Topics in Catalysis (2018) 61:643–651
https://doi.org/10.1007/s11244-018-0961-y

ORIGINAL PAPER

Heterogeneous Catalytic Aqueous Phase Oxidative Cleavage of Styrenes to Benzaldehydes: An Environmentally Benign Alternative to Ozonolysis

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Abstract

The oxidative cleavage of styrenes to benzaldehydes by an environmentally benign heterogeneous catalytic method is described. The commercially available, inexpensive KSF montmorillonite was applied as a catalyst for the cleavage reaction at moderate temperatures using air as a sustainable oxidant in aqueous medium. The approach has been thoroughly optimized by testing several commercially available heterogeneous catalysts, including supported Pd and Rh catalysts, acidic montmorillonites and other common oxides such as silica or alumina. A broad variety of reaction conditions were assessed, including catalyst/reactant/solvent ratios, temperature, solvent and reaction time. The optimized conditions yielded benzaldehyde from styrene with high yield and exclusive selectivity. The scope of the reaction has also been investigated by using substituted styrenes as substrates. The data indicate that KSF is an excellent and at the same time sustainable catalyst for the oxidative cleavage. When also considering the simplicity of this method, it makes for a good alternative that can serve as a green replacement for the traditional ozonolysis reaction.

Keywords Oxidative cleavage · KSF montmorillonite · Heterogeneous catalysis · Styrenes · Benzaldehydes · Pseudo-ozonolysis

1 Introduction

Alkenes are of utmost significance for many human endeavors; they are building blocks for pharmaceuticals, agrochemicals, fine chemicals, polymers and fragrances. Thus, their preparation and transformations are in the forefront of synthesis research [1–5]. The first oxidative cleavage of the C=C bond, also known as ozonolysis, to ketones, aldehydes or carboxylic acids was developed over a century ago [6]. Since the preparation of aldehydes is a notoriously difficult process as they easily suffer over-oxidation, the major goal is to selectively cleave and oxidize alkenes to corresponding aldehydes [7]. The two major methods that are available for this reaction are (i) dihydroxylation of alkenes and the subsequent oxidation of the diols by $KMnO_4$, $Pb(OAc)_4$ or periodate [8, 9], and (ii) ozonolysis of alkenes by O_3 gas [6]. The dihydroxylation uses superstoichiometric reagents and produces extensive amount of toxic, heavy metal-containing waste. Ozonolysis is carried out by O_3, a harmful gas, utilizing an ozone generator and high pressure oxygen and the intermediate ozonides are explosives. In addition, the quenching of ozonides requires multiple reagents generating significant amount of toxic waste further decreasing the appeal of this method [10]. Therefore, the traditional ozonolysis does not comply with the general requirements of sustainable or green chemistry [11, 12]. However, it could be especially useful in ring-opening procedures or multistep synthesis, when the C=C bond maybe considered as a latent carbonyl function [13]. Due to ever stricter environmental regulations and safety concerns none of the above mentioned methods appear feasible for the preparation of carbonyl compounds.

However, due to the utility for the synthesis of carbonyl compounds efforts have been made to make the ozonolysis reaction safer. A recent development of a flow system (Ice-Cube™) with a built in ozone generator made considerable

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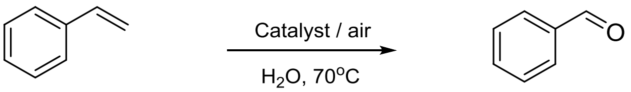
strides in this direction [14]. Nonetheless, the system still uses high pressure oxygen and reagents for ozonide cleavage which generates waste as well as the presence of the ozonide still represents hazardous conditions. Other efforts were focused on the development of environmentally benign oxidation processes that emulate the substrate-product pathway of ozonolysis; however, without the use of ozone. For example, the electrocatalytic oxidative cleavage of alkenes is a relatively underexplored area, despite its great potential benefits [15–19]. Other examples include a truly green, catalytic oxidation approach that applied $Fe(NO_3)_3$ as a catalyst and molecular oxygen as oxidant. While the conditions are appealing, the conversion is often low and the reaction results in complex product mixtures [20]. The application of Pd catalysts in supercritical carbon dioxide/poly(ethylene–glycol) solvent mixture achieved high yields and selectivities; the need for high pressure oxygen still makes the process less than desirable [21]. The most recent examples are focused on catalytic approaches using oxygen, air, organic peroxides or hydrogen peroxide [22–27]. While most of these reports describe efficient systems, the use of oxygen and peroxides is still undesirable. In other cases the catalysts used require tedious synthesis, which makes the easy reproduction and scale-up challenging.

