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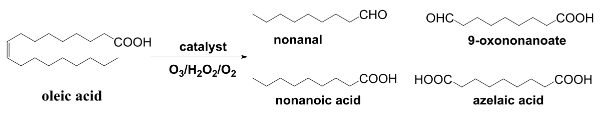
Sodium Stannate Promoted Double Bond Cleavage of Oleic Acid by Hydrogen Peroxide over Heterogeneous WO_3 Catalyst

Xiukai Li, Joel Choo Ping Syong and Yugen Zhang*

The production of valuable mono- and dicarboxylic acids from abundant and renewable vegetable oil sources is of great industrial interest. It is demonstrated a simple and eco-friendly heterogeneous catalytic system for direct oleic acid (OA) cleavage by hydrogen peroxide to produce azelaic acid (AA) and nonanoic acid (NA). Commercially available tungsten oxide was used as the heterogeneous catalyst without any modification or pretreatment, and sodium stannate was used as an H_2O_2 stabilizer to improve the efficiency of the oxidant. The sodium stannate additive notably improved the product yields and it could be recycled together with the tungsten oxide catalyst. Isolated product yields up to 89% for azelaic acid and 65% for nonanoic acid were achieved from oleic acid in this simple system, which should be among the best results for oleic acid cleavage in heterogeneous systems. This strategy is also applicable for other catalytic systems for the cleavage of OA or its derivatives. This work provides a potential method for the large scale upgrading of oleic acid.

Renewable biomass feedstock is a potential alternative to fossil resources for the production of chemicals and fuels. Oils from vegetable origins are abundant, nontoxic, and biodegradable, making them very promising candidates for the sustainable chemical industry. In fact, the nonfood consumption of vegetable oils has increased steadily in the past two decades.[1] The hydrolysis of triglycerides (the main constituents of vegetable oils and animal fats) generates glycerol and various saturated and unsaturated fatty acids such as palmitic acid, oleic acid, and linolenic acid. The fatty acid products as well as glycerol have functional groups possible for further derivatization and chemical modification. The oxidative cleavage of unsaturated fatty acid at the C=C bond for the production of shorter-carbon-chain monocarboxylic acids and dicarboxylic acids is of particlular interest.[1a, 2] For instance, the ozonolysis of oleic acid enables the production of azelaic acid (C9 dicarboxylic acid) and nonanoic acid (C9 monocarboxylic acid) (Scheme 1),[2d-f] both acid products being useful intermediates for the manufacture of polymers and a variety of materials.



Scheme 1. Oxidative cleavage of oleic acid into aldehydes and carboxylic acids.

Though the ozonolysis of oleic acid (OA) into azelaic acid (AA) and nonanoic acid (NA) is efficient and has already been industrialized on a large scale, the use of hazardous ozone as an oxidant is obviously a big challenge for safety and environmental management. As such, safer, greener, and economically viable processes for oleic acid cleavage are highly sought-after. Noncatalytic and catalytic systems with oxidants alternative to ozone have therefore been explored extensively. Reagents such as nitric acid, organic peracids, potassium monopersulfate, potassium permanganate, sodium periodate, and sodium hypochlorite were used as strong oxidants for oleic acid cleavage in homogeneous systems with or without the aid of a catalyst;[1a, 2a, c, 3] however, these oxidants are not eco-friendly. Transition metal-based catalytic systems with molecular oxygen and hydrogen peroxide as green oxidants are more attractive. Fe, W, Mo, and Ru organometallic complexes are homogeneous catalysts, activating O_2 or H_2O_2 for oleic acid cleavage.[1a, 2a, 4] Among those, the quaternary ammonium salts of W-based heteropoly acids gave the best product yield varying from 80–97% in two phase reaction systems.[4d-h] Besides the direct cleavage of oleic acid, there have also been trials on the two-step conversions of oleic acid via 9,10-dihydroxysteric acid (DSA) as an intermediate.[5] Oleic acid was first dihydroxylated to DSA by H_2O_2 in the presence of H_2WO_4, then DSA was further cleaved by sodium hypochlorite[5b] or molecular oxygen in the presence of homogeneous cobalt catalysts.[5a, c, d] A heterogeneous Au/AlO_3 catalyst could cleave DSA to afford a high yield of azelaic acid (86%) and nonanoic acid (99%) under 5 bar of O_2; however, the catalyst recyclability suffered from the problem of Au leaching.[5e, f] Compared with the one-step processes, the two-step processes were more complicated and afforded comparable or even lower product yield.

