Selective catalytic dehydration of furfuryl alcohol to 2, 2′-difurfuryl ether using a polyoxometalate catalyst

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The spice flavour compound 2, 2′-difurfuryl ether (DFE) is widely utilised in the food industry as it has a coffee-like, nutty, earthy, mushroom-like odour. However, despite intensive research efforts, to date, an environmentally friendly and practical synthetic preparation technique for 2, 2′-difurfuryl ether is still unavailable. Here, we investigate a new approach using polyoxometalate catalysts to selectively catalytically dehydrate furfuryl alcohol to 2, 2′-difurfuryl ether. We have successfully applied this methodology using the polyoxometalate (POMs) catalyst \[[\text{[(CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{)}_4\text{N]}\text{][SMo}_{12}\text{O}_{40}]\] to produce 2,2′-difurfuryl ether in a 30.86% isolated yield.

Furfuryl alcohol (FA) is considered as an important template chemical for the production of a range of useful chemicals, such as levulinic acid, alkyl levulinate and various other useful polymer products. FA is synthesised by a selective hydrogenation process from furfural and its conversion into oligomer (Oligomerized FA, OFA) and polymer (Polymerized FA, PFA) products has been widely explored owing to their utility in a range of applications. Several molecular structures of OFAs and PFAs have been proposed using a combination of NMR, IR, UV–Vis, Raman spectroscopy, XRD and DFT calculations. From these studies a variety of dimer products have been proposed including: 2,2′-difurfuryl ether (DFE); 2,2′-difurfurylmethane (DFM); 2,2′-difuryl-ethylene (DFEt) and a hydroxyl-carbon bridge dimer. Further examples include, 4-furfuryl-2-pentenoic acid γ-lactone (PAL) which can be produced over γ-alumina during FA polymerisation and 2-hydroxymethyl-5(5-furfuryl) furan (HFF) which is a maleic anhydride product. However, studies reveal that HFF and PAL cannot co-exist in either acid-polymerized or γ-alumina-polymerized FA, although analytical results were not enough to support PAL existence.

A particularly valuable chemical product of FA is 2,2′-difurfuryl ether (DFE), which is a spice flavour compound with an aroma described as a mixture of coffee and mushroom scents combined with nutty and earthy odours. It can be eaten according to the Flavour Extract Manufacturers’ Association (FEMA), Joint FAO/WHO Expert Committee on Food Additives (JECFA) and National Health and Family Planning Commission of the People’s Republic of China (NHFPC) regulation guidelines. DFE is referred to by the FEMA No. 3337, the JECFA No. 1522 and the Chinese Standards for Food Additives No. S1108.

DFE is synthesised from FA in a two-step process comprised of bromination followed by etherification. However, this particular synthetic method poses significant environmental hazards, such as pollution, and thus, a search for an alternative cleaner, safer and more environmentally friendly approach is a key priority. Interestingly, DFE can also be obtained as a side-product during FA oligomerization reactions over heterogeneous catalysts. Polyoxometalate (POMs) catalysts are one example of a heterogeneous catalyst which could be used for this purpose; however, to the best of our knowledge, very little quantitative analysis information is available on the presence of DFE during such FA oligomerization reactions. Indeed, we have previously reported, the successful synthesis of another flavour compound (−)-Ambrox, which was prepared using (−)-schreol as a starting material which was oxidised using hydrogen peroxide in the presence of the POMs catalyst \[[\text{[C}_5\text{H}_5\text{N}][\text{H}_2\text{PMo}_{12}\text{O}_{40}]]\], which is a quaternary ammonium phosphomolybdate catalyst. Therefore,

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in this study, we investigate the feasibility of using selective catalytic dehydration of furfuryl alcohol in the presence of various POM catalysts to produce 2,2′-difurfuryl ether—thus producing a more environmentally friendly synthetic approach.