The ideal process for the target reaction would involve a commercially available catalyst free of toxic metals to ensure easy reproducibility and scale up. In addition, the most environmentally sustainable and economic oxidant is the natural oxygen content of air, possibly at atmospheric pressure using water as a medium. Based on our earlier experience, the semi-synthetic K-10 montmorillonite carries the promise to fulfill such role under the outlined conditions. It is safe and moderately active heavy metal free oxidation catalyst that worked well for the oxidative coupling of amines or the aromatization of various heterocycles [28–31]. Herein, we extend our earlier efforts on the development of environmentally benign synthetic processes [32–39] and describe a sustainable alternative to the traditional ozonolysis for the cleavage of styrene derivatives to substituted benzaldehydes.

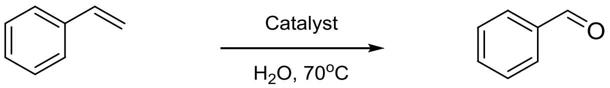
2 Results and Discussion

We have selected the oxidation of styrene as a model reaction, as our goal was to develop a sustainable process for the heterogeneous catalytic oxidative cleavage of styrenes to produce benzaldehydes (Scheme 1).



Scheme 1 Heterogeneous catalytic oxidative cleavage of styrene to benzaldehyde under aqueous conditions with air as oxidant

Table 1 Oxidative cleavage of styrene using different commercial catalysts



Entry	Catalyst	Reaction time	Yield^a (%)
1	5% Pd/C	27 h	Trace
2	Rh/Al_2O_3	27 h	45
3	Al_2O_3	3 days	26
4	SiO_2	44 h	Trace
5	K-10	42 h	40
6	KSF	22 h	47
7	Amberlite IRC-86	24 h	Trace

Standard reaction conditions: 50 mg catalyst, 0.5 mmol styrene, H_2O as medium, 70 °C

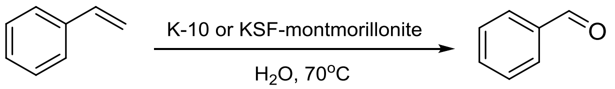
^{b}Yield determined by GC–MS

Initially, we investigated different solid catalysts to find the optimal system for the desired transformation. Given our fundamental goal, we exclusively focused on using readily, commercially available catalyst samples under aqueous conditions with atmospheric pressure air as an oxidant. A summary of the data is provided in Table 1. While palladium on carbon yielded only Wacker-type chemistry [40] (Table 1, entry 1), rhodium on alumina was found to be active producing benzaldehyde in 45% yield after 27 h reaction time (Table 1, entry 2). It appears that the presence of the noble metals is not absolutely necessary, the reaction can also be performed when only the catalyst support, Al_2O_3 was used (Table 1, entry 3), although with low yield even after extended reaction time. With this observation we decided to further explore the use of oxides and related compounds including silica and semi-synthetic montmorillonites. The use of the well-known solid acid K-10 montmorillonite allowed the reaction to be performed in 42 h yielding 40% benzaldehyde (Table 1, entry 5). Substituting K-10 with the similar KSF montmorillonite, the reaction time can be further reduced to 22 h (Table 1, entry 6) while increasing the yield to 48%. The use of other polystyrene-based solid acids such as Amberlite IRC-86 proved to be unsuccessful (Table 1, entry 7).

