Scientific paper

Carbon-based Solid Acid Catalyzed Highly Efficient Selective Oxidations of Sulfides to Sulfoxides or Sulfones with Hydrogen Peroxide

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Abstract

Carbon-based solid acid catalyst was found to be highly efficient, eco-friendly; recyclable heterogeneous catalyst for selective oxidation of sulfides to sulfoxides or sulfones in excellent yields under mild reaction conditions using 30% hydrogen peroxide as an oxidant.

Keyword: Carbon-based solid acid, oxidation, hydrogen peroxide, heterogeneous catalyst, sulfoxides, sulfones

1. Introduction

Replacement of conventional toxic and pollutant Brønsted and Lewis acid catalysts with environmentally benign and reusable solid heterogeneous catalysts is an active area of current research. New catalysts may include acidic zeolites, sulfated zirconia and acidic groups containing resins. Using solid acid catalyst have some advantages such as lower of equipments, ease of products separation, recycling of the catalyst and environmental acceptability as compared to liquid acid catalyst.[1]

Moreover, ideal solid acid catalysts should have high stability and numerous strong protonic acid sites. Carbon-based solid acid catalyst has many advantages. It is insoluble in common organic solvents, causes low corrosion, and shows environmental acceptability. Also the products could be easily separated from the reaction mixture and the catalyst is recoverable without decreasing its activity. Therefore, it can be successfully used instead of sulfuric acid as catalyst.[2–5]

Organosulfur compounds, such as sulfoxides and sulfones, are useful compounds in organic chemistry. In particular, sulfoxides are valuable synthetic intermediates for the production of different varieties of chemically and biologically active molecules.[6–16] The main synthetic route for preparation of these valuable materials is oxidation of corresponding sulfides.[17]

Various reagents including high valent metal and nonmetal oxides, mineral salts, e.g. potassium permanganate, potassium bromate, organic peroxides and hydrogen peroxide, have been used for the oxidation of functional groups.[18,19] There is also some limitations for using of mineral oxidants because they require rigorous control of the reaction conditions. Moreover, the lack of selectivity in multistage organic synthesis, tedious work-up and toxicity are their main disadvantages.[20] Aqueous H_2O_2 is an ideal oxidant for its high content of active oxygen (47%) and cleanness of the method.[21–23]

This work represent the continuation of our studies using carbon-based solid acid in organic transformations.[24] We introduce an efficient, rapid, and clean procedure for the oxidation of sulfides through using carbon-based solid acid and hydrogen peroxide in a suitable solvent. There is also a good selectivity in the oxidation of sulfides to sulfoxides or sulfones, which depend on the reaction conditions (see Scheme 1).

2. Experimental

Chemicals were purchased from Fluka, Merck and Aldrich chemical companies. The products were characterized by comparison of their spectral (IR, ^{1}H NMR), TLC and physical data with the authentic samples. Carbon-based solid acid was prepared according to the reported procedure.[2]

2. 1. General Experimental Procedure for the Preparation of Sulfoxides

A mixture of carbon-based solid acid (0.10 g), sulfide substrate (1 mmol), hydrogen peroxide (aq. 30%, 1 mmol) and 1,2-dichloroethane (5 ml) was refluxed for the specified reaction time (see Table 1). The progress of reaction was monitored by TLC and GC method. At the end of reaction, catalyst was removed by filtration and the resulting solution was concentrated under reduced pressure. Then, residue was purified by column chromatography on silica gel. After removing the solvent, the corresponding sulfoxide was obtained in good to excellent yield (Table 1).

Table 1. Oxidation of sulfides (1 mmol) to sulfoxides with hydrogen peroxide (1 mmol)/carbon-base solid acid (0.10g).

Entry	R–S–R’	Reaction time (min)	Yield (%)[a]
1	R=R’=C_6H_5	10	98
2	R=C_6H_5; R’=CH_3	10	94
3	R=C_6H_5; R’=$CH_2C_6H_5$	10	95
4	R=C_6H_5; R’=n–C_4H_9	10	88
5	R=R’ $CH_2C_6H_5$	8	95
6	R=R’=n–C_4H_9	7	95
7	R=R’=n–C_3H_7	7	95
8	R= $CH_2C_6H_5$; R’=n–C_4H_9	10	90
9	Dibenzothiophene	30	70

[a] Isolated yields.

