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N-Hydroxyphthalimide on a Polystyrene Support Coated with Co(II)-Containing Ionic Liquid as a New Catalytic System for Solvent-Free Ethylbenzene Oxidation

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Abstract: The oxidation of ethylbenzene using dioxygen was carried out applying a new catalytic system—heterogeneous *N*-hydroxyphthalimide (PS-NHPI) coated with an ionic liquid containing CoCl₂. The catalytic system represents a combination of solid catalyst with ionic liquid layer (SCILL) and supported ionic liquid phase (SILP) techniques, wherein the resulting system utilizes CoCl₂ dissolved in the 1-ethyl-3-methylimidazolium octyl sulphate ([emim][O₈OSO₃]) ionic liquid phase that is layered onto the solid catalyst support. PS-NHPI was obtained by immobilizing *N*-hydroxyphthalimide on chloromethyl polystyrene resins by ester bonds. It was observed that novel SCILL/SILP systems significantly improved the selectivity toward acetophenone. We also demonstrate that these systems can be separated from the reaction mixture and recycled without appreciably reducing its activity and selectivity.

Keywords: supported catalysts; oxidation; ionic liquids; *N*-hydroxyphthalimide; hydrocarbons

1. Introduction

Hydrocarbon oxidations represent an important family of reactions in organic synthesis, and they play a key role in the chemical industry. For environmental and economic reasons, it is advantageous to use dioxygen or air as the oxidizing agent for such transformations, which is made possible by using catalytic systems containing often transition metal compounds, e.g., Co and Mn [1,2]. The high activity of *N*-hydroxyphthalimide (NHPI) in this type of reaction has been also demonstrated repeatedly in the literature [3–5]. This compound's activity is related to the fact that, during turnover, it generates the phthalimide-*N*-oxyl (PINO) radical, which effectively abstracts the hydrogen atom from the hydrocarbon being oxidized (Scheme 1).

The PINO radical in this system can be generated by various additives, including azo compounds, transition metal complexes, aldehydes, oximes, and quinones [4,6]. For example, azobisisobutyronitrile (AIBN) was used in the oxidation of cumene to its hydroperoxide using dioxygen at 60 °C, aided by 10 mol% NHPI [7]. After allowing the reaction to proceed for three hours in acetonitrile, a 46% conversion of cumene reagent was obtained, with nearly 100% selectivity toward production of cumene hydroperoxide. In contrast, in the presence of NHPI and Co(acac)₂, 2-phenyl-2-propanol and acetophenone were obtained as main products [8]. Transition metal compounds can indeed generate the PINO radical, but they also decompose the hydroperoxide formed during the reaction [3].

NHPI-catalyzed oxidation of hydrocarbons with dioxygen are most often carried out in polar solvents, such as acetonitrile, benzonitrile, or acetic acid [7–10]. This is because of the low solubility of NHPI in non-polar media and the fact that the catalyst must be fully dissolved to ensure promotion of the catalytic cycle shown in Scheme 1. Recently, researchers have investigated replacing classic organic solvents with supercritical CO₂ (scCO₂) [11,12] or ionic liquids (ILs) [11,13–18].

Scheme 1. Mechanism of hydrocarbon oxidation in the presence of NHPI [19].

A key issue in the context of applying NHPI in industrial processes involves its potential separation and reuse. Unfortunately, simple isolation methods, such as solvent evaporation [7,20] or, in the case of scCO₂, decompression by changing the pressure and temperature parameters [11,12], are ineffective if the reaction product is highly polar and effectively dissolves NHPI. However, this issue can be avoided by immobilizing NHPI on solid supports, such as silicas [21–23], polymers [24–29], or zeolites [30]. For example, heterogeneous NHPI was used to oxidize toluene with dioxygen in the presence of heterogeneous Co(II) in acetic acid [21]. After 20 h, benzaldehyde was obtained as a product in 12% yield. In the second reaction cycle, the activity of the catalytic system allowed the product to be obtained with a yield of 10%. Heterogenization of NHPI effectively simplifies the separation and therefore reuse of the catalyst; however, it adversely affects the catalytic activity. In the oxidation of cyclohexane with dioxygen at 130 °C in the presence of heterogeneous NHPI (0.85 mmol/g catalyst; 0.1 mol% NHPI), oxygen consumption after 4 h was about 8.5 mmol [22]. In an analogous process carried out in the presence of 0.1 mol% of homogeneous NHPI in acetonitrile, the oxygen consumption surpassed 11 mmol.

Recently, in order to increase the activity of heterogeneous catalysts, scientists have applied the so-called solid catalyst with ionic liquid layer (SCILL) technique, which involves covering the catalyst's surface with a layer of ionic liquid [31]. The addition of an ionic liquid may increase both the activity and the selectivity of the solid catalyst by tuning its chemical properties (i.e., co-catalytic effect) and/or by changing the concentration of intermediates and semi-products at the catalyst surface (i.e., physical solvent effect). Contrary to processes that use ionic liquids as solvents, the SCILL technique allows their use in minimal amounts, thereby avoiding high additional costs. The aim of SCILL is to modify the activity and selectivity of a heterogeneous catalyst while maintaining the ease of its separation and recycling [32]. To date, the SCILL technique has been used mainly in hydrogenation processes, including those involving cyclooctadiene [31], citral [33,34], toluene [35], and propyne [36]. Additionally, several studies regarding oxidation of alcohols and oxidative coupling of thiols have been published [37–39]. In 2011, a SCILL system consisting of the 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) radical covalently immobilized on SBA-15 silica (Figure 1a) coated with a [bmim][Br] (bmim = 1-butyl-3-methylimidazolium) ionic liquid effectively promoted oxidation of alcohols to aldehydes using dioxygen [37]. The benzyl alcohol oxidation reactions were carried out in the presence

