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N-Hydroxyphthalimide Supported on Silica Coated with Ionic Liquids Containing $CoCl_2$ (SCILLs) as New Catalytic System for Solvent-Free Ethylbenzene Oxidation

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Abstract: *N*-Hydroxyphthalimide was immobilized via ester bond on commercially available silica gel (SiOCONHPI) and then coated with various ionic liquids containing dissolved $CoCl_2$ (SiOCONHPI@$CoCl_2$@IL). New catalysts were characterized by means of FT IR spectroscopy, elemental analysis, SEM and TGA analysis and used in ethylbenzene oxidation with oxygen under mild solvent-free conditions (80 °C, 0.1 MPa). High catalytic activity of SiOCONHPI was proved. In comparison to a non-catalytic reaction, a two-fold increase in conversion of ethylbenzene was observed (from 4.7% to 8.6%). Coating of SiOCONHPI with [bmim][$OcOSO_3$], [bmim][Cl] and [bmim][CF_3SO_3] containing $CoCl_2$ enabled to increase the catalytic activity in relation to systems in which IL and $CoCl_2$ were added directly to reaction mixture. The highest conversion of ethylbenzene was obtained while SiOCONHPI@$CoCl_2$@[bmim][$OcOSO_3$] were used (12.1%). Catalysts recovery and reuse was also studied.

Keywords: oxidation; *N*-hydroxyphthalimide; immobilization; ionic liquids; SCILL

1. Introduction

Hydrocarbon oxidation processes play an important role in organic synthesis and industrial processes. Processes which use oxygen or air as an oxidizing factor often require the use of suitable catalytic systems. The most commonly used ones include compounds of transition metals, such as Co and Mn [1,2]. High activity of *N*-hydroxyphthalimide (NHPI) has also been proved in reactions of this kind [3–5]. Its catalytic activity is attributed to a PINO radical generated in the system, which abstracts a hydrogen atom from oxidized hydrocarbon, from 2 to 20 times faster than peroxyl radicals in an autocatalytic process [3] (Figure 1). PINO is generated by various additives, e.g., azo compounds, peroxides, transition metals salts, aldehydes, and quinones and its derivatives [6].

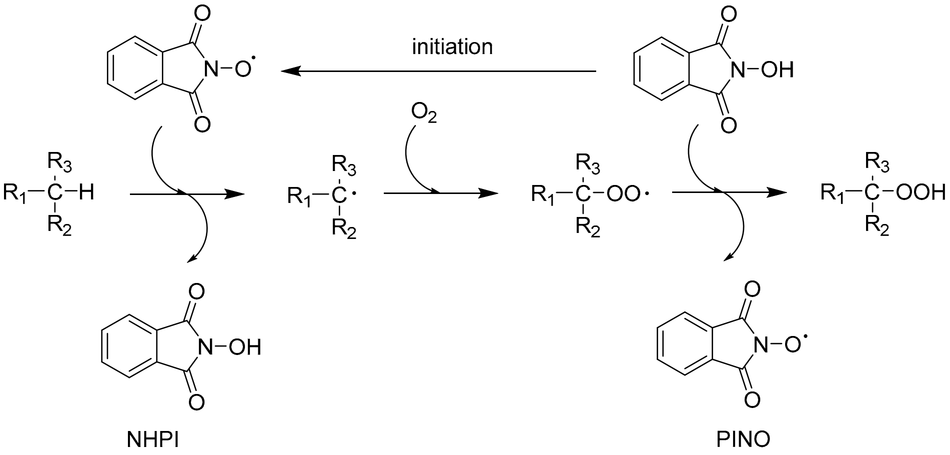

Figure 1. Mechanism of hydrocarbons oxidation using *N*-hydroxyphthalimide (NHPI).

The advantage of NHPI is its availability, low price, and a simple method of its synthesis from phthalic anhydride and hydroxylamine [3]. Because of its poor solubility in hydrocarbons, the processes are usually carried out in polar solvents, e.g., in acetic acid [7], acetonitrile [8], or benzonitrile [9]. The use of compressed CO_2 [10–12] and ionic liquids [11,13–18] has also been reported. In order to use NHPI in industrial processes, it is necessary to develop efficient methods of its recovery and reuse. NHPI separation by evaporation of organic solvent [8,19] or CO_2 has been described in literature [10,11]. However, this simple method may prove to be ineffective, if the product of the reaction will be characterized by high polarity and related good solubility of NHPI. Therefore, there were attempts to immobilize NHPI on solid carriers: Silicas [20,21], polymers [22–25], and zeolites [26]. As an example, Hermans [20] et al., in the process of oxidation of cyclohexane, used NHPI immobilized by simple impregnation on silica gel. Attempts of heterogeneous NHPI reuse, proved that the activity of catalyst in the first cycle drops down twofold, but in the following two cycles it is maintained at a constant level. In the work [21], in the reactions of toluene oxidation in acetic acid as a solvent, NHPI immobilized on silica via amide bond was used. It was proven that it is possible to reuse heterogeneous NHPI with only a slight decrease in activity. In our work [22] the results of oxidation of *p*-methoxytoluene with oxygen, Co(II) salt, and NHPI immobilized via amide bond on aminomethyl polystyrene or via ester bond on a chloromethyl polystyrene, were discussed. We proved that two-fold recovery and reuse of catalysts is possible. Examples of use of NHPI immobilized in ionic liquids was also described [17,18]. NHPI was incorporated into the structure of imidazolium [17] cation and pirydinium [18] cation. The catalysts belong to the so called task-specific ionic liquids, compounds built of ionic liquid with an introduced functional group with specific properties [27], in this case—NHPI (Figure 2). They were used in the processes of oxidation of 1-phenylethanol [17], *N*-alkylamides, and various benzylic hydrocarbons [18]. The authors of [17] claim that IL-NHPI has higher activity than NHPI. For example, acetophenone was obtained in 98% yield in the presence of IL-NHPI, after two hours, and in 93% yield with NHPI, after six hours. It is also possible to use IL-NHPI five times without decrease in activity.

