Catalysis Letters 56 (1998) 237–239

Clay-catalysed dealkylation of organic sulfides

Kannan P. Naicker[a], A. Lalitha[b], K. Pitchumani[a,*] and C. Srinivasan[b]

[a] School of Chemistry, Madurai Kamaraj University, Madurai 625 021, India
[b] Department of Materials Science, Madurai Kamaraj University, Madurai 625 021, India

Received 23 July 1998; accepted 30 October 1998

Both K10- as well as modified montmorillonites such as cation-exchanged and surfactant-pillared clays catalyse the cleavage of carbon–sulfur single bonds resulting in dealkylation of organic sulfides. The corresponding disulfides are obtained in high yield.

Keywords: montmorillonite clays, catalysis, organic sulfides, dealkylation

1. Introduction

Clays and various cation-exchanged clays serve as efficient solid-state catalysts in a number of acid-site-assisted reactions [1] and clay-supported reagents were extensively employed in organic syntheses. Pillared bentonite was found to be an efficient catalyst for the O–methyl bond cleavage of anisoles (e.g., *meta*-methylanisole, guaiacol, and creosol) under mild, static conditions (150 °C, inert atmosphere). Dealkylation and transalkylation reactions occurred to a large extent and the conversion was $>95\%$ after two days [2]. Formation of *ortho*- and *para*-isomers was exclusive without any evidence of *meta*-substitution. The clay–organic complexes went through various color changes as the reaction progressed and when examined by UV-visible spectroscopy suggested some quinone formation. This high catalytic activity of pillared bentonite towards dealkylation was attributed mainly to the Brønsted acidity. Among the various forms of clays, those with larger surface area (e.g., pillared bentonite) were found to be more efficient. The analogous demethylation of an N-methyl group was also observed (along with Fischer–Hepp rearrangement), when N-methyl-N-nitrosoaniline was placed [3] in clay microenvironment. However, the corresponding dealkylation of sulfides, which is difficult to achieve, is worth attempting as this will have significance and relevance in various industrial processes, waste degradation, control of pollution, fine chemical production, etc.

These observations, coupled with our interest in organic sulfur compounds (we have synthesised substituted sulfides by thiol addition to styrenes [4], by the reaction between benzyl chloride and thiols [5]) prompted us to study the analogous carbon–sulfur bond cleavage in clay heterogeneous media. To our knowledge, this is the first report of dealkylation of sulfides in the aluminosilicate layers of clay.

2. Experimental

2.1. Reagents and catalysts

K10-montmorillonite (Aldrich) was used as received. Cation-exchanged montmorillonite clays were prepared by reported procedures [6,7]. Surfactant-pillared clays were prepared by stirring 6 g of 0.15 M solution of cetryltrimethylammonium chloride (CTAC) for 100 h at 53 °C. The filtered solution was washed repeatedly with distilled water and dried overnight in a hot air oven. Inclusion of surfactant in between the clay interlayers is evidenced by an increase in the spatial distance in the 001 plane from 9 to 16 Å in XRD and observation of characteristic stretching frequencies of long-chain alkyl groups in FT-IR.

All the organic sulfides employed in the study were prepared by reported procedures [8,9].

2.2. Reaction procedure

A 1 : 1 solid mixture of clay and sulfide was heated in a water bath for 11 h. The reaction mixture was then extracted with diethyl ether and dried over anhydrous sodium sulphate. After removing the solvent, the products were separated by column chromatography using hexane as the eluant. The reaction in the case of CTAC-pillared clay is heated in the water bath for 41 h.

2.3. Analysis of the reaction mixture

The percentage conversion was obtained by analysing the reaction mixture in a Shimadzu LC-8A modular hplc system (reverse-phase ODS column, UV detector at 258 nm) using 70% methanol as the mobile phase and in each case the retention time for the starting material was taken as the internal reference.

---

[*] To whom correspondence should be addressed.

