Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Selective dehydrosulfurization of 3-mercaptopropionic acid to acrylic acid on silicalite catalyst

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ARTICLE INFO

Article history: Received 2 October 2009 Received in revised form 19 November 2009 Accepted 23 November 2009 Available online 26 November 2009

Dedicated to the humanity and scientific creativity of Prof. Mauro Graziani in the occasion of his 75th birthday.

Keywords: Acrylic acid 3-Mercaptopropionic acid Acid catalysis Dehydrosulfurization Silicalite

1. Introduction

Decomposition products of organosulfur compounds and chlorinated organic compounds have been found to be toxic to humans [1]. Petroleum and natural gas contain various organosulfur compounds and their removal by hydrodesulfurization (HDS) over heterogeneous catalysts (reaction (1)) produces decontaminated hydrocarbons along with H₂S [2–10], the latter to be transformed into safe elemental sulfur by the Claus process (reactions (2) and (3)) [11,12].

$$C_x H_y S + 2H_2 \rightarrow C_x H_{y+2} + H_2 S \tag{1}$$

 $2H_2S + 3O_2 \ \to \ 2SO_2 + 2H_2O \eqno(2)$

$$2H_2S + SO_2 \rightarrow 3S + 2H_2O \tag{3}$$

Although soluble metal derivatives, particularly aluminium, vanadium and nickel, are able to promote the desulfurization of some simple organosulfur compounds [13] the present industrial HDS process is based on alumina-supported Mo and Co catalysts [14–17], whereas recent interest has also been devoted to the use of gold catalysts [18].

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ABSTRACT

Dehydrosulfurization of 3-mercaptopropionic acid has been investigated in a fixed bed reactor using a silicalite catalyst in order to recover the hydrocarbon core. Under reductive conditions, acrylic acid was formed in high yield at 350 °C and atmospheric pressure as the desired product along the toxic H₂S, whereas, carrying out the reaction in the presence of air, safer dihydrogenpolysulfides resulted as the co-product.

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Beside H_2S , environmental pollution of sulfur is mainly related to the emission of gaseous SO_2 and SO_3 because these latter compounds have a strong impact on the health of animals and vegetables. Reducing emissions of sulfur compounds by selective catalytic reduction (SCR) and flue gas desulfurization (FGD) systems by basic compounds (the "scrubbers") remains a crucial component of strategy to clean air and, consequently, international agencies are developing several control programs.

Considering the fate of sulfur in chemical wastes, the deep oxidation produces SO_x compounds which are removed by the above cited gas desulfurization process according to the common practice whereas less care has been paid to selective processes allowing hydrocarbons recovery similarly to the petrol-HDS process.

Considering the importance of chemicals recycling, we have investigated a process for recovering the hydrocarbon core of 3-mercaptopropionic acid (3-MPA), selected as a model compound by using silicalite as a metal free dehydrosulfurization catalyst. 3-Mercaptopropionic acid and its derivatives are currently employed as ion exchange catalysts, PVC-stabilizers, chain-transfer and crosslinking agents and UV-curable formulations. From literature data we know that this compound can be desulfurized by means of stoichiometric reactions. In particular, by using 2-chloro-1,3-dimethylimidazolium chloride the valuable commercial compound acrylic acid was produced [19], whereas, to our knowledge, no catalytic processes have been investigated for removing sulfur from this molecule.



^{1566-7367/\$ -} see front matter @ 2009 Elsevier B.V. All rights reserved. doi:10.1016/j.catcom.2009.11.022

Although silicalites are widely used as acid catalysts for industrial processes, particularly in petroleum refining (hydrocracking, isomerization, alkylation and reforming) [20,21], minor interest has been devoted to laboratory-scale catalytic applications. In this paper we show that silicalite can be advantageously applied in the absence of heavy metals as a catalyst for removing sulfur from 3-mercaptopropionic acid according to a selective process, preserving the hydrocarbon core.

2. Experimental

2.1. Reagents and instruments

3-Mercaptoproprionic acid (Fluka, $\geq 99.0\%$), NaOH (Fluka, $\geq 98\%$), KMnO₄ (Fluka, $\geq 99.0\%$), H₂SO₄ 95% (Prolabo), CH₃OH (Fluka, >99.5%), CH₃I (Fluka, $\geq 99.5\%$), Na₂SO₄ anhydrous (Fluka, >99%). N₂ and air (SIAD, 99.99%), silikalite-1 pellets (1 mm × 4 mm size, Si = 44%, Al < 0.01%, Fe < 0.005%, micropore volume = 0.18 ml/g were provided by BASF).