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The direct cleavage of oleic acid in heterogeneous catalytic systems is preferred for better simplicity of the system and easier post-treatment. However, so far there have been quite limited reports on such heterogeneous systems probably because of the poor catalyst performances.[6] About 80% product yield was achieved from methyl oleate cleavage over ruthenium nanoparticles supported on hydroxyapatite, however, with $NaIO_4$ as the oxidant instead of greener O_2 and H_2O_2.[7] Using Cr/Co/Mn-doped MCM-41 molecular sieves[6c] and supported/unsupported WO_3[6e] as catalysts, only 30% yield of azelaic acid and nonanoic acid were produced from oleic acid oxidation by molecular oxygen or hydrogen peroxide. Surfactant-functionalized WO_3 and MoO_3 nanoparticles afforded higher product yield (near 80%) due to the better compatibility of catalysts in the reaction system.[6a, d, 8] Sophisticated procedures were carried out to synthesize such nanoparticles with hydrophobic surfaces. Thus, all the current catalytic sytems are restricted for the large-scale cleavage of oleic acid.

In this work, we report a simple system for direct oleic acid cleavage by hydrogen peroxide employing commercial tungsten oxide as a catalyst and sodium stannate as an additive. The tungsten oxide is easily avaliable in large amounts and it was used without any modification or pretreatment. Sodium stannate served as an H_2O_2 stabilizer and it promoted the reaction notably. An isolated yield up to 89% for AA was achieved from this simple system, in contrast to the 30–80% yield for AA from other heterogeneous systems.[6a, 6c-e, 8] Moreover, both the tungsten oxide catalyst and the sodium stannate additive could be recycled. This work provides a possible strategy for improving product yields from oleic acid and its derivatives by H_2O_2 oxidation. This work may also open up the study of new W/Sn-based catalysts for this reaction.

Tungsten-based catalysts are attractive for oleic acid cleavage in both the homogeneous and heterogeneous systems.[4d-h, 6a, e, 8] The use of tungsten oxide as a solid catalyst for oleic acid cleavage by hydrogen peroxide usually requires a reaction temperature above 100 °C to achieve high OA conversion.[6a, e, 8] Table 1 (Entries 2−4) reports the results of OA cleavage by hydrogen peroxide in the presence of commercial WO_3 catalyst under different reaction tempratures. The WO_3 was in a monoclinic crystal structure and had micron particle sizes. A rapid sample derivatization method (esterification in BF_3-methanol)[9] was used to speed up GC analysis in our preliminary catalyst screening and reaction optimization, with the extents of esterification at 70% for AA and 85% for NA, respectively. One can see that both OA conversion and the apparent yields for NA and AA increased with the reaction temperature. Full OA conversion was achieved at the reaction temperature of 130 °C, and the apparent yields for NA and AA were 38.1% and 22.9%, respectively. Octanoic acid, suberic acid, nonanal and 9-oxononanoate were observed as the major side products. As the decomposition of hydrogen peroxide at above 130 °C is rapid and dangerous,[10] reaction temperatures should be capped at 130 °C. As we envision that suppressing the rapid decomposition of hydrogen peroxide might improve reaction efficiency, we added H_2O_2 stabilizers into the system. Different types of stabilizers were screened (Table 1 & S1), including inorganic acids, inorganic salts, metal oxides, and chelating agents.[11] Most of the stabilizers did not give positive effects except sodium stannate. The combination of sodium stannate with the tungsten oxide catalyst resulted in product yields improving to 51.1% for NA and 42.0% for AA (Entry 5, Table 1). It is also noted that the addition of sodium stannate did not change the product distribution. Other tin-containing compounds were not as effective as sodium stannate (Entries 6−8). Our control reaction (Entry 9, Table 1) revealed that sodium stannate itself is inactive for oleic acid cleavage. To study the thermal decomposition of H_2O_2 in the presence of sodium stannate stabilizer, we carried out the tests at 130 °C without oleic acid and WO_3 in the system (Figure 1). It turned out that 91% of H_2O_2 remained in 4 h and 66% of H_2O_2 remained in 16 h. This is a sharp contrast to the fact that H_2O_2 was almost fully decomposed in 4 h at 130 °C in the absence of sodium stannate. Thus, it is feasible to improve OA cleavage by adding sodium stannate as a H_2O_2 stabilizer into the reaction system. Similar positive effects of adding H_2O_2 stabilizer were also observed in Fenton oxidations.[12]

