [M + H]+ calcd. for C11H10O2S, 229.0898; found, 229.0896.

1-(Isobutylsulfonyl)-2-methoxybenzene (3l): White solid; m.p.: 88–90 °C. 1H NMR (500 MHz, CDCl3): δ (ppm) 7.97 (dd, J = 8.5 Hz, J = 2.0 Hz, 1H), 7.60–7.56 (m, 1H), 7.10 (td, J = 7.5 Hz, J = 1.0 Hz, 1H), 7.04 (d, J = 8.5 Hz, 1H), 3.98 (s, 3H), 3.25 (d, J = 6.5 Hz, 2H), 2.28–2.23 (m, 1H), 1.03 (d, J = 6.5 Hz, 6H). 13C NMR (125 MHz, CDCl3): δ (ppm) 163.8, 131.1, 130.4, 114.6, 56.8, 55.8, 31.8, 29.1, 29.0, 28.4, 23.0, 22.7, 14.2. HRMS-ESI: m/z [M + H]+ calcd. for C15H18O3S, 285.1524; found, 285.1522.

1-Methoxy-4-(octylsulfonyl)benzene (3m): White solid; m.p.: 104–106 °C. 1H NMR (500 MHz, CDCl3): δ (ppm) 7.84–7.81 (m, 2H), 7.03–7.00 (m, 2H), 3.88 (s, 3H), 3.06–3.03 (m, 2H), 1.70–1.67 (m, 2H), 1.35–1.32 (m, 2H), 1.27–1.23 (m, 2H), 0.86 (t, J = 7.0 Hz, 3H). 13C NMR (125 MHz, CDCl3): δ (ppm) 163.8, 131.1, 130.4, 114.6, 56.8, 55.8, 31.8, 29.1, 29.0, 28.4, 23.0, 22.7, 14.2. HRMS-ESI: m/z [M + H]+ calcd. for C15H18O3S, 285.1524; found, 285.1522.

2,3-Dimethyl-1-(tosylbenzene (3o): White solid; m.p.: 130–132 °C. 1H NMR (500 MHz, CDCl3): δ (ppm) 8.07 (d, J = 8.0 Hz, 1H), 7.73 (d, J = 8.5 Hz, 2H), 7.37 (d, J = 7.5 Hz, 1H), 7.29–7.27 (m, 3H), 2.41 (s, 3H), 2.35 (s, 3H), 2.26 (s, 3H). 13C NMR (125 MHz, CDCl3): δ (ppm) 143.9, 139.7, 139.5, 139.0, 136.4, 135.2, 129.8, 127.8, 127.5, 125.9, 21.7, 20.5, 16.1. HRMS-ESI: m/z [M + H]+ calcd. for C18H17NO3, 261.0949; found, 261.0954.

2,4-Dimethoxy-1-(tosylbenzene (3p): White solid; m.p.: 159–161 °C. 1H NMR (500 MHz, CDCl3): δ (ppm) 8.04 (d, J = 8.5 Hz, 1H), 7.80 (d, J = 8.5 Hz, 2H), 7.23 (d, J = 8.0 Hz, 2H), 6.55 (dd, J = 8.5 Hz, J = 2.0 Hz, 1H), 6.36 (d, J = 2.0 Hz, 1H), 3.81 (s, 3H), 3.72 (s, 3H), 2.38 (s, 3H). 13C NMR (125 MHz, CDCl3): δ (ppm) 165.6, 158.7, 143.5, 139.4, 133.1, 129.2, 128.3, 121.9, 104.7, 99.6, 56.0, 55.8, 21.7. HRMS-ESI: m/z [M + Na]+ calcd. for C15H16O4S, 315.0667; found, 315.0632.

1,3-Dimethoxy-2-(tosylbenzene (3q): White solid; m.p.: 101–103 °C. 1H NMR (500 MHz, CDCl3): δ (ppm) 7.84 (d, J = 8.0 Hz, 2H), 7.37 (t, J = 8.5 Hz, 1H), 7.24 (d, J = 8.0 Hz, 2H), 6.54 (d, J = 8.5 Hz, 2H), 3.77 (s, 6H), 2.39 (s, 3H). 13C NMR (125 MHz, CDCl3): δ (ppm) 199.5, 143.0, 141.7, 134.8, 130.9, 128.8, 127.4, 118.4, 105.4, 56.5, 21.5. HRMS-ESI: m/z [M + Na]+ calcd. for C15H16O4S, 315.0667; found, 315.0642.