As the results presented in Table 1 show, K-10 and KSF montmorillonites gave the best yield for the desired transformation without the need for a noble metal catalyst. K-10 and KSF montmorillonites are solid acids that are derived from bavarian bentonite, a natural clay, and treated with different mineral acids [41]. Such montmorillonite-based semi-synthetic solid acids are well-characterized and commonly applied catalysts in a broad variety of synthetic applications [41–50]. These two materials differ mainly in their iron-content and specific surface area. K-10 containing only 1.99% iron and possesses a significant surface area of 229 m^2/g. In contrast, KSF has a much smaller surface of 9 m^2/g; however, over one and half times higher iron content (3.17%) than K-10 [41]. In the light of an earlier paper [20] that used Fe-based catalysts for the target reaction, the higher iron content of KSF montmorillonite could result in much higher reaction rates and improved yields, despite its one order of magnitude lower surface area. Thus it has been decided to investigate the effect of Fe-content on the reaction. In order to further investigate the role of the iron, the reaction was performed using the montmorillonites with various iron-containing additives. The data are collected in Tables 2 and 3.

In agreement with an earlier work [20], it was observed that $Fe(NO_3)_3$ can catalyze the oxidation without the presence of K-10 (Table 2, entry 6), however, the major product is a diol not benzaldehyde, indicating that the major pathway is dihydroxylation not oxidative cleavage. Additional experiments in which K-10 and $FeCl_3$ or $FeSO_4$ were used as a co-catalyst, respectively, resulted in only minor improvements (Table 2 entries 3, 4). The use of $Fe(NO_3)_3$ with K-10 (Table 2, entry 5), however, increased the benzaldehyde yield to 65%. As this result clearly indicates that the iron content of the catalyst can play a crucial role in the reaction, we turned our attention back to KSF montmorillonite. Besides the use of Fe-additives, conditions applying KSF in different amounts were also tested (Table 3).

Table 2 Oxidative cleavage of styrene catalyzed by K-10 montmorillonite with different Fe-salts as additives



Entry	Catalyst	Additive	Reaction time	Yield[a] (%)
1	K-10 (50 mg)	–	42 h	40
2	KSF (50 mg)	–	22 h	47
3	K-10 (50 mg)	$FeCl_3$ (50 mg)–	24 h	41
4	K-10 (50 mg)	$FeSO_4$ (50 mg)	22 h	47
5	K-10 (50 mg)	$Fe(NO_3)_3$ (50 mg)	22 h	65
6	–	$Fe(NO_3)_3$ (200 mg)	3 days	16[b]

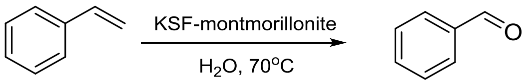
The neat KSF data is shown for comparison

Standard reaction conditions: 50 mg catalyst, 0.5 mmol styrene, H_2O as medium, 70 °C

[a] Yield determined by GC–MS

[b] 67% phenylethane-1,2-diol and 17% benzoic acid are formed as byproduct

Table 3 Oxidative cleavage of styrene catalyzed by KSF montmorillonite with and without additives



Entry	Amount of KSF (mg)	Additive	Reaction time (h)	Yield[a] (%)
1	50	–	22	47
2	100	–	22	55
3	200	–	22	88
4	300	–	22	73
5	400	–	22	70
6	500	–	22	62
7	200	HNO_3	24	22[b]
8	200	H_2SO_4	24	6[b]
9	–	KSF/$Fe(NO_3)_3$ (200 mg)[c]	17	67
10	–	KSF/$FeSO_4$ (200 mg)[c]	17	66

Standard reaction conditions: catalyst, 0.5 mmol styrene, 2 mL H_2O as medium, 70 °C

[a] Yield determined by GC–MS

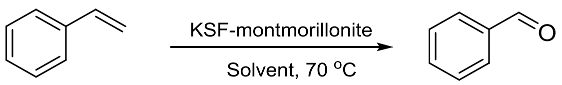
[b] Increased amount of hydration product, 1-phenylethanol, was observed

[c] KSF was pretreated in $Fe(NO_3)_3$ (1 g/10 ml H_2O, 1 g KSF) or $FeSO_4$ (1 g/10 ml H_2O, 1 g KSF) for 24 h, filtered, then air dried