Acrylic acid was identified by the ¹H NMR and ¹³C NMR spectra recorded on a Bruker 300 MHz instrument and quantified by HPLC method using a Shimadzu LC-10 instrument equipped with a refractive index detector Shimadzu RID-10A, a Varian MetaCarb H Plus column (300 mm × 7.8 mm) and using aqueous 0.01 M H₃PO₄ as the eluant. XRD spectra were recorded using a Rigaku D III-MAX horizontal-scan powder diffractometer with Cu Kα radiation. SEM images were collected by using a LEO 1430 microscope.

The polysulfides were identified by UV–vis spectroscopy (230 nm) on a Hewlett Packard 8453 instrument using chloroform as solvent and quantified by a LECO SC-132 Sulfur Determinator instrument.

2.2. Catalytic tests and analysis for the reactions under N_2 flow

The reactions were carried out in a fixed bed vertical glass reactor (l = 25 cm, diameter = 3.5 cm) fitted with a porous septum carrying the catalyst (2.5 g) and provided with an electronically controlled furnace. The gas stream (N₂ = 268 mmol/h) was controlled by a Brooks mass-flow instrument and the liquid reagent (18.4 mmol/h) was supplied through an automatic syringe pump ensuring that liquid vaporization occurred on the reactor wall prior to the catalytic bed. The condensable reaction products were collected for 1 h by bubbling the effluent into trap A containing an aqueous solution of H₃PO₄ 0.01 M, cooled in an ice-water bath. The non-condensable products were collected in the second trap B containing NaOH 10 M. In order to detect further reducible gaseous products, a trap C containing KMnO₄ 1 M was connected at the end of the system.

2.3. Catalytic tests and analysis for the reaction in the presence of air

These tests were carried out as above but using a mixture of gas stream ($N_2 = 224 \text{ mmol/h}$, air = 54 mmol/h) along with the liquid 3-MPA stream (18.4 mmol/h) in the range of temperature 250–370 °C. Acrylic acid, collected in trap A as aqueous solution, was analysed by HPLC chromatography, while polysulfides were collected at the bottom of the same trap as a dark brown insoluble liquid. This fraction was methylated by reacting with CH₃I in methanol [20] and analysed by UV–vis spectroscopy in order to identify the products and quantified by a standard combustion method [21]. No products were collected in the second trap B and in the last trap C.

3. Results and discussion

The catalytic dehydrosulfurization of 3-MPA was investigated in a range of temperature between 200 °C and 370 °C, in the presence of a catalyst (silicalite), either in the absence or in the presence of dioxygen.

The experimental apparatus is represented in Scheme 1.

Fig. 1 shows the results obtained in the tests carried out under N2 stream.

During these experiments, the main product, acrylic acid, was collected in the trap containing a weakly acid aqueous solution (H_3PO_4 0.01 M) cooled at 0 °C, whereas H_2S was collected in a second trap containing NaOH 10 M solution. According to the KMnO₄ analysis in final trap, almost no oxidable products were present in the vent gas.

Starting from 200 °C and increasing the temperature we noted that the dehydrosulfurization process started at ca. 250 °C forming acrylic acid and H₂S. No other products have been detected except non-quantified amounts of polyacrylic acid solidified at the exit of the reactor. Owing to this loss of acrylic acid, yields below 100% have been observed in trap A by HPLC determination: however, acrylic acid was recovered up to 76.5% by converting 3-MPA at 370 °C. In any case, total conversion of 3-mercaptopropionic acid occurred by passing the feed on the catalyst at 350 °C and over this temperature, as the reagent resulted absent in the products. Iodimetric titration of H₂S collected in trap B showed its stoichiometric equivalence to the converted 3-mercaptopropionic acid according to reaction (4):



Scheme 1. Apparatus used for the experiments.



Fig. 1. Catalytic test in nitrogen stream. Reaction conditions: 3-MPA = 18.4 mmol/h, N₂ = 268 mmol/h, catalyst amount = 2.5 g. Yield and selectivity as acrylic acid.



Fig. 2. Catalytic test in air stream. Reaction conditions: 3-MPA = 18.39 mmol/h, N₂ = 224 mmol/h, air = 54 mmol/h, catalyst amount = 2.5 g. Yield and selectivity as acrylic acid.



