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Nanoparticles of organosilane-based nitrite ionic liquid immobilized on silica for the diazotization of aniline derivatives and subsequent synthesis of azo dyes

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ABSTRACT

Imidazolium based nitrite ionic liquid containing trimethoxysilyl group was prepared from the reaction of N-methylimidazole and (3-chloropropyl) trimethoxysilane. This ionic liquid was immobilized on silica covalently to give nanoparticles with the imidazolium nitrite moiety remaining intact. The diazotization reaction was performed as a model reaction to examine the activity of these nanoparticles as a nitrosonium source. Excellent performance was exhibited in the diazotization reaction of various aniline derivatives in the presence of HCl under mild heterogeneous conditions (room temperature and short reaction time). In-situ coupling of diazonium salts to a range of tertiary anilines, phenols and naphthols afforded the requisite azo dyes in good yield, using standard experimental procedures.

1. Introduction

Organosilanes containing covalently bonded catalyst were used as a linker or coupling agent to an oxide support. The complexes of metals with organosilane-based ligands were synthesized and immobilized on the oxide supports [1]. Organosilane-based *N*- heterocyclic carbene–palladium complex immobilized on silica particles was reported as a catalyst for the Suki reaction [2]. Ionic liquids are growing in importance over the past few years due to their unique physical and chemical properties [3]. Ionic liquids containing a functional group which is covalently tethered to its cation or anion, TSILs, have been increasingly used as solvents and reagents or catalysts due to their specific properties [4–9].

Very recently we used nitrite functionalized ionic liquid as a nitrosonium source for the diazotization reaction of a variety of aniline derivatives [10]. Ionic liquids immobilized on metal oxides such as silica was used as catalyst in some organic reactions [11–14]. Sugimura and co-workers synthesized the immobilized acidic ionic liquids by copolymerization with styrene and used them as catalyst for the acetal formation [15]. Diphenylmethane and its derivatives were synthesized using immobilized chloroferrate ionic liquid as an efficient and reusable catalyst [16].

Diazoniums are an important group of organic compounds which have interesting applications in synthetic organic chemistry. These compounds can be reduced into radicals and used for the covalent surface modification of carbon [17], metal [18], and semiconductors [19]. Diazoniums also have been used for the preparation of the important synthetic azo dyes via well-known azo-coupling reaction [20–22]. Nitrous acid is well-known reagent for the diazotization of aniline derivatives under acidic conditions. Many methods have been reported for the diazotization and subsequent azo-coupling reaction [23–31].

In continuation of our work on the using of task-specific nitrite ionic liquid (IL-ONO) as solvent and reagent for the diazotization and synthesis of azo dyes [10], we now introduce nitrite ionic liquid immobilized on silica as a new reagent that can act as a nitrosonium source for the efficient conversion of aryl amines to their corresponding diazonium salts. In-situ azo-coupling of these diazonium salts afforded the related azo dyes in good yields.

2. Experimental

2.1. General information

All reagents were purchased from Merck Company and used without further purification. Infrared spectra were recorded in KBr and were determined on a Perkin Elmer FT-IR spectrometer. ^{1}H NMR spectra were recorded on a Bruker Avance AC-400 MHz using

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DMSO-d_6 or $CDCl_3$ as the deuterated solvents and TMS as internal standard. All melting points measured in open glass-capillaries using a Stuart melting point apparatus.

2.1.1. Synthesis of 1-methyl-3-(3-trimethoxysilylpropyl) imidazolium chloride

1-Methylimidazole (20 mL, 0.25 mol) and (3-chloropropyl) trimethoxysilane (6.04 g, 0.25 mmol) were refluxed at 80 °C for three days in the absence of any catalyst and solvent. The unreacted materials were washed by diethyl ether (3 × 8 mL). The diethyl ether was removed under reduced pressure at room temperature, followed by heating under high vacuum, to yield a yellowish viscous liquid. Isolated yield was 98%. FT-IR (KBr, cm^{-1}): 1656, 1612, 1584. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm): 10.22 (broad, 1H, Ar–H), 7.59 (1H, dd, $J = 7.89$ and 2.86 Hz, Ar–H), 7.26 (1H, dd, $J = 7.89$ and 2.79 Hz, Ar–H), 4.06 (2H, t, $J = 7.25$ Hz, $-NCH_2$), 3.86 (3H, s, $-NCH_3$), 3.30 (9H, s, OCH_3), 1.74 (2H, tt, $J = 7.14$ Hz, $-CH_2$), 0.37 (2H, t, $J = 7.09$ Hz, $SiCH_2$).