of *tert*-butyl nitrite and acetic acid at 40 °C for about 3 h. The addition of [bmim][Br] increased the benzaldehyde yield from less than 5% to over 99%. The authors further reported that this SCILL system showed unchanged activity over as many as 11 reaction cycles [37]. There are also several studies that employed SCILL systems containing transition metal salts dissolved in the ionic liquid phase [40,41]. For example, Liu et al. [40] described the oxidation of 4-methoxybenzyl alcohol to 4-methoxybenzaldehyde using dioxygen as the oxidant and TEMPO immobilized on polystyrene (PS-TEMPO) (Figure 1b) covered with a [bmim][PF₆] ionic liquid containing dissolved CuCl₂ as the heterogeneous catalyst. Modification of the PS-TEMPO/CuCl₂ system by adding an ionic liquid increased the alcohol conversion from 58% to 85%. Research into the possibility of recycling the SCILL system containing CuCl₂ revealed that this system can be used four times with only a slight decrease in activity (i.e., in the fourth cycle, a decrease in aldehyde yield from 93% to 79% was noted). It was determined that this decrease results from partial elution of the ionic liquid from the PS-TEMPO surface. In previous work in our laboratory [41], we used a SCILL system consisting of NHPI immobilized via ester bonds on silica gel (SiOCONHPI; Figure 1c), in combination with various ionic liquids containing CoCl₂ (SiOCONHPI@CoCl₂@IL) for the oxidation of ethylbenzene. The positive impact of the ionic liquid, [bmim][OcOSO₃], on the catalytic activity of the studied system was clearly observed. Specifically, the SiOCONHPI@CoCl₂@[bmim][OcOSO₃] system achieved 12.1% conversion of ethylbenzene, while using SiOCONHPI/CoCl₂ alone led to only 8.2% conversion. The observed effect, might be a result of interaction between N-OH groups and [bmim][OcOSO₃], better contact between CoCl₂ dissolved in a layer of IL and N-OH groups, as well as between reagents and N-OH groups and CoCl₂, and also undesired washing out of ionic liquid containing CoCl₂ from the surface of silica. We also demonstrated that it is possible to recycle SiOCONHPI@CoCl₂@[bmim][OcOSO₃], and that the decrease in activity observed in the fourth reaction cycle (i.e., 8% conversion) was due to partial elution of the IL and CoCl₂ from the catalyst surface. Promising results were obtained for the system using a slightly different ionic liquid, SiOCONHPI@CoCl₂@[emim][OcOSO₃] (emim = 1-ethyl-3-methylimidazolium), which could obtain an ethylbenzene conversion of 9.5% in the fourth reaction cycle.

Figure 1. Catalysts employed in SCILL systems reported in the literature (see text for further details). (a) SBA-15-TEMPO, (b) PS-TEMPO, (c) SiOCONHPI.

This paper describes investigations regarding the use of a novel SCILL system containing heterogeneous NHPI coated with IL containing CoCl₂ (NHPI@CoCl₂@IL) to carry out ethylbenzene oxidation reactions. First, solid catalysts (PS-NHPI; Figure 2a) were obtained according to the procedure described in [24], by immobilizing NHPI on commercially available polymer supports, differing in (i) their functional group content (according to the manufacturer, this was in the range of

2.0–5.5 mmol Cl/g), (ii) their grain size (from 16 to 400 mesh), and (iii) the amount of divinylbenzene (DVB) used as a cross-linking agent (1%, 2%, or 5.5%). The obtained PS-NHPI material was characterized by SEM, FT-IR, and elemental analysis. Previously, catalysts of this type with 0.35–1.65 mmol NHPI/g were active for the oxidation of toluene and *p*-methoxytoluene using dioxygen and $\text{Co}(\text{OAc})_2$ (as co-catalyst), either in acetic acid or without solvent, and the catalyst could be separated twice in reactions without a solvent [24]. Herein, the synthesized heterogeneous PS-NHPI catalysts were covered with a thin layer of ionic liquid, [emim][O₂SO₃], which contained cobalt(II) chloride (Figure 2b). The activities of the obtained systems were tested in a model ethylbenzene oxidation reaction conducted at 80 °C under dioxygen atmosphere for 6 h. This work aims to compare the activity of various obtained catalysts PS-NHPI@CoCl₂@[emim][O₂SO₃], referred to as SCILL/SILP systems (SILP = supported ionic liquid phase), with systems composed of heterogeneous PS-NHPI and CoCl₂ (PS-NHPI/CoCl₂) or IL (PS-NHPI/IL) added separately to the reaction mixture. Their potentials for reuse was also tested.

Figure 2. Catalyst systems tested and compared in this work, i.e., with and without ionic liquid. (a) PS-NHPI (b) PS-NHPI@CoCl₂@[emim][O₂SO₃].

2. Results and Discussion

2.1. Preparation of the Catalytic System

The PS-NHPI heterogeneous catalyst was obtained by immobilizing NHPI on commercially available chloromethyl polystyrene (PS-Cl) resins (Table 1). The resins (carriers) were characterized by elemental analysis and SEM, as well as by FT-IR spectroscopy applying an attenuated total reflectance (ATR) method. The results of the elemental analysis showed that the functional group content in the PS-Cl-1, PS-Cl-3, and PS-Cl-4 did not differ from the values provided by the manufacturer. Two resins, PS-Cl-2 and PS-Cl-5, were found to contain slightly more functional groups than reported by the vendor.

Table 1. Types of applied resins and selected properties.

Resin	Loading (mmol Cl/g) a	DVB (%) b	DVB (%)	Practical Size (mesh)	Practical Size (μm)	FT-IR (ATR; cm^{-1})
PS-Cl-1	~5.5	5.5	5.5	16–50	297–1190	3023, 2921, 1611, 1511, 1443, 1421, 1264, 1111, 1019, 913, 823, 744, 672
PS-Cl-2	2.5–4.0	4.24	1	50–100	149–297	3025, 2920, 1602, 1510, 1493, 1451, 1421, 1265, 1111, 1019, 908, 823, 760, 699, 674
PS-Cl-3	3.5–4.5	3.94	1	100–200	74–149	3025, 2920, 1602, 1510, 1493, 1452, 1421, 1265, 1111, 1019, 909, 822, 760, 699, 673
PS-Cl-4	3.5–4.5	4.39	1	200–400	37–74	3024, 2919, 1602, 1510, 1493, 1451, 1421, 1264, 1111, 1019, 909, 823, 746, 700, 673
PS-Cl-5	2.0–2.5	2.78	2	200–400	37–74	3025, 2919, 1601, 1510, 1493, 1452, 1420, 1265, 1112, 1028, 907, 823, 757, 697, 676

^a given by the manufacturer; ^b based on elemental analysis: PS-Cl-1: %C: 74.41, %H: 6.14; PS-Cl-2: %C: 78.29, %H: 6.69; PS-Cl-3: %C: 79.34, %H: 6.70; PS-Cl-4: %C: 77.86, %H: 6.56; PS-Cl-5: %C: 83.08, %H: 7.05.

The FT-IR spectra allowed for identification of the deformation vibration bands ($\delta_{\text{C-Cl}}$) at approximately 1265 cm^{-1} and the bands corresponding to the stretching vibrations ($\nu_{\text{C-Cl}}$) at around 823 cm^{-1} , which are characteristic of the chloromethyl group (Table 1). The SEM analysis showed that the resins have a consistent circular grain shape within the size range specified by the manufacturer (Figures S1–S5). According to the procedure described in [24], trimellitic anhydride was first immobilized on a PS-Cl supports through formation of ester bonds, and in the second reaction step, the N-OH group was formed following a reaction with hydroxylamine hydrochloride (Scheme 2). The obtained heterogeneous catalysts PS-NHPI were characterized using FT-IR analysis (Figure 3, Figures S11–S14, Table 2), elemental analysis (Table 2), and SEM (Figures S6–S10).