Table 1 The oxidative cleavage of OA by H_2O_2 in the presence of commercial WO_3 catalyst and tin additives.

Entry	Catalyst	Additive	Yield (%)[a]					Conv. (%)
			C_8-acid	C_9-al	NA	C_9-al-acid	AA	
1	-	-	1.8	4.7	3.6	2.7	1.2	60.0
2	WO_3 [b]	-	3.2	2.9	14.6	1.5	10.6	53.2
3	WO_3 [c]	-	4.6	11.7	28.1	10.8	20.9	76.1
4	WO_3	-	5.0	3.9	38.1	2.0	22.9	100.0
5	WO_3	Na_2SnO_3	2.4	1.3	**51.1**	2.6	**42.0**	100.0
6	WO_3	$Sn(OH)_4$	0.0	0.0	37.2	0.0	27.1	100.0
7	WO_3	SnO_2	7.1	7.5	32.2	6.7	24.7	100.0
8	WO_3	$SnCl_4$	5.0	7.6	24.4	6.0	17.0	100.0
9	-	Na_2SnO_3	2.7	0.6	5.4	0.0	3.9	52.7

OA 283 mg (1 mmol), WO_3 30 mg, Na_2SnO_3 10 mg, *tert*-butanol 4 mL, 31% H_2O_2 1 mL, 130 °C 4 h. [a] GC yield; [b] 60 °C 4 h; [c] 100 °C 4 h. C_8-acid: octanoic acid; C_9-al: nonanal; NA: nonanoic acid; C_9-al-acid: 9-oxononanoate; AA: azelaic acid.

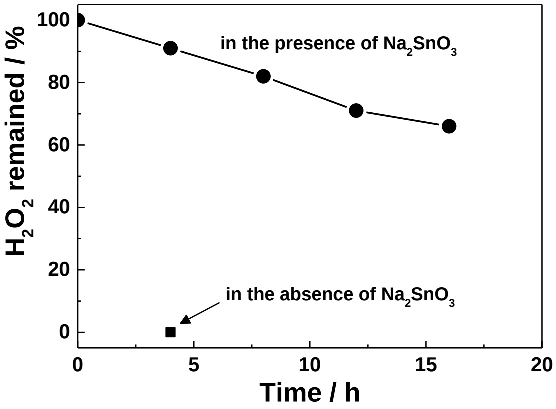

Figure 1. Rate of H_2O_2 decomposition in the presence or absence of Na_2SnO_3. Na_2SnO_3 10 mg, *tert*-butanol 4 mL, 31% H_2O_2 1 mL, 130 °C.