1,4-Dimethoxy-2-(tosylbenzene (3r): White solid; m.p.: 111–113 °C. 1H NMR (500 MHz, CDCl3): δ (ppm) 7.85 (d, J = 8.5 Hz, 2H), 7.68 (d, J = 3.0 Hz, 1H), 7.27 (d, J = 8.0 Hz, 2H), 7.06 (dd, J = 9.0 Hz, J = 3.0 Hz, 1H), 6.84 (d, J = 9.0 Hz, 1H), 3.84 (s, 3H), 3.71 (s, 3H), 2.41 (s, 3H). 13C NMR (125 MHz, CDCl3): δ (ppm) 153.5, 151.4, 144.0, 138.7, 130.1, 129.3, 128.6, 121.7, 114.5, 113.9, 56.7, 56.3, 21.7. HRMS-ESI: m/z [M + Na]+ calcd. for C15H16O4SCl, 315.0700; found, 315.0700.

4-((4-Chlorophenyl)sulfonyl)phenol (3s): White solid; m.p.: 146–147 °C. 1H NMR (500 MHz, CDCl3): δ (ppm) 7.83 (d, J = 8.5 Hz, 2H), 7.80 (d, J = 9.0 Hz, 2H), 7.45 (d, J = 8.5 Hz, 2H), 6.91 (d, J = 9.0 Hz, 2H), 4.57 (s, J = 125 MHz, CDCl3): δ (ppm) 160.5, 140.9, 139.8, 132.8, 130.3, 129.7, 128.9, 116.4. HRMS-ESI: m/z [M + Na]+ calcd. for C12H9O3SCl, 290.9859; found, 290.9894.
2-((4-Chlorophenyl)sulfonyl)phenol (3r): White solid, m.p.: 158–159 °C, 1H NMR (500 MHz, CDCl₃): δ (ppm) 9.11 (s, 1H), 7.88–7.86 (m, 2H), 7.63 (dd, J = 8.0 Hz, J = 1.5 Hz, 2H), 7.51–7.45 (m, 3H), 7.01–6.96 (m, 2H). 13C NMR (125 MHz, CDCl₃): δ (ppm) 155.9, 140.5, 140.2, 136.4, 129.8, 129.1, 128.3, 123.2, 110.1, 119.3. HRMS-ESI: m/z [M + Na]⁺ calcd. for C₁₂H₈O₂Cl₂, 290.8959; found, 290.8959.

2-(Phenylsulfonyl)naphthalene (3s): White solid, m.p.: 123–125 °C, 1H NMR (500 MHz, CDCl₃): δ (ppm) 8.58 (s, 1H), 7.79 (t, J = 7.5 Hz, 3H), 7.93 (d, J = 9.0 Hz, 1H), 7.88–7.84 (m, 2H), 7.64–7.62 (m, 2H), 7.56–7.50 (m, 3H). 13C NMR (125 MHz, CDCl₃): δ (ppm) 138.3, 134.9, 133.1, 132.2, 129.5, 129.3, 129.2, 129.1, 129.0, 128.7, 127.8, 127.6, 127.5, 122.6. HRMS-ESI: m/z [M + Na]⁺ calcd. for C₁₆H₁₂O₂S, 291.0456; found, 291.0445.

4-(Phenylsulfonyl)dibenzon[b,d]thiophene (3t): White solid, m.p.: 117–119 °C. 1H NMR (500 MHz, CDCl₃): δ (ppm) 8.15 (d, J = 8.0 Hz, 1H), 7.71 (d, J = 8.0 Hz, 2H), 7.27 (d, J = 7.5 Hz, 2H), 6.85 (dd, J = 8.5 Hz, J = 2.5 Hz, 1H), 6.71 (d, J = 2.5 Hz, 1H), 3.83 (s, 3H), 2.39 (s, 6H). 13C NMR (125 MHz, CDCl₃): δ (ppm) 163.5, 143.7, 140.3, 139.3, 132.0, 131.2, 129.7, 127.6, 118.2, 111.1, 55.6, 21.7, 20.6. HRMS-ESI: m/z [M + Na]⁺ calcd. for C₁₅H₁₅O₂S, 297.0918; found, 297.0915.

2-Methoxy-4-methyl-1-tosylbenzene (3v): White solid; m.p.: 128–130 °C. 1H NMR (500 MHz, CDCl₃): δ (ppm) 8.00 (d, J = 8.0 Hz, 1H), 7.83 (d, J = 8.5 Hz, 2H), 7.25 (d, J = 7.5 Hz, 2H), 6.89 (d, J = 8.0 Hz, 1H), 6.68 (s, 1H), 3.74 (s, 3H), 2.40 (s, 3H), 2.37 (s, 3H). 13C NMR (125 MHz, CDCl₃): δ (ppm) 156.9, 146.5, 143.4, 138.9, 129.7, 129.0, 128.2, 126.5, 121.1, 113.0, 55.7, 21.8, 21.4. HRMS-ESI: m/z [M + Na]⁺ calcd. for C₁₅H₁₄O₂S, 299.0718; found, 299.0746.