First the role of the catalyst amount on the reaction was investigated by testing masses between 50 and 500 mg KSF (Table 3, entries 1–6). While the desired product was obtained under all conditions, it was found that using 200 mg KSF gave the highest yield of 88% (Table 3, entry 3). When performing the reaction using strong mineral co-acids with oxidative character (Table 3, entries 7 and 8) the yield of benzaldehyde decreased significantly and instead, the product of the hydration reaction (1-phenylethanol) was obtained. As increasing the iron content was somewhat beneficial in the case of K-10 (Table 2) the reaction was performed using iron-enriched KSF (prepared according to Clayfen formulation method [51]). Both materials, prepared with $Fe(NO_3)_3$ and $FeSO_4$, yielded in slightly lower amounts of benzaldehyde than neat KSF (Table 3, entries 9 and 10), indicating that additional iron doping of KSF montmorillonite has no beneficial effect on the oxidative cleavage. Therefore, 200 mg KSF montmorillonite to 0.5 mmol styrene ratio was selected to perform all further studies with this catalyst.

After having determined the optimal catalyst amount we turned our attention towards the solvent as an important additional variable in the reaction (Table 4). It is important to note that our efforts using neat organic solvents were not successful; when water, at least as a co-solvent, was not present the reaction did not yield benzaldehyde. Thus, we

Table 4 Effect of solvents on the oxidative cleavage of styrene to benzaldehyde catalyzed by KSF montmorillonite



Entry	Solvent	Amount (mL)	Conversion (%)	Yield[a] (%)	Byproducts
1	H_2O	1	88	62	26% diol formed
2	H_2O	2	88	88	–
3	H_2O	3	100	0	Polymeric products
4	EtOH (neat)	2	33	0	Polymeric products
5	H_2O/EtOH (1:1)	2	91	0	Polymeric products
6	EtOAc	2	NR	0	–
7	H_2O/EtOAc (1:1)	2	NR[b]	0	–
8	DCE (neat)	2	100	0	Polymeric products
9	H_2O/DCE (1:1)	2	NR[b]	0	–

Standard reaction conditions: 200 mg catalyst, 0.5 mmol styrene, 70 °C, 22 h reaction time

[a] Yield determined by GC–MS

[b] *NR* no reaction

focused on the use of aqueous medium. While water is a preferred solvent from a green perspective [52, 53] the relatively low solubility of styrene in water adds mass transport as a limiting factor to the reaction. Different co-solvents were applied to overcome this drawback (Table 4, entries 4–9). All solvent systems used resulted in a lower product yield than that in neat H_2O even after greatly increased reaction times. Having identified neat water as the optimum medium for the reaction we investigated the influence of the water/reagent ratio, by changing the volume of water and keeping the amount of reagent and catalyst the same (Table 4, emtries 1–3). While the conversion was high in all three cases, the selectivity toward benzaldehyde decreased when smaller amount of water was used. Increasing the water amount led to a complete shift in selectivity and only the formation of polymeric byproducts was observed. It was thus concluded that the 2 mL water/0.5 mmole styrene ratio was the optimum condition to perform the desired transformation.

As the next step in the optimization approach the temperature dependence of the process was investigated. The results, obtained for performing the reaction at temperatures ranging from 50 to 100 °C, are depicted in Fig. 1. As clearly indicated in Fig. 1 the reaction is best performed at 70 °C, both decreasing and increasing the temperatures led to a dramatic drop in yield. It should be noted that increasing the temperature leads to an increased amount of styrene in the gas phase not being available for the reaction. This culminates in the absence of any product when the reaction is performed at 100 °C.

