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Production of Renewable Oleo-Furan Surfactants by Cross-Ketonization of Biomass-Derived Furoic Acid and Fatty Acids

Hannah Nguyen, a Yunzhu Wang, b David Moglia, a Jiayi Fu, b Weiqing Zheng, b Marat Orazov* a,b and Dionisios G. Vlachos* a,b

Synthesis of 2-dodecanoyl furan is a crucial step in the formulation of oleo-furan sulfonates as bio-surfactants from biomass-derived furans and vegetable-oil-derived molecules. Herein, cross-ketonization of 2-furoic acid and lauric acid is proposed to produce the bio-surfactant precursor. Among the commonly reported metal oxide ketonization catalysts, the inexpensive and abundant iron oxides are demonstrated as effective and recyclable catalysts, enabling up to 77% selectivity to 2-dodecanoyl furan at 56% lauric acid conversion. Catalyst characterization by X-ray diffraction, H2 temperature-programmed reduction, and X-ray photoelectron spectroscopy indicates that Fe3O4 is the catalytically active and stable phase. 13C isotopic tracing experiments suggest that cross-ketonization on Fe3O4 proceeds via a β-keto acid intermediate.

The OFSs preparation involves the formation of a 2-alkoylfuran intermediate via Friedel-Crafts acylation of furan with a vegetable-oil-derived, long-chain (Cn-C18) carboxylic acid or fatty acid anhydride. Optionally, hydrodeoxygenation of the ketone group may be used to increase the hydrophobicity of the alkyl chain. Finally, sulfonation introduces the hydrophilic head of the surfactant. Among these steps, the C-C coupling reaction is equilibrium limited for long chains, resulting in low yields (see SI for equilibrium estimations). Due to the disadvantages of the current approaches, herein, we propose a new synthesis of 2-alkoyl furan via cross-ketonization of 2-furoic acid and lauric acid using heterogeneous catalysts (Figure 1, pathway C). The cross-ketonization strategy offers ease of separation and recyclability of solid catalysts and produces only water and carbon dioxide as byproducts. It also does not suffer from the equilibrium limitations of acylation (see SI for equilibrium estimations).

Introduction

Recent research in biomass conversion has significantly advanced the science and technology of converting the most naturally abundant renewable source of carbon to chemicals. Specifically, the non-edible biomass-derived furans can be upgraded to valuable chemicals, such as plastics, rubber, lubricants, and detergents.1-7 Examples include the synthesis of para-xylene via cycloaddition of dimethyl furan and ethylene,1 butadiene via “dehydra-decyclization” of tetrahydrofuran,4 C33-45 base-oil lubricants,5 and oleo-furan sulfonates (OFSs), which possess excellent detergency. The structure of OFSs (shown in Figure 1) includes a central furan moiety that links a hydrophobic hydrocarbon chain to a hydrophilic sulfonate. Park et al. evaluated the surfactant properties of OFSs using the critical micelle concentration (CMC), defined as the minimum surfactant concentration for micelle formation, the Kraft point (TKraft), below which surfactants form solid crystals, and their stability in hard water.7 OFSs with linear alkyl chains exhibit enhanced surfactant performance as evidenced by their lower CMC and TKraft than petroleum-derived alkylbenzene sulfonates (LAS). The furan moiety improves surfactant’s solubility compared to the benzene moiety. Moreover, the OFS function in hard water, i.e., in the presence of Ca2+, is much better than the LAS’s. Overall, OFSs enable the (1) utilization of renewable lignocellulosic feedstock, (2) enhanced detergency in cold water applications, and (3) improved stability in hard water, eliminating the need for costly chelating agents used in conventional LAS.

