

Addition of hydrogen sulfide to methyl acrylate over solid basic catalysts

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Abstract

H₂S was added to methyl acrylate in a batch reactor at 313 K, 450 rpm, 0.2 M (in decane) in methyl acrylate, 5.5 bar of hydrogen sulfide pressure in the presence of solid bases. The bases differed in their chemical composition, structural properties, and acid–base properties. The bases were cation-exchanged X-faujasites, magnesium oxide, alkaline- and alkaline-earth-doped magnesium oxides, and commercially available and synthesized mixed magnesium/aluminum oxides. All of these catalysts were shown to achieve, in terms of both activity and selectivity, the addition of H₂S to methyl acrylate as compared with the patent literature. Catalytic runs have also been conducted on a fixed-bed continuous-flow reactor with performances, in terms of selectivity, better than those observed in batch mode, particularly with a Cs-exchanged X zeolite, which featured a selectivity level similar to that of modified ion-exchange resins. As previously assumed from kinetics and IR studies on H₂S and methyl acrylate adsorption and co-adsorption, the prerequisite for the title reaction to occur is the dissociation of H₂S into HS[−] and H⁺ species over weak acid/strong basic Lewis pair sites. This assumption is confirmed in this work and is in agreement with the HSAB principle; H₂S is dissociated into a soft HS[−] nucleophilic species associated with a soft M^{x+} acid, and the hard H⁺ species is associated with the hard O^{2−} basic species.

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1. Introduction

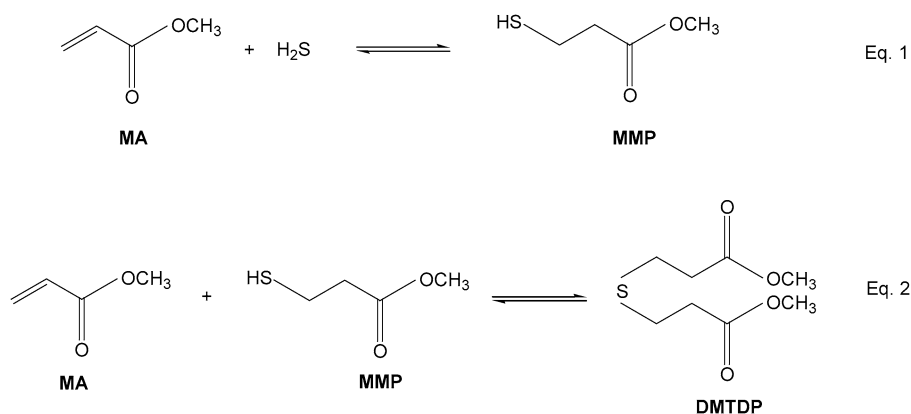
Methyl-3-mercaptopropionate (MMP) is of primary importance as a feedstock for the production of various industrial chemicals, pharmaceuticals, and agrochemicals, as indicated by a significant number of patents granted in the period from the 1970s to the 1990s that used homogeneous catalysts [1–7]. For practical and environmental reasons, most of the companies involved in this area have considered this reaction in the presence of solid bases, namely anion-exchanged resins, basic oxides, and hydroxides [8–11]. Satisfactory selectivities in MMP were generally claimed, between 82 and

97%, depending on the operating conditions and catalysts used; the highest selectivity has been obtained under high H₂S pressure, where H₂S is partially liquid and plays the role of solvent [9]. However, a high selectivity for MMP is generally achieved in the presence of a large excess of H₂S, whatever the catalysts used.

MMP is obtained through the nucleophilic Michael-type reaction addition of H₂S to methyl acrylate (MA) over basic catalysts (Scheme 1, Eq. (1)). Apart from MMP, dimethyl 3,3'-thiodipropionate (DMTDP) is the main secondary product, resulting from the addition of MMP to methyl acrylate (MA) (Scheme 1, Eq. (2)). Other side-reactions may also take place, namely the condensation of two molecules of MMP to give the corresponding disulfide and polymerization of methyl acrylate.