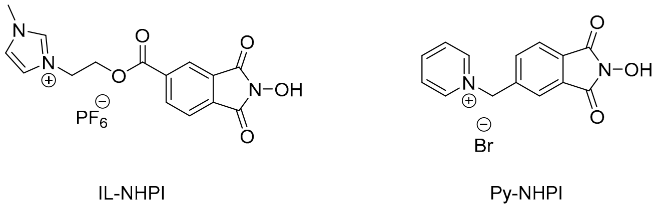

Figure 2. NHPI immobilized in ionic liquids.

Heterogenization of catalysts, is often related to the decrease in their activity. Recently, in order to minimize or even to eliminate this problem, studies on supported catalysts with ionic liquid layer (SCILL) have been undertaken [28,29]. In this case, heterogeneous catalysts, not inert support as in the case of the supported ionic liquid phase (SILP) catalysis [30–32], are coated with ionic liquids. It was confirmed that ionic liquid can positively influence properties of catalyst (cocatalytic effect) and may cause an increase in concentration of substrates or intermediate products on its surface, because of ionic properties of ionic liquid phase (solvent effect) [29]. However, it is important that the organic phase and ionic liquid compose biphasic system, otherwise IL film will be washed out from a catalyst [28,29]. SCILL method has been already used in hydrogenation [33–35] and oxidation [36,37] processes. Karimi and Badreh [36], in the oxidation reactions of a great variety of alcohols, used a system composed of TEMPO chemically bonded to silica SBA-15 coated with ionic liquid [bmim][Br]. Catalyst IL@SBA-15-TEMPO showed higher activity than not modified by ionic liquid SBA-15-TEMPO. In addition, it was possible to obtain 11-fold recycling values of this catalyst without loss in activity. In a similar system, a catalyst composed of TEMPO immobilized on a polymer support coated with ionic liquid [bmim][PF_6], containing $CuCl_2$, was used in oxidation reactions of 4-methoxybenzyl alcohol [37]. In oxidation process carried out in the presence of this catalyst, a significantly higher conversion of alcohol was acquired (85%) than in the presence of the same catalyst without ionic liquid (58%). However, catalyst recycling attempts showed that the activity of this catalyst drops down insignificantly, together with every reaction cycle, what results from washing out [bmim][PF_6] from the support surface.

Herein, NHPI was immobilized via ester bond on silica (SiOCONHPI), which was coated with a layer of ionic liquid containing dissolved $CoCl_2$ salt (SiOCONHPI@$CoCl_2$@IL). To the best of our knowledge, both catalysts have not been previously described. Consequently, catalytic activity of SiOCONHPI as well as SCILL system was examined for the first time, in oxidation reaction using oxygen. The influence of the type of ionic liquid on activity of the system and a possibility of recovery and reuse was determined. In the previous work [38] it was proved that selected ionic liquid, used in catalytic amounts, can positively influence the hydrocarbons oxidation process using NHPI/Co(II) system without solvent additive.

2. Results and Discussion

2.1. Preparation of Catalyst

2.1.1. SiOCONHPI Synthesis

Immobilization of NHPI was carried out on commercially available silica. For that purpose, in accordance with the procedure described for polymer support [22], in the first stage, trimellitic anhydride was immobilized on chloropropyl-functionalized silica gel via ester bond and consequently it underwent the reaction with hydroxylamine hydrochloride (Figure 3).

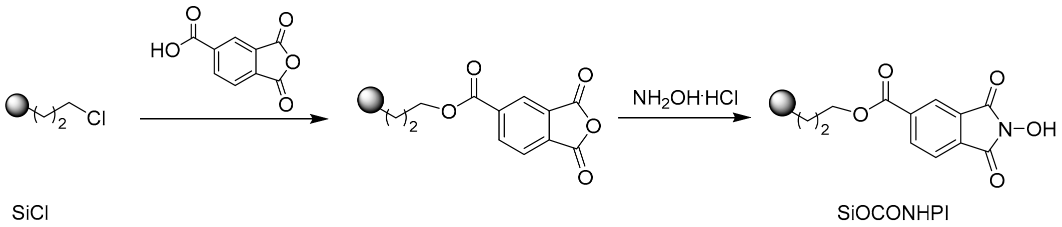

Figure 3. Synthesis of NHPI immobilized on chloropropyl silica gel via ester bond.

On the basis of elemental analysis, it was confirmed that the content of immobilized NHPI was equal to 0.45 mmol NHPI/g.

Comparing FT-IR spectra of chloropropyl functionalized silica SiCl (Figure 4I) and of NHPI immobilized on silica SiOCONHPI (Figure 4II) it is possible to unambiguously identify only signals of carbonyl groups at around 1650 cm^{-1}. *N*-hydroxyl group signals at around 3300 cm^{-1} overlap with vibration band of SiO–H hydroxyl groups of silica support. Because of intensive vibration bands characteristic for silica gel, this is silicon-oxygen bond peaks 1007 cm^{-1} and hydroxyl group bonded with silicon atom 793 cm^{-1}, it was not possible to identify a signal originating from C–O in ester bond.

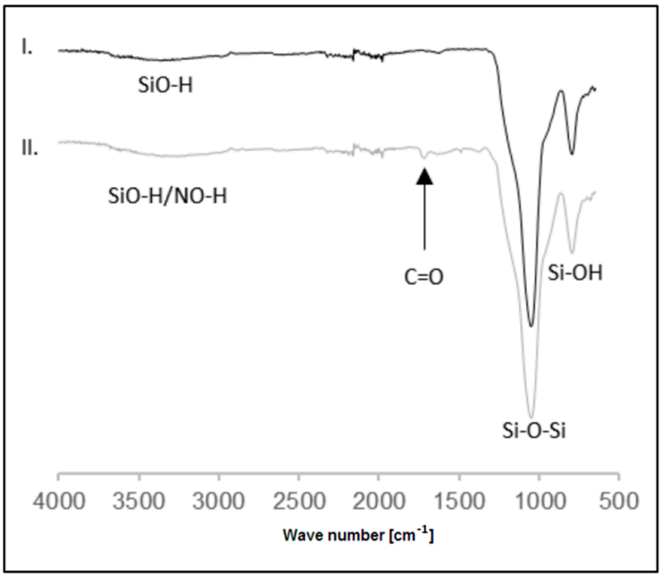

Figure 4. FT-IR spectra of I. SiCl and II. SiOCONHPI.