Results and Discussion

With respect to FA oligomerization reactions, the catalyst tungsten oxide in the liquid phase (100 °C) has been successfully employed to produce a range of OFAs. These include: five dimers (2,2′-difurylmethane, 2-(2-furylmethyl)-5-methylfuran, difurfuryl ether, 4-furfuryl-2-pentenoic acid γ-lactone and 5-furfuryl-furfuryl alcohol) and two trimers (2,5-difurfurylfuran and 2,2′-(furylmethylene)bis(5-methylfuran)) were observed, difurfuryl ether and 5-Furfuryl-furfuryl alcohol were the dominant products 23–25. Another class of catalysts are POMs, which are discrete metal-oxide clusters containing W, Mo, V or Nb that have attracted increasing interest owing to their multi-electronic redox activities, and photochemical, acidic and magnetic properties. Importantly, there are a wide range of potential applications that POMs can be envisaged for, such as catalysts and functional materials26.

As with all catalysis, the first step in utilising POMs for the selective catalytic dehydration of furfuryl alcohol to 2,2′-difurfuryl ether, will be to choose an appropriate POM catalyst. For thus, a series of POMs catalysts were prepared as summarised in Table 127–31. In order to relatively assess the utility of these synthetic catalysts a set of standard experimental conditions was employed (i.e., in toluene at 100 °C for 7 h). The results are given in Table 2, revealing catalytic activities in the following order: sulfo-polyoxometalates > quaternary ammonium phosphomolybdates > quaternary ammonium phosphotungstates and heteropolyacid salts. With respect to the heteropolyacid salts, the catalysts 4d and 4h showed greater yields (entry 4, 8 Table 2) than the other heteropolyacid salt catalysts (entry 1–8 Table 2). We also found that the heteropolyacid Al 3+ salts showed a much better catalytic ability than the Na+, K+ and Fe3+ salts. Furthermore, of the quaternary ammonium phosphomolybdates with the same phosphomolybdic group, we found that the character of the quaternary ammonium cation groups have a very limited influence on the catalytic activity (entries 13–17, Table 2). Moreover, although Mo and W belong to the same main group, they display difference catalytic activities in this reaction. We also found that the quaternary ammonium phosphomolybdates usually displayed better catalytic ability (entries 13–17, Table 2) than the other heteropolyacid salt catalysts (entry 1–8 Table 2).

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Table 1. Synthesis of the catalysts.

| Entry | Catalyst 4 | Chemical compositions of catalyst | Yield (%) | IR (cm\(^{-1}\)) |
|-------|------------|----------------------------------|-----------|----------------|
| 1     | 4a         | Na₃PW₁₂O₄₀                        | 81        | 1079, 976, 895, 802 |
| 2     | 4b         | FePW₁₂O₄₀                         | 85        | 1063, 968, 897, 807 |
| 3     | 4c         | K₃PW₁₂O₄₀                         | 79        | 1079, 976, 895, 802 |
| 4     | 4d         | AlPW₁₂O₄₀                         | 82        | 1076, 981, 897, 803 |
| 5     | 4e         | Na₃PMo₁₂O₄₀                       | 80        | 1063, 964, 893, 802 |
| 6     | 4f         | FePMo₁₂O₄₀                        | 86        | 1067, 961, 893, 802 |
| 7     | 4g         | K₃PMo₁₂O₄₀                        | 77        | 1092, 964, 893, 802 |
| 8     | 4h         | AlPMo₁₂O₄₀                        | 80        | 1064, 961, 896, 782 |
| 9     | 4i         | [(CH₃)₄N][H₂PW₁₂O₄₀]              | 88        | 2922, 1851, 1635, 1486, 1079, 976, 895, 802 |
| 10    | 4j         | [(CH₃)₂C₅H₅N][H₂PW₁₂O₄₀]          | 80        | 2922, 2851, 1623, 1481, 1062, 959, 879, 803 |
| 11    | 4k         | [(CH₃)NC₅H₅][H₂PW₁₂O₄₀]           | 76        | 2922, 2851, 1635, 1486, 1079, 976, 895, 802 |
| 12    | 4l         | [(CH₃CH₂CH₂CH₂N][H₂PW₁₂O₄₀]      | 83        | 2971, 2867, 1615, 1474, 1080, 976, 894, 816 |
| 13    | 4m         | [(CH₂N][H₂PMo₁₂O₄₀]               | 88        | 2922, 2851, 1635, 1471, 1062, 956, 880, 798 |
| 14    | 4n         | [(CH₂N][C₅H₅N][H₂PMo₁₂O₄₀]        | 72        | 2922, 2851, 1671, 1471, 1080, 977, 897, 805 |
| 15    | 4o         | [(CH₂NC₅H₅N][H₂PMo₁₂O₄₀]          | 82        | 2922, 2851, 1635, 1486, 1079, 976, 895, 802 |
| 16    | 4p         | [(CH₃CH₂CH₂CH₂N][H₂PMo₁₂O₄₀]      | 70        | 2922, 2851, 1671, 1471, 1080, 977, 897, 805 |
| 17    | 4q         | [(CH₂NC₅H₅N][HPMo₁₂O₄₀]           | 78        | 2921, 2851, 1640, 1478, 1062, 961, 879, 794 |
| 18    | 4r         | [(CH₃CH₂CH₂CH₂N][SMo₁₂O₄₀]        | 75        | 2921, 2851, 1634, 1488, 1079, 976, 895, 799 |

