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Epoxidation of biodiesel with hydrogen peroxide over Ti-containing silicate catalysts

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Dedicated to Prof. Dr. Ing. Jens Weitkamp on the occasion of his 70th birthday

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ABSTRACT

The heterogeneously catalyzed epoxidation of methyl oleate with hydrogen peroxide in the liquid phase is reported using different catalysts such as TS-1, Ti-MCM-41, TiO_x–SiO_2, and MO_x and WO_x supported on Al_2O_3 or SiO_2. At 323 K, in acetonitrile as the solvent and with an industrial TS-1 catalyst, an epoxide selectivity of 87% at 93% conversion is achieved after 24 h. Variation of the catalyst mass, particles size and the reaction temperature proove that the conversion is limited by mass transport to the outer crystal surface of the catalyst. With TS-1 as the catalyst, also the unsaturated fatty acid methyl esters (FAME) in biodiesel can be epoxidized with a conversion of 90% and selectivity of 76%. A higher TON than over Ti-MCM-41 or even the industrial TS-1 catalysts is reached, when TS-1 with nanoscaled particles and stacked morphology is applied as the epoxidation catalyst. The latter was synthesized by microwave-assisted synthesis and possesses Ti sites in similar coordination geometry as conventional TS-1 as shown by DR-UV–Vis spectroscopy.

1. Introduction

The current chemical industry has to respond to a steadily increasing demand of synthetic products on the one hand and the shortage of fossil and mineral raw materials as well as their decreasing quality on the other hand [1,2]. Therefore, renewable feedstocks have recently gained considerable interest as raw materials for chemical production. By far the largest share of utilized renewables in the chemical industry is held by fats and oils [3]. Among the applications of fats and oils, their conversion to fatty acid methyl esters (FAME) for biodiesel production is one of most prominent. FAME can be further converted to epoxidized fatty acid esters which play an important role for a broad range of large-scale industrial synthesis of chemicals and intermediates such as plasticizers and stabilizers in PVC, intermediates in the production of polyurethane polyols, components for lubricants, cosmetics or pharmaceuticals [4–6].

Currently, epoxy fatty acid compounds are mainly obtained on the industrial scale by the Prileshajew reaction, in which the unsaturated oils are converted with percarboxylic acids, such as peracetic or performic acid. This route suffers from several drawbacks: (I) in the acidic reaction media, the selectivity for epoxides is relatively low due to oxirane ring opening, (II) the handling of peracids and highly concentrated hydrogen peroxide solutions is strongly hazardous, and (III) the aqueous solutions of C1–C3 carboxylic acids formed as by products are strongly corrosive [7,8].

In view of the principles of green chemistry, catalyzed epoxidations are the preferred alternatives to conventional stoichiometric epoxidation reactions such as the Prileshajew reaction. Catalysts based on titanium, tungsten and molybdenum were investigated for epoxidations of unsaturated olefins, with high yields and/or selectivity of the target products [9–12]. Molybdenum complexes or oxides on silica and alumina supports were extensively studied in the epoxidation of cyclooctene and limonene as well as allyl alcohol [13–15]. For the epoxidation of fatty acids esters, the tungsten-based active compound "tetrakis", i.e., $([(C_8H_{17})_3NCH_3]_3^+ [PO_4[W(O)(O_2)_2]_4]_3^-)$ was reported [16]. In the presence of H_2O_2, acid reaction conditions result favoring ring opening of the epoxide formed.

In several recent studies, catalytic epoxidations of FAME were reported using organic hydroperoxides, such as *tert*-butyl- or cumene hydroperoxide, as epoxidizing agents [17–19]. Typically, TiO_2–SiO_2 and Ti-MCM-41 were used as catalysts. However, hydrogen peroxide would be an economically and environmentally largely preferred oxidant. In fact, MCM-41 and MCM-48 with Ti sites grafted onto the surface were found to be efficient catalysts in the epoxidation of methyl oleate with aqueous hydrogen peroxide [20]. Conversions up to 96% and yields of the methyl epoxystearate up to 91% were obtained over Ti/MCM-41 after 24 h at 358 K in liquid acetonitrile. Suarez et al. [21] and Sepulveda et al. [22] reported on the performance of different aluminas as catalysts for the epoxidation of fatty acid methyl esters with anhydrous and