Scheme 2. Immobilization of NHPI on chloromethyl polystyrene resin via an ester bond.

For example, characteristic bands are observed in the FT-IR spectrum of the PS-Cl-2 carrier (Figure 3, Table 1) at 3025, 2920, 1602, 1510, 1493, 1451, 1421, 1265, 1111, 1019, 908, 823, 760, 699, and 674 cm^{-1} . In the FT-IR spectrum of PS-NHPI-2 (Figure 3, Table 2) there is an additional a broad band at 3398 cm^{-1} corresponding to the stretching vibrations of the N-OH group (ν_{OH}), an intense band at 1720 cm^{-1} of the carbonyl groups' stretching vibrations ($\nu_{\text{C=O}}$), and a band at 1236 cm^{-1} , which is characteristic of the stretching vibration of a C-O single bond ($\nu_{\text{C-O}}$), thus confirming the presence of an ester group. Elemental analysis indicated the presence of nitrogen, which verifies the immobilization of NHPI on the support (Table 2). The amount of NHPI immobilized on the support ranged from 1.70 to 2.63 mmol/g.

Figure 3. FT-IR spectra of PS-Cl-2 (I) and PS-NHPI-2 (II).

Table 2. Elemental analysis and FT-IR characterization of obtained resin-immobilized NHPI catalysts.

Immobilized NHPI	Loading (mmol NHPI/g) ^a	Size ^b (μm)	Shape ^b	FT-IR (ATR; cm^{-1})
PS-NHPI-1	2.60	2–15	irregular	3397br, 2925, 1786, 1717, 1449, 1362, 1275, 1245, 1183, 1103, 1070, 962, 817, 770, 746, 709
PS-NHPI-2	2.63	149–297 20–170	spherical irregular	3398br, 2925, 1784, 1720, 1668, 1452, 1363, 1274, 1236, 1182, 1103, 1069, 817, 747, 701
PS-NHPI-3	2.13	74–149	spherical	3398br, 2925, 1788, 1721, 1601, 1452, 1361, 1274, 1235, 1182, 1110, 1069, 1018, 817, 747, 701
PS-NHPI-4	2.17	37–74	spherical	3439br, 2918, 1783, 1717, 1451, 1361, 1274, 1237, 1182, 1109, 818, 746, 701
PS-NHPI-5	1.70	37–74	spherical	3439br, 3025, 2917, 1785, 1723, 1601, 1492, 1452, 1373, 1278, 1246, 1182, 1108, 819, 748, 699

^a based on elemental analysis: PS-NHPI-1: %C: 68.97, %H: 5.73, %N: 3.64; PS-NHPI-2: %C: 72.42, %H: 6.34, %N: 3.68; PS-NHPI-3: %C: 73.83, %H: 6.48, %N: 2.98; PS-NHPI-4: %C: 71.12, %H: 6.12, %N: 3.05; PS-NHPI-5: %C: 79.49, %H: 6.41, %N: 2.38; ^b based on SEM analysis.

The SEM images (Figures S1 and S6) show that the macroporous PS-Cl-1 carrier undergoes mechanical degradation during the synthesis, and consequently, the NHPI-containing catalyst consists

of small, irregularly-shaped grains, approx. 2–15 μm in size. Similarly, in the case of the PS-NHPI-2 catalyst, the regular grains of the PS-Cl-2 polymer resin (149–297 μm) were partially degraded to irregularly-shaped grains in the size range of 20–170 μm (Figures S2 and S7). The PS-NHPI-3 catalyst grains underwent very little mechanical degradation, resulting in grain sizes of approx. 30–50 μm in diameter, as compared with the carrier grain sizes in the range of 74–149 μm (Figures S3 and S8). The sizes of the PS-NHPI-4 and PS-NHPI-5 catalyst grains corresponded closely to the grain sizes (37–74 μm) of the support resins, and their regular shape indicates that they did not undergo mechanical degradation (Figures S4, S5, S9 and S10).

The obtained PS-NHPI was coated with a layer of [emim][OcOSO₃] ionic liquid containing dissolved cobalt(II) chloride to form PS-NHPI@CoCl₂@[emim][OcOSO₃]. The ionic liquid was selected from a wide range of potential imidazolium ionic liquids based the research presented in [41] regarding SCILL systems containing NHPI immobilized on silica gel (Figure 1c). It was then shown that using [emim][OcOSO₃] gives the best results in terms of recycling the SCILL system.

2.2. Ethylbenzene Oxidation

We determined the effect of the developed five novel SCILL/SILP systems PS-NHPI@CoCl₂@[emim][OcOSO₃] on the oxidation of ethylbenzene with dioxygen at 80 °C, and compared it with the activity of the systems containing (i) PS-NHPI in combination with separately added CoCl₂ (PS-NHPI/CoCl₂), and (ii) PS-NHPI in combination with separately added CoCl₂ and [emim][OcOSO₃] (PS-NHPI/CoCl₂/[emim][OcOSO₃]) (Table 3). The blank experiment was also performed. CoCl₂ has limited solubility in ethylbenzene, which reduces the extent to which it leaches from the catalyst surface and dissolves in the reaction mixture. In the NHPI-catalyzed hydrocarbon oxidation reactions, Co(II) compounds participate in the generation of the PINO radical but also accelerate hydroperoxide decomposition. The oxidation reactions (carried out by all catalytic systems) resulted in the production of a mixture of unreacted ethylbenzene, ethylbenzene hydroperoxide (EBOOH), acetophenone (AP), and 1-phenylethanol (PEOH), as shown in Scheme 3.

Scheme 3. Ethylbenzene oxidation with dioxygen in the presence of PS-NHPI/CoCl₂ or PS-NHPI@CoCl₂@[emim][OcOSO₃].