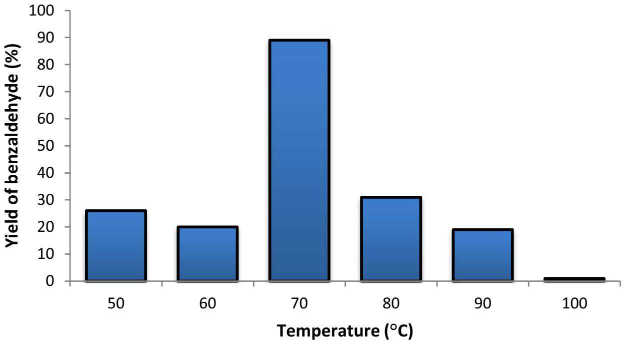


Fig. 1 Effect of temperature on the oxidative cleavage of styrene to benzaldehyde catalyzed by KSF montmorillonit in water under standard conditions

Applying the above optimum conditions determined for most reaction parameters, the time dependence of benzaldehyde formation was assessed (Fig. 2). Benzaldehyde, as all aldehydes, is prone to over-oxidation, thus by finding the appropriate reaction time one can avoid the formation of benzoic acid and other byproducts. It was found that the formation of benzaldehyde underwent a lag phase, yielding only about 10% product even after 9 h reaction time. Despite the long lag phase a significant amount of benzaldehyde formed after 12 h (33%). The product yield continuously increases up to 18 h reaction time (89%). At this point there was no more increase in yield and the benzaldehyde amount remained stable up to 22 h (88%). After 22 h the product amount slowly decreases and the amount of byproducts increases. The analysis of the product mixture showed that this is due to

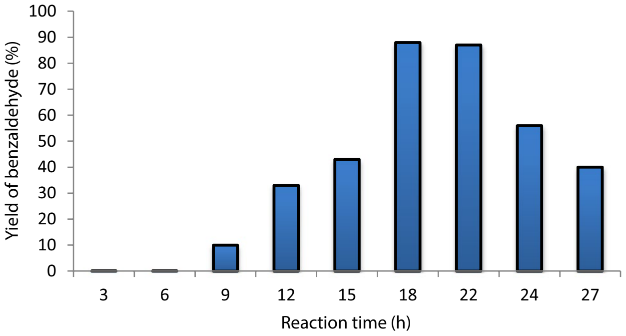


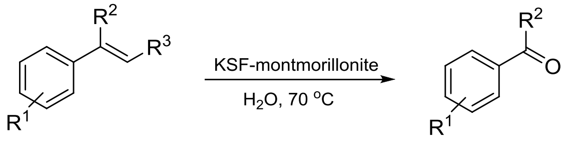
Fig. 2 Oxidative cleavage of styrene using KSF montmorillonite at different reaction times under standard conditions

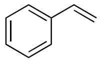
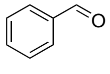
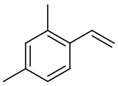
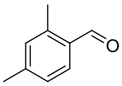
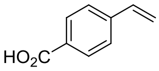
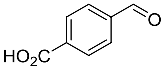
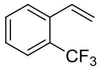
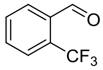
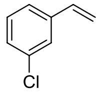
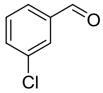
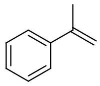
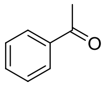
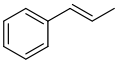
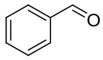
the subsequent transformations of the product benzaldehyde into secondary oxidation products such as benzoic acid (see Scheme 3d).

During the above investigations several reaction parameters have been optimized and led us to devise a general set of reaction conditions that would produce the best performance toward the direct oxidative cleavage to benzaldehyde. Thus, we decided to explore the scope of the reaction and different substituted styrenes were submitted to the same reaction conditions. The results are tabulated in Table 5. While unsubtituted styrene underwent the oxidation in high conversion and excellent selectivity, substituted starting materials gave varying results. The lower conversion values are usually accompanied by high selectivities for benzaldehyde; however, as the conversion of the starting styrene increased so did the amount of byproducts resulting in lower selectivities for the substituted benzaldehydes.