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aqueous hydrogen peroxide. Over a sol–gel derived alumina, methyl oleate and soy bean oil methyl ester conversion of 95% and epoxide selectivities >95% were achieved after 24 h at 353 K in ethyl acetate as a solvent [22]. Titanosilicate molecular sieves, especially titanium silicalite-1 (TS-1), were widely studied for the selective epoxidation of a variety of organic substrates using aqueous H_2O_2 as the sole oxidant [23–26]. Often high selectivities up to 94% at essentially complete conversion are achieved. The present work was, thus, devoted to investigate the heterogeneously catalyzed epoxidation of unsaturated fatty acid methyl esters with aqueous hydrogen peroxide as the sole oxidant over solid catalysts. In particular, the catalytic activity, selectivity and stability of different supported transition metal oxide catalysts, e.g., TiO_x, MoO_x or WO_x on SiO_2 or Al_2O_3, were studied and compared to that over a commercial titanium silicalite-1 (TS-1) and Ti-MCM-41 with methyl oleate as a model substrate. After a screening of the catalysts, the influence of the solvent and the reaction temperature was studied. It was also of interest whether the catalysts can be reused and if a deactivation takes place. An additional goal was to clarify, whether the conversion of the rather bulky FAME molecules is limited by mass transport processes and, if yes, whether strategies for an improved catalyst design can be derived. Finally, it was investigated whether the knowledge obtained for methyl oleate can be transferred to the conversion of FAME from “real” biodiesel with aqueous hydrogen peroxide over Ti-containing silica catalysts.

2. Experimental section

2.1. Catalyst synthesis

Supported MO_x–Al_2O_3 (M: W, Mo) as well as MoO_x–SiO_2 catalysts were prepared by incipient wetness impregnation of γ-Al_2O_3 (bimodal, 99.7%, Alfa Aesar, specific surface area: 80–120 $m^2\ g^{-1}$) or SiO_2 (Aerosil 380, Degussa) with aqueous solutions of $(NH_4)_6H_2W_{12}O_{40}\cdot H_2O$ (≥85% WO_3 basis, Aldrich) and $(NH_4)_2MoO_4$ (99%, Aldrich) under constant stirring at room temperature. Typically, 5 g of γ-Al_2O_3 or SiO_2 were used. The molar ratio of metal to aluminum or silicon, respectively, for impregnation was kept constant at $n_M/n_{Al\ or\ Si} = 1/10$. After removal of water under UV irradiation for 180 min, the impregnated catalysts were further dried at 428 K for 16 h and calcined in air for 4 h at 823 K.

TiO_x–SiO_2 was obtained according to [27] by grafting of titanium sites on SiO_2 (Aerosil 380, Degussa) using a solution of titanium(IV) isopropoxide (TIP, ≥97%, Aldrich) in cyclohexanol (99%, Sigma–Aldrich). Typically, 5 g SiO_2 were treated with 150 cm^3 of the TIP solution ($c_{TIP} = 0.02\ mol\ l^{-1}$) under reflux for 2 h at 433 K. After evaporation of the solvent in vacuum, the obtained solid was calcined in air for 5 h at 823 K.

Ti-containing MCM-41 (Ti-MCM-41) was synthesized according to [28] starting from silica gel beads (Licrospher® Si 60, Merck) as the silica source, $Na_2Ti_3O_7$ as the titanium source (Aldrich) and cetyltrimethylammonium hydroxide (CTMAOH) as the structure-directing agent. CTMAOH was prepared by ion exchange of 1 g CTMABr (99%, Acros) dissolved in 42 cm^3 demineralized water with 10 g Ampersep (900 OH, Fluka). The silica gel beads, a defined amount of $Na_2Ti_3O_7$ (Aldrich) and a 0.08 M CTMAOH aqueous solution were mixed under stirring for 10 min to obtain the synthesis gel of the molar composition 0.012 TiO_2 : SiO_2 : 0.004 Na_2O : 0.202 CTMAOH : 140.2 H_2O. The resulting suspension was transferred to a polypropylene flask (Nalgene®, 60 cm^3 volume) and held at 383 K for 1 day. Then, the resulting solid was removed by filtration, washed five times with 25 cm^3 deionized water and once with 20 cm^3 anhydrous ethanol, and dried in air at 363 K for 15 h. The obtained materials were calcined stepwise in air with a heating rate of 10 K min^{-1}, i.e., 2 h at 473 K, 2 h at 673 K and 15 h at 813 K.