1-Methoxy-3-methyl-1-tosylbenzene (3v’): White solid; m.p.: 107–109 °C. 1H NMR (500 MHz, CDCl₃): δ (ppm) 7.79 (d, J = 8.5 Hz, 2H), 7.33 (t, J = 8.0 Hz, 1H), 7.25 (d, J = 8.0 Hz, 2H), 6.87 (d, J = 7.5 Hz, 1H), 6.73 (d, J = 8.5 Hz, 1H), 3.61 (s, 3H), 2.84 (s, 3H), 2.40 (s, 3H). 13C NMR (125 MHz, CDCl₃): δ (ppm) 158.3, 143.2, 142.1, 141.1, 133.8, 128.9, 128.3, 127.4, 125.5, 110.9, 56.0, 22.4, 21.6. HRMS-ESI: m/z [M + Na]⁺ calcd. for C₁₅H₁₄O₂S, 297.0918; found, 297.0702.

1,2-Dimethoxy-4-tosylbenzene (3w) white solid; m.p.: 130–132 °C. 1H NMR (500 MHz, CDCl₃): δ (ppm) 7.80 (d, J = 8.5 Hz, 2H), 7.55 (dd, J = 8.5 Hz, J = 2.0 Hz, 1H), 7.37 (d, J = 2.5 Hz, 1H), 7.28 (d, J = 8.0 Hz, 2H), 6.91 (d, J = 8.5 Hz, 1H), 3.91 (s, 3H), 3.90 (s, 3H), 2.39 (s, 3H). 13C NMR (125 MHz, CDCl₃): δ (ppm) 152.9, 149.3, 149.3, 134.8, 139.4, 133.6, 129.8, 127.3, 123.1, 121.7, 110.9, 109.9, 56.3, 56.2, 21.5. HRMS-ESI: m/z [M + H⁺]⁺ calcd. for C₁₅H₁₄O₃S, 293.0847; found, 293.0850.

1,2-Dimethoxy-3-tosylbenzene (3w’): White solid; m.p.: 128–130 °C. 1H NMR (500 MHz, CDCl₃): δ (ppm) 7.85 (d, J = 8.0 Hz, 2H), 7.70 (d, J = 8.0 Hz, 1H), 7.26 (d, J = 7.5 Hz, 2H), 7.18 (t, J = 8.0 Hz, 1H), 7.11 (d, J = 8.5 Hz, 1H), 3.86 (s, 3H), 3.83 (s, 3H), 2.39 (s, 3H). 13C NMR (125 MHz, CDCl₃): δ (ppm) 153.8, 147.4, 144.0, 139.1, 135.8, 129.4, 128.3, 123.9, 120.6, 117.8, 61.5, 56.3, 21.7. HRMS-ESI: m/z [M + H⁺]⁺ calcd. for C₁₅H₁₄O₃S, 293.0847; found, 293.0846.

4. Conclusions

Using contemporary green chemistry, a chlooroaluminate ionic liquid immobilized on magnetic nanoparticles was developed and applied in the solvent-free sulfonylation of substituted aromatic compounds with sulfonyl chlorides, as well as p-toluenesulfonic anhydride, to afford sulfones in moderate to good yields. The Friedel–Crafts sulfonylation had preferred arenes and sulfonyl chlorides with electron-donating substituents. The more electron-donating substituents on the aromatic rings, the more the yields of sulfones, and the shorter the reaction times. In addition, another interesting result was that the size of the Fe₃O₄ particles, which originally were around 20 nm in diameter, became smaller, in
the range of 6–14 nm in diameter, owing to the immobilization of the chloroaluminate ionic liquid on the particles. Furthermore, Fe$_2$O$_4@$O$_2$Si[PrMIM]Cl·AlCl$_3$ is an ecofriendly, efficient, and highly recyclable catalyst, especially evidenced by the yields of sulfones without a significant drop after four catalytic cycles of recovery and reuse.

**Supplementary Materials:** The following are available online. $^1$H-NMR, $^{13}$C-NMR, and HRMS of unknown products. Figure S1. BET surface area of Fe$_2$O$_4@$O$_2$Si[PrMIM]Cl·AlCl$_3$. Figure S2. 1H-NMR of 1-((4-chlorophenyl)sulfonyl)-2-methylbenzene (3c′); Figure S3. 13C-NMR of 1-((4-chlorophenyl)sulfonyl)-2-methylbenzene (3c′).

**Author Contributions:** T.X.T.L. conceived and designed the experiments and wrote the paper; N.-L.T.N. mainly performed the experiments and wrote the original draft preparation; Q.-A.N., K.-N.T.T., and P.-B.P. performed the experiments and analyzed the data; T.K.L. analyzed the data and reviewed and edited the paper. All authors have read and agreed to the published version of the manuscript.

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