During the synthesis irregular chloropropyl silica granules were mechanically degraded to smaller, irregular granules with size equal to 1–20 μm (Figure 5).

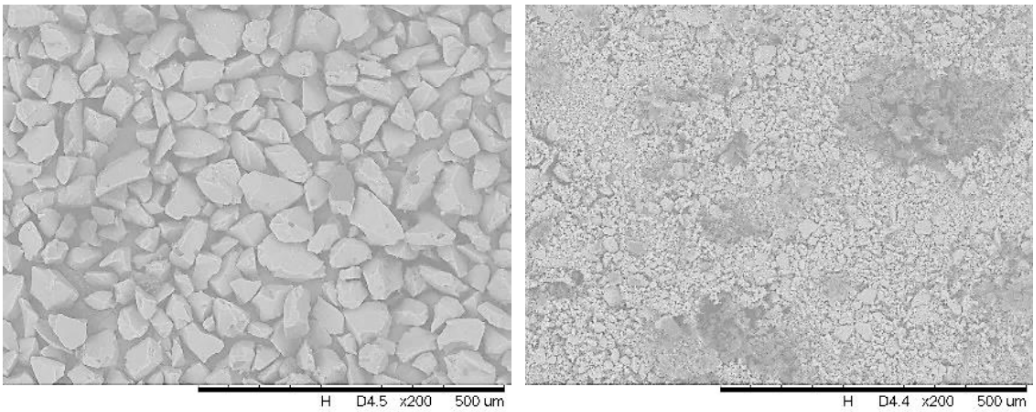

Figure 5. SEM analysis of support (SiCl) and NHPI immobilized on chloropropyl silica gel (SiOCONHPI).

2.1.2. SiOCONHPI@CoCl$_2$@IL Preparation

Obtained SiOCONHPI was coated with a layer of ionic liquid containing dissolved cobalt(II) chloride (SiOCONHPI@CoCl$_2$@IL). Ionic liquids with the following cations were selected for the study: 1-ethyl-3-methylimidazolium [emim], 1-butyl-3-methylimidazolium [bmim], 1-hexyl-3-methylimidazolium [hmim], 1-octyl-3-methylimidazolium [omim], 1-decyl-3-methylimidazolium [C$_{10}$mim], and anions: [CH$_3$OSO$_3$], octylsulfate ([OcOSO$_3$]),

[$C_{12}H_{25}OSO_3$], [Br], [Cl], [CF_3SO_3], [BF_4], [PF_6], and [$(CF_3SO_2)_2N$] ([NTf_2]). Used ionic liquids differ in polarity, solubility of oxygen, and ethylbenzene.

2.2. Study on Ethylbenzene Oxidation Reaction

The catalytic activity of SiOCONHPI and SiOCONHPI@$CoCl_2$@IL was studied in oxidation reaction of ethylbenzene, used as a model alkylaromatic hydrocarbon, with the use of oxygen. The selection of $CoCl_2$ as cocatalyst resulted from known activity of cobalt(II) salt in oxidation reactions using NHPI as well as from limited solubility of $CoCl_2$ in the hydrocarbon in order to limit its leaching from the surface of catalyst. It is known that the cobalt(II) salts in NHPI catalyzed oxidation reactions of hydrocarbons with oxygen not only influence the generation of PINO radical but also accelerate decomposition of hydroperoxides to stable products. As a result of ethylbenzene oxidation mixtures composed of unreacted ethylbenzene, ethylbenzene hydroperoxide (EBOOH), acetophenone (AP), and 1-phenylethanol (PEOH) were obtained (Figure 6).

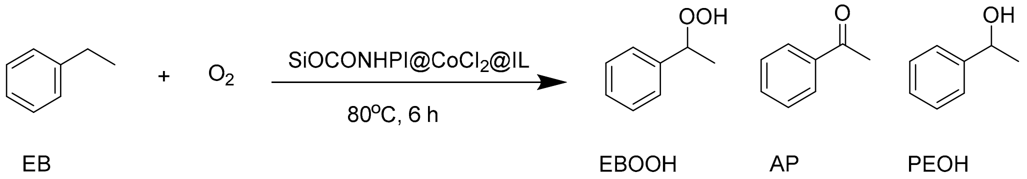

Figure 6. Ethylbenzene oxidation with oxygen in the presence of SiOCONHPI@$CoCl_2$@IL.

2.2.1. Ethylbenzene Oxidation with Oxygen using SiOCONHPI or SiOCONHPI/$CoCl_2$ System

High catalytic activity of NHPI immobilized on silica was proved in the studied oxidation process. In comparison to a non-catalytic reaction carried out only with the use of azo initiator a two-fold increase in conversion was observed (Table 1, entries 1, 3). At the same time a minimal decrease in selectivity to EBOOH was observed, what may result from the influence of silica support on its stability.

Table 1. Ethylbenzene oxidation with oxygen in the presence of SiOCONHPI@$CoCl_2$@[bmim][X].