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We further applied the sodium stannate additive to similar systems for OA cleavage by H_2O_2 but with tungstic acids and molybdenum oxide as the catalysts (Figure 2A). In the absence of sodium stannate, the WO_3 catalyst enabled the best NA (38.1%) and AA (22.9%) yields and the MoO_3 catalyst gave the lowest NA (24.1%) and AA (14.3%) yields. The two tungstic acids afforded only modest product yields among the four catalysts. With sodium stannate addition, the product yields improved notably for all the four catalytic systems. The yield for AA was enhanced by 34–77% and the yield for NA was enhanced by 84–127%. The $H_2W_2O_7$ catalyst in combination with Na_2SnO_3 additive afforded product yields comparable to that from the system of WO_3 and Na_2SnO_3. However, $H_2W_2O_7$ is an unstable heterogeneous catalyst because it reacts with H_2O_2 to form water-soluble pertungstic acid.[5b-d] The best-performing system with WO_3 as a catalyst and Na_2SnO_3 as an additive was applied to other substrates such as technical grade oleic acid (TOA), 9,10-epoxyoctadecanoic acid (EOA), and 9,10-dihydroxysteric acid (DSA), with the results shown in Figure 2B. The technical grade OA contains 90% oleic acid, with stearic acid as the major impurity, and it is much cheaper than refined OA. EOA and DSA are possible intermediates in OA oxidative cleavage by H_2O_2.[4f, 5] Similarly, the addition of Na_2SnO_3 as a hydrogen peroxide stabilizer improved the product yields for all substrates including OA, TOA, EOA, and DSA. These results also provide information for the understanding of the reaction mechanism. In the current work, the use of Na_2SnO_3 did not change the product distribution from OA cleavage, as shown in Table 1. The epoxidation of OA to EOA and the subsequent hydrolysis of EOA to DSA are rather straightforward in the presence of H_2O_2.[13] Product yields similar to those from OA cleavage could be achieved from EOA and DSA under the same conditions. Thus, we propose that the reactions of OA cleavage with or without the Na_2SnO_3 additive proceed by the same pathway (Scheme 2). However, adding Na_2SnO_3 as a H_2O_2 stabilizer made better utilization of the oxidant and enabled higher reaction efficiency. Thus, adding Na_2SnO_3 as a H_2O_2 stabilizer is a general strategy to improve the cleavage of OA and its derivatives by H_2O_2.

The reaction conditions were optimized for the system with WO_3 catalyst and Na_2SnO_3 additive, including the reaction temperature, the reaction time, and the loading amounts of WO_3, Na_2SnO_3, and H_2O_2. Figure 3A shows the temperature dependence of OA cleavage by H_2O_2 in the presence of WO_3 and Na_2SnO_3. In the presence of Na_2SnO_3, the fast decomposition of H_2O_2 was suppressed and a reaction temperature higher than 130 °C could therefore be applied. The product yields increased with the reaction temperature and maximized at 130 °C, then dropped at higher temperature. In view that similar temperature dependence was observed for the system without Na_2SnO_3 (Entries 2–4, Table 1), it is deduced that the Na_2SnO_3 addition does not decrease the activation energy for OA cleavage. However, Na_2SnO_3 affects the reaction efficiency significantly even at a very small quantity. The addition of several milligrams of Na_2SnO_3 resulted in notable improvement in the product yields (Figure 3B), and the loading amount of 10 mg was the most optimal. From Figure 3C, the product yields increased remarkably with WO_3 loading and the rate slowed down when the loading amount exceeded 30 mg. Thus, the minimum loading amount for WO_3 is 30 mg. It is noted that the optimal loading amount of WO_3 for the current system (10.6 wt%) is much lower than that (45 wt%) of surfactant-functionalized WO_3.[8] The reaction time was studied for different loading amounts of H_2O_2 (Figure 3D). For each loading amount of H_2O_2, the product yields increased quickly in the first 4 h, then changed slowly after 4 h. At the same reaction time, the best product yields were achieved at 1.5 mL of H_2O_2 and reached 61.4% yield for NA and 56.3% yield for AA at 12 h.

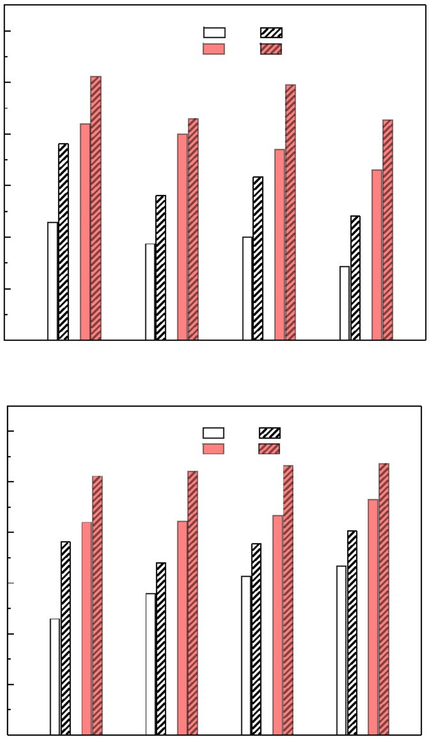
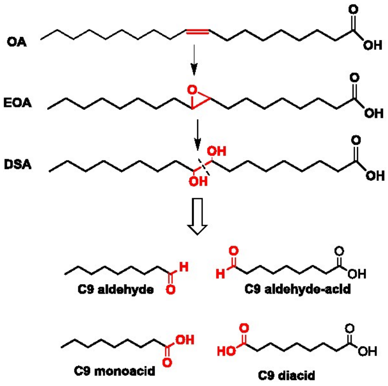