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Ketonization is an established C-C coupling reaction to prepare symmetrical dialkyl ketones or cyclic ketones from aliphatic acids or diacids, respectively. Common examples include the ketonization of acetic acid to acetone\(^8,9\) and adipic acid cyclization to cyclopentanone.\(^9\) Two different carboxylic acids lead to self- and cross-ketonization, with the former reducing the selectivity to the desired cross-ketonization product.\(^10-12\) Early work on ketonization of acetic acid was facilitated by alkali and alkaline earth oxides via decomposition of the acetate salts, which forms via the reaction of the acid with the bulk oxides.\(^13,14\) Recent catalyst developments show that ketonization occurs on the surface of zeolites and high-lattice-energy metal oxides, such as TiO\(_2\), ZrO\(_2\), CeO\(_2\), their mixed oxides, and transition metal (e.g., Pd, Ru, Co)-doped oxides.\(^15-19\) Catalyst properties that may affect ketonization activity include, but are not limited to, redox, acid-base properties, and interaction of the carboxylic acid with the oxide surface. Comprehensive reviews on the catalysis and ketonization mechanism of short-chain carboxylic acids have been reported elsewhere.\(^20,21\) Extensive mechanistic research has shown that \(\alpha\)-hydrogen (\(\alpha\)-H) in at least one of the carboxylic acid molecules is critical for the surface reaction to take place.\(^15,22\) The reaction rate increases monotonically with the number of \(\alpha\)-H atoms in the absence of steric hindrance. For instance, the self-ketonization of propionic acid (with two \(\alpha\)-H) occurs ten times faster than 2-methyl propionic acid (with one \(\alpha\)-H).\(^23\) Accordingly, one may expect a slower reaction rate for cross-ketonization since 2-furoic acid does not contain an \(\alpha\)-H. While most prior ketonization studies focused on small gas-phase molecules, the high boiling point of lauric acid requires a liquid reaction. Therefore, the proposed cross-ketonization chemistry entails challenges, namely (1) slow rate of cross-ketonization, (2) lack of mechanistic insights, and (3) limited related literature. This report demonstrates the selective production of 2-dodecanoyl furan bio-surfactant precursor from biomass-derived 2-furoic acid and vegetable-oil-derived lauric acid, using earth-abundant metal oxide catalysts. The reaction mechanism and catalyst active sites are elucidated to guide further research on catalyst design.

**Experimental section**

**Materials**

2-furoic acid and n-dodecanoic (lauric) acid were purchased from Sigma Aldrich. Solvents n-dodecane, cyclohexane, and dimethyl sulfoxide (DMSO) were acquired from Fisher Scientifics. The metal oxides, including iron (II) oxide (FeO\(_2\)), iron (III) oxide (Fe\(_2\)O\(_3\)), and iron (II, III) oxide (Fe\(_3\)O\(_4\)), titanium oxide (TiO\(_2\)), zirconium oxide (ZrO\(_2\)), gamma aluminum oxide (\(\gamma\)-Al\(_2\)O\(_3\)), and cerium oxide (CeO\(_2\)) were obtained from Sigma Aldrich. All chemicals were used as received.

**Catalytic reaction and analysis**

Reactions were carried out in a 100 mL Parr reactor vessel, with a glass liner, containing 30 mL of n-dodecane solvent, 2-furoic acid and lauric acid as reactants, 0.2 g metal oxide catalyst, under 20 bar \(N_2\) pressure, with lauric acid as the limiting reagent. N-dodecane was chosen as the solvent due to its inertness, low vapor pressure, and the ability to solubilize lauric acid and the desired product, 2-dodecanoyl furan. The reactor was heated up to the desired temperature in a fitted band heater, using an inhouse made PID controller, on a magnetic stir bar. After a designated time, the reactor was quenched in an ice bath to stop the reaction. Due to its low solubility in n-dodecane at room temperature, 2-furoic acid was extracted from the post-reaction solution by DMSO for further quantification. The samples were then filtered for further analysis. In recyclability experiments, the spent catalysts were collected, washed with cyclohexane, which can dissolve dodecane and quickly evaporate in air, and air-dried at room temperature overnight before used for the next catalytic experiment. Due to the 10-15% typical loss of spent catalysts during filtering, washing, and handling, three repeated experiments (run 1) were conducted with a fresh catalyst to collect enough spent catalysts for the second recycle (run 2), and two repeated experiments were conducted for run 2 to collect enough spent catalysts for the third recycle (run 3). Products were identified and quantified with a gas chromatogram-mass spectrometer (GC-MS) system (Agilent 7890B) and with a gas chromatogram-flame ionization detector (GC-FID) instrument, respectively. Both the GC-MS and GC-FID were equipped with an HP-1 column (Agilent). When available, calibration curves from commercial standards were used to quantify the concentrations of reactants and products. Because a commercial standard of 2-dodecanoyl furan was unavailable, this product was quantified using the effective carbon number (ECN) method.\(^23\) The ECN of 2-dodecanoyl furan was determined from the ECN of the commercially available 2-acetyl furan and hexane. The method was verified with the agreement between experimentally measured and calculated calibration slope for 2-hexanoyl furan (see Figure S.1 and Table S.1).