All of the obtained heterogeneous PS-NHPI catalysts showed activity in the oxidation of ethylbenzene with dioxygen in the presence of CoCl₂ addition (Table 3, entries 5–9). Compared with the Co(II)-catalyzed reaction (Table 3, entry 4), the presence of PS-NHPI led to about a twofold increase in conversion (α). Among the catalysts immobilized on carriers with 1% DVB (Table 3, entries 6–8), the highest TON (8.2) was obtained with PS-NHPI-4. It was further determined that heterogeneous NHPI activity is influenced by the size of the catalyst grains, which vary as follows: PS-NHPI-2 (149–297 and 20–170 μm) > PS-NHPI-3 (74–149 μm) > PS-NHPI-4 (37–74 μm). As supported by the reactivity results, smaller grains likely provide a larger contact surface area between the catalyst active centers and the reactant. SEM images (Figures S2 and S7) showed that, during the synthesis of the PS-NHPI-2 catalyst, the PS-Cl-2 carrier (grain sizes: 149–297 μm) was partially mechanically degraded to irregularly-shaped grains with sizes of approx. 20–170 μm . However, the degradation probably did not increase the availability of the catalyst active sites, since higher ethylbenzene conversions were not recorded.

Table 3. Effect of the PS-NHPI/CoCl₂ and PS-NHPI@CoCl₂@IL systems on ethylbenzene oxidation.

Entry	Catalyst	Loading (mmol NHPI/g)	DVB in Resin (%)	PS-NHPI ^h		nO ₂ ⁱ (mmol)	α (%)	S _{EB} OOH (%)	S _{AP} (%)	S _{PEOH} (%)	TON ^j
				Size (μm)	Shape						
1	—	—	—	—	—	0.49	3.0	57.8	12.9	29.2	—
2 ^a	PS-NHPI-4	2.17	1	37–74	spherical	0.84	5.1	29.0	12.7	58.3	3.9
3 ^b	PS-NHPI-4@[emim][OcOSO ₃]	2.17	1	37–74	spherical	0.90	5.5	19.1	20.4	60.5	4.1
4 ^c	CoCl ₂	—	—	—	—	0.73	4.5	46.3	22.1	31.4	—
5 ^d	PS-NHPI-1/CoCl ₂	2.60	5.5	2–15	irregular	1.71	10.5	4.7	78.1	17.2	6.6
6 ^d	PS-NHPI-2/CoCl ₂	2.63	1	149–297 20–170	spherical irregular	1.55	9.5	18.7	50.4	30.9	5.9
7 ^d	PS-NHPI-3/CoCl ₂	2.13	1	74–149	spherical	1.18	7.2	23.2	45.1	31.7	5.5
8 ^d	PS-NHPI-4/CoCl ₂	2.17	1	37–74	spherical	1.78	10.9	1.8	64.8	33.4	8.2
9 ^d	PS-NHPI-5/CoCl ₂	1.70	2	37–74	spherical	1.31	8.0	14.4	53.3	32.3	7.7
10 ^e	PS-NHPI-1@CoCl ₂ @[emim][OcOSO ₃]	2.60	5.5	2–15	irregular	1.08	6.6	12.7	73.7	11.6	4.2
11 ^e	PS-NHPI-2@CoCl ₂ @[emim][OcOSO ₃]	2.63	1	149–297 20–170	spherical irregular	0.99	6.1	14.6	55.5	28.3	3.8
12 ^e	PS-NHPI-3@CoCl ₂ @[emim][OcOSO ₃]	2.13	1	74–149	spherical	0.96	5.9	10.6	67.9	20.3	4.5
13 ^e	PS-NHPI-4@CoCl ₂ @[emim][OcOSO ₃]	2.17	1	37–74	spherical	1.18	7.2	5.6	76.5	16.5	5.4
14 ^e	PS-NHPI-5@CoCl ₂ @[emim][OcOSO ₃]	1.70	2	37–74	spherical	1.08	6.6	10.3	63.9	25.8	6.3
15 ^f	CoCl ₂ /[emim][OcOSO ₃]	—	—	—	—	0.56	3.4	34.3	23.5	39.5	—
16 ^g	PS-NHPI-4/CoCl ₂ /[emim][OcOSO ₃]	2.17	1	37–74	spherical	1.13	6.9	23.3	35.7	40.0	5.2

Ethylbenzene (2 mL; 16.31 mmol), AIBN 0.1% mol, 80 °C, 6 h, 0.1 MPa O₂, 1200 rpm; ^a PS-NHPI 0.1 g; ^b PS-NHPI 0.1 g and [emim][OcOSO₃] 0.05 g dissolved in 5 mL acetone, stirred for 3 h, then the acetone was evaporated; ^c CoCl₂ 0.0021 g; ^d PS-NHPI 0.1 g, CoCl₂ 0.0021 g (0.1 mol% vs. ethylbenzene); ^e PS-NHPI 0.1 g, CoCl₂ 0.0021 g, [emim][OcOSO₃] 0.05 g dissolved in 5 mL acetone, stirred for 3 h, then the acetone was evaporated; ^f CoCl₂ 0.0021 g, [emim][OcOSO₃] 0.05 g; ^g PS-NHPI 0.1 g, CoCl₂ 0.0021 g, [emim][OcOSO₃] 0.05 g; ^h based on SEM analysis;

ⁱ nO₂ = O₂ consumed; ^j TON = $\frac{n_{O_2}}{n_{NHPI}} \frac{mmol}{mmol}$.

The results presented in Table 3 illustrate that higher content of the DVB cross-linker leads to lower TONs (entries 5,8,9). Similar results were obtained in [24], where the authors determined that higher DVB content may hinder the reagent's access to the catalytic active centers. Accordingly, the lowest TON (6.6) calculated in this study was recorded for the PS-NHPI-1 catalyst, which had the highest DVB content.

In terms of the PS-NHPI/CoCl₂ systems (Table 3, entries 5–9), mixtures of ethylbenzene hydroperoxide, acetophenone, and 1-phenylethanol products were obtained, with a preference toward ketone production (selectivity from 45.1% to 78.1%). For the PS-NHPI-4 and PS-NHPI-5 catalysts, which were characterized by a regular grain shape and a similar size (see Figures S9 and S10), the presence of a greater amount of cross-linking agent allowed higher selectivity (by approx. 12%) toward production of ethylbenzene hydroperoxide. This may indicate a reduction in the contact between the hydroperoxide and CoCl₂ due to weaker binding of the cobalt(II) salt to the catalyst surface.