Figure 1. The two-step synthesis of DFE from FA via bromination and etherification reactions.
In this study, the reasons these different POMs catalysts showed different activities on this selective catalytic dehydration reaction were unclear. In order to optimise the synthetic conditions for DFE using the 4r POMs catalyst, we systematically varied the parameters of catalyst quantity and reaction time. The amount of catalyst 4r in the reaction was optimised firstly (entries 1–10, Table 3). We found that DFE was produced in the highest yield (26.90%) when 1% equivalent of the catalyst was used (entry 6, Table 3). The yield decreased significantly, from 26.90% to 8.29%, when the catalyst loading was lowered from 1% to 0.1% equivalents, whereas the yield did not increase with incremental catalyst loading from 1% to 5% equivalents. We subsequently optimised the reaction time, the results were shown in Table 3 (entries 11–20). We found that the DFE yield increased gradually with extended reaction times from 1 h to 9 h (entries 11–19, Table 3), however, the yield did not increase furthermore up to 10 h (entries 19, 20, Table 3). Overall, the optimised conditions for DFE synthesis are a reaction time of 9 h at 100 °C with a 1% equivalent of 4r catalyst, resulting in a yield of 34.50% (entries 19, Table 3). The reaction was repeated under the above optimised conditions and 2,2′-difurfuryl ether (DFE) was obtained in an average isolated yield of 30.86%.

As per previous literature preparations of DFE[25], other compounds appear in the oligomerization reaction (Fig. 2, Figure S1), as determined by GC/MS. As shown in Table 4, these include: compound 5 (5-furfuryl-furfuryl alcohol, Figure S5); compound 6 (2, 2′-difurymethane, Figure S6) and compound 7 (2, 5-difurfurylfuran,

### Table 2. Optimization of the catalyst. “Reaction conditions: FA (10 mmol), catalyst (0.1 mmol), toluene (10 mL), 100 °C and 7 h. GC yield.”

| Entry | Catalyst | DFE yield (%) |
|-------|----------|---------------|
| 1     | 4a       | 2.08          |
| 2     | 4b       | 5.41          |
| 3     | 4c       | 7.85          |
| 4     | 4d       | 13.30         |
| 5     | 4e       | 3.55          |
| 6     | 4f       | 3.97          |
| 7     | 4g       | 4.90          |
| 8     | 4h       | 14.58         |
| 9     | 4i       | 13.09         |

### Table 3. Optimization of the Reaction Conditions using the 4r catalyst. “Reaction conditions: FA (10 mmol), catalyst 4r (relative equiv.), toluene (10 mL), 100 °C and 7 h. GC yield.”