**Catalyst characterization**

Surface area and porosity were determined from \(N_2\) physisorption data at 77 K using the Micromeritics ASAP 2020 instrument. The crystallinity of the fresh and spent catalysts were measured by a Bruker D8 X-ray diffraction (XRD) instrument equipped with a monochromatic Cu K\(\alpha\) line (\(\lambda = 0.154 \text{ nm}\)) at 40 kV and 40 mA, operating in 20 range of 5-80° at a scanning rate of 0.02°/s. Temperature programmed reduction (TPR) by hydrogen was performed on a thermogravimetric analysis (TGA) instrument (TA Q600 HT) using 50 mL/min of 5% \(H_2\) in \(N_2\) as the flowing gas in the 25-1200 °C temperature range. In addition, \(H_2\)-TPR was also conducted in a downward flow reactor. X-ray photoelectron spectra (XPS) of the catalysts were...
collected on a Thermo-Fisher K-alpha XPS, equipped with Al-Kα X-ray monochromatic source with 400 μm spot size. The spent catalysts were handled in an air-free glovebox and transferred to a vacuum transfer module (Thermo Scientific) before XPS measurements to eliminate air exposure. Iron species concentration in the post-reaction filtrates was measured by ICP. One milliliter of the filtrate was heated in a vacuum oven at 200 °C to evaporate the dodecane. The remaining solids were dissolved in a 20 mL mixture containing 50 v/v % ethanol, 2.5 v/v % HNO₃ and 47.5 v/v % water, and sonicated in a 50 °C water bath for 30 min. The mixture was further diluted 50 times using a 5 v/v % HNO₃ solution for ICP analysis. Six standards containing 1 ppb, 10 ppb, 50 ppb, 100 ppb, 500 ppb, and 1000 ppb of Fe (SPEX CertiPrep) were used for calibration. The Fe content in each sample was measured using a Thermo Scientific iCAP triple quad-inductively coupled plasma-mass spectrometer (TQ-ICP-MS). The results were averaged from triplicates. 45Sc (VHG Lab product # LIS2-100) was used as an internal standard to monitor the machine drift throughout the measurement. 45Sc was used due to its m/z ratio close to the target element Fe and was presumably not present in the samples. Results with recovery rates between 80 to 120% were considered valid.

Results and discussion

The catalytic activity of metal oxides for cross-ketonization of 2-furoic acid and lauric acid

We screened various commercial metal oxides with high lattice energies, which are active for surface-catalyzed ketonization, 8, 15, 24, 25 for the reaction of 2-furoic acid and lauric acid in dodecane at 300 °C (Figure S.2) and 316 °C (Figure 2), with the molar ratio of 5 (see SI for tests at other 2-furoic acid to lauric acid molar ratios (Figure S.3), and test for external mass transfer limitations in Figure S.4).

GC-detected products included long-chain ketones, 2-dodecanoyl furan (desired product), and 12-tricosanone, resulting from the cross- and self-ketonization of the lauric acid, respectively, and furan, from the decarboxylation of 2-furoic acid, as proposed in Figure 3.