Entry	Catalyst	α (%)	S_{EBOOH} (%)	S_{AP} (%)	S_{PEOH} (%)
1	-	4.7	67.1	12.3	20.6
2 [a]	$CoCl_2$	2.8	81.4	-	-
3 [b]	SiOCONHPI	8.6	51.0	19.4	29.6
4 [c]	SiOCONHPI/$CoCl_2$	8.2	20.0	52.9	26.2
5 [d]	SiOCONHPI/[bmim][$OcOSO_3$]	6.4	71.2	19.0	9.8
6 [e]	SiOCONHPI/$CoCl_2$/[bmim][$OcOSO_3$]	11.3	25.4	50.0	24.6
7 [f]	SiOCONHPI@[bmim][$OcOSO_3$]	6.1	70.0	19.1	10.9
8 [g]	SiOCONHPI@$CoCl_2$@[bmim][$OcOSO_3$]	12.1	23.0	50.6	26.3
9 [g]	SiOCONHPI@$CoCl_2$@[bmim][Cl]	10.2	26.8	55.0	17.9
10 [g]	SiOCONHPI@$CoCl_2$@[bmim][CF_3SO_3]	9.0	19.8	54.3	25.9
11 [g]	SiOCONHPI@$CoCl_2$@[bmim][BF_4]	8.4	36.5	49.1	14.4
12 [g]	SiOCONHPI@$CoCl_2$@[bmim][CH_3COO]	8.4	21.1	55.6	23.3
13 [g]	SiOCONHPI@$CoCl_2$@[bmim][PF_6]	7.3	23.0	69.7	7.7
14 [g]	SiOCONHPI@$CoCl_2$@[bmim][Br]	6.9	29.9	51.7	18.4
15 [g]	SiOCONHPI@$CoCl_2$@[bmim][NTf_2]	6.6	23.5	50.2	26.3

Ethylbenzene 2 mL, AIBN 1.0 mol%, 80 °C, 0.1 MPa, 6 h, 1200 rpm [a] only $CoCl_2$ 0.1 mol% (0.0021 g), [b] SiOCONHPI 0.033 g [c] SiOCONHPI 0.033 g, $CoCl_2$ 0.0021 g, [d] SiOCONHPI 0.033 g, [bmim][$OcOSO_3$] 0.017 g, [e] SiOCONHPI 0.033 g, [bmim][$OcOSO_3$] 0.017 g, $CoCl_2$ 0.0021 g, and [f] SiOCONHPI 0.033 g, [bmim][$OcOSO_3$] 0.017 g was dissolved in 3 mL of acetone and stirred for 3 h, then the acetone was evaporated [g] SiOCONHPI (0.033 g), [bmim][X] (0.017 g), $CoCl_2$ (0.0021 g) was dissolved in 3 mL of acetone and stirred for 3 h, then the acetone was evaporated.

It was confirmed that the addition of $CoCl_2$ directly to a reaction mixture does not influence the conversion of ethylbenzene, in comparison to non-catalytic reaction, as well as to the one carried out with the use of SiOCONHPI (Table 1, entries 3, 4). In the second case, however, it was observed that the selectivity to EBOOH dropped down from 51.0% to 20.0%. The obtained results are probably influenced by poor solubility of $CoCl_2$ in hydrocarbon, which can, however, increase together with the progress of the reaction and increase in polarity of the mixture.

2.2.2. Ethylbenzene Oxidation with Oxygen using SiOCONHPI@$CoCl_2$@[bmim][X] System

Catalytic activity of SCILL systems SiOCONHPI@$CoCl_2$@IL was studied. In those systems, ionic liquids with [bmim] cation and following anions: [$OcOSO_3$], [Br], [Cl], [CF_3SO_3], [BF_4], [PF_6], [CH_3COO], and [NTf_2] containing dissolved $CoCl_2$ were applied. The results are presented in the Table 1. For comparison, reactions in which [bmim][$OcOSO_3$] and/or $CoCl_2$ were added directly to reaction mixture containing SiOCONHPI were also carried out (Table 1, entry 5, 6).

It was confirmed that coating of SiOCONHPI with a layer of [bmim][$OcOSO_3$] influences the decrease in conversion from 8.6% to 6.1% (Table 1, entries 3, 7) and at the same time the increase in selectivity to EBOOH, from 51% to 70%. It indicates that the IL layer can limit the contact between hydrocarbon and active center of the catalyst (N–OH), as well as between EBOOH and support (silica may accelerate EBOOH decomposition). On the other hand, coating heterogeneous catalyst SiOCONHPI with ionic liquids [bmim][$OcOSO_3$], [bmim][Cl], and [bmim][CF_3SO_3] containing dissolved $CoCl_2$ (Table 1, entries 8–10) enabled to increase the catalytic activity in relation to systems in which IL and $CoCl_2$ were added directly to reaction mixture (Table 1, entries 4–6). The highest conversion of ethylbenzene was obtained while SiOCONHPI@$CoCl_2$@[bmim][$OcOSO_3$] were used (12.1%). Our previous study [38] on the influence of catalytic amounts of various ILs on ethylbenzene oxidation catalyzed by Co(II) and NHPI/Co(II) system, has proved a positive effect of [bmim][$OcOSO_3$].

The effect observed while using SiOCONHPI@$CoCl_2$@IL, may be influenced by such factors as: Interaction between N-OH and IL, better contact between $CoCl_2$ dissolved in a layer of IL and N-OH, as well as between reagents and N-OH groups or NO radicals and $CoCl_2$, and also undesired washing out of ionic liquid containing $CoCl_2$ from the surface of silica. Among all of the studied ionic liquids, [bmim][$OcOSO_3$] is characterized by the highest solubility of oxygen as well as used hydrocarbon. It was observed that after the reaction catalyzed by SiOCONHPI@$CoCl_2$@[bmim][$OcOSO_3$] post-reaction mixture had a pale-green shade, what suggests that a part of Co(II) salt was leaching from the surface of the catalyst during the reaction. Similar selectivities to EBOOH, obtained while using SiOCONHPI@$CoCl_2$@[bmim][$OcOSO_3$] and SiOCONHPI/$CoCl_2$, respectively equal to 23.0% and 20.0% (Table 1, entries 4, 8), may indicate similar concentration of $CoCl_2$ in the reaction mixture. Amount of [bmim][$OcOSO_3$] introduced together with the catalyst, this is 0.017 g, can dissolve in ethylbenzene as showed in [38]. In this case, it can cause an increase in polarity of reaction mixture and solubility of $CoCl_2$. Among studied ILs it is the [bmim][$OcOSO_3$] which is characterized by the highest solubility in ethylbenzene.

