1,4-diazoniabicycle[2.2.2]octane-chloride modified rice husk silica as a basic catalyst for the synthesis of phosphoryloxy phosphonate

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Abstract

The high surface area hybrid 1,4-diazoniabicycle[2.2.2] octane chloride xerogel, RH@DABCO, was prepared and used as an environmentally friendly catalyst in the synthesis of phosphoryloxy phosphonate compounds. The present methodology offers several advantages such as mild reaction condition, short reaction time, excellent product yield, simple procedure, recycle exploitation and use of a green and reusable catalyst. Moreover, the ^{1}H and ^{13}C chemical shift values of phosphate-phosphonates were computed and the scaled values were compared with those of experimental NMR spectra. The calculated ^{1}H and ^{13}C chemical shifts were in good accordance with the experimental data.

RH@DABCO:
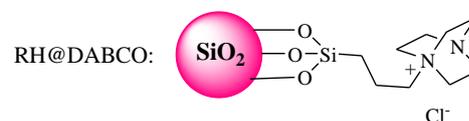
Keywords: Rice husk silica, Phosphate-phosphonates compounds, DABCO, Heterogeneous catalyst, Theoretical simulation.

Introduction

Using green reagents in organic reactions have attracted the attention of chemists in recent years. Therefore, solid heterogeneous catalysts can play a significant role in development of environmentally-friendly technologies. Compare to homogeneous catalysts, these materials have many advantages such as their efficiency, good stability, high surface area, facile and good functionalization, easy separation, low toxicity, and cost which are important in industry.[1-3]

Silica is one of the more extensively used solid supports for preparation of heterogeneous catalysts. Rice husk as a thin but abrasive skin in nature is a green source for preparation of silicon and silicon compounds,[4] such as silica, silicon nitride,[5] and silicon carbide.[6] Moreover, amine grafted solid materials such as silica particles have been approved as a type of good heterogeneous catalysts for organic reactions. 1,4-diazabicyclo[2.2.2]octane (DABCO) is a bicyclic base compound with two tertiary nitrogen, which has been widely used as a homogenous catalyst in polymerization and organic reactions. DABCO is an inexpensive, non-toxic, high reactive, and easy to handle base catalyst for a number of organic transformation reactions. However, DABCO cannot be recovered, and eliminated as residue in many reported procedures. To solve this problem, supporting or immobilizing of DABCO is desirable.[7,8]

Phosphorus compounds and its derivatives containing the P-C bond are known as enzyme inhibitors,[9] herbicides,[10] antibiotic and diverse biological activities.[11] Also, phosphonates have attracted extensionally synthetic proceeding of chemists because of their use in the production of the flame retardance[12,13] and organic synthesis[14] and their pharmacological interests.[15,16] Moreover, organophosphates are important molecular patterns in living organisms such as DNA, ATP, RNA, and cell membranes.[17] In particular, α-hydroxyketone phosphate have attracted interest of chemists serving as substantial intermediates and sugar analogues for construction of oligonucleotide and phospholipid.[18-20] as a result, various methods have been appeared expounding novel synthesis of phosphonate compounds.[21,22] In addition, due to environmental considerations, performing this reaction in aqueous media has become highly attractive in recent years.[23-25] Considering these factors, we attempted to prepare hybrid 1,4-diazoniabicycle[2.2.2]octane chloride xerogel, RH@DABCO and used them in the synthesis of phosphoryloxy phosphonate derivatives (Scheme 1). It should be noted that this is the first report on the use of RH@DABCO as catalyst for these compounds. Some theoretical investigations were also performed on one of the phosphoryloxy phosphonate compounds in water.

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Scheme 1. *Synthesis of phosphoryloxy phosphonate derivatives.*

Experimental

General

All reagents and solvents used were provided from Fluka or Merck and used without further purification. Rice husk (RH) was prepared from a rice farm in Khozestan-Baghmalek (Iran). The ^{1}H and ^{13}C spectra were measured on a Bruker Advance DPX 400 MHz instrument spectrometer using TMS as internal standard. FT-IR measurements were performed using KBr disc on a BOMEM MB-Series 1998 FT-IR spectrometer. Thermal analysis was done by using a thermogravimetric analyzer (TGA, BAHR, SPA 503) in N_2 at a heating rate of 10 ^{o}C min^{-1}. Scanning electron microscope, (Philips XL30 scanning electron microscope) was also used to obtain SEM images.

Synthesis of RH@DABCO

First, chloropropyl-grafted rice husk silica (RH-PrCl) was prepared based on the reported method by immobilizing of chloropropyl groups through co-condensation of RH-SiO$_2$ and 3-chloropropyl trimethoxysilane (CPTMS).[26] Then, 3.0 g of RH-PrCl was added to a flask containing DABCO (3 mmol) and 30 mL of anhydrous acetone. The reaction mixture was refluxed with stirring for 24 h. Then, the reaction mixture was cooled, filtered and washed for several times with water and acetone. Finally, the DABCO-functionalized rice husk ash (RH@DABCO) was dried at 50°C for 8h.

General procedure for the synthesis of phosphoryloxy phosphonate derivatives

RH@DABCO (0.1 g) was added slowly to a mixture of the acid chloride **1** (5 mmol) and dialkyl (aryl) phosphite **2** (4 mmol). Then, water (5 ml) was added, and the mixture was heated at 60 ^{o}C. After completion of the reaction (20-50 min) as indicated by TLC (n-hexane:ethylacetate 8:1), the resulting solid was separated by filtration, washed with water and diethylether, and dried to acquire the pure compounds.