2.3. Synthesis of silica nanoparticles

Ammonia solution 25% (750 μL, 10 mmol) and water (1.98 mL) were added into a 250 mL round bottom flask containing absolute methanol (100 mL). The solution is stirred for 10 min at room temparature. While stirring of the solution, tetraethoxysilane, TEOS (10.41 g, 500 mmol) was added dropwise. The final solution is stirred *continuously* for three days at ambient temperature. The particle size was examined under scanning electron microscopy.

2.4. Procedure for the immobilization of chloride ionic liquid onto silica nanoparticles

The silica nanoparticles suspension are precipitated with n-hexane and extracted through centrifugation (twice at 6000 rpm) before being re-suspended in dichloromethane. Silica (1.016 g) was suspended in CH_2Cl_2 (5 mL) and the solution of 1-methyl-3-(3-trimethoxysilylpropyl)imidazolium chloride (300 mg, 0.929 mmol) in CH_2Cl_2 was then added. The mixture was stirred for 3 days at 40–50 °C. In the following step, the solvent and the methanol created in the grafting step were distilled off and the remaining solid dried under high vacuum and the excess of 1-methyl-3-(3-trimethoxy silylpropyl) imidazolium chloride removed by extraction with boiling dichloromethane. After drying of residue under vacuum at room temperature, the nanoparticles of immobilized chloride ionic liquid on to silica was prepared.

2.5. Anion exchange in the immobilized ionic liquid

Immobilized chloride ionic liquid **6** and an excess amount of $NaNO_2$ were added into the deionized water and stirred for 24 h at room temperature. NaCl which was prepared during the exchange of chloride anion with NO_2, was removed by washing the mixture with deionized water (3 × 30 mL). Immobilized nitrite ionic liquid was obtained typically in 98% yield as a white powder (Scheme 2). Immobilized nitrite ionic liquid nanoparticles were examined under scanning electron microscopy.

Comparing of the IR spectra of chloride ionic liquid **5** and nitrite ionic liquid **8** showed that a broad bond signal at 1349 cm^{-1} was appeared in the spectrum of nitrite ionic liquid which was not observed in the spectrum of chloride ionic liquid. This difference was also observed comparing the two IR spectra of immobilized chloride ionic liquid **6** and immobilized nitrite ionic liquid **7** and a broad bond signal at 1335 cm^{-1} was appeared in the spectrum of ionic liquid 7.

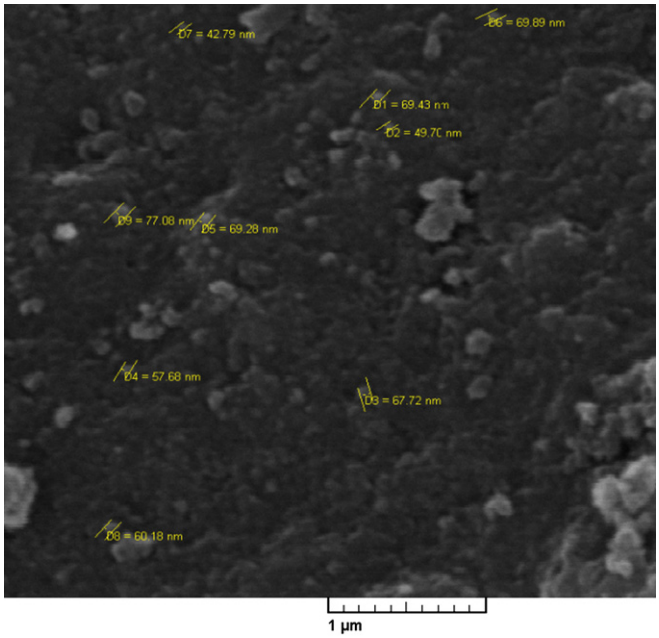


Fig. 1. The SEM image of immobilized nitrite ionic liquid 7.

