UC Berkeley

UC Berkeley Previously Published Works

Title

Production of renewable lubricants: Via self-condensation of methyl ketones

Permalink

<https://escholarship.org/uc/item/07n475wf>

Journal

Green Chemistry, 18(12)

ISSN

1463-9262

Authors

Balakrishnan, M
Arab, GE
Kunbargi, OB
et al.

Publication Date

2016

DOI

10.1039/c6gc00579a

Peer reviewed

Cite this: *Green Chem.*, 2016, **18**, 3577

Production of renewable lubricants *via* self-condensation of methyl ketones†

Madhesan Balakrishnan,^a George E. Arab,^a Omar B. Kunbargi,^a Amit A. Gokhale,^b Adam M. Grippo,^a F. Dean Toste^{*c} and Alexis T. Bell^{*d}

Self-condensation of biomass-derived methyl ketones catalyzed by solid bases or acids produces corresponding cyclic trimers exclusively in excellent yields. Condensates containing 24–45 carbon atoms are shown to be suitable lubricant base-oils after the removal of residual unsaturation and oxygen. Properties of cycloalkanes produced from biomass are very similar to those of conventional lubricant base-oils. The process reported here offers an environmentally benign alternative to the current non-selective production of lubricant base-oils from α -olefins, and avoids the production of corrosive waste products.

Received 28th February 2016,
Accepted 10th March 2016

DOI: 10.1039/c6gc00579a

www.rsc.org/greenchem

The past decade has seen significant progress in the development of renewable alternatives to fossil fuels stimulated, in part, by governmental mandates and incentives. The regulatory environment has also motivated the search for carbon-neutral substitutes for petroleum-based lubricants. For example, the United States Department of Agriculture (USDA) has recently added crankcase oils to the bio-preferred program, which requires federal agencies and their contractors to give preferential treatment to lubricants containing more than 25% renewable content.¹

The use of bio-based lubricants is not new and indeed some of the oldest lubricants used in industry were bio-esters sourced from plants.² However, with the advent of the petroleum age, lubricant formulations came to depend on the superior properties of mineral base-oils obtained as a cut from some refineries.³ Today even superior properties are achieved with poly- α -olefins (PAOs) base-stocks produced by the cationic oligomerization/hydrogenation of ethylene-derived linear α -olefins (usually C₁₀, Scheme 1).⁴ The PAO process is, however, environmentally unfriendly since it utilizes corrosive catalysts such as BF₃, HF, or AlCl₃. Moreover, the product distribution cannot be tightly controlled and it is quite common to get mixtures of dimers, trimers, and tetramers of 1-decene in the product mixture. Research efforts in homogeneous⁵ and heterogeneous⁶ catalysis have tried to overcome the selectivity and corrosivity issues; however, the discovery of an environ-

ment-friendly, efficient heterogeneous catalyst with high selectivity has proved elusive. As alternative to PAOs, we report here an entirely new class of lubricant base-oils exhibiting properties comparable to those of mineral oils and PAOs. The method of producing these base-oils features two-step approach involving a highly selective self-condensation of methyl ketones (MKs) and subsequent hydrodeoxygenation (Scheme 1). Several pathways are amenable for sourcing MKs (C₈–C₁₅) needed for this process from renewable feedstocks. For *e.g.*, biomass-derived terminal alkenes serve as potential precursors which undergo alkylation⁷ with acetone or Wacker oxidation⁸ to produce requisite MKs. These alkenes can be sourced from the corresponding primary alcohols obtained from hydrogenation of triglycerides⁹ or Guerbet reaction¹⁰ of fermented alcohols. Alternatively, direct coupling of alcohols with acetone is also known to give MKs in moderate yields.¹¹ In addition, biological routes have been developed to produce mid-/long-chain MKs directly from sugars.¹² Other less-common approaches are listed in ESI.† In this report, we

^aEnergy Biosciences Institute, 2151 Berkeley way, Berkeley, CA-94720, USA

^bBASF Corporation., 33 Wood Avenue South, Iselin, NJ 08830, USA

^cDepartment of Chemistry, University of California, Berkeley, CA-94720, USA.
E-mail: fdtoste@berkeley.edu

^dDepartment of Chemical and Biomolecular Engineering, University of California, Berkeley, CA-94720, USA. E-mail: alexbell@berkeley.edu

†Electronic supplementary information (ESI) available. See DOI: 10.1039/c6gc00579a

Industrial synthesis of lubricants:

Our approach to bio-lubricants:

Scheme 1 A novel approach to synthetic bio-lubricants.

summarize our efforts to produce various lubricant base-oils starting from MKs, understand the structure–property relationship, and compare the properties of this new class of lubricants base-oils to those obtained *via* the PAO route.