Next, the influence of the [emim][OcOSO₃] ionic liquid layer on the activity of studied systems was determined. First, we observed that coating the most active heterogeneous catalyst PS-NHPI-4 with a layer of [emim][OcOSO₃] ionic liquid barely affected its activity (Table 3, entries 2,3). The similar conversions of ethylbenzene (approx. 5%) carried out in these two cases suggest that the ionic liquid does not limit the contact between the reactant and the active centers of the NHPI catalyst (i.e., –NOH groups). However, the addition of [emim][OcOSO₃] caused a slight decrease in selectivity toward ethylbenzene hydroperoxide (from 29.0% to 19.1%) and an increase in selectivity toward acetophenone (from 12.7% to 20.4%). Based on Figure 4, the oxidation reactions performed by the PS-NHPI-4 and PS-NHPI-4@[emim][OcOSO₃] systems followed very similar trajectories. A different relationship was observed in our previous work [41], which discussed ethylbenzene oxidation by a system containing a heterogeneous NHPI catalyst immobilized on silica gel (SiOCONHPI; Figure 1c). Specifically, covering the SiOCONHPI catalyst with the ionic liquid, [bmim][OcOSO₃], caused a decrease in the conversion of ethylbenzene, from 8.6 to 6.1%.

Figure 4. The reaction evolution of ethylbenzene oxidation with dioxygen in the presence of PS-NHPI-4 and PS-NHPI-4@[emim][OcOSO₃].

The results demonstrate that coating PS-NHPI-4 with a layer of [emim][OcOSO₃] containing CoCl₂ leads to increase ethylbenzene conversion (Table 3, entries 2,3,13). However, the conversion and TON decrease, as compared to the conversion observed for the analogous PS-NHPI-4/CoCl₂ system (Table 3, entries 8,13). For the PS-NHPI-2, PS-NHPI-3, and PS-NHPI-5 catalysts (Table 3, entries 6, 7, 9 and 11, 12, 14), the presence of an ionic liquid caused a decrease in selectivity toward ethylbenzene hydroperoxide production. For PS-NHPI-2, PS-NHPI-3, PS-NHPI-4, and PS-NHPI-5 (Table 3, entries 6–9 and 11–14), addition of the ionic liquid led to increased selectivity toward production of acetophenone.

A particularly significant increase in selectivity toward ketone production was observed as a result of ionic liquid addition in the systems containing PS-NHPI-3, PS-NHPI-4, and PS-NHPI-5 catalysts (Table 3, entries 7–9 and 12–14). These catalysts are characterized by essentially regular grain sizes even after NHPI binding (Figures S8–S10). The relatively lower selectivities toward hydroperoxide production, in favor of ketone production, obtained for these SCILL/SILP systems may result from the higher CoCl_2 concentration in the IL layer, which promotes better contact between the co-catalyst and the EBOOH oxidation product. Selectivities comparable to those reported here for acetophenone production (~70%) were reported for the oxidation of ethylbenzene with dioxygen (0.1 MPa) in the presence of stearate and a Co(II) acetylacetonate catalyst, which had high solubility in the reaction mixture at 80 °C [42]. For comparison, as part of this study, the ethylbenzene oxidation reaction was carried out using PS-NHPI-3 and CoCl_2 in benzonitrile, and the products obtained were acetophenone ($S_{\text{AP}} = 66.7\%$), 1-phenylethanol ($S_{\text{PEOH}} = 26.2\%$), and ethylbenzene hydroperoxide ($S_{\text{EBOOH}} = 7.1\%$). These results indicate that the addition of an ionic liquid makes the heterogeneous catalyst similar to a homogeneous catalyst. This is an important aspect of the SILP technique, which involves covering the inert carrier with an ionic liquid that contains dissolved forms of the transition metal catalyst [32].

Employing a catalytic system consisting of three separately introduced components (PS-NHPI-4, CoCl_2 , and $[\text{emim}][\text{OcOSO}_3]$; i.e., the PS-NHPI-4/ CoCl_2 /[emim][OcOSO₃] system described in Table 3 (entry 16) for the oxidation reaction led to 6.9% ethylbenzene conversion. This was a similar result to that obtained with the analogous integrated system, PS-NHPI-4@ CoCl_2 @[emim][OcOSO₃] (7.2%; entry 13), although the composition of the product mixture differed significantly between the two cases. Specifically, much greater amounts of ethylbenzene hydroperoxide ($S_{\text{EBOOH}} = 23.3\%$) and 1-phenylethanol ($S_{\text{PEOH}} = 40.0\%$) products were obtained using the PS-NHPI-4/ CoCl_2 /[emim][OcOSO₃] system. This is most likely due to the poor solubility of CoCl_2 and [emim][OcOSO₃] in the ethylbenzene reagent, and the resulting formation of a separate IL phase, which was observed in the CoCl_2 /[emim][OcOSO₃]-catalyzed reaction. The ionic liquid can partially dissolve CoCl_2 , which is poorly soluble in ethylbenzene, thus hindering the contact between the reaction products (including hydroperoxide) and the active centers of PS-NHPI-4, as indicated by the decrease in its ethylbenzene conversion compared to the PS-NHPI-4/ CoCl_2 system.

The higher selectivities toward acetophenone production observed for the SCILL/SILP systems may also result from a solvent “cage” effect. The ionic liquid, which acts as a solvent, surrounds the alkoxy radical ($\text{Ph-CH}(\text{O}\cdot)\text{-CH}_3$) formed in the reaction and limits the possibility of its exit from the “cage” to react with ethylbenzene to form 1-phenylethanol. At the same time, this phenomenon favors the reaction to cleave the alkoxy radical into a ketone. For example, studies on the influence of the solvent properties on the initiation efficiency have shown that a solvent with higher viscosity provides less opportunity for radicals to leave the “cage”, which lowers the initiator efficiency [43]. Like most ionic liquids, [emim][OcOSO₃] is characterized by a higher viscosity than classic organic solvents [44], therefore the “cage” effect may influence the course of the reaction.

Reuse of both the PS-NHPI/ CoCl_2 and PS-NHPI@ CoCl_2 @[emim][OcOSO₃] catalytic systems were attempted, such that, after the completion of the ethylbenzene oxidation process, the reaction mixture was decanted and the catalyst was washed with hexane and dried. Then, a fresh batch of ethylbenzene and new AIBN were introduced. The results obtained over at least 3 reaction cycles are summarized in Table 4.