2.6. Diazotization using pure nitrite ionic liquid 8, general procedure

Aniline derivative (20 mmol) was dissolved in 10 mL of 37% HCl. The mixture was stirred at 0–5 °C for 35 min. Pure nitrite ionic liquid (25 mmol) was added to aniline solution. Diazonium salt product was assayed by well-known azo-coupling reaction of phenol or aniline derivatives. For the coupling reaction with phenolic compounds, the reaction mixture was continuously added to the solution of phenolic compound (20 mmol) and NaOH (1 g) in 10 ml water. The participated dyes were filtered off and washed three times with cold water to afford the crude azo dyes. The crude

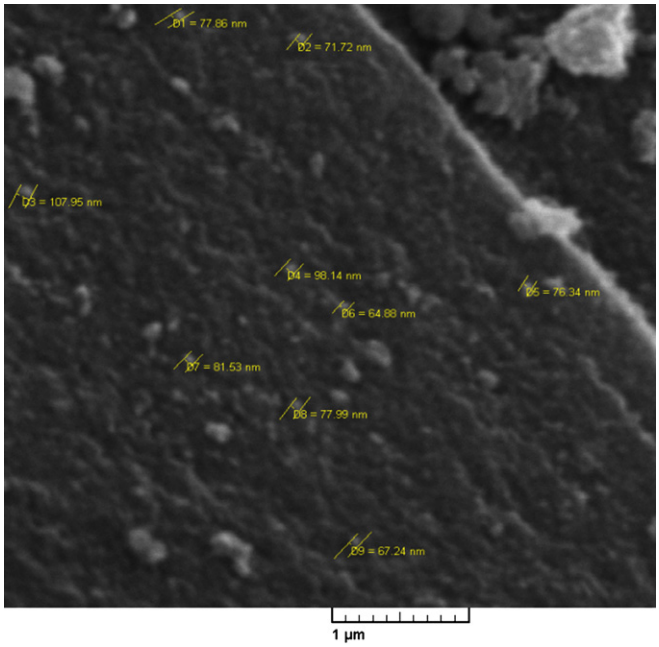
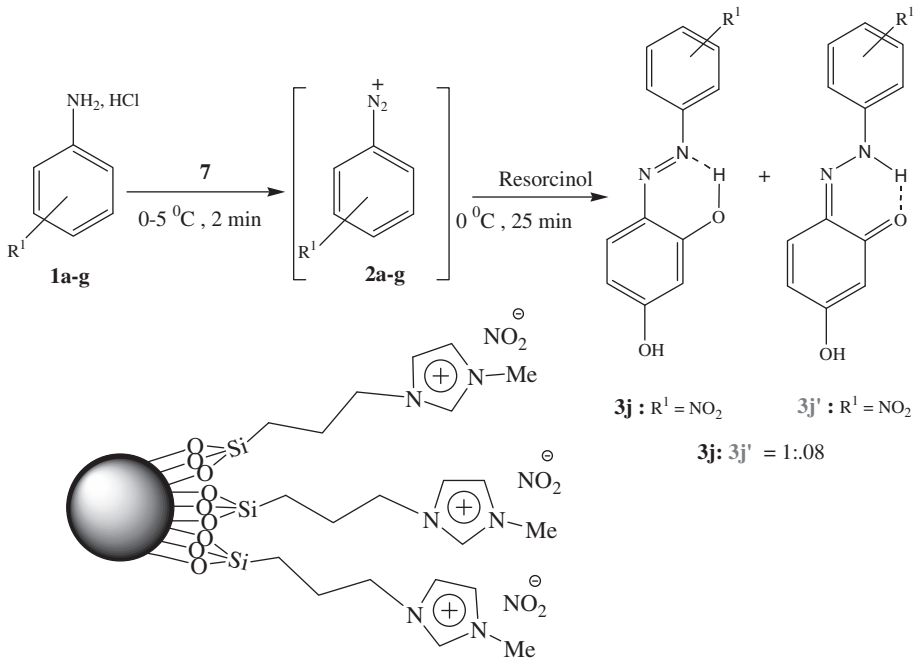


Fig. 2. The SEM image of silica nanoparticles.