While the furan yield, based on 2-furoic acid, was >30% on all catalysts, ketones only formed over iron oxides (FeₓOᵧ), ceria, and titania after 90 min. Among these, the highest selectivity (up to 77% at 316 °C and 84% at 300 °C) to the cross-ketonization product, based on the lauric acid conversion and 2-dodecanoyl yield, was on iron oxides (FeₓOᵧ). This demonstrates the feasibility of cross-ketonization for the oleo-furan sulfonate production. However, the 2-dodecanoyl furan yield is still lower than the 90% yield of the pathway A.⁶ The yield to 2-dodecanoyl over iron oxides for three consecutive cycles at 316 °C (Figure 4) was within experimental error. These recyclability experiments were conducted at near to full conversion of furoic acid to assess yields. A detailed catalyst stability/deactivation study in future work should be carried out at low conversions.

The post-reaction solutions were yellowish, and the total GC carbon balance for 2-furoic acid was lower than 80%, indicating the formation of organic deposits (see Figure S.5 for carbon balance analysis). Di-furfuryl ketone was not detected from 2-furoic acid self-ketonization, consistent with the critical role of α-H in the ketonization and the fact that the reaction takes place on the catalyst surface instead of in the bulk, using alkali, alkaline earth, and rare earth metal oxides, 13, 20 where an α-H is not required.

![Figure 2](image1.png)

**Figure 2.** Performance of various commercial metal oxides in the reaction of 2-furoic acid with lauric acid in n-dodecane. Reaction conditions: 0.05 M lauric acid, 0.25 M 2-furoic acid, 0.2 g catalyst, 316 °C, 90 min, 20 bar N₂, 800 rpm. Pressure at reaction temperature = 47 bar.

![Figure 3](image2.png)

**Figure 3.** Proposed reaction network for the reaction of 2-furoic acid and lauric acid in n-dodecane by iron oxide catalyst. Only paths to detectable products are shown. R represents the n-C₁₃H₂₇ group. Other chains could also be used.

![Figure 4](image3.png)

**Figure 4.** Lauric acid conversion (a) and 2-dodecanoyl furan yield (b) in dodecane for three consecutive uses of the catalyst. Reaction conditions: 0.05 M lauric acid, 0.25 M 2-furoic acid, 0.2 g catalyst, 316 °C, 90 min, 20 bar N₂, 800 rpm. Pressure at reaction temperature = 47 bar.

Interestingly, the filtered solutions from the FeO-catalyzed reactions turned reddish upon exposure to air, and iron species were determined with ICP analysis (Table S.2). After removing the spent FeO particles in the first cycle by filtration, fresh 2-furoic acid and lauric acid were added to the iron-containing filtrate solution, and the mixture was brought to reaction temperature = 47 bar. These recyclability experiments were conducted at near to full conversion of furoic acid to assess yields. A detailed catalyst stability/deactivation study in future work should be carried out at low conversions.
cross-ketonization. No homogeneous iron species were detected in Fe$_2$O$_3$ and Fe$_3$O$_4$ their post-reaction filtrates exhibited no activity. CeO$_2$ is promising but gives higher carbon loss of lauric acid (Figure S.5). Given their promising performance at the test conditions, the commercial iron oxides were down-selected to provide further insights into the cross-ketonization of fatty acids and furoic acid.

**Determination of catalyst active centers**

The BET surface area and pore volumes of the fresh iron oxides increased in the order of FeO < Fe$_3$O$_4$ < Fe$_2$O$_3$ and were overall the lowest (≤ 35 m$^2$/g and ≤ 0.08 cm$^3$/g) among the screened catalysts, indicating that the materials are almost nonporous and the catalytic reactions take place mostly on their external surfaces (Table S.3). After the third reaction cycle, the surface area and pore volume substantially increased, remained unchanged, and decreased for FeO, Fe$_3$O$_4$, and Fe$_2$O$_3$, respectively. The unexpected enhancement of surface area by more than 2-orders of FeO indicated a significant alteration in the catalyst morphology. XRD patterns of the fresh iron oxides displayed their expected polymorphs (Figure 5). The XRD patterns of γ-Fe$_2$O$_3$ (maghemite) in the tetragonal structure and Fe$_3$O$_4$ (magnetite) are not distinguishable because both oxides have the inverse spinel-type structure. However, some maghemites contain other cations in the octahedral Fe vacancies, giving additional XRD peaks in the fresh commercial Fe$_2$O$_3$ of this work (matched with maghemite-Q-00-0251402).