| Entry | Catalyst amount (mmol)* | Yield (%) | Entry | Reaction time ** | Yield (%) |
|-------|-------------------------|-----------|-------|------------------|-----------|
| 1     | 0.01                    | 8.29      | 11    | 1 h              | 10.58     |
| 2     | 0.03                    | 14.16     | 12    | 2 h              | 10.99     |
| 3     | 0.05                    | 15.72     | 13    | 3 h              | 15.51     |
| 4     | 0.07                    | 20.65     | 14    | 4 h              | 16.28     |
| 5     | 0.09                    | 23.16     | 15    | 5 h              | 18.47     |
| 6     | 0.1                     | 26.90     | 16    | 6 h              | 19.40     |
| 7     | 0.2                     | 26.12     | 17    | 7 h              | 26.90     |
| 8     | 0.3                     | 26.08     | 18    | 8 h              | 27.24     |
| 9     | 0.4                     | 25.24     | 19    | 9 h              | 34.50     |
| 10    | 0.5                     | 25.07     | 20    | 10 h             | 34.25     |

**Figure 2.** The selective catalytic dehydration process converting furfuryl alcohol to 2,2′-difurfuryl ether using a polyoxometalate (POM) catalyst.
Figure S7). Although other compounds have been proposed as side-products in such reactions, we found no evidence of them under our experimental and equipment conditions.

As shown in Tables 3 and 4, the reaction time has an obvious influence on the yields of compound 4 (DFE), compound 5, compound 6 and compound 7. As expected, the yields of compound 5, compound 6 and compound 7 decrease and yields of compound 4 increases with reaction time. The yield of compound 5 increased gradually with extended reaction times from 1 h to 7 h (entries 1–7, Table 4), but decreased with reaction time from 7 h to 10 h (entries 7–10, Table 4). Compound 5 was obtained in the highest yield of 20.30% after 7 h (entries 7, Table 4). The yield of compound 6 increased gradually with extended reaction times from 1 h to 6 h (entries 1–6, Table 4), but the yield decreased with reaction time from 6 h to 10 h (entries 6–10, Table 4). Compound 6 has the highest yield of 23.20% after 6 h (entries 6, Table 4). The yield of compound 7 increased gradually with extended reaction times from 1 h to 7 h (entries 1–7, Table 4), but the yield decreased with the increment of reaction time from 7 h to 10 h (entries 7–10, Table 4). Compound 7 has highest yield of 10.86% after 7 h (entries 7, Table 4). Therefore, it was fortunate that compound 4 (DFE) was obtained in the highest yield of 34.50% after 9 h (entries 19, Table 3). These results clearly illustrate that catalyst 4r was a strong candidate as a heterogeneous catalyst for the selective catalytic dehydration of FA to DFE.

Conclusions
In this paper, a comprehensive study on the utility of POMs catalysts for the selective catalytic dehydration of furfuryl alcohol to 2, 2′-difurfuryl ether has successfully been carried out. Through assessing a range of potential POMs catalysts, we found that \([(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{)}_4\text{N}]_2[\text{SMo}_{12}\text{O}_{40}]\) was the most effective, accomplishing the reaction in an overall 30.86% yield. Thus, we have present a novel synthetic avenue for the efficient and environmentally benign synthesis of 2, 2′-difurfuryl ether, which employs an inexpensive and simple POMs catalyst. Further studies are underway to further improve the yield of 2, 2′-difurfuryl ether using other POMs catalysts and various synthetic conditions.

Methods
Synthesis of the catalysts a-h. All of the catalysts a-h were synthesised by the same approach. This method is illustrated following for catalyst 4a as an example.