### Diphenyl[[diphenoxyphosphoryl)oxy](4-chlorophenyl)methyl]phosphonate

Yellow powder. mp: 157-160 °C. IR (KBr) (cm^{-1}): 1584, 1461, 1385, 1291, 1157. ^{1}H-NMR (500 MHz, CDCl$_3$): δ = 6.08 (dd, 1 H, CH), 6.90-7.27 (22 H, m, 22 CH), 7.47 (2 H, 2 CH) ppm. ^{13}C-NMR (125 MHz, CDCl$_3$): δ = 74.7 (CH), 119.9 (CH), 120.2 (2 CH), 121.1 (2 CH), 120.9 (2 CH), 124.9 (CH), 125.7 (2 CH), 125.9 (CH), 129.1 (2 CH), 129.8 (2 CH), 130.0 (2 CH), 130.2 (2 CH), 130.3 (2 CH), 130.6 (2 CH), 136.1 (C), 140.1 (C), 150.2 (C), 150.3 (2 C), 150.5 (C) ppm. ^{31}P-NMR (202 MHz, CDCl$_3$): δ = -11.69 ($^3J_{PP}$ = 39.9 Hz), 7.68 ($^3J_{PP}$ = 39.9 Hz) ppm.

Diphenyl[[diphenoxyphosphoryl)oxy](phenyl)methyl]phosphonate

Yellow powder. mp: 143-146 °C. IR (KBr) (cm^{-1}): 1539, 1488, 1455, 1360, 1288, 1149. ^{1}H-NMR (500 MHz, CDCl$_3$): δ = 6.18 (CH), 6.71-7.41 (25 CH) ppm. ^{13}C-NMR (125 MHz, CDCl$_3$): δ = 75.9 (CH), 119.8 (2 CH), 120.4 (2 CH), 120.7 (2 CH), 121.7 (2 CH), 125.6 (2 CH), 125.8 (2 CH), 128.8 (2 CH), 128.9 (2 CH), 129.1 (2 CH), 129.2 (2 CH), 129.7 (2 CH), 129.9 (CH), 130.2 (2 CH), 131.6 (C), 149.8 (C), 150.2 (C), 150.5 (C), 150.8 (C) ppm. ^{31}P-NMR (202 MHz, CDCl$_3$): δ = -11.68 ($^3J_{PP}$ = 40.2 Hz), 8.36 ($^3J_{PP}$ = 40.2 Hz) ppm.

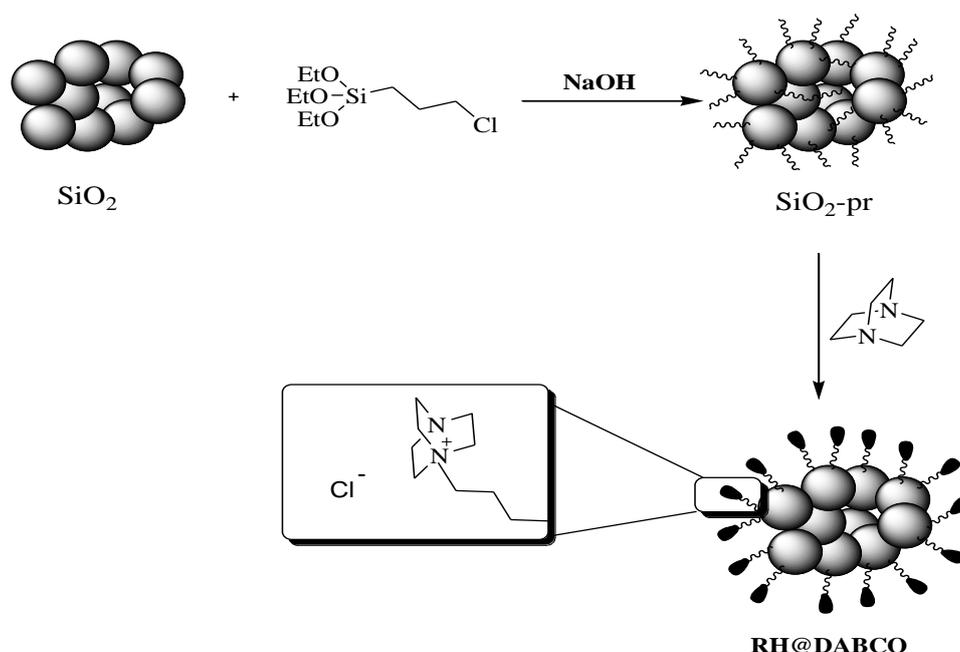### Diphenyl[[diphenoxyphosphoryl)oxy](4-nitrophenyl)methyl]phosphonate