Attempts to recycle the PS-NHPI/ CoCl_2 systems (Table 4, entries 1–16) revealed that their activity gradually decreases in subsequent cycles, with the slowest decrease occurring in the case of PS-NHPI-5. As a result, in the 3rd reaction cycle using PS-NHPI-2/ CoCl_2 , PS-NHPI-3/ CoCl_2 , and PS-NHPI-4/ CoCl_2 , and in the 4th cycle using PS-NHPI-5/ CoCl_2 , these systems achieve an overall conversion similar to that obtained by PS-NHPI-4 alone in its first cycle (5.1%; shown for comparison in entry 33). The observed decrease in activity was likely related to the gradual removal of CoCl_2 (which was not physically bound to the PS-NHPI) with the reaction products. Despite the poor solubility of CoCl_2 in ethylbenzene, the polarity of the organic phase increased as the reaction progressed due to the

generation of polar products, which suggests that some of the CoCl_2 was dissolved in the organic phase during the reaction, and then was decanted during the separation of the catalyst. As a result, the concentration of CoCl_2 was lower and lower in each subsequent reaction cycle. This concept is supported by the observed concomitant increase in selectivities toward ethylbenzene hydroperoxide, because the Co(II) compounds would otherwise accelerate the decomposition of the EBOOH to AP and PEOH. Comparative analysis of the course of the ethylbenzene oxidation reaction, as carried out by the PS-NHPI-4/ CoCl_2 system in three consecutive reaction cycles, showed that the activity of reused PS-NHPI-4/ CoCl_2 (i.e., in the 2nd and 3rd cycles) was similar to PS-NHPI-4 alone in the 1st cycle (Figure 5).

Another important aspect to consider in the analysis is the stability of the various PS-NHPI catalyst systems. The ester bond formed between the NHPI catalyst and the support can be decomposed. Comparing the FT-IR spectra (Figure 6) of the PS-NHPI-2 catalyst before the reaction to the PS-NHPI-2/ CoCl_2 system after the 3rd reaction cycle confirms the stability of the catalyst. The presence of a wide band at 3373 cm^{-1} (ν_{OH}) indicates the presence of the N-OH group, the intense band at around 1716 cm^{-1} ($\nu_{\text{C=O}}$) is evidence of carbonyl groups, and the band at around 1236 cm^{-1} ($\nu_{\text{C-O}}$) confirms the presence of an ester group.

Table 4. Recovery and recycling of PS-NHPI/ CoCl_2 and PS-NHPI@ CoCl_2 @IL systems.

Entry	Cycle	Catalyst	Loading (mmol NHPI/g)	DVB in resin (%)	PS-NHPI Size ^c (μm)	PS-NHPI Shape ^e	α (%)	SEBOOH (%)	S _{AP} (%)	S _{PEOH} (%)
1 ^a	1	PS-NHPI-1/ CoCl_2	2.60	5.5	2–15	irregular	10.5	4.7	78.1	17.2
2	2						7.8	13.6	54.3	32.0
3	3						6.5	26.8	40.5	32.7
4 ^a	1	PS-NHPI-2/ CoCl_2	2.63	1	149–297 20–170	spherical irregular	9.5	18.7	50.4	30.9
5	2						6.2	37.8	36.1	26.1
6	3						4.6	40.5	35.4	24.1
7 ^a	1	PS-NHPI-3/ CoCl_2	2.13	1	74–149	spherical	7.2	23.2	45.1	31.7
8	2						7.1	28.7	36.7	34.6
9	3						4.3	35.3	38.5	26.2
10 ^a	1	PS-NHPI-4/ CoCl_2	2.17	1	37–74	spherical	10.9	1.8	64.8	33.4
11	2						5.9	31.1	39.2	29.7
12	3						4.2	45.7	30.3	24.0
13 ^a	1	PS-NHPI-5/ CoCl_2	1.70	2	37–74	spherical	8.0	14.4	53.3	32.3
14	2						6.1	15.6	50.6	32.5
15	3						7.2	13.4	49.8	36.8
16	4						5.8	19.1	45.3	35.6
17 ^b	1	PS-NHPI-1@ CoCl_2 @[emim][O ₂ SO ₃]	2.60	5.5	2–15	irregular	6.6	12.7	73.7	11.6
18	2						6.1	13.2	71.2	15.6
19	3						5.2	18.5	69.4	10.3
20 ^b	1	PS-NHPI-2@ CoCl_2 @[emim][O ₂ SO ₃]	2.63	1	149–297 20–170	spherical irregular	6.1	14.6	55.5	28.3
21	2						5.8	18.9	49.5	30.7
22	3						5.4	19.3	50.6	30.1
23 ^b	1	PS-NHPI-3@ CoCl_2 @[emim][O ₂ SO ₃]	2.13	1	74–149	spherical	5.9	10.6	67.9	20.3
24	2						5.7	9.0	68.0	22.5
25	3						5.4	10.9	66.2	22.4
26 ^b	1	PS-NHPI-4@ CoCl_2 @[emim][O ₂ SO ₃]	2.17	1	37–74	spherical	7.2	5.6	76.5	16.5
27	2						6.5	7.6	70.5	21.1
28	3						6.7	7.1	63.9	28.4
29 ^b	1	PS-NHPI-5@ CoCl_2 @[emim][O ₂ SO ₃]	1.70	2	37–74	spherical	6.6	10.3	64.1	25.6
30	2						6.1	11.9	57.7	30.4
31	3						5.6	13.5	54.5	32.0
32 ^c	1	CoCl_2	–	–	–	–	4.5	46.3	22.1	31.4
33 ^d	1	PS-NHPI-4	2.17	1	37–74	spherical	5.1	29.0	12.7	58.3

Ethylbenzene 2 mL, AIBN 0.1% mol, 80 °C, 6 h, 0.1 MPa O_2 , 1200 rpm; ^a PS-NHPI 0.1 g, CoCl_2 0.0021 g; ^b PS-NHPI 0.1 g, CoCl_2 0.0021 g, [emim][O₂SO₃] 0.05 g was dissolved in 5 mL acetone, stirred for 3 h, then the acetone was evaporated; ^c CoCl_2 0.0021 g; ^d PS-NHPI-4 0.1 g; ^e based on SEM analysis.

Figure 5. The course of ethylbenzene oxidation with dioxygen in the presence of PS-NHPI-4 and the PS-NHPI-4/CoCl₂ system reused in three successive reaction cycles.

Figure 6. FT-IR spectra of fresh PS-NHPI-2 (I) and PS-NHPI-2/CoCl₂ after the 3rd cycle (II).

The results presented in Table 4, entries 17–31, illustrate that it is possible to recycle the PS-NHPI@CoCl₂@[emim][O₂SO₃] systems while suffering only a slight decrease in overall catalytic activity and selectivity toward acetophenone production. For example, the conversions achieved by PS-NHPI-3@CoCl₂@[emim][O₂SO₃] decreased from 5.9% > 5.7% > 5.4%, in the 1st, 2nd, and 3rd reaction cycles, respectively. The system's selectivity toward producing acetophenone over those three cycles remained essentially constant, and it was as high as 66.2% in the third reaction cycle. None of the PS-NHPI@CoCl₂@[emim][O₂SO₃] systems showed the significant increase in selectivity toward ethylbenzene hydroperoxide in subsequent reaction cycles, as was observed for the PS-NHPI/CoCl₂ systems without IL. The obtained results suggest significantly limited elution of CoCl₂ from the IL layer,

which indicates greater potential for recycling and reusing SCILL/SILP systems. Analyzing the course of the ethylbenzene oxidation reaction carried out by the PS-NHPI-4@CoCl₂@[emim][OcOSO₃] system over three reaction cycles showed no significant differences in the oxidation rate during subsequent cycles (Figure 7).