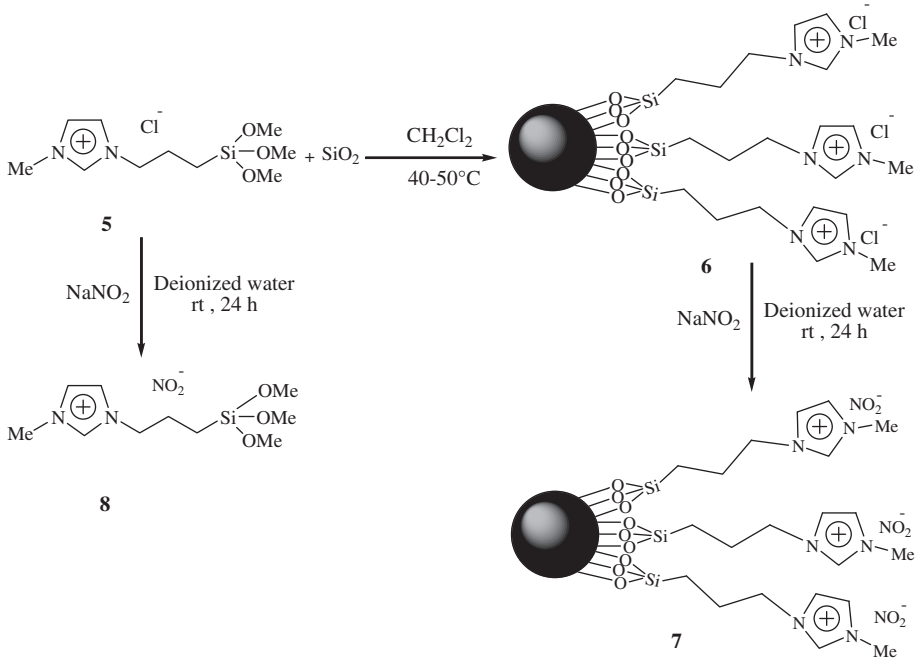


Scheme 1. Diazotization of anilines using ionic liquid 7 and azo-coupling with resorcinol.

dyes were purified by recrystallization on ethanol/water. For azo-coupling with aniline derivatives, the reaction mixture containing diazonium salts was continuously added to the solution of aniline derivative (20 mmol) in 10 ml water at 0–5 °C. The pH of mixture was adjusted to 6–7 by addition of NaOH solution (1 M) during stirring for 20 min. The participated dyes were isolated and purified as described above.

*2.7. Diazotization using immobilized nitrite ionic liquid **7**, general procedure*

The aniline derivative (20 mmol) was dissolved in 37% HCl (10 mL). The mixture was stirred at 0–5 °C for 10 min. While stirring of the mixture, immobilized nitrite ionic liquid **7** was added slowly until removal of aniline derivative from the reaction



Scheme 2. Preparation of immobilized nitrite ionic liquid 7.

Table 1
Diazotization of anilines using immobilized nitrite ionic liquid on silica and synthesis of azo-dyes.