In order to gain insights into the reaction mechanism, a series of reactions were performed as summarized in Scheme 2. When the reaction was performed in the presence of (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) (Scheme 2a) the rate was significantly slowed down and only 4% of benzaldehyde was obtained after 3 days of heating. As TEMPO is a known reagent to inhibit radical reactions, this result strongly suggests that the mechanism

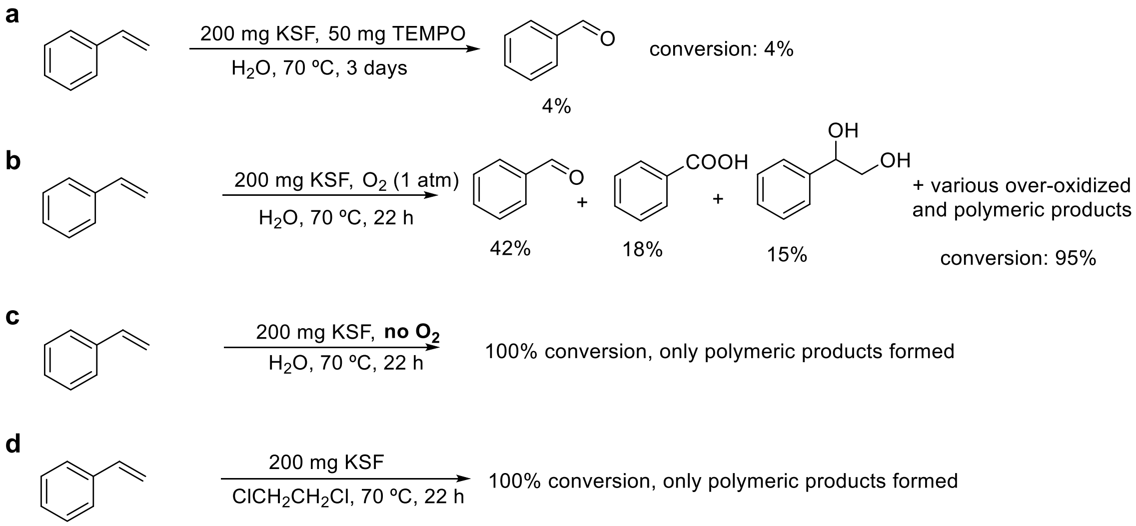
Table 5 KSF montmorillonite-catalyzed oxidative cleavage of substituted styrenes to benzaldehydes in aqueous medium



Entry	Substrate	Product	Reaction time	Conversion[a] (%)	Selectivity[a] (%)
1			18 h	89	100
2			22 h	81	47
3			4 days	7	100
4			22 h	68	63
5			22 h 44 h	7 94	71 48
6			22 h	89	70
7			22 h 45 h	50 73	41 31

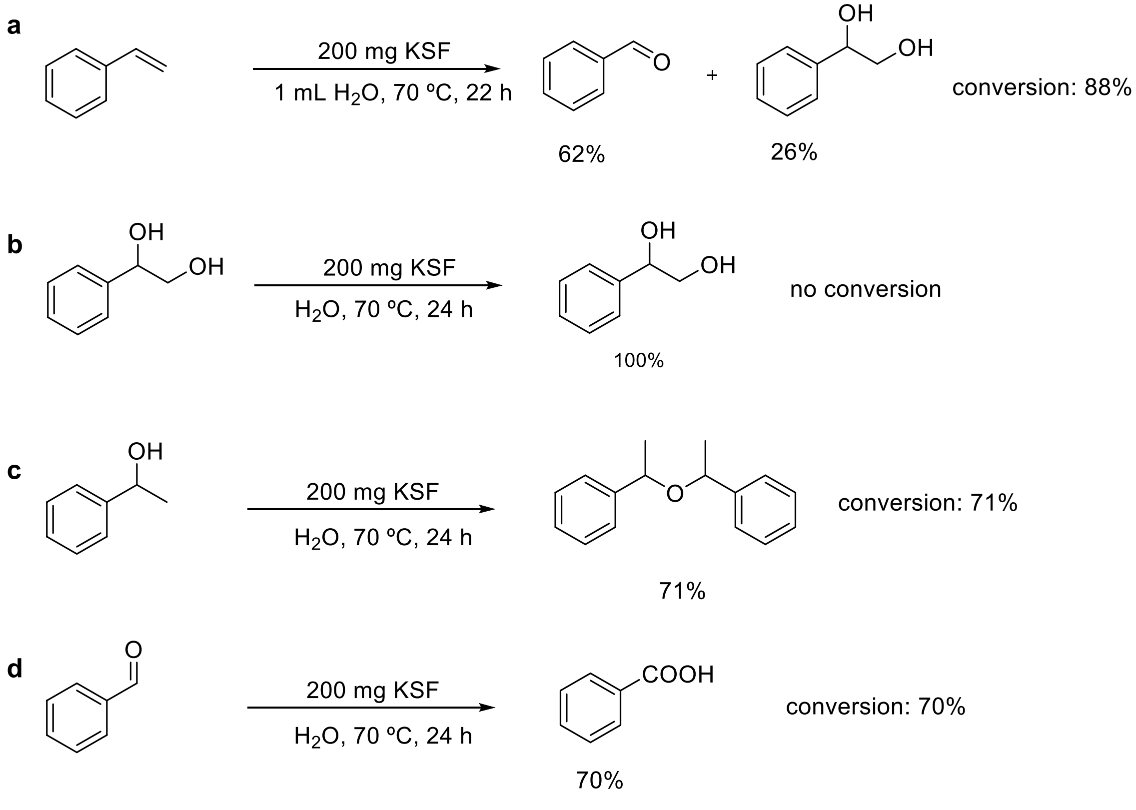
[a] Standard reaction conditions: 200 mg catalyst, 0.5 mmol substituted styrene, H2O as medium, 70 °C