In the reactions, in which [bmim][$OcOSO_3$] and $CoCl_2$ was introduced directly into the reaction mixture containing heterogeneous SiOCONHPI (Table 1, entry 6), also it was possible to observe a positive influence of [bmim][$OcOSO_3$]. However, during the reaction, the polar ionic liquid can also physically interact with the layer of silica. Therefore, it is difficult to explicitly determine, whether the observed effect results from the presence of IL dissolved in the system or supported onto the surface of silica.

As opposed to [bmim][$OcOSO_3$], [bmim][Cl] and [bmim][CF_3SO_3] poorly dissolve in ethylbenzene. Additionally, in the previous work [38] we ascertained that the addition of catalytic amounts of [bmim][CF_3SO_3] to the process of ethylbenzene oxidation catalyzed by Co(II) or NHPI/Co(II), in both cases influenced the decrease in conversion of substrate. However, in the studies presented in this paper, it was observed that there was a slight increase in conversion, which was related to the process of coating SiOCONHPI with a layer of [bmim][CF_3SO_3] containing $CoCl_2$, what would indicate a positive influence of IL bonded with silica on the whole process.

The main product of the oxidation of ethylbenzene using SiOCONHPI@$CoCl_2$@[bmim][X] was AP obtained with selectivities equal to ca. 50% (only in the case of using [bmim][PF_6] additive, it was obtained with selectivity equal to 70%), furthermore, selectivities to EBOOH and PEOH were varying respectively between 21.1% and 36.5% and between 7.7 and 26.3%.

2.2.3. Influence of the Structure of Alkyl Substituent in Cation or Anion of Ionic Liquid on Catalytic Activity of SiOCONHPI@CoCl$_2$@IL

The study on the influence of the length of alkyl chain in 1-alkyl-3-methylimidazolium cation or alkyl sulfate anion on catalytic activity of SiOCONHPI@CoCl$_2$@IL, in the processes of oxidation of ethylbenzene with oxygen, was carried out. Results are presented in Table 2.

Table 2. Influence of the ionic liquid structure on catalytic activity of SiOCONHPI@CoCl$_2$@IL.

Entry	Catalyst	α (%)	S_{EBOOH} (%)	S_{AP} (%)	S_{PEOH} (%)
1 [a]	SiOCONHPI/CoCl$_2$	8.2	20.0	52.9	26.2
2	SiOCONHPI@CoCl$_2$@[bmim][Cl]	10.2	26.8	55.0	17.9
3	SiOCONHPI@CoCl$_2$@[hmim][Cl]	11.1	21.8	52.6	25.4
4	SiOCONHPI@CoCl$_2$@[omim][Cl]	11.3	17.5	57.0	25.2
5	SiOCONHPI@CoCl$_2$@[C$_{10}$mim][Cl]	11.9	20.0	57.1	22.6
6	SiOCONHPI@CoCl$_2$@[bmim][CH$_3$OSO$_3$]	10.2	36.2	38.7	25.1
7	SiOCONHPI@CoCl$_2$@[bmim][OcOSO$_3$]	12.1	23.0	50.6	26.3
8	SiOCONHPI@CoCl$_2$@[bmim][C$_{12}$H$_{25}$OSO$_3$]	14.3	15.8	58.3	25.9
9	SiOCONHPI@CoCl$_2$@[emim][OcOSO$_3$]	12.8	28.8	44.6	26.6

Ethylbenzene 2 mL, AIBN 1.0 mol%, 80 °C, 0.1 MPa, 6 h, 1200 rpm, SiOCONHPI@CoCl$_2$@IL: SiOCONHPI (0.033 g), IL (0.017 g), CoCl$_2$ (0.0021 g, 0.1 mol%) was dissolved in 3 mL of acetone and stirred for 3 h, then the acetone was evaporated [a] SiOCONHPI 0.033 g, CoCl$_2$ 0.1 mol%.

It was proved that together with the increase of the number of carbon atoms in the alkyl group, both in anion and cation, conversion of ethylbenzene is increased. At the same time selectivity to EBOOH slightly decreases. Lipophilicity increase of IL influences the increase of oxygen and hydrocarbon solubility in IL supported on silica, as well as solubility of IL in non-polar starting material and related greater solubility of CoCl$_2$ in ethylbenzene. The decrease in selectivity to EBOOH may indicate that IL containing CoCl$_2$ is washed out from the surface of the catalyst.

2.2.4. Attempts to Reuse SiOCONHPI@CoCl$_2$@[bmim][X] System.

The advantage of heterogeneous catalysts is the possibility to recover them in a simple way. Therefore, attempts were made to reuse studied catalytic systems. After the reaction (first cycle) the mixture was decanted, and the catalyst was washed with hexane and subsequently the hexane was also decanted. Before the reuse, the catalyst was dried under vacuum. Table 3 compares the results of conversion of ethylbenzene in four reaction cycles, obtained with the use of the most active catalytic systems, i.e., SiOCONHPI@CoCl$_2$@[bmim][X] containing layers of [bmim][OcOSO$_3$], [bmim][Cl], and [bmim][CF$_3$SO$_3$]. For comparison also SiOCONHPI was recycled 3 times from the reaction carried out in the presence of CoCl$_2$ introduced directly to the reaction mixture. Portions of fresh CoCl$_2$ were not introduced in the following cycles.