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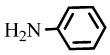
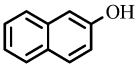
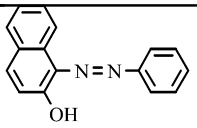
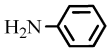
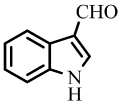
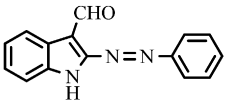
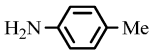
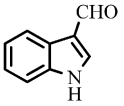
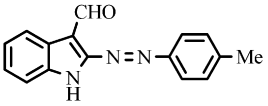
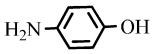
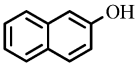
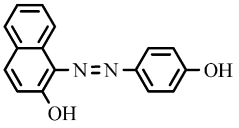
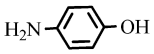
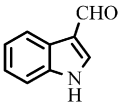
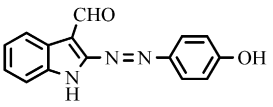
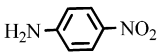
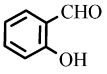
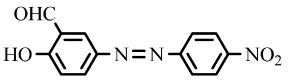
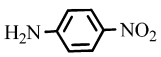
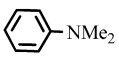
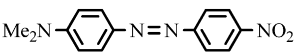
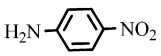
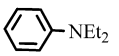
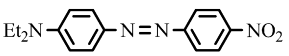
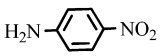
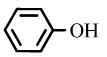
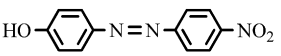
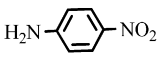
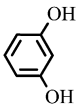
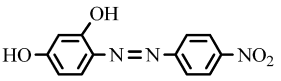
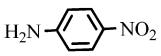
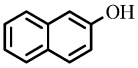
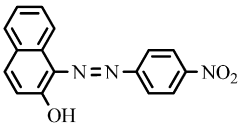
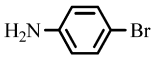
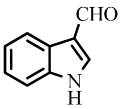
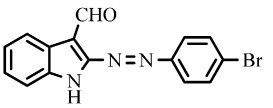
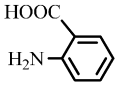
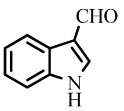
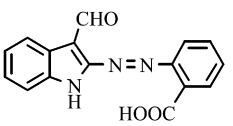
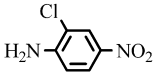
1		**2a**			**3a**
2		**2a**			**3b**
3		**2b**			**3c**
4		**2c**			**3d**
5		**2c**			**3e**
6		**2d**			**3f**
7		**2d**			**3g**
8		**2d**			**3h**
9		**2d**			**3i**
10		**2d**			**3j**
11		**2d**			**3k**
12		**2e**			**3l**
13		**2f**			**3m**
14		**2g**			**3n**

mixture. After 25 min, the diazonium salt in filtered solution was reacted with active benzene derivatives. For the coupling reaction with phenolic compounds, the filtered solution was continuously added to the solution of phenolic compound (20 mmol) and NaOH (1 g) in water (10 mL). The participated dye was filtered and washed three times with cold water. For coupling with aniline derivatives, the filtered solution containing diazonium salts was continuously added to the solution of aniline derivative (20 mmol) in water (10 mL) at 0–5 °C. The pH of mixture was adjusted to 6–7 by addition of NaOH solution (1 M). The participated dyes were isolated and purified as described above. The immobilized ionic liquid in the feed was washed tree times with ethanol and reused after exchanging of the chloride anion with nitrite ionic liquid. No significant decrease in yield of azo dyes **3b** and **3f** was observed after three times recycled immobilized ionic liquid.

2.8. Selected spectroscopic data

Compound ***3a***: $C_{16}H_{12}N_2O$: FT-IR (KBr, cm^{-1}): 3420 (bs), 1660, 1605. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 12.13 (OH); 8.02 (1H, dd, J = 7.38 and 2.14 Hz); 7.65 (2H, m); 7.49 (1H, d, J = 7.82 Hz); 7.45 (1H, dd, J = 7.21 and 2.10 Hz); 7.43 (1H, dt, J = 7.73 and 2.03 Hz); 7.39 (1H, d, J = 7.82 Hz); 7.36 (1H, dt, J = 7.55 and 1.89 Hz); 7.15 (3H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 140.01, 138.20, 135,35, 128.96, 128.31, 127.54, 124.52, 121.31, 120.28, 120.06, 119.12, 117.17, 116.29, 110.28.

Compound ***4a***: $C_{16}H_{12}N_2O$: FT-IR (KBr, cm^{-1}): 3391, 1685, 1667, 1612. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 14.26 (NH); 8.42 (1H, dd, J = 7.78 and 2.35 Hz); 7.62 (1H, d, J = 7.74 Hz); 7.58 (2H, m); 7.44 (1H, dd, J = 7.61 and 2.13 Hz); 7.41 (1H, dt, J = 7.81 and 2.42 Hz); 7.39 (1H, dt, J = 7.60 and 2.05 Hz); 7.35 (3H, m); 6.70 (1H, d, J = 7.74 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 159.69, 139.45, 137.8 4, 130.13, 129.19, 126.23, 124.51, 122.12, 122.00, 121.56, 120.02, 117.12, 113.80, 109.28.