Figure 2. (A) The oxidative cleavage of OA over various catalysts w/wo Na_2SnO_3 additive. (B) The oxidative cleavage of various substrates over WO_3 catalyst w/wo Na_2SnO_3 additive. Substrate 1 mmol, catalyst 30 mg, Na_2SnO_3 10 mg, *tert*-butanol 4 mL, 31% H_2O_2 1 mL, 130 °C 4 h. NA: nonanoic acid; AA: azelaic acid; TOA: technical grade OA (90%); EOA: 9,10-epoxyoctadecanoic acid; DSA: 9,10-dihydroxysteric acid. GC yields.



Scheme 2. The proposed reaction pathway for OA cleavage by H_2O_2 in the presence of WO_3 and Na_2SnO_3.

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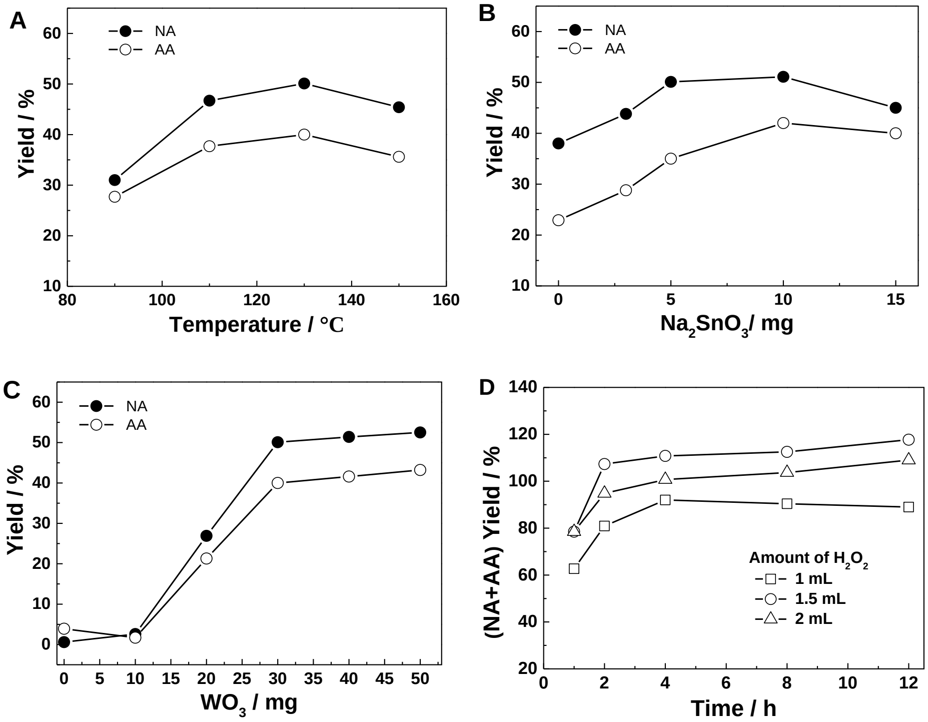

Figure 3. Deferred reaction conditions: OA 283 mg (1 mmol), WO_3 30 mg, Na_2SnO_3 10 mg, *tert*-butanol 4 mL, H_2O_2 1 mL, 130 °C, reaction time 12 h. (A) The temperature dependence of OA cleavage by H_2O_2 in the presence of WO_3 and Na_2SnO_3. (B) The changing of loading amount of Na_2SnO_3 at 4 h reaction time. (C) The changing of loading amount of WO_3. (D) The loading amount of H_2O_2 and the reaction time.