Yellow powder. mp: 176-178 °C. IR (KBr) (cm^{-1}): 1519, 1481, 1362, 1292, 1145, 1087. ^{1}H-NMR (500 MHz, CDCl$_3$): δ = 6.27 (CH), 7.02-
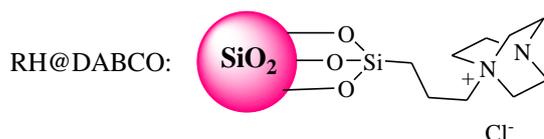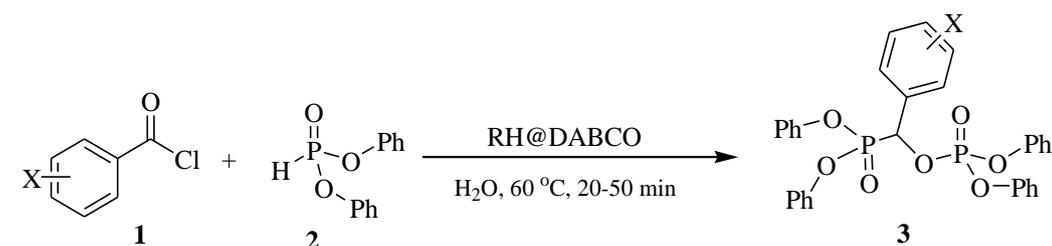
1, 3	X
a	Ph
b	4-Cl-C$_6$H$_4$
c	4-Br-C$_6$H$_4$
d	4-NO$_2$-C$_6$H$_4$
e	4-Me-C$_6$H$_4$
f	4-OMe-C$_6$H$_4$
g	Et
h	t-Bu

Scheme 2. *Synthesis of phosphoryloxy phosphonate derivatives.*

Scheme 3. *Synthesis of RH@DABCO.*

7.35 (20 CH), 7.64 (2 CH), 8.09 (2 CH) ppm. ^{13}C-NMR (125 MHz, CDCl$_3$): δ = 75.0 (CH), 120.0 (2 CH), 120.3 (2 CH), 120.5 (2 CH), 123.8 (2 CH), 125.9 (2 CH), 126.2 (CH), 126.6 (CH), 128.8 (2 CH), 129.3 (2 CH), 130.1 (2 CH), 130.3 (2 CH), 130.4 (2 CH), 130.9 (2 CH), 132.6 (C), 148.6 (C), 150.1 (C), 150.2 (C), 150.3 (C), 150.5 (C) ppm. ^{31}P-NMR (202 MHz, CDCl$_3$): δ = -10.28 ($^3J_{PP}$ = 40.0 Hz), 12.4 ($^3J_{PP}$ = 40.1 Hz) ppm.

Diphenyl[[diphenoxyphosphoryl)oxy](4-bromophenyl)methyl]
phosphonate
White powder. mp: 166-168 °C. IR (KBr) (cm^{-1}): 1556, 1409, 1382, 1301, 1151, 1025. ^{1}H-NMR (500 MHz, CDCl$_3$): δ = 6.85 (CH), 6.89-7.39 (22 CH), 7.55 (2 CH) ppm. ^{13}C-NMR (125 MHz, CDCl$_3$): δ = 78.6 (CH), 118.7 (2 CH), 120.1 (2 CH), 120.4 (2 CH), 122.0 (2 CH), 124.9 (CH), 125.5 (2 CH), 125.7 (CH), 128.9 (2 CH), 129.7 (2 CH), 129.8 (2 CH), 129.9 (2 CH), 130.1 (2 CH), 130.3 (2 CH), 133.1 (C), 138.8 (C), 150.1 (C), 150.3 (2 C), 151.6 (C) ppm. ^{31}P-NMR (202 MHz, CDCl$_3$): δ = -9.81 ($^3J_{PP}$ = 38.6 Hz), 8.47 ($^3J_{PP}$ = 38.4 Hz) ppm.

Results and discussion

In continuation of our interest in using silica heterogeneous catalysts in organic transformations,[26-29] herein, we design an organic-inorganic hybrid nanocatalyst as a basic organocatalyst for the synthesis of phosphoryloxy phosphonate compounds (Scheme 2).

Recently, we have synthesized a new organic-inorganic nano-silica based catalyst, n-propyl-4-aza-1-azoniabicyclo[2.2.2]octane chloride supported rice husk silica (RH@DABCO).[30] Based on that report, in this study the catalyst (RH@DABCO) was prepared with some modifications by the direct incorporation of chloropropyl groups through co-condensation of rice husk nanosilica and CPTMS and then grafting of DABCO onto the surface of the silica by the simple nucleophilic substitution reaction (Scheme 3).