Table 1
Percentage of the various products in dealkylation of organic sulfides in clay microenvironment.[a]

Substrate	Catalyst	Conversion	Percentage of products		
		(%)	Disulfide	PhPh/PhSPh	Unidentified
Methyl phenyl sulfide	K10-mont.	84	77.0	0.6/1.2	5.8
Methyl phenyl sulfide	K10-mont.–Cr^{3+}	91	88.0	0.4/1.0	1.6
Methyl phenyl sulfide	K10-mont.–Fe^{3+}	64	41.0	1.6/3.9	17.5
Methyl phenyl sulfide	K10-mont.–Al^{3+}	93	75.8	2.8/2.06	12.3
Methyl phenyl sulfide	K10-mont.–Mn^{2+}	89	65.0	13.5/7.27	3.2
Methyl phenyl sulfide	K10-mont.–Ni^{2+}	91	73.4	8.45/6.50	2.6
Methyl phenyl sulfide	K10-mont.–Na^{+}	82	77.0	0.6/1.2	3.2
p-anisyl methyl sulfide	K10-mont.	0	–	–	–
p-nitrophenyl methyl sulfide	K10-mont.	0	–	–	–
p-carboxyphenyl methyl sulfide	K10-mont.	0	–	–	–
Methyl phenyl sulfide	CTAC-pillared	7	0.2	2/0.80	4
n-butyl phenyl sulfide	CTAC-pillared	0	0	0	0
n-butyl phenyl sulfide	CTAC-pillared[b]	11	7	0.58/0.70	2.70
n-butyl phenyl sulfide	CTAC-pillared[c]	97	85	3.9/3	5.10

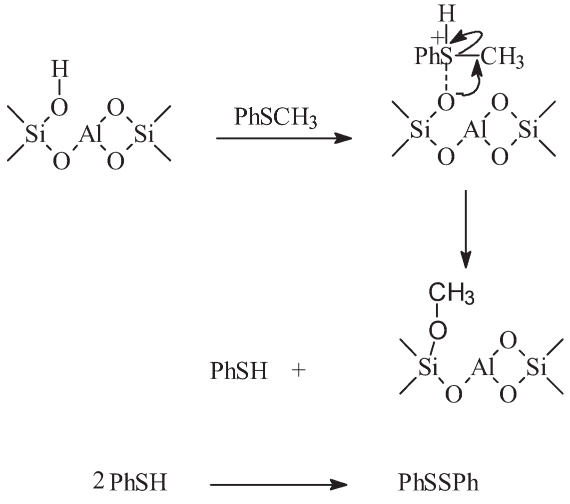
[a] A solid mixture of clay and sulfide is heated to 95 °C for 11 h.
[b] The reaction mixture in CTAC-pillared clay is heated at 95 °C for 41 h.
[c] At 145 °C for 41 h.

3. Results and discussion

We have employed K10-, various cation-exchanged and CTAC-pillared montmorillonite clays for the dealkylation of methyl phenyl sulfide, substituted phenyl methyl sulfides and n-butyl phenyl sulfide. In all the cases, diphenyl disulfide is the major product with small amounts of diphenyl sulfide, diphenyl and some other unidentified products. The percentage conversion and products distribution are shown in table 1.

It is interesting to observe that with substituted phenyl methyl sulfides (i.e., *para*-methoxy, *para*-nitro and *para*-carboxylic groups), there is neglible reaction with K10-, cation-exchanged and pillared clays. This may be attributed to the decreased mobilities of substituted phenyl methyl sulfides (in comparison with phenyl methyl sulfides) when placed in a solid environment. Though smaller benzenoid derivatives are fairly mobile in the clay microenvironment, as reported by Carrado et al. [2] in the dealkylation of anisole on clays (based on their MAS-^{13}C-NMR experiments), we believe that the presence of an additional substituent makes the mobility more difficult leading to a significant size effect in this reaction.

The reaction of sulfides with CTAC-pillared clay is slow when compared with natural and cation-exchanged clays. It is likely that on introducing a surfactant pillar, the effective clay surface area may have decreased. This factor, coupled with its low-surface acidity [8], may be responsible for the low catalytic activity of a CTAC-pillared clay. It is relevant to recall that surface acidity in pillared clays was attributed to sites on the alumina pillars [9] and these sites were found to be stronger than those in synthetic Y-zeolites [10]. As CTAC-pillared clay is less active than the unpillared (i.e., natural and cation-exchanged) clays, the pillaring group, i.e., trimethylammonium group, is not catalytically active in these reactions. The yield, however, has improved slightly with a longer reaction time. Use of elevated temperatures and longer reaction time increases the mobility of the substrate inside the CTAC-pillared clay, thereby improving the percentage conversion significantly. There is also a possibility of generation of more Brønsted acidic sites at elevated temperatures.



Scheme 1. Dealkylation of organic sulfides in sheet silicate.