Comparison of the FT-IR spectra recorded for the PS-NHPI-4 and PS-NHPI-4@CoCl₂@[emim][OcOSO₃] catalysts before the reaction and for the PS-NHPI-4@CoCl₂@[emim][OcOSO₃] catalyst after the 3rd reaction cycle is presented in Figure 8. As expected, the FT-IR spectrum of the PS-NHPI-4@CoCl₂@[emim][OcOSO₃] system has bands indicating the presence of PS-NHPI-4, including one characteristic of the OH group (ν_{OH}) at about 3449 cm⁻¹ and one typical carbonyl stretching band ($\nu_{\text{C=O}}$) at 1720 cm⁻¹. The bands at about 1234 and 1573 cm⁻¹ are evidence presence of the ionic liquid (see Figure S15). The very strong, broad band at around 1234 cm⁻¹ presumably corresponds to also the ester stretching vibrations ($\nu_{\text{C-O}}$) in PS-NHPI-4. The FT-IR spectrum of the PS-NHPI-4@CoCl₂@[emim][OcOSO₃] system acquired after the third reaction cycle contains bands confirming the presence of PS-NHPI-4, intensive of the hydroxyl group stretching vibration bands (ν_{OH}) at about 3243 cm⁻¹ and the carbonyl stretching band ($\nu_{\text{C=O}}$) at 1713 cm⁻¹. The bands observed at 1574 and 1237 cm⁻¹ indicate the presence of the ionic liquid (Figure S15), while the new, very strong band at 1086 cm⁻¹ ($\nu_{\text{C-O}}$) indicates that the PEOH (Figure S16) product was not completely washed off of the surface of the recycled catalyst.

In order to unequivocally confirm the presence of the ionic liquid in the recycled PS-NHPI-4@CoCl₂@[emim][OcOSO₃], thermogravimetric analysis (TGA) was conducted (Figure 9) to compare the fresh PS-NHPI-4@CoCl₂@[emim][OcOSO₃] catalyst, with that which was separated after three reaction cycles. The analysis revealed that, in both cases, a weight loss of approx. 71% (from 95% to 24%) was observed over the temperature range from 200–500 °C. This confirms the presence of an ionic liquid on the catalyst surface and excludes the idea that the IL gets washed away during the catalyst recycling process. Therefore, we suppose that the slight decrease in the activity of the studied catalysts may be caused by the absorption of polar products in the IL layer. This may influence the activity of the catalytic system, e.g., by influencing the solubility of the substrate in the IL layer.

Figure 7. The course of ethylbenzene oxidation with dioxygen in the presence of PS-NHPI-4@CoCl₂@[emim][OcOSO₃] over three reaction cycles, as compared to the 3rd cycle using only PS-NHPI-4/CoCl₂.

Figure 8. FT-IR spectra of PS-NHPI-4 (I), PS-NHPI-4@CoCl₂@[emim][OcOSO₃] (as-prepared, before any oxidation reaction) (II), and PS-NHPI-4@CoCl₂@[emim][OcOSO₃] after the 3rd reaction cycle (III).

Figure 9. TGA curves obtained for fresh PS-NHPI-4@CoCl₂@[emim][OcOSO₃] and PS-NHPI-4@CoCl₂@[emim][OcOSO₃] after the 3rd reaction cycle.

3. Materials and Methods

3.1. Materials

Ethylbenzene (Acros 99.8%, Geel, BE) was purified by washing with H₂SO₄ and vacuum distillation. All chemicals were purchased from commercial sources. Solvents were purified and dried with standard methods. Chloromethyl polystyrene resins (PS-Cl) were supplied by Sigma Aldrich (St. Louis, MO, USA).

3.2. PS-NHPI Synthesis

PS-NHPI catalysts were synthesized following the procedure described in [24] (see Table 5 for details). Each chloromethyl polystyrene resin was first swollen in 1,4-dioxane. Next, the trimellitic anhydride (TA) and triethylamine (Et₃N) were added. The reaction was allowed to proceed under reflux for 48 h. The product was filtered and washed at 50 °C with H₂O (2 × 25 mL), MeOH (2 × 25 mL), THF (4 × 25 mL), and CH₂Cl₂ (2 × 25 mL), and dried under vacuum. Immobilized TA was added to a (3:1, v/v) solvent mixture of pyridine:1,2-dichloroethane, followed by the addition of hydroxylamine hydrochloride. The mixture was stirred for 24 h at 75 °C. The product (PS-NHPI) was filtered and washed at RT with H₂O (2 × 25 mL), H₂O:MeOH (1:1, v/v; 1 × 25 mL), and then at 50 °C with MeOH (2 × 25 mL), DMF (2 × 25 mL), THF (2 × 25 mL), and CH₂Cl₂ (2 × 25 mL), and finally dried under vacuum. (Volume of solvents are given per 1 g of resin.)

Table 5. Quantities of reagents used in NHPI immobilization on chloromethyl polystyrene resins.

Resin	Loading (mmol Cl/g)	Amount of resin (g)	TA (mmol)	Et ₃ N (mmol)	Dioxane (mL)	NH ₂ OH·HCl (mmol)	Pyridine: C ₂ H ₄ Cl ₂ (mL)	Immobilized NHPI	Amount of immobilized NHPI (g)
PS-Cl-1	5.5	2	44	110	60	110	220	PS-NHPI-1	3.34
PS-Cl-2	2.5–4.0	2	32	80	60	80	160	PS-NHPI-2	3.42
PS-Cl-3	3.5–4.5	2	36	90	60	135	270	PS-NHPI-3	4.68
		1	18	45	30				
PS-Cl-4	3.5–4.5	2	36	90	60	90	180	PS-NHPI-4	3.10
PS-Cl-5	2.0–2.5	2	20	50	60	50	100	PS-NHPI-5	1.86

3.3. PS-NHPI@CoCl₂@[emim][OcOSO₃] Preparation

Catalysts PS-NHPI@CoCl₂@[emim][OcOSO₃] were prepared analogously to the procedure described in [37]. The ionic liquid (0.05 g), heterogeneous NHPI (PS-NHPI; 0.1 g), and CoCl₂ (0.0021 g; 0.1 mol% relative to ethylbenzene) were introduced into a two-neck flask. Approximately 5 mL of acetone was added, and the flask was placed on a magnetic stirrer and stirred for 3 h, before the acetone was removed using a rotary evaporator.