The catalyst has been characterized by a Fourier transform infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA), scanning electron microscope (SEM) (Figures 1-2), and by their comparisons with that of valid sample. The FT-IR spectra of RH-SiO$_2$ and RHA@DABCO are shown in Figure 1a. The two spectra exhibit basic characteristic peaks at approximately 990-1220, 801, and 473 cm^{-1}, which were attributed to the presence of Si-O-Si
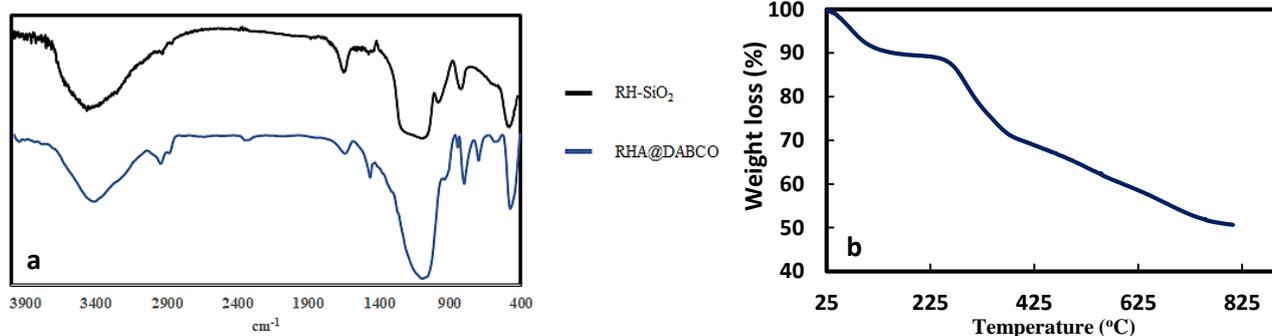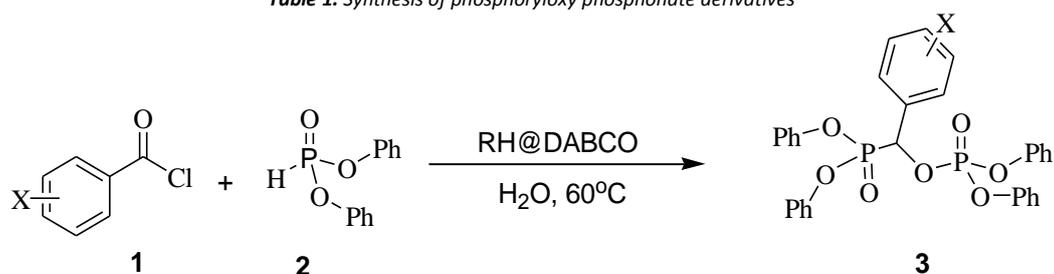

Figure 1. (a) *The FT-IR spectra of RH-SiO$_2$ and RH@DABCO and **(b)** TGA profile of RH@DABCO.*

Entry	X	Time	Yield %
1	Ph	20	92
2	4-Cl-C_6H_4	20	85
3	4-Br-C_6H_4	20	90
4	4-NO_2-C_6H_4	20	90
5	4-Me-C_6H_4	35	87
6	4-OMe-C_6H_4	35	85
7	Et	50	89
8	t-Bu	50	80

network. The presence of peaks at 1200-1500 and 2870-3040 cm^{-1} were characteristic of the C-H bonds in catalyst spectrum. Also, a band at 1465 cm^{-1} is due to the tertiary amine group. The bands around 1635 and 3400 cm^{-1} are assigned to the bending vibration of surface adsorbed water molecules. The presence of a broadband near 3450 cm^{-1} is also owing to a stretching vibration of SiO-H bond and HO-H vibration of water molecules adsorbed on the surface.

Thermal stability of catalyst was checked by thermal gravimetric analysis (TGA) (Figure 1b). The TG curve indicates an initial weight loss of 10% up to 125 °C due to the adsorbed water and organic solvent adsorbed onto the surface of silica support. The significant weight loss occurs at 250-450 °C, comes from the decomposition of organic substances. This result conveys the clear information that the surface of silica is successfully modified by pr-DABCO.

The morphology of the samples was observed by scanning electron microscopy (Figure 2). Accordingly, the RH@DABCO particles have spherical shape with nano dimension ranging from 70 to 300 nm.

After characterization, the catalytic efficiency of this basic nanocatalyst has been systematically studied in the rapid and efficient preparation of phosphate-phosphonates compounds. In the prime stage of examination, we focused on the model reaction of benzyl chloride, di phenyl phosphite.

After testing different reaction conditions, it was found that upon simple mixing of acid chlorides (1 mmol), dialkyl (aryl) phosphites (2 mmol), in the presence of RH@DABCO (0.1 g), a quantitative conversion to phosphoryloxy phosphonates **3** was observed with good to excellent yields in water (Table 1). In addition, compounds (3a-3h) does not perform without catalyst.

A possible mechanism for this transformation is proposed in Scheme 4, indicating the role of DABCO as a nucleophile and leaving group in the formation of phosphate-phosphonates compounds.

In order to show the merit of the presented protocol in phosphate-phosphonates synthesis, we compared the results of RHA@DABCO catalyst with some of those reported in the literature (Table 2).