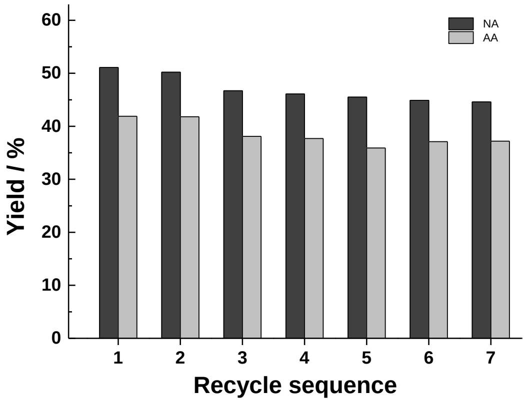

Figure 4. The recyclability tests for WO_3 and Na_2SnO_3. OA 283 mg (1 mmol), catalyst 30 mg, Na_2SnO_3 10 mg, *tert*-butanol 4 mL, H_2O_2 1 mL, 130 °C 4 h. Catalyst was separated by centrifuge and washed with *tert*-butanol twice for the next test.

Catalyst recyclability was tested for OA cleavage with the results reported in Figure 4. In seven runs of use and reuse of the catalyst, the product yields dropped slightly for NA and AA. Since the product yields in the recycled reactions are higher than that in the reaction with WO_3 catalyst alone (Entry 4, Table 1), we assumed that the Na_2SnO_3 additive was recycled together with WO_3. The fresh and the used catalysts were characterized by scanning electron microscopy (SEM). The fresh WO_3 catalyst contains cubes in micron sizes (Figure 5A). After the first round of catalytic reaction, the cubes broke into smaller irregular particles (Figure 5B). After seven rounds of recyclability testing, the catalyst morphology changed into uniform nanoparticles (Figure 5C). The XRD analysis (Figure S1) shows that the fresh WO_3 catalyst is in a monoclinic crystal structure. After several runs of reaction for OA cleavage, the catalyst gradually changed to monoclinic $WO_{2.72}$.[14] The interaction between WO_3 and aqueous H_2O_2 is profound under solvothermal conditions. WO_3 could be converted to various hydrates and tungsten-peroxo complexes under the conditions,[8] and this would induce the restacking and phase transition of the crystals, and also the changes in sample morphology. Because the tungsten-peroxo complexes are the active oxidants for OA cleavage and their formation is independent of the crystal structure of WO_3, WO_3 with various crystal structures can activate H_2O_2 for this reaction.[8] The tungsten-peroxo complexes are unstable and gradually decomposed, converting to the oxygen-deficient metal oxide after prolonged reaction. The catalyst after the seventh reaction was subjected to the energy dispersive X-ray analysis (EDXA). The elemental mapping spectra (Figure 5D & E) for the used catalyst show that both W and Sn were uniformly dispersed over the sample, confirming that the tin additive was recovered together with the WO_3 catalyst. The elemental emission spectrum (Figure 5F) indicates that the W/Sn ratio (2.1 in molar) in the used catalyst is close to the initial ratio (2.7) in the first round of reaction. It is noteworthy that Na_2SnO_3 is soluble in *tert*-butanol/water mixture but it can be recycled together with the WO_3 catalyst. We presume

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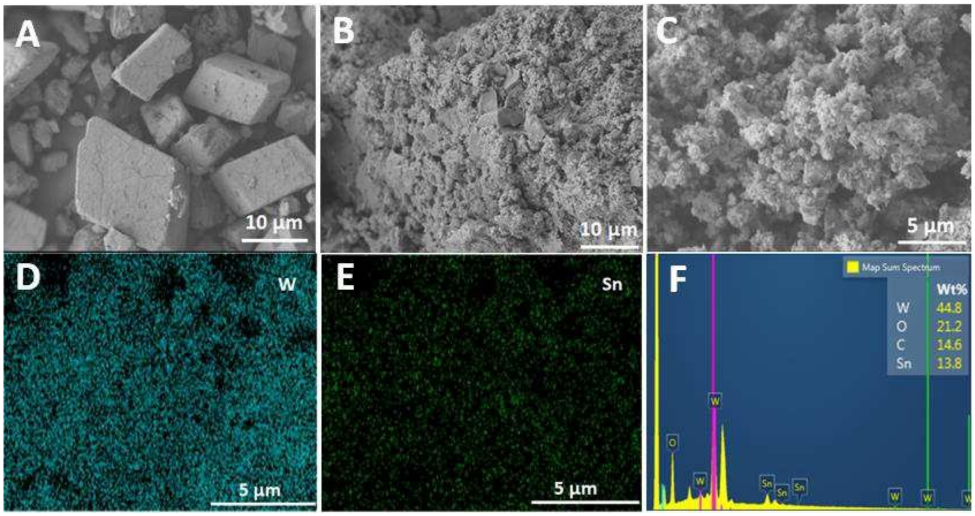