Our procedure for the synthesis of lubricants builds on the self-condensation of *n*-alkyl methyl ketones (**1**) catalyzed by solid acids and bases (Table 1).¹³ The condensates produced are exclusively cyclic trimers the structures of which vary greatly with the nature of the catalyst. The condensation of **1** carried out in the presence of bases such as calcined hydrotalcite (MgAlO)¹⁴ results in a quantitative yield of **2a'** and **2a''** (17 : 3) (entry 1, condition A). On the other hand, acid catalysts (*e.g.*, Ta₂O₅/SBA-15)¹⁵ promote dehydration leading to the production of aromatic condensates (**3a'**/**3a''** = 1 : 1 approx.) under nearly identical conditions (entry 2). The formation of trimer condensates **2** and **3** differ in the number of moles of water molecules released per mole of substrate at the end of the reaction (0.667 *vs.* 1), but involve the same, observable dimer condensates **I** and **II** as intermediates (Scheme 2).

To explain the observed intermediates and products, we propose the reaction pathways illustrated in Scheme 2. Methyl

Scheme 2 Reaction pathways during the self-condensation of methyl ketone.

ketone **1** undergoes self-condensation to generate **I** and **II** promoted by a base or acid catalyst. The first step in the reaction sequence is the formation of the respective enolate/enol species (**A–D**). Subsequently, 1,2-/1,4-addition of **A/B** to **I** and **II** occurs in the presence of a base catalyst to generate intermediates **III–V**. On the other hand, acid catalysis proceeds exclusively through 1,2-addition of **C/D** to give **VI**. Finally, ring

Table 1 Syntheses of various cycloalkane lubricant base-oils using the sequence of self-condensation and hydrogenation/hydrodeoxygenation

Entry	Ketone (C _n)	Conditions A ^a	Condensate (C _{3n})	Conditions B ^b	Cyclic alkane (C _{3n})
1	1a (C ₆) R ¹ = <i>n</i> -propyl	MgAlO ^c , 160 °C, 3 h	2a (C ₁₈) R ¹ = <i>n</i> -propyl	Pt/NbOPO ₄ ^e , H ₂ (3.45 MPa), 160 °C, 6 h	4a (C ₁₈) R ² = <i>n</i> -propyl
2	1a (C ₆) R ¹ = <i>n</i> -propyl	Ta ₂ O ₅ /SBA-15 ^d , 200 °C, 24 h	3a R ¹ = <i>n</i> -propyl	Rh/C ^h , H ₂ (3.45 MPa), 200 °C, 16 h	5a R ² = <i>n</i> -propyl
3	1b–f (C ₈ –C ₁₂) R ¹ = <i>n</i> -pentyl– <i>n</i> -nonyl	MgAlO ^c , 160 °C, 6 h	2b–f (C ₂₄ , C ₂₇ , C ₃₀ , C ₃₃ , C ₃₆) R ¹ = <i>n</i> -pentyl– <i>n</i> -nonyl	Pt/NbOPO ₄ ^e , H ₂ (3.45 MPa), 160 °C, 6 h	4b–f (C ₂₄ , C ₂₇ , C ₃₀ , C ₃₃ , C ₃₆) R ² = <i>n</i> -pentyl– <i>n</i> -nonyl
4	1g (C ₁₅) R ¹ = <i>n</i> -dodecyl	MgAlO ^c , 160 °C, 12 h	2g (C ₄₅) R ¹ = <i>n</i> -dodecyl	Pt/NbOPO ₄ ^e , H ₂ (3.45 MPa), 200 °C, 12 h	4g (C ₄₅) R ² = <i>n</i> -dodecyl
5	1h (C ₁₀)	MgAlO ^c , 160 °C, 12 h	2h (C ₃₀) R ¹ = benzyl	Rh/C ^h , H ₂ (3.45 MPa), 120 °C, 6 h and then Pt/NbOPO ₄ ^e , H ₂ (3.45 MPa), 160 °C, 6 h	4h (C ₃₀) R ² = <i>c</i> -hexylmethyl
6	1i (C ₁₁)	MgAlO ^c , 160 °C, 16 h	2i (C ₃₃) R ¹ = 2-ethylhexyl	Pt/NbOPO ₄ ^e , H ₂ (3.45 MPa), 160 °C, 6 h	4i (C ₃₃) R ² = 2-ethylhexyl
7	1j (C ₈) and 1k (C ₉)	MgAlO ^c , 160 °C, 16 h	2j (C ₂₄) R ¹ = furfuryl and 2k (C ₂₇) R ¹ = 5-methylfurfuryl	Pd/C ⁱ , H ₂ (2 MPa), 100 °C, 5 h and then Pt/NbOPO ₄ ^j , H ₂ (3.45 MPa), 220 °C, 6 h	4j ≅ 4b (C ₂₄) R ² = <i>n</i> -pentyl and 4k ≅ 4c (C ₂₇) R ² = <i>n</i> -hexyl
8	1l (C ₁₅)	MgAlO ^c , 190 °C, 16 h	2l (C ₄₅) R ¹ = 2,2-bis(5-methylfuran-2-yl)ethyl	Pd/C ⁱ , H ₂ (2 MPa), 100 °C, 5 h and then Pt/NbOPO ₄ ^g , H ₂ (3.45 MPa), 250 °C, 6 h	4l (C ₄₅) R ² = 2-pentylheptyl
9	1d (C ₁₀)	Ta ₂ O ₅ /SBA-15 ^d , 230 °C, 24 h	3b (C ₃₀) R ¹ = <i>n</i> -heptyl	Rh/C ^h , H ₂ (6.9 MPa), 200 °C, 24 h	5b (C ₃₀) R ² = <i>n</i> -heptyl