Volatile compounds such as alcohol and alkyl ether are not detected under the reaction conditions. Based on the observed results and also from the analogous dealkylation of anisoles, we believe that the high catalytic activity of the natural and cation-exchanged clays in this reaction depends on the Brønsted acidity in clay interlayer and propose the following mechanism for dealkylation of organic sulfides (scheme 1). Protonation of the sulfide moiety by the Brønsted acidic sites of clay, followed by subsequent cleavage, would result in a silyl ether and thiophenol, which then undergoes facile oxidation on the surface to give rise to diphenyl disulfide. From the surface methoxy group, methyl migration among the adjacent Si atoms is likely to take place.

The formation of small amounts of biphenyl and also diphenyl sulfide may be explained by an electron-transfer process. This side reaction, involving initial electron transfer to the Lewis acidic sites in clay interlayer, generates a sulfide radical cation. Combination of this with another radical ion/neutral molecule may have resulted in diphenyl and diphenyl sulfide. The observed significant increase in the yield of diphenyl sulfide and biphenyl with various M^{2+}-exchanged clays supports the operation of an electron-transfer process. The formation of a light green color when methyl phenyl sulfide is placed in clay may also be considered as an evidence for radical ion intermediates. It is pertinent to note here that when electron-rich substrates such as olefins are brought in contact with inorganic solid supports such as zeolites, an intense color is developed [11,12] and this phenomenon is attributed to the generation of radical cation intermediates which are stabilised in the framework.

4. Conclusions

The efficiency of K10- as well as modified montmorillonites such as cation-exchanged and surfactant-pillared clays in cleaving carbon–sulfur single bonds (to yield the corresponding disulfides as the major product) is demonstrated in the present work. Though the analogous O–methyl and N–methyl cleavages are reported, this dealkylation of organic sulfides is the first report of its kind in clay microenvironment.

Acknowledgement

Financial assistance from CSIR is gratefully acknowledged.

References

[1] (a) J.A. Ballantine, J.H. Purnell and J.M. Thomas, Clay Miner. 18 (1983) 347;
(b) T.J. Pinnavaia, Science 220 (1983) 4595;
(c) J.M. Adams, S.E. Davies, S.H. Graham and J.M. Thomas, J. Catal. 78 (1982) 197;
(d) J.A. Ballantine, M. Davies, H. Purnell, M. Rayanakorn, J.M. Thomas and K.J. Williams, J. Chem. Soc. Chem. Commun. (1981) 8;
(e) J.H. Clark, ed., *Catalysis of Organic Reactions by Supported Inorganic Reagents* (VCH, Weinheim, 1994);
(f) M. Ogawa and K. Kuroda, Chem. Rev. 95 (1995) 399;
(g) P. Kannan, R. Sevvel, S. Rajagopal, K. Pitchumani and C. Srinivasan, Tetrahedron 53 (1997) 7635.

[2] K.A. Carrado, R. Hayatsu, R.E. Botto and R. Winans, Clays Clay Miner. 38 (1990) 250.

[3] P. Kannan, K. Pitchumani, S. Rajagopal and C. Srinivasan, J. Mol. Catal. 118 (1997) 189.

[4] P. Kannan and K. Pitchumani, Catal. Lett. 45 (1997) 271.

[5] P. Kannan, K. Pitchumani, S. Rajagopal and C. Srinivasan, J. Chem. Soc. Chem. Commun. (1996) 369.

[6] K. Pitchumani and A. Pandian, J. Chem. Soc. Chem. Commun. (1990) 1613.

[7] A. Cornelis and P. Laszlo, Synthesis (1985) 909.

[8] K. Urabe, S. Hiroaki and Y. Izumi, J. Chem. Soc. Chem. Commun. (1988) 1520.

[9] G. Poncelet and A. Schutz, in: *Chemical Reactions in Organic and Inorganic Constrained Systems*, ed. R. Setton (Reidel, Dordrecht, 1986) p. 165.

[10] (a) D. Tichit, F. Fajula, F. Figueras, J. Bousquet and C. Gueguen, in: *Catalysis by Acids and Bases*, eds. B. Imelik, C. Naccache, G. Coudurier, Y.B. Taarit and J.C. Vedrine (Elsevier, Amsterdam, 1985) p. 351.

[11] K. Pitchumani, P.H. Lakshminarasimhan, N. Prevost, D.R. Corbin and V. Ramamurthy, J. Chem. Soc. Chem. Commun. (1997) 181.

[12] V. Fornes, H. Garcia, S. Jananovic and V. Marti, Tetrahedron 53 (1997) 4715.