A solution of H₃PW₁₂O₄₀ (2.88 g, 1 mmol) in deionized water (10 mL) was added into a 50 mL beaker. The reaction mixture was stir for 5 min at 25 °C, and Na₂CO₃ (1.06 g, 10 mmol) in deionized water (10 mL) was added over 5 min. After addition, the mixture was stir for 1 h at 25 °C, then filtered and washed with deionized water and dried in vacuo and subsequently calcined at 450 °C for 2 h to afford 4a as a white solid (2.38 g, 81%) [33]. The elemental analysis data for the purified salts were as follows.

| Entry | Reaction time | Compound 5 yield (%) | Compound 6 yield (%) | Compound 7 yield (%) | FA conversion (%) |
|-------|---------------|----------------------|----------------------|----------------------|-----------------|
| 1     | 1 h           | 5.85                 | 6.84                 | 1.63                 | 28.42           |
| 2     | 2 h           | 6.61                 | 6.33                 | 2.81                 | 30.70           |
| 3     | 3 h           | 13.97                | 7.20                 | 5.47                 | 43.27           |
| 4     | 4 h           | 14.18                | 11.72                | 6.53                 | 50.59           |
| 5     | 5 h           | 18.7                 | 17.03                | 6.75                 | 57.4            |
| 6     | 6 h           | 20.2                 | 23.20                | 10.1                 | 75.1            |
| 7     | 7 h           | 20.3                 | 20.60                | 10.86                | 80.9            |
| 8     | 8 h           | 17.47                | 13.80                | 8.94                 | 82.56           |
| 9     | 9 h           | 14.20                | 8.94                 | 6.93                 | 89.81           |
| 10    | 10 h          | 13.10                | 6.87                 | 6.81                 | 89.82           |

Table 4. The yields for the oligomerization reaction using the 4r catalyst. *Reaction conditions: FA (10 mmol), catalyst 4r (0.01 equiv.), toluene (10 mL) and 100 °C. GC yield.

Synthesis of the catalysts 4i-q. Synthesis of catalysts was illustrated by the synthesis of catalyst 4n.

H₅PMo₁₇O₄₃ (1.82 g, 1 mmol) and deionized water (10 mL) were combined in a 50 mL three-neck flask. The mixture was stir for 5 min at 25 °C, and Na₂CO₃ (1.06 g, 10 mmol) in deionized water (10 mL) was added over 5 min. After addition, the mixture was stir for 1 h at 25 °C, then filtered and washed with deionized water and dried in vacuo and subsequently calcined at 450 °C for 2 h to afford 4a as a white solid (2.38 g, 81%) [33]. The elemental analysis data for the purified salts were as follows.
The residue was extracted with ether, the organic phases were then washed with a saturated solution of Na₂CO₃. The mixture was stirred for 9 h at 100 °C. The toluene was subsequently removed under reduced pressure.

Synthesis of the catalyst 4r. A solution of Na₂MoO₄·2H₂O (6.05 g, 25 mmol) in deionized water (200 mL) was added into a 500 mL beaker. The reaction mixture was stir for 5 min at 25 °C, and then NH₄VO₃ (0.6 g, 10 mmol) was added. After stirring for 1 h at 25 °C, tetrabutylammonium bromide (10 g, 31 mmol) was added. After addition, the mixture was stir for 0.5 h at 25 °C, then filtered, washed with deionized water, ethanol and acetonitrile, and dried in vacuo to afford 4r as a yellow solid (3.60 g, 75%).

Synthesis of the DFE. Each of the catalysts were employed, respectively, for this reaction and the overall synthetic conditions are illustrated following 4r as an example (Fig. 3).

Synthetic met. FA (0.98 g, 10 mmol), 4r (0.23 g, 0.1 mmol, 1% equiv.) and toluene (10 mL) were added into a 50 mL three-neck flask. The mixture was stirred for 9 h at 100 °C. The toluene was subsequently removed under reduced pressure. The residue was extracted with ether, the organic phases were then washed with a saturated solution of Na₂CO₃ and brine and then dried over MgSO₄. After solvent removal, the residue was purified by flash chromatography (petroleum/EtOAc, 40:1) to afford DFE as a colourless liquid (0.55 g, 30.86%).

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Author Contributions
S.X.Y., H.Y.T. and B.G.S. conceived of the project and designed the experiments. S.X.Y. wrote most of the paper. Y.E.H., J.L.W., Y.M.Z., H.W. and Y.G.L. carried out the experiments, analysed the data. All authors discussed the results and commented on the manuscript.

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