Theoretical section
^{1}H and ^{13}C-NMR study
Figure 3 depicts the relaxed geometry structure of diphenyl[(diphenoxyphosphoryl)oxy](4-methylphenyl)methyl]phos
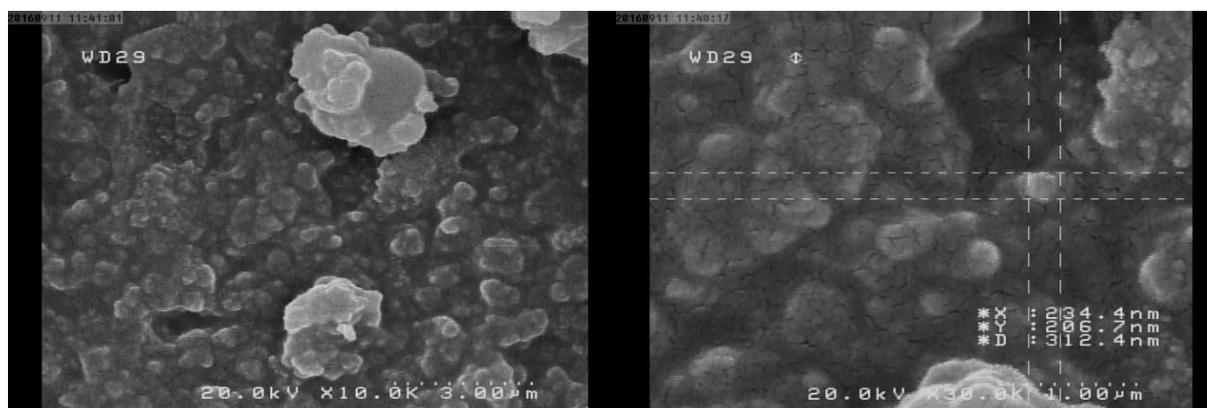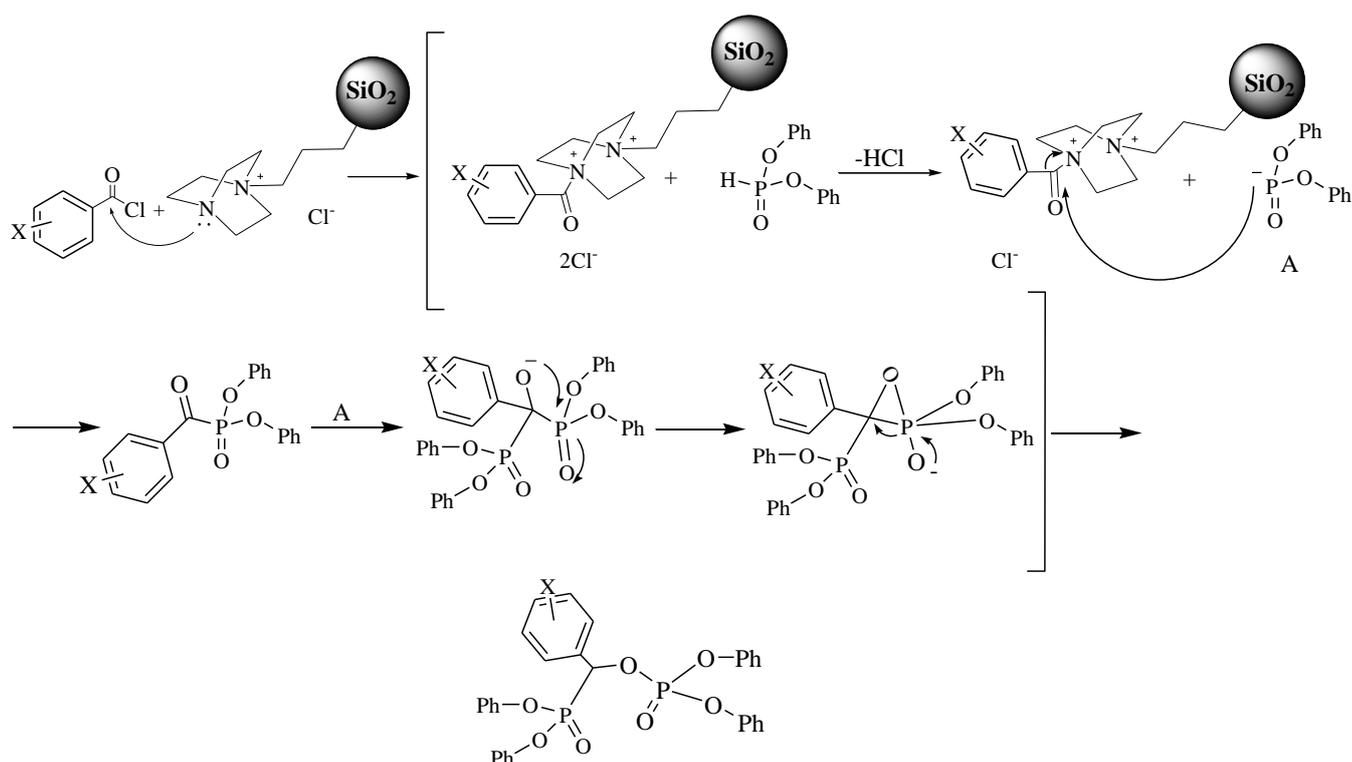

Figure 2. SEM images of RHA@DABCO.

Scheme 4. Plausible Reaction Mechanism.

phonate.[35] The entry 5 in Table 1 is selected to determine each peak to the corresponding atom. Figure 4 shows the experimental and the theoretical ^{1}H and ^{13}C-NMR spectra of the studied compounds. Base on the chemical shift values collected in Table 3, it can be observed that the experimental values are at 2.357–7.459/21.26–150.46 ppm while for the calculated ^{1}H/^{13}C chemical shifts are in the range of 2.304–8.209/21.649–160.348

ppm. A remarkable correlation (R^2 = 0.98, R^2 = 0.97) are found between the experimental and calculated ^{1}H/^{13}C chemical shifts, respectively. Due to the estimated slopes for both of the graphs 1.048 and 1.004 for ^{1}H and ^{13}C spectra, it can be concluded that the calculated spectra are in well accordance with the corresponding experimental spectra (Figures 5 and 6).[27]
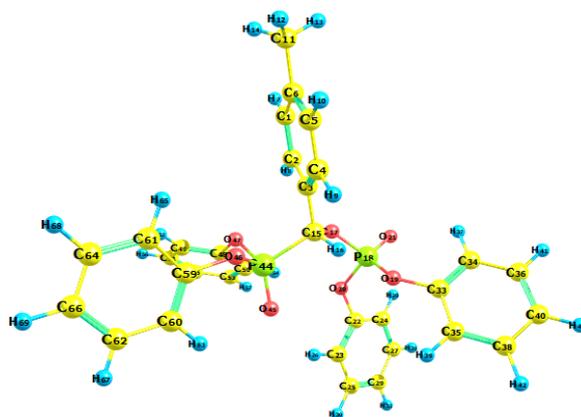

Figure 3. The optimized geometry of entry 5 in Table 1.