Compound ***3b***: $C_{15}H_{11}N_3O_1$: FT-IR (KBr, cm^{-1}): 1789, 1604, 1549, 1134; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 11.99 (1H, s, NH); 9.97 (1H, s, CHO); 8.10 (1H, dd, J = 7.56 and 2.11 Hz); 7.43 (1H, dd, J = 7.49 and 2.04 Hz); 7.87 (2H, m); 7.45 (2H, m); 7.23 (3H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 163.69, 131.48, 130.98, 125.73, 124.50, 123.16, 122.79, 122.43, 121.65, 121.02, 118.43, 116.25, 113.80.

Compound ***3f***: $C_{13}H_9N_3O_4$: FT-IR (KBr, cm^{-1}): 3413, 3104, 1658, 1606, 1524, 1478, 1342, 1284. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 11.43 (1H, s); 10.05 (1H, s); 8.39 (2H, d, J = 7.26 Hz); 8.27 (1H, d, J = 2.21 Hz); 8.22 (1H, dd, J = 7.21 and 2.21 Hz); 8.01 (2H, d, 7.26 Hz); 7.14 (1H, d, J = 7.21 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 160.09, 135.87, 134,14, 130.25, 129.36, 128.63, 121.54, 120.23, 117.68, 112.17, 110.95.

Compound ***3g***: $C_{14}H_{14}N_4O_2$: FT-IR (KBr, cm^{-1}): 1611, 1531, 1519, 1475, 1345. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.78 (2H, d, J = 8.02 Hz); 7.75 (2H, d, J = 8.02); 7.70 (2H, d, J = 7.95 Hz); 6.69 (2H, d, J = 7.95 Hz); 3.65 (6H, s, $-NMe_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 135.54, 128.89, 126.63, 125.54, 123.35, 120.19, 117.85, 115.12, 35.12.

Compound ***3m***: $C_{16}H_{11}N_3O_3$: FT-IR (KBr, cm^{-1}): 3402, 3098, 1658, 1525, 1343; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 11.98 (1H, s, NH); 11.05 (1H, s, COOH); 9.95 (1H, s, CHO); 8.19 (2H, d, J = 7.61 Hz); 7.92 (2H, d, J = 7.46 Hz); 7.78 (2H, m); 7.45 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 163.25, 160.23, 134.50, 131.25, 130.89, 128.89, 127.98, 126.63, 125.54, 124.56, 124.06, 123.35, 122.56, 120.19, 117.85, 115.12.

3. Results and discussions

N-methyl-3-(3-trimethoxysilylpropyl) imidazolium chloride **5**, $[MTMSPIM]Cl^-$, was prepared from the reaction of *N*-methyl imidazole with (3-chloropropyl)trimethoxysilane at 80 °C. The solution of ionic liquid **5** in CH_2Cl_2 was then added to the suspension of freshly prepared silica nanoparticles in CH_2Cl_2. After stirring the mixture for 3 days at 40–50 °C, ionic liquid immobilized on silica **6** was prepared. Immobilized nitrite ionic liquid **7** was obtained in 98% yield as a white powder by stirring of **6** with excess amount of $NaNO_2$ in deionized water for 24 h at room temperature (Scheme 2).

The SEM image of silica nanoparticles was obtained and compared with the SEM images of immobilized nitrite ionic liquid **7.** Comparing the SEM image of silica nanoparticles with immobilized nitrite ionic liquid showed that the mean size of silica nanoparticles is larger than immobilized nitrite ionic liquid (Figs. 1 and 2).

Diazotization of aniline derivatives was examined using the new immobilized nitrite ionic liquid **7** at 0–5 °C in the presence of HCl. Diazotization of 4-nitroaniline was chosen as a model reaction. 4-Nitrodiazonium intermediate **2d** (R^1 = 4-NO_2) was prepared by the stirring of the mixture of 4-nitroaniline, immobilized nitrite ionic liquid and 37% HCl for 40 min in aqueous media. This intermediate was trapped by the addition in to the solution of *N*, *N*-dimethylaniline to obtain the azo dye **3g** via the well-known azo-coupling reaction (Scheme 1)). The product was characterized by ^1H, ^{13}C NMR and IR spectroscopic data and by comparing of the melting point with literature value.

Table 2
Comparison of the reaction times and yields of azo dyes of present method with the reported values.