^a Entries 1, 3–8 were carried out in a Dean–Stark separator; entries 2 and 9 were carried out in Parr reactor; toluene was used as solvent for entries 1–7, and 9; mixture of xylenes was used as solvent for entry 8. ^b Hydrogenations were carried out in a Parr reactor using octane as the solvent. ^c 50 wt% of the catalyst with respect to substrate. ^d 20 wt%. ^e 0.2 mol% of the total metal content with respect to substrate. ^f 0.25 mol%. ^g 0.5 mol%. ^h 0.2 mol%. ⁱ 0.1 mol%. ^j 0.2 mol%. MgAlO = calcined hydrotalcite.

closure of intermediates **III–VI** occurs either through cyclization or cyclodehydration to give products **2'**, **2''** and **3'**, **3''**. Formation of the kinetic enolate/enol intermediates (**A** and **C**) is highly favored due to steric/electronic factors and therefore the reaction proceeds predominantly *via* these intermediates rather than through the thermodynamic intermediates **B** and **D**.

Since synthetic PAOs used for lubricant formulations are primarily composed of C₃₀ and C₄₀ alkanes, we targeted the production of cyclic trimers containing 24–45 carbon atoms *via* condensation of biomass-derived C₈–C₁₅ methyl ketones. The reaction conditions were optimized to enable the complete conversion of starting materials to trimers **2** and **3** (Table 1, conditions A). This condensation reaction is reversible and the retro-condensation is facilitated by water formed as a by-product of the reaction. To minimize this effect, we employed a Dean–Stark apparatus to continuously remove water from the reaction mixture. Using such an approach and MgAlO as the catalyst we were able to produce trimers (**2**) in near-quantitative yields (>98%) for *n*-alkyl (**1b–g**, Table 1, entries 3 and 4), branched alkyl (**1i**, entry 5), arylalkyl (**1h**, entry 6), and heteroarylalkyl (**1j–l**, entries 7 and 8) methyl ketones as reactants. The time required for the completion of the reaction was directly proportional to the complexity of the alkyl substitution in **1** (entries 3–8). For example, the most complex ketone, **1l**, required refluxing xylenes for completion (entry 8). As expected, the choice of catalyst also influenced the conditions required for the near-complete conversion of the reactants. For example, Ta₂O₅/SBA-15-catalyzed reactions required higher temperatures and longer times compared to MgAlO-catalyzed reactions for a given methyl ketone (entries 3 *vs.* 9). At this point, we thought about industrially relevant reactive distillation method as an alternative to Dean–Stark set-up to remove water by-product. Such a method would also eliminate the need for solvents during the reaction. In order to examine the efficiency of self-condensation in solvent-free conditions, 2-nonanone was heated with MgAlO catalyst under

vacuum to facilitate water removal (see ESI† for details). The results indicated that the combined selectivity to **2c'** and **2c''** is >95% even at an elevated temperature (190 °C). Usually, process optimization for industrial production would consider temperature and duration as important parameters. Here we show that increasing the process temperature allows us to reduce the residence time from 6 h (Table 1) to 90 minutes (Table S1†) while achieving high conversion (>90%) without any loss in selectivity.