2. 2. General Experimental Procedure for the Preparation of Sulfones

A mixture of carbon-based solid acid (0.20 g), sulfide substrate (1 mmol), hydrogen peroxide (aq. 30%, 5 mmol) and 1,2-dichloroethane (5 ml) was refluxed for the specified reaction time (see Table 2). After completion of the reaction, carbon-based solid acid catalyst was removed by filtration and the resulting solution was concentrated under reduced pressure. Then, the residue was subjected to column chromatography using silica gel to obtain pure compound in good yield (Table 2).

Table 2. Oxidation of sulfides (1 mmol) to sulfones with hydrogen peroxide (5mmol)/carbon-base solid acid (0.20g).

Entry	R–S–R’	Reaction time (min)	Yield (%)[a]
1	R=R’=C_6H_5	10	95
2	R=C_6H_5; R’=CH_3	10	95
3	R=C_6H_5; R’=$CH_2C_6H_5$	10	98
4	R=C_6H_5; R’=n–C_4H_9	10	93
5	R=R’ =$CH_2C_6H_5$	10	95
6	R=R’=n–C_4H_9	7	95
7	R=R’=n–C_3H_7	7	97
8	R= $CH_2C_6H_5$; R’=n–C_4H_9	10	98
9	Dibenzothiophene	45	75

[a] Isolated yields.

3. Results and Discussion

Carbon-based solid acid was prepared according to the procedure reported by Hara et al.[2] The density of SO_3H group was measured using NaOH (0.01 mol/L) as titrant by acid–base potentiometric titration method. The amount of SO_3H groups attached to polycyclic aromatic carbon was obtained to be 4.75 mmol/g.

We have used the carbon-based solid acid as a heterogeneous catalyst in the presence of hydrogen peroxide as an oxidizing agent for the oxidation of both aliphatic and aromatic sulfides to the corresponding sulfoxides or sulfones. The optimum ratio of sulfide to H_2O_2 (1:1 equivalent) in the presence of carbon-based solid acid (0.1 g) is found to be ideal for complete conversion of sulfides to sulfoxides (with a few amount of sulfone), which the reaction remains incomplete in lesser amounts.

The use of excess reagent (the higher molar ratio of H_2O_2 relative to the sulfide (5:1) in the presence of carbon-based solid acid (0.2 g)) affords the corresponding sulfone in a clean reaction. The yield and selectivity of oxidation of diphenyl sulfide to the corresponding sulfoxide or sulfone as a function of time is indicated in Table 3.

As shown in Tables 1 and 2, the generality of this approach has been demonstrated by a facile and effortless oxidation of a wide variety of alkyl, aryl and aromatic sulfides. To check the reusability and recyclability of the catalyst, we have carried out the oxidation of dibutyl sulfide to dibutyl sulfone under similar reaction conditions. After completion of the reaction, the catalyst was separated by filtration and the same reaction course was repeated with fresh substrate and oxidant (aqueous 30% H_2O_2). It was found that the activity of catalyst has been remained unchanged after four catalytic cycles.

To compare the carbon-based solid acid with other catalysts including zeolite HZSM-5, USY-BEA, amberlyst-15 resins, Nafion NR-50, and silica sulfuric acid,

Table 3. Oxidation of diphenyl sulphide with hydrogen peroxide/carbon-base solid acid under different reaction conditions.