[b] Yield determined by GC–MS



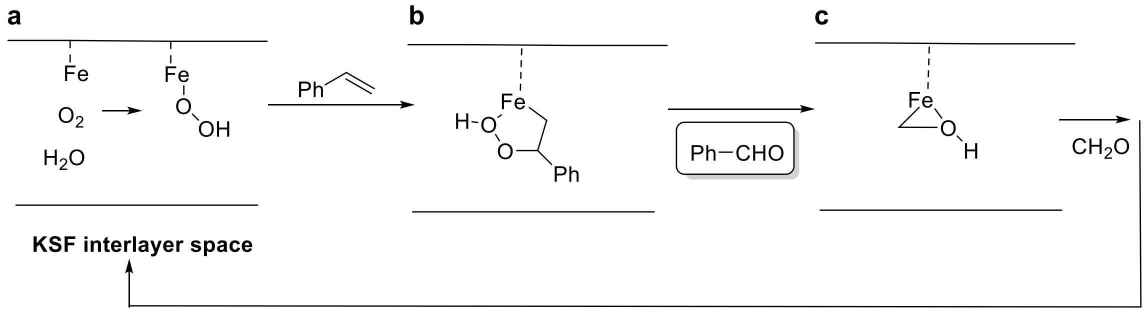
[a] yield determined by GC-MS.

Scheme 2 Investigation towards the mechanism of the oxidative cleavage of styrene to benzadehyde catalyzed by KSF montmorillonite



[a] conversion/selectivity determined by GC-MS.

Scheme 3 Investigation of the potential contributions of different byproducts under oxidative cleavage conditions using KSF montmorillonite



Scheme 4 Proposed schematic mechanistic pathway for the oxidative cleavage of styrene using KSF montmorillonite

involves radical intermediates. We then investigated the role of oxygen and the reaction was performed under a pure oxygen atmosphere (Scheme 2b) and using degassed solvent under argon atmosphere (Scheme 2c). The use of oxygen atmosphere has resulted nearly quantitative conversion, the selectivity, however, significantly decreased. The presence of benzoic acid and other over-oxidized products indicate that high oxygen concentration in the system is not beneficial for the aldehyde formation. In contrast, when the reaction was performed under oxygen free conditions the system only yielded polymerization products with 100% conversion. Thus, it appears that without the presence of oxygen the oxidation does not occur. Performing the reaction in the absence of water using only 1,2-dichloroethane (DCE) as solvent led to styrene polymerization only (Scheme 2d), no trace of oxidation was observed. This suggests the involvement of water in a critical step in the mechanism, most likely as, at least partial, source of oxygen in the cleavage reaction or catalyst regeneration.