The study on recovery and recycling of SiOCONHPI catalyst from reaction mixture containing only an additive of CoCl$_2$, in the first cycle, proved that the catalyst maintains its activity. In the successive cycles conversion between 8.9% and 8.1% was obtained. These conversion values are higher than the one obtained in non-catalytic process (4.7%) (Table 1, entry 1) and are comparable to the one obtained using SiOCONHPI only (8.6%) (Table 1, entry 3). Selectivity to EBOOH gradually increased in every recycling from 20% to 43% (Table 3, entry 1–4) and got close to the selectivity obtained while using SiOCONHPI without CoCl$_2$, this is 51% (Table 1, entry 3). It indicates binding of CoCl$_2$, introduced to the reaction mixture, in the first cycle, on the surface of silica and consequently its gradual wash out in the following cycles two to four.

Table 3. Recovery and recycling of SiOCONHPI@$CoCl_2$@[bmim][X] systems in ethylbenzene oxidation reaction.

Entry	Cycle	Catalyst	α (%)	S_{EBOOH} (%)	S_{AP} (%)	S_{PEOH} (%)
1 [a]	1	SiOCONHPI/$CoCl_2$	8.2	20.0	52.9	26.2
2	2		8.9	28.5	48.1	23.3
3	3		8.4	30.7	46.3	23.0
4	4		8.1	43.4	34.2	22.3
5 [b]	1	SiOCONHPI@$CoCl_2$@[bmim][$OcOSO_3$]	12.1	23.0	50.6	26.3
6	2		12.4	24.3	43.8	31.8
7	3		11.3	30.5	36.2	33.3
8	4		8.0	44.1	37.1	18.6
9 [b]	1	SiOCONHPI@$CoCl_2$@[bmim][Cl]	10.2	26.8	55.0	17.9
10	2		10.1	42.5	40.2	17.3
11	3		7.4	59.0	25.2	15.8
12	4		7.7	61.6	24.0	14.4
13 [b]	1	SiOCONHPI@$CoCl_2$@[bmim][CF_3SO_3]	9.0	19.8	54.3	25.9
14	2		9.5	26.8	48.4	24.5
15	3		9.0	38.3	40.6	20.7
16	4		7.4	57.1	32.8	10.1

Ethylbenzene 2 mL, AIBN 1.0 mol%, 80 °C, 0.1 MPa, 6 h, 1200 rpm [a] SiOCONHPI 0.033 g, $CoCl_2$ 0.1 mol% [b] SiOCONHPI@$CoCl_2$@IL: SiOCONHPI (0.033 g), IL (0.017 g), $CoCl_2$ (0.0021 g, 0.1 mol%) was dissolved in 3 mL of acetone and stirred for 3 h, then the acetone was evaporated.

In the reactions carried out with the use of SiOCONHPI@$CoCl_2$@[bmim][$OcOSO_3$] and SiOCONHPI@$CoCl_2$@[bmim][CF_3SO_3] systems, it is possible to recycle the catalyst two times, and a significant decrease in conversion and an increase in selectivity to EBOOH related to washing out of $CoCl_2$ was observed no sooner than in the fourth cycle. In case of SiOCONHPI@$CoCl_2$@[bmim][Cl] the decrease in activity occurred already in the third cycle.

Figure 7 compares the FTIR spectra of SiOCONHPI@$CoCl_2$@[bmim][$OcOSO_3$] before the reaction and after the fourth cycle. Based on that, it is possible to determine that after the fourth cycle the IL was washed out from the surface of silica (Figure 7). Thermogravimetric analysis of fresh and recovered SiOCONHPI@$CoCl_2$@[bmim][$OcOSO_3$] also demonstrates that after the fourth cycle the IL was partly washed out from the surface of silica (Figure 8). The weight loss of 34% was observed between 200 and 500 °C for fresh SiOCONHPI@$CoCl_2$@[bmim][$OcOSO_3$] and 13% for recovered catalyst (Supplementary Materials; Figure S1–S3).

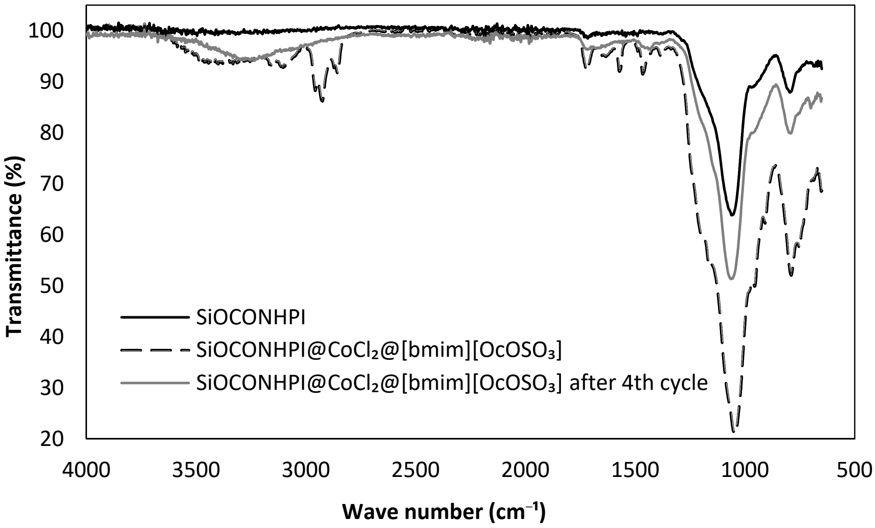

Figure 7. FT-IR spectra of SiOCONHPI, SiOCONHPI@$CoCl_2$@[bmim][$OcOSO_3$] and SiOCONHPI@$CoCl_2$@[bmim][$OcOSO_3$] after the fourth cycle.