After the reaction, the spectrum of Fe$_2$O$_3$ remained unchanged, the aforementioned additional XRD peaks in the spent Fe$_2$O$_3$ disappeared, and the diffraction pattern of the used FeO transformed to that of Fe$_3$O$_4$. In short, all Fe$_2$O$_3$ catalysts displayed the crystallinity pattern of magnetite, suggesting reduction of Fe$_2$O$_3$ and oxidation of FeO during the reaction. The same phenomenon was reported for iron oxides supported on silica after acetic acid ketonization. The drastic change in the iron oxides’ surface area and porosity may be attributed to their corresponding oxidation state transformation.

![Figure 5](image)

**Figure 5.** XRD pattern of the fresh and spent iron oxides FeO (a), Fe$_2$O$_3$(b), Fe$_3$O$_4$(c) with assigned diffraction peaks for FeO (■), Fe$_2$O$_3$ or γ-Fe$_2$O$_3$ (*), and additional octahedral Fe cation peaks (†).

To better understand the reduction of the Fe$_2$O$_3$ temperature-programmed reduction by H$_2$ coupled with thermogravimetric analysis were performed on the fresh iron oxides. Standard reduction of Fe$_2$O$_3$ was previously postulated to take place via a 3-step mechanism: Fe$_2$O$_3$ → Fe$_3$O$_4$ → FeO → Fe$^{3+}$. However, the TPR-TGA profiles of the commercial iron oxides indicate that the reduction is more complex and involves multiple convoluted steps, in agreement with other literature.

![Figure 6](image)

**Figure 6.** XPS spectra of Fe 2p on the iron oxide catalysts surfaces (a) before and (b) after the cross-ketonization reaction.

A shoulder at 709.0 eV, assigned to Fe 2p$_{3/2}$ of FeO, was observed in all XPS spectra of the spent catalysts. Therefore, the catalyst surfaces of all Fe$_2$O$_3$ catalysts were reduced from Fe$^{3+}$ to a mixture of Fe$^{2+}$ and Fe$^{3+}$ post-reaction. The disappearance of the satellite peaks in the spent catalysts provides further evidence for cross-ketonization.
support that the catalyst surfaces contain Fe₃O₄. Therefore, the initially oxidized catalyst surfaces of all iron oxide catalysts are reduced to Fe₂O₃ during the reaction, in agreement with the XRD results of the bulk FeO/Fe₂O₃. Interestingly, a closer look at the reaction evolution over Fe₂O₃ shows no 2-dodecanoyl furan production during the first 20 min of the reaction followed by rapid formation (Figure S.8).

This induction period suggests that the initial Fe₂O₃ surface (as measured by XPS) transformed to the catalytically active form – potentially Fe₃O₄. To verify the hypothesis, we reduced the commercial Fe₂O₃ with H₂ at 316 °C for 30 min in the dodecane solvent before using it for the cross-ketonization reaction. The resulting material exhibited much higher activity, i.e., 36% of 2-dodecanoyl furan yield (Figure 7), whereas the starting material resulted in no measurable yield. The XPS spectrum of Fe 2p of the pre-reduced Fe₂O₃ is similar to that of the spent Fe₂O₃ after a standard reaction experiment (Figure S.9). Specifically, the Fe 2p₃/₂ binding energy shifted to a lower value of 710.6 eV, with a shoulder at 709 eV, assigned to Fe²⁺ 2p₃/₂. The absence of a satellite peak confirmed the generation of Fe₂O₃ on the surface. The enhancement of Fe₂O₃ catalytic activity after H₂ pretreatment indicates that the newly formed Fe²⁺ centers on the catalyst surface are responsible for cross-ketonization. The improvement in the ketonization activity of Fe₂O₃ in the presence of H₂ has been reported for acetic acid ketonization.34, 35 We hypothesize that even though the standard reaction conditions were under inert N₂, either the reagents, intermediates, or the solvent in Figure 3 act as reducing agents during the induction time, thereby reducing the Fe³⁺ centers to generate a catalytically active surface for ketonization. To better understand this finding, further experiments were conducted. When the catalysts were pretreated with a dodecane solution of 2-furoic acid or lauric acid individually at 316 °C for 30 min prior to the catalytic reaction, similar enhancements in catalytic activity were observed at 20 min (Figure 7).
product show one unit shift to a higher m/z ratio (Figure S.12b) compared to that in the unlabeled lauric acid (Figure S.12a), suggesting a $^{13}$C in the structure of self-ketonization of lauric acid. The GCMS fragmentation of the cross-ketonization product and the standard 2-dodecanoyl furan are the same.