Fig. 3. Evaluation of the catalytic decay. Experimental conditions: $T = 370 \degree C$ the rest as in Fig. 1.

A blank test in the absence of catalyst showed the thermal stability of 3-mercaptopropionic acid up to 370 °C. Considering that the dangerous H_2S is commonly converted to harmless elemental sulfur by the Claus process, we have investigated the dehydrosulfurization process in the presence of air in order to promote reactions (2) and (3).

Counts

As reported in Fig. 2, in the presence of a small excess of O_2 ($O_2/S = 0.6$) 3-mercaptopropionic acid was completely converted to acrylic acid with fairly good selectivity (>90%) at 300–330 °C.

In this case, no H_2S was collected in trap B whereas an insoluble oily material was collected in trap A along with the acrylic acid solution. It was identified as dihydrogenpolysulfide by means of UV–vis spectroscopy after methylation [22] and quantified by infrared spectroscopy [23]. Its formation is due to the incomplete oxidation of 3-mercaptopropionic acid to H_2S which is able to react with the formed sulfur according to reaction (5):

$$H_2S + {}_nS \rightarrow H_2S_{n+1} \tag{5}$$

The amount of sulfur transformed into polysulfides in the experiments of Fig. 2 accounts for 81% of the converted 3-mercaptopropionic acid.

The results of the tests carried out in air stream are important as the process allows either the recovery of a great part of acrylic acid or the removal of total sulfur in form of harmful material; for the economic balance, it is interesting to note that polysulfides are commercially valuable products [24].

Finally, a preliminary test was performed at 370 °C for evaluating the catalyst life under reductive dehydrosulfurization conditions. According to Fig. 3, 100% conversion was preserved for 24 h, while the yield of acrylic acid gradually decreased from 80% to 50% owing to formation of non-characterised products, probably polyacrylates, collected in the aqueous solution. No attempts were done either to regenerate the catalyst under oxidative conditions or to optimize typical engineering aspects (diffusion problems and catalyst bed dilution).

The XRD spectra and SEM pictures of the fresh silicalite and the used silicalite are recorded in Figs. 4 and 5, respectively: no significant changes of the silica framework appear after 24 h on stream, to be related to the observed decline of selectivity.

In the absence of specific mechanistic investigations we believe that the dehydrogenation mechanism of the 3-mercaptopropionic acid on silicalite should be similar to that reported for hydroxycompounds dehydrogenation [25,26]. Accordingly, the starting activation occurs at the silica surface where strained Si–O–Sibridges are taken part in dissociative adsorption preceding hydrogen abstraction. In the case of alcohols, competition between C₁ and C₂ abstraction leads to the more favoured carbonyl compound, whereas in the case of thiol it leads selectively to the olefinic compound (Scheme 2).

In the presence of oxygen, partial oxidation of sulfur occurs producing the polysulfides according to reaction (5).



Fig. 4. XRD spectra of fresh silicalite (A) and 24 h on stream silicalite (B).



Fig. 5. SEM pictures of fresh silicalite (A) and silicalite used for 24 h (B).

$\begin{aligned} \text{HOOC-CH}_2\text{-CH}_2\text{-SH} + \text{Si-O-Si} &= \text{Si-S-CH}_2\text{-CH}_2\text{-COOH} + \text{Si-OH} \\ \text{Si-S-CH}_2\text{-CH}_2\text{-COOH} + \text{Si-OH} &= \text{Si-O-Si} + \text{H}_2\text{S} + \text{CH}_2\text{=CH-COOH} \end{aligned}$

Scheme 2. Dehydrosulfuridation mechanism.

4. Conclusions

Silicalite has been evaluated as a catalyst in the reductive and oxidative dehydrosulfurization of 3-mercaptopropionic acid in order to recover a valuable product, namely acrylic acid. Under N_2 flow, sulfur can be totally removed as H_2S . The possibility to couple this process to a Claus type process has been demonstrated by reacting 3-mercaptopropionic in the presence of air: under these conditions, sulfur can be removed in form of the much safer dihydrogenpolysulfides with respect to the noxious H_2S .

Acknowledgements

We are grateful to Dr. Valter Mantelli, Dr. Gianfranco Bagnara and Dr. Giorgio Mirabelli of IPLOM S.p.a. Busalla (Genova) for analytical determinations. BASF is also acknowledged for supplying the silicalite catalyst.

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