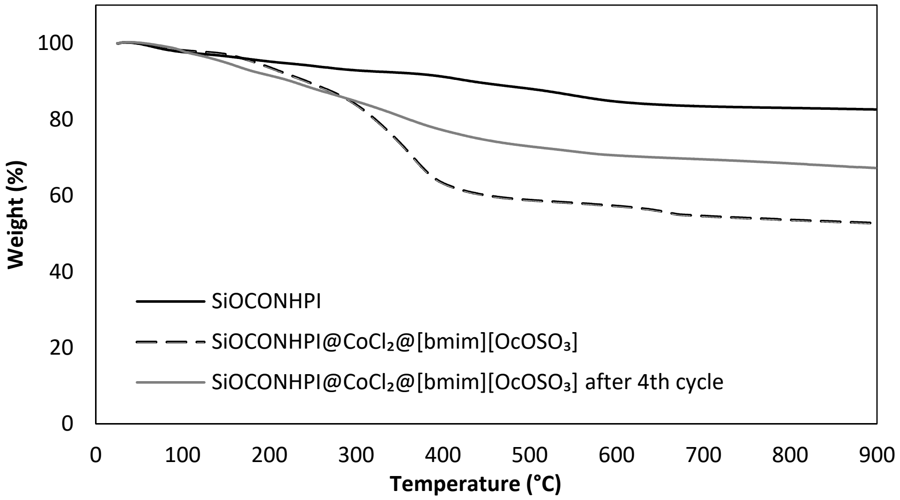

Figure 8. TGA curves obtained for SiOCONHPI, SiOCONHPI@$CoCl_2$@[bmim][$OcOSO_3$] and SiOCONHPI@$CoCl_2$@[bmim][$OcOSO_3$] after the fourth cycle.

The influence of the length of carbon chain in alkyl substituent in the alkyl sulfate anion and 1-alkyl-3-methylimidazolium cation, on the possibility of SiOCONHPI@$CoCl_2$@IL system recycling (Table 4), was also studied.

Table 4. Influence of ionic liquid structure on possibility to recycle SiOCONHPI@$CoCl_2$@IL.

Entry	Cycle	Catalyst	α (%)	S_{EBOOH} (%)	S_{AP} (%)	S_{PEOH} (%)
1 [a]	1	SiOCONHPI@$CoCl_2$@[bmim][CH_3OSO_3]	10.2	36.2	38.7	25.1
2	2		9.3	47.7	30.0	22.3
3	3		8.2	58.8	25.5	15.7
4	4		6.8	61.4	23.2	14.5
5 [a]	1	SiOCONHPI@$CoCl_2$@[bmim][$OcOSO_3$]	12.1	23.0	50.6	26.3
6	2		12.4	24.3	43.8	31.8
7	3		11.3	30.5	36.2	33.3
8	4		8.0	44.1	37.1	18.6
9 [a]	1	SiOCONHPI@$CoCl_2$@[bmim][$C_{12}H_{25}OSO_3$]	14.3	15.8	58.3	25.9
10	2		11.6	26.3	50.5	23.2
11	3		9.8	37.5	36.8	25.7
12	4		8.8	47.8	30.2	22.0
13 [a]	1	SiOCONHPI@$CoCl_2$@[emim][$OcOSO_3$]	12.8	28.8	44.6	26.6
14	2		10.0	36.0	38.1	25.9
15	3		9.9	36.4	34.6	29.0
16	4		9.5	44.9	27.1	28.0

Ethylbenzene 2 mL, AIBN 1.0 mol%, 80 °C, 0.1 MPa, 6 h, 1200 rpm [a] SiOCONHPI@$CoCl_2$@IL: SiOCONHPI (0.033 g), IL (0.017 g), $CoCl_2$ (0.0021 g, 0.1 mol%) was dissolved in 3 mL of acetone and stirred for 3 h, then the acetone was evaporated.

The results presented in Table 4, indicate that the greatest decrease in conversion and increase in selectivity to EBOOH in subsequent cycles is observed while using SiOCONHPI@$CoCl_2$@[bmim][CH_3OSO_3]. In the fourth cycle, the higher conversion, in comparison to the reaction carried out with the use of SiOCONHPI (8.6%) (Table 1, entry 3), was obtained with the use of SiOCONHPI@$CoCl_2$@[emim][$OcOSO_3$] (Table 4, entry 16).

3. Materials and Methods

3.1. Materials

Ethylbenzene (Acros 99.8%, Geel, BE) was purified by washing with H_2SO_4 and vacuum distillation. Cobalt(II) chloride, *N*-hydroxyphthalimide (NHPI) were purchased from commercial sources and used without purification. 3-Chloropropyl-functionalized silica gel were purchased from Sigma Aldrich (St. Louis, MO, USA) (Si–Cl): Loading 1.0 mmol Cl/g, 230–400 mesh.

Ionic liquids: 1-butyl-3-methylimidazolium chloride ([bmim][Cl]), 1-butyl-3-methylimidazolium bromide ([bmim][Br]), 1-butyl-3-methylimidazolium methyl sulfate ([bmim][CH_3OSO_3]), 1-butyl-3-methylimidazolium octyl sulfate ([bmim][$OcOSO_3$]), 1-butyl-3-methylimidazolium acetate ([bmim][CH_3COO]), 1-butyl-3-methylimidazolium trifluoromethanesulfonate ([bmim][CF_3SO_3]), 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]), 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]), 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([bmim][NTf_2]), 1-hexyl-3-methylimidazolium chloride ([hmim][Cl]), 1-octyl-3-methylimidazolium chloride ([omim][Cl]), 1-decyl-3-methylimidazolium chloride (C_{10}mim][Cl]), 1-ethyl-3-methylimidazolium octyl sulfate ([emim][$OcOSO_3$]) were commercial materials and were dried under vacuum before use (50 °C, 0.1 bar). 1-Butyl-3-methylimidazolium lauryl sulfate ([bmim][$C_{12}H_{25}OSO_3$]) was prepared according procedure described in literature [38].