Entry	Product number	Time (min)			M.P (°C)		Yield[a] (%)		
		IL-ONO [9]	Pure IL 8	Immobilized IL	Found reported [Ref.]		IL-ONO [9]	Pure IL 8 [32]	Immobilized IL
1	**3a**	25	22	21	131–132	131–132 [10]	87%	87%	89%[b]
2	**3b**	40	39	40	188–193	190–195 [32]	75%	76%	77%
3	**3c**	38	37	35	129–134	130–135 [32]	71%	75%	74%
4	**3d**	20	20	22	194–198	192–193 [10]	85%	85%	88%[b]
5	**3e**	38	35	33	194–197	194–197 [32]	80%	79%	81%
6	**3f**	24	23	20	184–186	184–186 [10]	84%	84%	90%
7	**3g**	20	20	20	219–223	225–228 [10]	83%	83%	87%
8	**3h**	25	25	22	145–146	145 [10]	85%	85%	85%
9	**3i**	22	20	25	203–204	207 [10]	86%	86%	85%
10	**3j**	25	23	22	183–188	185 [10]	89%	89%	90%[b]
11	**3k**	22	21	23	250–252	248–252 [10]	89%	89%	92%[b]
12	**3l**	35	35	32	161–164	162–163 [32]	85%	83%	82%
13	**3m**	36	35	34	191–194	190–195 [32]	80%	82%	84%
14	**3n**	22	20	20	126–128	127–128 [10]	90%	90%	90%

[a] Isolated yield.
[b] Total yield of azo and hydrazone isomers.

In comparison with the nitrite containing ionic liquid derived from the *O*-nitrosation of *N*-methyl-*N*-hydroxybutylimidazolinium chloride, IL-ONO [10], this immobilized nitrite ionic liquid similarly produced high yield of product under the identical reaction conditions. We studied the optimization of the reaction conditions with different molar ratios of the aniline, ionic liquid and β-naphthol. The best ratio of equivalents was found to be 1:1.25:1. In order to investigate the scope and limitation of IL/silica gel as reagent for diazotization and subsequent azo-coupling, different anilines and phenolic compounds as the reactants were also tested and the results were summarized (Table 1).

It could be found that IL/silica gel could act as nitrosonium source for diazotization. Good to excellent yields ranging from 73% to 92% were obtained in all systems under investigation. The diazotization of aniline, 4- hydroxyaniline and 4-nitroaniline and subsequent coupling reaction with 2-naphthol or resorcinol gave expected mixture of products (**3a** and **3a′**), (**3d** and **3d′**), (**3j** and **3j′**) and (**3K** and **3K′**) in 89%, 88%, 90% and 92% yields respectively. The mixture of isomers (**3a** and **3a′**), (**3d** and **3d′**), (**3j** and **3j′**) and (**3K** and **3K′**) with ratio of (1: 0.11), (1: 0.09), (1: 0.08) and (1: 0.13) respectively were determined by ^{1}H NMR spectroscopic data. We also examined the diazotization of anilines using the pure N-methyl-3-(3-trimethoxysilylpropyl) imidazolium nitrite **8** and subsequent azo-coupling with active benzenes under the same conditions.

These results suggest that the immobilized ionic liquid **7**, IL-ONO and pure N-methyl-3-(3-trimethoxysilylpropyl) imidazolium nitrite **8** can act as nitrosonium source for diazotization of anilines. As it can be seen from Table 2, the reaction times are shorter in the presence of immobilized ionic liquid in comparison with other IL's as a result of its larger interface area.

4. Conclusion

In conclusion, immobilized nitrite ionic liquid was prepared and used as an efficient nitrosonium source for the convenient diazotization and subsequent azo-coupling. Azo dyes were synthesized in good yields in short reaction times under mild heterogeneous conditions. Using of the ionic liquids, pure N-methyl-3-(3-trimethoxysilylpropyl) imidazolium nitrite and IL-ONO as nitrosonium sources in this procedure no significant difference in the results were observed. The reaction times are slightly shorter and the yields were slightly higher in the presence of immobilized ionic liquid in comparison with other IL's as a result of its larger interface area. The heterogenisation of nitrite ionic liquid can offer important advantages in handling and in separation and reuse thus lowering the risks and hazards of a chemical process, as well as simplifying the work up procedure.

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