3.4. General Procedure for Ethylbenzene Oxidation

The oxidation reactions were performed in a gasometric apparatus (Figure S17), as described in [45]. Ethylbenzene, AIBN, and the appropriate catalyst were placed in a 10 mL flask connected to a gas burette filled with dioxygen under atmospheric pressure. The oxygen uptake (n_{O₂}) was measured and recalculated for normal conditions (273 K, 1 atm), and this value was used to calculate the total ethylbenzene conversion (α) using the equations given below:

$$n_{O_2} = \frac{V_{O_2} \cdot 273 \cdot p}{101325 \cdot 22.415 \cdot T} \text{ (mol)} \quad (1)$$

$$\alpha = \frac{n_{O_2}}{n} \cdot 100\% \quad (2)$$

The quantity of ethylbenzene hydroperoxide (EBOOH) produced was determined iodometrically according to the method described in [46], and the result was used to calculate the reaction selectivity (S_{EBOOH}) using the equation below:

$$S_{EBOOH} = \frac{n_{OOH}}{n_{O_2}} \cdot 100\% \quad (3)$$

EBOOH is thermally unstable and easily decomposes to 1-phenylethanol (PEOH) and/or acetophenone (AP). Thus, before GC analysis, the hydroperoxide was quantitatively reduced to PEOH by adding triethyl phosphite ((EtO)₃P), which gets oxidized to triethyl phosphate ((EtO)₃PO) [47]. The quantity of PEOH measured by GC was equal to the sum of the alcohol and hydroperoxide formed. In order to calculate the PEOH selectivity, we simply subtracted the amount of ethylbenzene hydroperoxide that was determined independently by iodometric analysis. The quantity and selectivity related to acetophenone were determined based on analogous GC analysis.

3.5. Analytic Methods

Infrared spectra (IR) were recorded on a Nicolet 6700 FT-IR Spectrometer (Thermo Scientific, Madison, WI, USA), using the Attenuated Total Reflectance (ATR) technique. Thermogravimetric analysis (TGA) was performed using a TGA851e thermobalance (Mettler Toledo, Greifensee, Switzerland). Samples of approximately 10 mg were heated from 25 °C to 900 °C at a rate of 10 °C/min in standard 70 µL Al₂O₃ crucibles under a dynamic nitrogen flow of 60 mL/min (99.9992%). Scanning electron microscopy (SEM) images were obtained with a Phenom Pro desktop SEM instrument equipped with an EDS detector (15 kV). Gas chromatography analysis (GC) was performed using an Agilent Technologies 7890 C (Agilent Technologies, Santa Clara, CA, USA) gas chromatograph (Zebtron ZB-5HT capillary column) with an FID detector and *p*-methoxytoluene as the internal standard. Elemental analysis (EA) was carried out using a Thermo Scientific FlashSmart elemental analyzer (Thermo Fisher Scientific, Waltham, MA, USA).

4. Conclusions

In this study, a series of new, efficient catalytic systems of the general form, PS-NHPI@CoCl₂@[emim][O₂SO₃], which embody a combination of SCILL and SILP techniques, were used for ethylbenzene oxidation reactions. In order to prepare these systems, five heterogeneous chloromethyl polystyrene-NHPI (PS-NHPI) catalysts, differing in particle size distribution and content of the cross-linking agent, were synthesized by immobilizing the NHPI on the polymer supports. The obtained heterogeneous catalysts were characterized by SEM, FT-IR, and elemental analysis, and then were covered with the ionic liquid, [emim][O₂SO₃], which contained dissolved CoCl₂. The ethylbenzene oxidation capabilities and outcomes obtained by the prepared PS-NHPI@CoCl₂@[emim][O₂SO₃] systems were compared with the systems composed of heterogeneous PS-NHPI and CoCl₂ (PS-NHPI/CoCl₂) or IL (PS-NHPI/IL) added separately to the reaction mixture. Ethylbenzene was selected as a model hydrocarbon, and the reactions were carried out using dioxygen under atmospheric pressure.

We showed that PS-NHPI catalysts exhibit catalytic activity for ethylbenzene oxidation using dioxygen in the presence of CoCl₂. Compared to the CoCl₂ reference reaction, they performed with a twofold increase in conversion, from about 4% to about 7–11%. Attempts to recycle PS-NHPI/CoCl₂ catalysts revealed that the systems' catalytic activities gradually decrease in each successive cycle, due to the removal of CoCl₂ with the reaction products.

Covering the PS-NHPI-4 catalyst with the [emim][O₂SO₃] ionic liquid layer did not affect the catalytic activity of immobilized NHPI. For example, both the PS-NHPI-4 and PS-NHPI-4@[emim][O₂SO₃] achieved conversions around 5%. This indicates that the ionic liquid covering PS-NHPI does not limit the contact between the reactants and the active centers of the catalyst, as is often observed in SCILL systems [38,39,41].

The integrated PS-NHPI@CoCl₂@[emim][O₂SO₃] systems constructed using a combination of SCILL and SILP techniques showed increased acetophenone selectivity, but decreased ethylbenzene conversion, compared with the systems where PS-NHPI and CoCl₂ were added separately. The higher selectivities toward ketone production and lower selectivities toward ethylbenzene hydroperoxide observed for the SCILL/SILP systems may result from the higher CoCl₂ concentration in the IL layer, which promotes better contact between the co-catalyst and the products, including ethylbenzene hydroperoxide. The relatively high viscosity of the ionic liquid [44] also likely influences the course of the reaction due to the solvent “cage” effect [43]. Based on the results presented herein, it is possible to recycle the PS-NHPI@CoCl₂@[emim][O₂SO₃] systems with only a slight decrease in the activity and selectivity to acetophenone observed in successive reaction cycles. The ionic liquid layer significantly reduces the leaching of CoCl₂, which leads to better recyclability and reuse options than for the PS-NHPI/CoCl₂ systems.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4344/10/12/1367/s1>, Figures S1–S5: SEM images of the PS-Cl resins; Figures S6–S10: SEM images of the PS-NHPI catalysts; Figure S11: FT-IR spectra of PS-Cl-1 and PS-NHPI-1; Figure S12: FT-IR spectra of PS-Cl-3 and PS-NHPI-3; Figure S13: FT-IR spectra of PS-Cl-4 and PS-NHPI-4; Figure S14: FT-IR spectra of PS-Cl-5 and PS-NHPI-5; Figure S15: FT-IR spectra of [emim][O₂SO₃]; Figure S16: FT-IR spectra of 1-phenylethanol; Figure S17: gasometric apparatus.

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