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Scheme 1. Reaction scheme for the base-catalyzed addition of H₂S to methyl acrylate.

Resins exchanged with tertiary amines or quaternary ammonium ions were not found to be stable enough. However, an increase in both stability and efficiency was found with the use of guanidine-grafted resins [11]. MMP is produced in a continuous process without solvent, with a selectivity of 98% at 318 K and a H₂S/MA molar ratio of 6.

In a recent work we reported on a detailed study (kinetics, FT-IR adsorption, and coadsorption experiments) of the mechanism of the addition of H₂S to methyl acrylate in the presence of a commercial hydrotalcite (KW2200 from Kyowa) and magnesium oxide as catalysts. Under this chemical regime, it was shown that chemisorbed H₂S species like HS⁻, which result from H₂S dissociative adsorption, were the active species and that strongly adsorbed MA was not involved in the reaction [12]. It was then anticipated that selective and active catalysts should contain weak Lewis acid/strong base pairs.

In order to corroborate the conclusion of our kinetic approach, the goal of the work reported in this paper was to perform the title reaction with a series of catalysts ensuring a large range of basicity regarding, on one hand, the Brønsted or Lewis nature of their sites, and on the other hand, the very different strength of the Lewis-type acid–base pairs. For this purpose alkaline-exchanged X zeolites, Mg(Al)O mixed oxides obtained from hydrotalcite precursor, meixnerite, and alkaline- or alkaline-earth-doped MgO were investigated. They indeed cover a wide range of basic strength, from weak for X zeolites [13] to moderate and strong for Mg(Al)O mixed oxides and very strong for doped MgO. Furthermore, meixnerite, in contrast to previous samples, exhibits Brønsted-type basic sites assigned to the OH⁻ compensating anions of this lamellar structure.

2. Experimental

2.1. Reactants

MA (99% purity) and dimethyl 3,3'-thiodipropionate (99% purity) were obtained from Aldrich, MMP (98% purity) from Fluka, decane (99+% purity, solvent) and dode-

cane (99+% purity, internal standard) from Interchim, and hydrogen sulfide (99.8% purity) from AGA.

2.2. Sample characterization

Chemical analyses of the as-prepared solids were performed at the Service Central d'Analyses du C.N.R.S. (So-laize, France) by ICP-MS.

X-ray diffraction patterns were obtained on a powder X-ray Philips PW1380 diffractometer with Cu-K_α radiation ($\lambda = 1.540 \text{ \AA}$, 40 kV and 50 mA).

Specific surface areas (BET method) and pore volumes were calculated from the isotherms of nitrogen adsorption/desorption recorded at 77 K with a Micromeritics ASAP 2010 M apparatus. Samples ($\approx 100 \text{ mg}$) were calcined at 723 K and outgassed at 523 K and 10^{-4} Pa .

The total basicity of the catalysts was measured by thermal adsorption and desorption of CO₂ with a Setaram TG-DSC-111 microcalorimeter. The samples were previously outgassed at 723 K, cooled to 373 K, and brought into contact with flowing CO₂ (25 ml min^{-1}). The thermal event in the microcalorimetric cell was recorded.

The total acidity of the catalysts was measured by adsorption of deuterated acetonitrile followed by IR spectroscopy with a Nicolet FTIR 320 spectrometer. The IR spectra were recorded at room temperature at a resolution of 2 cm^{-1} (100 scans). The samples were pressed into a disk wafer of 11 mg cm^{-2} . The activation was performed in oxygen flow (150 ml min^{-1} at 773 K for 8 h, then evacuated at the same temperature and a pressure of $1.33 \times 10^{-4} \text{ Pa}$. After evacuation at 773 K, the sample was cooled to room temperature, and CD₃CN was admitted to the cell, at full coverage, then evacuated either at room temperature or at 333 K. IR spectra were then recorded.

2.3. Workup procedure

The procedure was typically as follows: 50 ml of decane containing MA (0.870 g, 0.01 mol) and dodecane (0.850 g, 0.005 mol) was poured into a 0.1-liter magnetically stirred

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