Figure 8. Proposed reaction mechanism of cross-ketonization of 2-furoic acid and lauric acid on Fe$_3$O$_4$.

The initial adsorption of 2-furoic acid and lauric acid to their corresponding surface carboxylates prior to the α-H abstraction from a basic oxygen site. C-C coupling between the adsorbed carboxylates generates the β-keto acid, thermally decomposing to the final product, 2-dodecanoyl furan. Coordinate unsaturated metal cations are necessary for surface carboxylate formation. As the density of the surface Fe$^{2+}$ increases, so does the probability of two adjacent carboxylates to form the β-keto acid. A similar reaction mechanism has been proposed for the vapor phase ketonization of propanoic acid to 3-pentanone over CeO$_2$-Mn$_2$O$_3$. In addition, the roles of redox properties and surface oxygen vacancy on maintaining ketonization activity have been demonstrated for other metal oxides, such as CeO$_2$, ZrO$_2$, and TiO$_2$. Numerous studies have utilized metal doping of metal oxides and/or catalyst pretreatment to create oxygen vacancies and unsaturated metal cations and by doing so to ultimately increase ketonization activity, suggesting a potential strategy for improved activity in this system.

Conclusions

In this work, we introduced a method to produce oleo-furan surfactant precursors via cross-ketonization of biomass-derived furoic acid and vegetable-oil-derived lauric acid to 2-dodecanoyl furan. The volatile byproducts and solid catalysts can easily be separated from the desired product stream. In addition, one can use fatty acids instead of their anhydrides, without the typical thermodynamic limitations of the acylation reaction. This aspect is expected to minimize process waste.

Among the tested catalysts, earth-abundant, commercially-available iron oxides are active and selective towards cross-ketonization and were employed for further mechanistic studies. Detailed catalyst characterization, structure-activity relationships, and elucidation of reaction pathways provide insights into the active catalysis centers, reaction mechanism, and stability of the catalysts. XRD and XPS measurements of the fresh and spent catalysts reveal that the bulk and surface of all tested iron oxides transform to a stable Fe$_3$O$_4$ phase during the reaction. Enhancement in the pre-reduced catalyst surface reactivity leads us to hypothesize that surface Fe$^{2+}$ is critical for the reaction. $^{13}$C isotopic labeling indicates that adjacent adsorbed laurate and furoate couple on the Fe$^{2+}$ sites to form the corresponding β-ketoacid, which is then decarboxylated to 2-dodecanoyl furan. The iron oxide catalysts maintain activity for three consecutive cycles tested herein. The insights obtained here can guide future work on process and catalyst optimization for this new path to renewable surfactants.

Author Contributions

Dionisios G. Vlachos: Conceptualization, Supervision, Writing - Review & Editing; Marat Orazov: Conceptualization, Supervision, Writing - Review & Editing; Hannah Nguyen: Methodology, Validation, Investigation, Data Curation, Writing - Original Draft; David Moglia: Investigation, Data Curation; Yunzhu Wang: Investigation, Data Curation; Jiayi Fu: Investigation; Weiqing Zheng: Methodology, Validation.

Conflicts of interest

There are no conflicts to declare.

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Notes and references