Titanium silicalite-1 with stacked morphology (TS-1_s) was prepared according to [23] by microwave-assisted synthesis using tetraethyl orthosilicate (TEOS, >99%, Merck), tetrapropylammonium hydroxide (TPAOH, 10 wt.% aqueous solution, Sigma Aldrich), titanium(IV) isopropoxide (TIP, 97%, Sigma Aldrich), isopropanol (99%, BDH Prolabo) and deionized water. Typically, TEOS (36.5 g), TPAOH solution (35.7 g) and deionized water (39.2 g) were mixed under stirring for 1 h. TIP (0.71 g) and Isopropanol (8.15 g) were mixed under stirring in a separate beaker for 45 min. Subsequently the solutions were added together and further stirred for 2 h at room temperature and then stirred at 353 K for 1 h to remove isopropanol. The resulting mixture was partitioned to a 100 cm^3 PTFE autoclave and transferred to a microwave oven (MLS, Start 1500) for crystallization. Therefore, the synthesis mixture were heated for 5 min with the irradiation power of 600 W to 438 K and hold at this temperature under autogeneous pressure for 20 min in case of TS-1_s_20 and 60 min for TS-1_s_60. The obtained solids were recovered by centrifugation, washed five times with 25 cm^3 deionized water, dried at 393 K for 6 h and calcined in air at 823 K for 6 h as well.

An industrial sample of titanium silicalite-1 (TS-1, powder) was supplied by Evonik.

Finally, all catalysts were pressed ($6 \times 10^8\ N\ m^{-2}$), crushed and sieved to obtain a fraction with a grain size between 50 and 150 μm for use in the catalytic experiments.

2.2. Catalyst characterization

The catalysts were characterized by powder X-ray diffraction (XRD, Siemens D 5000) using CuKα radiation (λ = 1.5418 Å) in the 2θ-range of 5° and 80° with a step size of 0.05°. The specific surface area A_{BET} were determined from N_2-sorption isotherms at 77 K using an ASAP 2000 (micromeritics) apparatus. Table 1 reports the values for A_{BET} of the samples. The metal loading of the samples was determined by elemental analysis via optical emission spectrometry with inductively coupled plasma (ICP-OES) after dissolving the solids in a mixture of HNO_3, HF, and H_3BO_3 by chemical extraction under pressure.

Diffuse reflectance UV–Vis (DR-UV–Vis) spectra were measured at room temperature on Perkin Elmer Lambda 650 S equipped with a 150 mm integrating sphere using spectralon® (PTFE, reflective value 99%) as a reference.

2.3. Catalytic Experiments

Catalytic experiments were carried out batchwise in a two-necked round-bottom glass reactor ($V = 25\ cm^3$) with a septum and a reflux condenser in the liquid phase at 323 K with magnetic stirring (400 rpm). Methyl oleate (MO, ⩾99%, Sigma–Aldrich) or biodiesel (FAME, methyl oleate: 72 wt.%, methyl linoleate + methyl

Table 1
Specific surface area A_{BET}, metal content of the catalysts as well as turnover number *TON* and turnover frequency *TOF* in the epoxidation of methyl oleate with hydrogen peroxide after 24 h.

Sample	Specific surface area A_{BET} ($m^2\ g^{-1}$)	Metal content (wt.%)	TON	TOF (h^{-1})
TS-1 (ind.)	448	1.5	5.9	0.24
Ti-MCM-41	994	1.2	0.6	0.02
TiO_x–SiO_2	330	1.8	1.4	0.06
WO_x-Al_2O_3	131	12.5	1.4	0.06
MoO_x-Al_2O_3	223	7.8	0.7	0.03
MoO_x-SiO_2	154	9.1	1.0	0.04