Table 2. Comparison of the efficacy of RHA@DABCO catalyst with some of those reported in the literature.

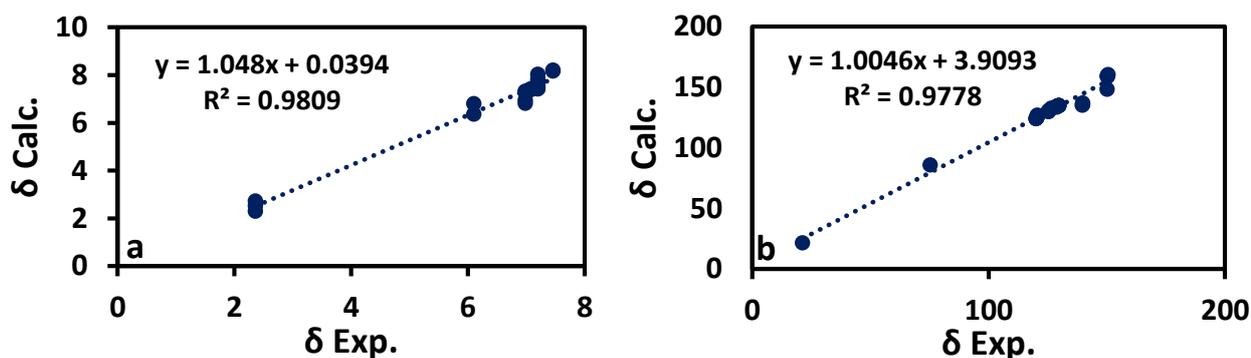| Entry	Catalyst	Time (min)	Yield (%)	Ref.
1	N-methylimidazole	35-40	74-92	31
2	KHSO$_4$	60-240	83-91	32
3	Et$_3$N + MgCl$_2$	60-120	85-98	33
4	Et$_3$N	120	63-89	34
5	This work	20-50	80-92	-

Figure 4. *The correlations between the experimental and calculated* ***(a)*** *^{1}H-NMR together with* ***(b)*** *^{13}C-NMR chemical shifts of the entry 5 in Table 1.*

Table 3. *The calculated (δ $_{Calc.}$) and experimental (δ $_{Exp.}$) chemical shift values of ^{1}H-NMR and ^{13}C-NMR for the entry 5 in Table 1 (all in ppm).*

| Atom	δ $_{Calc.}$	δ $_{Exp.}$	Atom	δ $_{Calc.}$	δ $_{Exp.}$
H-12	2.304	2.357	C-11	21.649	21.26
H-14	2.523		C-15	85.801	75.279
H-13	2.72		C-24	123.892	119.971
H-16	6.364	6.101(6.081-6.121)	C-34	124.027	120.011
H-52	6.797		C-35	124.24	120.164
H-65	6.819	6.985(6.917-7.053)	C-60	124.857	120.203
H-39	6.952		C-61	125.057	120.426
H-43	7.279		C-49	125.157	120.461
H-42	7.326		C-50	126.2	120.5
H-58	7.378	7.072(7.053-7.092)	C-23	126.995	120.532
H-31	7.415		C-40	129.804	125.255
H-56	7.415	7.196(7.107-7.285)	C-55	129.954	125.279
H-69	7.452		C-66	130.189	125.295
H-32	7.438		C-29	130.781	125.421
H-28	7.458		C-2	132.776	126.588
H-41	7.484		C-5	133.523	128.637
H-57	7.489		C-1	134.355	128.735
H-68	7.539		C-36	134.355	129.056
H-67	7.539		C-53	134.387	129.325
H-10	7.545		C-4	134.397	129.336
H-9	7.595		C-27	134.558	129.548
H-7	7.661		C-51	134.669	129.604
H-37	7.681		C-38	134.71	129.651
H-30	7.744		C-62	134.76	129.704
H-63	7.84		C-64	135.125	139.648
H-8	8.036		C-25	135.536	139.671
H-26	8.161	7.459(7.451-7.467)	C-3	136.901	139.67
H-54	8.209		C-6	148.236	150.054
			C-22	158.651	150.162
			C-59	158.654	150.199
			C-48	159.591	150.253
			C-33	160.348	150.46