The detailed analysis of the reaction products also revealed that phenylethane-1,2-diol was often found as the byproduct of the reaction (Scheme 3a). It was decided to further examine the potential formation and possible role of the byproducts. In order to test whether the diol observed was a dead-end byproduct or an intermediate, in a separate reaction it was subjected to the reaction conditions (Scheme 3b). After 22 h reaction time no conversion was observed confirming that phenylethane-1,2-diol is a byproduct formed by a different reaction pathway. When performing a similar reaction with 1-phenylethanol, the product of the traditional acid-catalyzed hydration, only the corresponding symmetric ether was obtained, likely with another acid catalyzed intermolecular dehydration, with no benzaldehyde formation. Thus, the simple hydration product cannot be considered as an intermediate to benzaldehyde. In order to explain the disappearance of the product after extended reaction time benzaldehyde was submitted to the reaction conditions. As expected most of the initial benzaldehyde was oxidized to benzoic acid (Scheme 3d).

Based on the above presented experimental evidence several pathways can be excluded. The diol (Scheme 3b) or the hydration product phenylethanol appear to be byproducts and not active intermediates. Considering literature reports [54] and our own data it is proposed that the reaction occurs in the interlayer space within the clay. Literature data suggest that in the presence of protons (KSF) and Fe, oxygen can undergo a two electron reduction to H_2O_2 [55]. It has also been proposed that in the presence of high spin Fe ions water can attack this over-oxidized species and H_2O_2 forms as a result [56]. We suggest that the formation of high spin Fe ions and their reaction with the solvent water is the most probable pathway that describes the reaction mechanism. This explains that the cleavage only occurs in aqueous media. The in situ formed Fe–O–O–H ions form an Fe–alkylperoxide complex with styrene. This complex is highly unstable and will undergo a disproportionation to two aldehydes in subsequent steps as described in several reports using Pd [57] and Fe [58] catalysts. The proposed pathway is described in Scheme 4. As an alternative mechanism the formation of a dioxetane was also suggested [54]; however, this pathway does not provide an explanation for the role of water in the process. In order to confirm the formation of formaldehyde the reaction was carried out under the standard conditions with the addition of phenylhydrazine. It was expected that the phenylhydrazine will trap the aldehydes and form the corresponding phenylhydrazones. After the reaction a large amount of hydrazone formed (~45% yield) from benzaldehyde, however, the hydrazone from $CH_2=O$ was not found. We believe that formaldehyde being a gas and slowly forming in a relatively small amount simply evaporated during the long reaction time at the high temperature and escaped the system.

3 Conclusions

In conclusion, KSF montmorillonite has been found as an inexpensive commercially available, environmentally benign catalyst for the catalytic oxidative cleavage of styrenes to benzaldehydes, an ultimately green version of ozonolysis. The catalyst provided high yields and excellent selectivity for styrene nearly reaching quantitative conversion. The reactions appear to be a broad scope approach, however, individual optimizations may be needed to achieve similar clean reactions with substituted styrenes. It is proposed that the elevated Fe-content of the catalyst contributed to the improved activity in the oxidative cleavage. The sustainable commercial catalyst, the simplicity of the method, the aqueous medium and using atmospheric pressure air as an oxidant makes this approach a green alternative to replace the traditional ozonolysis reaction.

4 Experimental

4.1 General Information

All starting materials were commercially available and were purchased from Sigma-Aldrich or AlfaAesar and used without further purification. The mass spectrometric identification of the products have been carried out by an Agilent 6850 gas chromatograph-5973 mass spectrometer system (70 eV electron impact ionization) using a 30 m long DB-5 type column (J&W Scientific). For thin-layer chromatography (TLC), silica gel plates EMD 60 F254 were used and compounds were visualized under UV light. All obtained products are commercially available and were identified by comparison to authentic samples.

4.2 General Procedure for the Oxidative Cleavage of Styrenes

Styrene (57 µL) and 200 mg KSF montmorillonite were introduced to a screw cap vial and 2 mL of water was added. The vial was closed and heated to 70 °C in an oil bath for 22 h under continuous stirring. After completion of the reaction the aqueous reaction mixture is extracted with ethyl acetate. The organic layer is then analyzed by GC-MS.

Acknowledgements Financial support provided by the University of Massachusetts Boston is gratefully acknowledged.

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