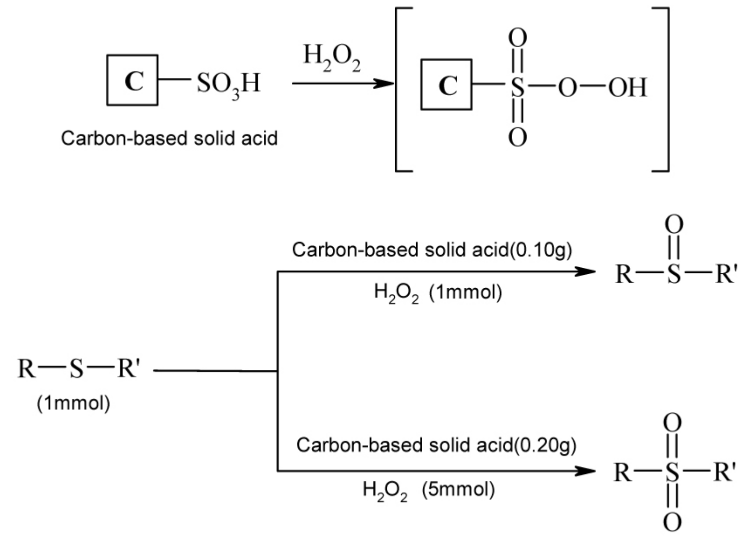
Entry	Solvent	Carbon-base solid acid (g/mmol of substrate)	H_2O_2 (mmol)	Reation time (min)	Yield (%)	
					sulfoxides	sulfones
1	Acetonitrile	0.20	5	20	–	90
2	Dichloromethane	0.20	5	20	–	85
3	1,2-Dichloroethane	0.20	5	10	–	95
4	1,2-Dichloroethane	0.05	1	15	86	–
5	1,2-Dichloroethane	0.10	1	10	90	Trace
6	1,2-Dichloroethane	0.20	1	10	90	5
7	1,2-Dichloroethane	0.00	5	60	–	Trace
8	1,2-Dichloroethane	0.05	5	20	5	80
9	1,2-Dichloroethane	0.10	5	15	–	89
10	1,2-Dichloroethane	0.15	5	15	–	92
11	1,2-Dichloroethane	0.20	5	10	–	95
12	1,2-Dichloroethane	0.30	5	8–10	–	95

the oxidation of diphenyl sulfide as a model compound with H_2O_2 was studied (see Table 4). Carbon-based solid acid affects the reaction course so that the reaction was completed in a shorter time (10-min) with a high yield.

As shown in Scheme 1, the reaction probably involves the in situ formation of persulfonic acid by the reaction of sulfonic acid groups of the carbon-based solid acid with hydrogen peroxide, followed by the oxygen transfer to the organic substrate.

4. Conclusion

In summary, we have reported a new, versatile, and efficient methodology for the selective oxidation of sulfides to sulfoxides or sulfones with aqueous hydrogen peroxide as an oxidant, in the presence of catalytic amounts of carbon-based solid acid. The usefulness of this methodology lies in the availability of the reagents, easy and clean work-up, and possibility of large scale synthesis. Moreover, the reagents are very cheap and the reaction proceeds



Scheme 1

Table 4. Comparison of the efficiency of carbon-based solid acid and the other catalysts for the oxidation of diphenyl sulfide to diphenyl sulfone with hydrogen peroxide.

Entry	Catalyst	Solvent	Catalyst load (g)	Time (min)	Yield, (%)	Ref.
1	Nafion NR-50	1,2-Dichloroethane	0.25	35	98	3
2	HZSM-5	1,2-Dichloroethane	0.25	60	40	3
3	USY-BEA	1,2-Dichloroethane	0.25	50	55	3
4	Amberlyst-15	1,2-Dichloroethane	0.25	45	75	3
5	Silica sulfuric acid	Acetonitrile	0.20	45	96	25
6	Carbon-based solid acid	Dichloromethane	0.20	20	85	This work
7	Carbon-based solid acid	1,2-Dichloroethane	0.20	10	95	This work

with relatively good yields. We believe that the present methodology would be an important improvement with respect to the other methodologies.

5. References

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Povzetek

V prispevku je opisana uporaba heterogenega, trdnega kislega katalizatorja na ogljikovi osnovi za seletivno oksidacijo sulfidov v sulfokside in sulfone. Reakcija poteka pod milimi reakcijskimi pogoji s 30 % vodikovim peroksidom kot oksidantom in z visokimi izkoristki. Uporabljeni heterogeni katalizator se je izkazal kot zelo učinkovit, okolju prijazen in enostaven za recikliranje.