a

b
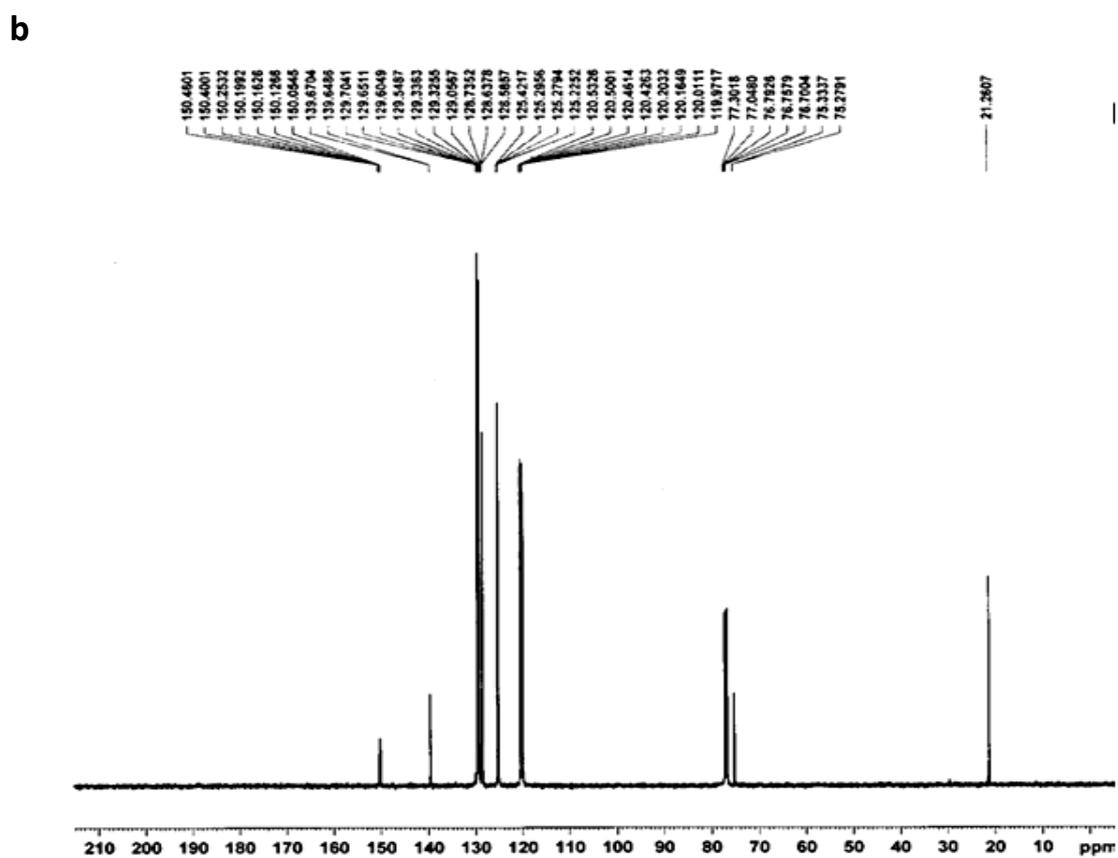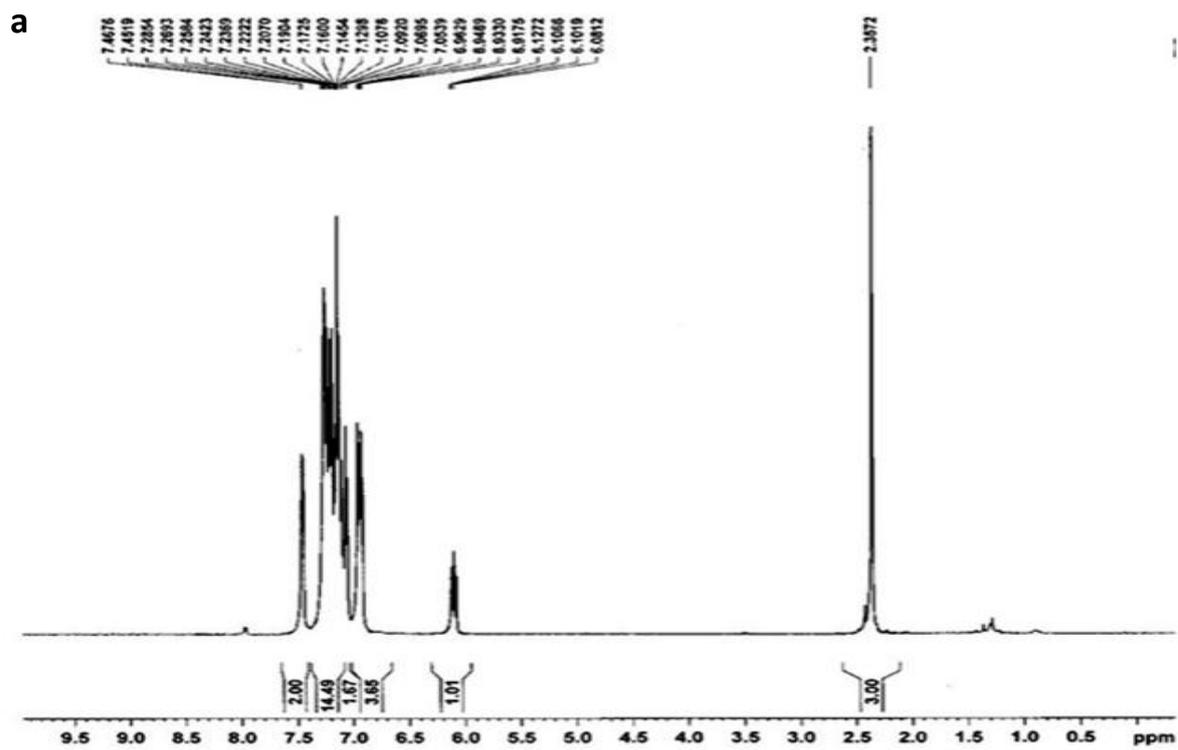
Figure 5. The obtained experimental (a) ¹H-NMR and (b) ¹³C-NMR spectra for the entry 5 in Table 1.
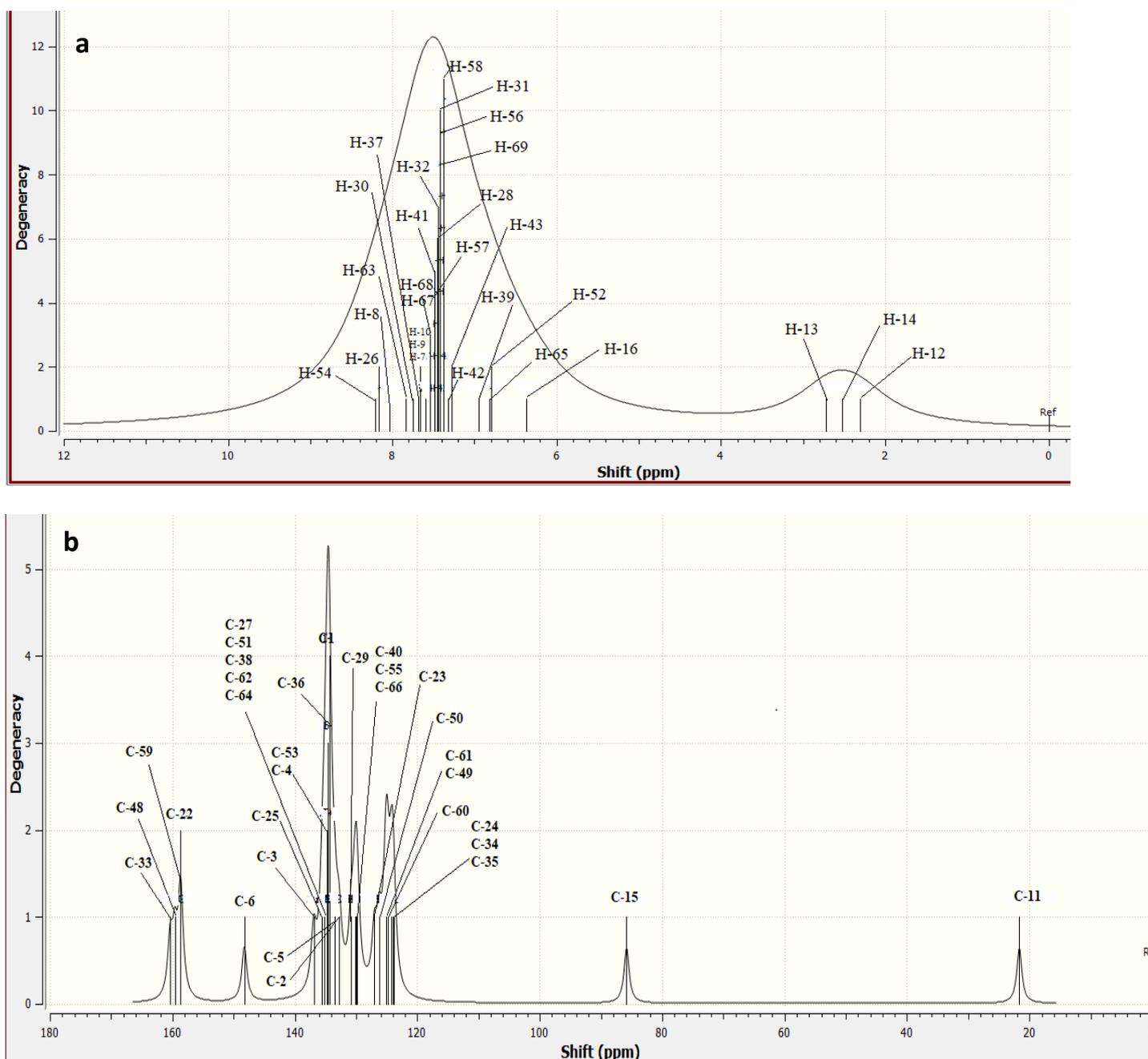
Figure 6. The **(a)** ¹H-NMR and **(b)** ¹³C-NMR spectra simulated at B3LYP /6-311++G** in CDCl₃ for the entry 5 in Table 1 (see Figure 3).

Conclusion

In this research, the performance of hybrid 1,4-diazoniabicycle [2.2.2]octane chloride xerogel, RH@DABCO as basic heterogeneous catalyst for the synthesis of phosphoryloxy phosphonate compounds was investigated. The catalytic system can combine the advantages of homogeneous and heterogeneous catalysts and therefore they can be selective, reactive, and recyclable. The most outstanding merits of this method were its simple process, controllable procedure, being recyclable after usage, reasonable yields, and environmentally benign solvent. The catalyst was characterized by the aid of FT-IR, SEM, and TGA. ¹H and ¹³C chemical shifts which were calculated for the titled compound were in good agreement with the experimental data.

Acknowledgements

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