Figure 5. The SEM image and the EDX mapping. (A) Fresh WO_3 catalyst. (B) Catalyst after the first round of reaction shown in Figure 4. (C) Catalyst after the seventh round of reaction shown in Figure 4. (D − F) The energy dispersive X-ray analysis (EDXA) for the catalyst after the seventh round of reaction shown in Figure 4.

that there might be certain interactions between the WO_3 hydrate and the Na_2SnO_3 hydrate. For instance, the intermolecular dehydration between the Na_2SnO_3 hydrate and the WO_3 hydrate could graft Na_2SnO_3 onto the surface of WO_3 (Scheme S1). Such binding between WO_3 and Na_2SnO_3 enabled the recyclability of Na_2SnO_3 together with WO_3. The WO_3-Na_2SnO_3 composite (W/Sn $\cong$ 2.1−2.7) is a bifunctional material; WO_3 is the active phase to activate H_2O_2 for oleic acid cleavage, while the Na_2SnO_3 species attached to the WO_3 surface serves as a H_2O_2 stabilizer. This observation may open the door for the design of new W-Sn based compounds as bifunctional catalysts for OA cleavage.

As we have demonstrated that adding Na_2SnO_3 could improve the yield for AA and NA from oleic acid cleavage, we further scaled up the reaction (8 mmol of OA) to verify the efficiency of this protocol (Supporting Information). After product isolation and purification, AA was achieved at 89% yield as a white solid (Figure S2), and NA was achieved at 65% yield as a clear liquid (Figure S3); the results should be among the best for oleic acid cleavage in heterogeneous systems.[6a, 6c-e, 8] The isolated yields, especially that for AA, are higher than those from GC analysis, because the extent of esterification for a dicarboxylic acid is lower than that for a monocarboxylic acid by the rapid sample derivatization method.[9]

Conclusions

In conclusion, we have demonstrated a very simple heterogeneous catalytic system for direct oleic acid cleavage to produce shorter carbon chain carboxylic acids by H_2O_2. Commercially available WO_3 was used as the catalyst and Na_2SnO_3 was used as an additive to stabilize H_2O_2. The Na_2SnO_3 additive did not change the reaction pathway but notably improved efficiency of the oxidant and product yield. This strategy is also applicable for other catalytic systems for the cleavage of OA and its derivatives. In a scale-up reaction, azelaic acid and nonanoic acid were produced at isolated yields of 89% and 65% from this system. The WO_3 catalyst and the Na_2SnO_3 additive can be recycled without remarkable loss in activity. It is proposed that the interaction between the WO_3 hydrate and the Na_2SnO_3 hydrate enabled the good recyclability of the catalyst and the additive.

Acknowledgements

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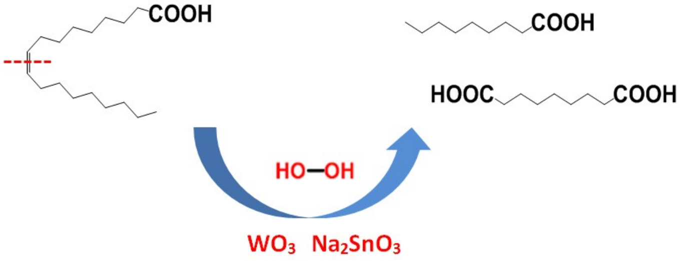

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