3.2. SiOCONHPI Synthesis

Chloropropyl silica gel SiCl (2.0 g, 1.0 mmol Cl/g), trimellitic anhydride (8 mmol) and triethylamine (20 mmol) were added to 20 mL of dioxane. The mixture was stirred for 48 h under reflux. The product was filtered and washed twice with H_2O (2 times 25 mL) at RT and of each of the following solvents at 50 °C: MeOH, THF and CH_2Cl_2. The solid was dried under vacuum and then was added to a 40 mL mixture of pyridine:1,2-dichloroethane (3:1, v/v) followed by the addition of hydroxylamine hydrochloride (20 mmol). The mixture was stirred for 24 h at 75 °C, then filtered. The filtrate was washed with H_2O (2 times 25 mL) and H_2O:MeOH (1:1, v/v, 25 mL) at RT and MeOH, DMF, THF, and CH_2Cl_2 (2 times 25 mL) at 50 °C. The product was died under vacuum to afford 1.26 g of immobilized NHPI (SiOCONHPI). SiOCONHPI was analyzed using FT-IR spectroscopy (Figure 4), SEM (Figure 5), TGA (Figure 8 and Figure S1) and elemental analysis (%C: 9.26; %H: 1.34; %N: 0.64). Based on the elemental analysis the content of immobilized NHPI was 0.45 mmol/g.

3.3. SiOCONHPI@Co(II)@IL Preparation

Catalysts were prepared in accordance with the described procedure [36]. Ionic liquid (0.017 g), NHPI immobilized on silica SiOCONHPI (0.033 g) and $CoCl_2$ (0.0021 g; 0.1 mol% in relation to etylbenzene) were introduced into a two-neck flask. Consequently, about 3 mL of acetone was added, and the flask was placed on a magnetic stirrer and stirred for 3 hours, the next step was evaporation of the acetone with the use of rotary evaporator.

3.4. Ethylbenzene Oxidation

The oxidation reactions were performed in a gasometric apparatus as described in [39]. Ethylbenzene, heterogeneous NHPI, AIBN and $CoCl_2$ were placed in a 10 mL flask connected to a gas burette filled with oxygen under atmospheric pressure. The reaction was conducted at 80 °C for 6 h with magnetic stirring at 1200 rpm. The oxygen uptake (n_{O2}) was measured, recalculated for normal conditions (273 K, 1 atm), and this value was used to calculate the ethylbenzene conversion (α). The amount of ethylbenzene hydroperoxide (EBOOH) was determined iodometrically according to the described method [40], and the result was used for the calculation of the reaction's selectivity (S_{EBOOH}).

$$n_{O2} = (V_{O2} \cdot 273 \cdot p)/(101325 \cdot 22.415 \cdot T)\ (\mathrm{mol})$$

$$\alpha = n_{O2}/n \cdot 100\%$$

$$S_{EBOOH} = n_{OOH}/n_{O2} \cdot 100\%$$

EBOOH is thermally unstable and easily decomposes to 1-phenylethanol (PEOH) and acetophenone (AP). Thus, before GC analysis, the hydroperoxide was quantitatively reduced to

1-phenylethanol by addition of triethylphosphite $(EtO)_3P$, which is oxidized to triethyl phosphate $(EtO)_3PO$ [41]. The amount of PEOH determined by GC was the sum of the alcohol and hydroperoxide formed. In order to calculate the PEOH selectivity, the amount of hydroperoxide determined by iodometric analysis was subtracted. The amount of acetophenone was determined based on the GC analysis and used for the calculation of the reaction's selectivity.

3.5. Analytic Methods

FT-IR analysis was carried out in Nicolet 6700 FT-IR Spectrometer (Thermo Electron Scientific Instruments Corporation, Madison, WI, USA), with the use of ATR technique (attenuated total reflection technique). Elemental analysis was carried out with the use of CHNS Vario Micro Cube equipment (Elementar Analysensysteme GmbH, Langenselbold, DE).

Morphology of the surface of solid carriers and immobilized NHPI was carried out with the use of Scanning Electron Microscope (SEM) (TM3000 TableTop, Hitachi High-Technologies Corporation brand, USA).

GC analysis was performed using a gas chromatograph (Agilent Technologies 7890C, Santa Clara, CA, USA) (Zebron ZB-5HT capillary column 30 m by 0.25 mm by 0.25 μm) with an FID detector. The injection port temperature was 200 °C. The detector temperature was 300 °C. The temperature program was: Hold at 80 °C for 10 min, then ramp at 3 °C/min to 110 °C, hold at 110 °C for 4 min, then ramp at 20 °C/min to 210 °C, hold for 4 min. Calibration curves for acetophenone and 1-phenylethanol were determined using *p*-methoxytoluene as the internal standard.

Thermogravimetric analysis (TGA) was performed using a TGA851e thermobalance (Mettler Toledo, Greifensee, CHE). Samples of approximately 10 mg were heated from 25 °C to 800 °C at a rate of 10 °C/min in standard 70 μL Al_2O_3 crucibles under a dynamic nitrogen flow of 60 mL/min (99.9992%).

4. Conclusions

For the first time, the catalytic activity of NHPI immobilized on silica via ester bond SiOCONHPI in oxidation of model ethylbenzene with oxygen without any solvent, as well as possibility of its (at least) three-fold recycling without any loss in activity, was reported.

It was also proved that coating the surface of SiOCONHPI with a layer of IL such as $[bmim][OcOSO_3]$, [bmim][Cl] and $[bmim][CF_3SO_3]$ containing dissolved $CoCl_2$, enables to obtain higher conversions of ethylbenzene. The highest conversion was obtained while using SCILL system $SiOCONHPI@CoCl_2@[bmim][OcOSO_3]$.

Study on recovery and reuse of reported new SCILLs systems $SiOCONHPI@CoCl_2@IL$ demonstrated that a significant decrease in conversion was observed no sooner than in the fourth cycle using $[bmim][OcOSO_3]$ and $[bmim][CF_3SO_3]$ or in the third cycle using [bmim][Cl]. Fortunately, after IL and $CoCl_2$ are washed out, SiOCONHPI preserves its catalytic activity.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4344/10/2/252/s1, Figure S1: TGA curves obtained for SiOCONHPI, Figure S2: TGA curves obtained for $SiOCONHPI@CoCl_2@[bmim][OcOSO_3]$, Figure S3: TGA curves obtained for $SiOCONHPI@CoCl_2@[bmim][OcOSO_3]$ after the fourth cycle.

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