Hydrogenation of the ketones **2** and alkyl benzenes **3** to the corresponding cyclic alkanes **4** and **5**, is an essential step for obtaining hydrocarbon base-oils (Table 1, conditions B). Conversion of **2** to **4** can be accomplished in >98% yield using Pt/NbOPO₄, a bifunctional catalyst that operates under mild conditions.¹⁶ Platinum catalyzes the reduction of the double bond functionalities of **2**, whereas the acidic support (NbOPO₄) facilitates the elimination of oxygen atoms. It is noted that condensates **2** and **3** possessing longer alkyl substituents required higher temperatures and longer reaction times for the complete reduction of the innermost double bonds (entries 3 *vs.* 4). The hydrodeoxygenations of furan-containing condensates **2j–l** were also carried out at relatively high temperature (>200 °C). To avoid C–C bond scissions at high temperatures, Pd/C mediated saturation of the furan rings was conducted prior to hydrodeoxygenation (>95% yield for two steps, entries 7 and 8). Saturation of aromatic rings in **2h**, **3a–b** was accomplished by hydrogenation over Rh/C using condition B (Table 1, entries 2, 5, and 9, >98% yield). For aromatic compounds, the final hydrogenation step is not absolutely essential for producing lubricant base-oils. Alkyl benzenes are often added to lubricant formulations³ as they have acceptable properties as seen from Table 2, entry 12.

As seen from their structures, hydrocarbons **3–5** contain the appropriate number of carbons (C₂₄–C₄₅), but differ significantly in structure from known lubricant base-oils. While the synthetic PAOs are mainly branched alkanes, the compounds that we synthesized are exclusively aromatics (**3**) or cyclo-

Table 2 Evaluation of lubricant properties of cycloalkane base-oils

Entry	Cycloalkanes	KV ₁₀₀ ^a (cSt)	KV ₄₀ ^a (cSt)	VI ^b	PP ^c (°C)	DSC oxidation ^d (°C)	TGA Noack ^e (wt%)
1	4b (C ₂₄) R ² = <i>n</i> -pentyl	3.35	17.01	40	−69	224	58.3
2	4c (C ₂₇) R ² = <i>n</i> -hexyl	4.07	21.19	82	−66	224	21.6
3	4d (C ₃₀) R ² = <i>n</i> -heptyl	4.87	26.06	109	−72	224	7.5
4	4e (C ₃₃) R ² = <i>n</i> -octyl	5.72	31.57	123	−69	226	2.6
5	4f (C ₃₆) R ² = <i>n</i> -nonyl	6.55	37.18	131	−60	225	1.2
6	4g (C ₄₅) R ² = <i>n</i> -dodecyl	9.64	59.48	146	−9	229	0
7	4h (C ₃₀) R ² = <i>c</i> -hexylmethyl	Too viscous to analyse				220	5.6
8	4i (C ₃₃) R ² = 2-ethylhexyl	7.09	59.74	66	−54	212	22.5
9	4j ≅ 4b (C ₂₄) R ² = <i>n</i> -pentyl	3.51	18.11	49	−51	203	56.5
10	4k ≅ 4c (C ₂₇) R ² = <i>n</i> -hexyl	4.38	25.59	62	−63	210	30.4
11	4l (C ₄₅) R ² = 2-pentylheptyl	11.49	106.46	94	−51	212	1.7
12	3b (C ₃₀) R ² = <i>n</i> -octyl	4.29	20.07	121	−75	219	14.4
13	5b (C ₃₀) R ² = <i>n</i> -octyl	3.99	18.74	110	−57	222	26.6
14	Commercial C ₃₀ PAO	3.63	15.23	124	−72	221	9.6

^a KV₁₀₀ and KV₄₀ are kinematic viscosities at 100 °C and 40 °C, respectively (ASTM standard D7279-14). ^b Viscosity index calculated from KV₁₀₀ and KV₄₀ (ASTM standard D2270). ^c Pour point (ASTM standard D7346-07). ^d Oxidation stability (ASTM standard E2009-99). ^e Volatility (ASTM standard D972).

hexanes (**4** and **5**). The lubricant properties of these compounds – the viscosity index (VI), pour point (PP), oxidation stability (DSC oxidation), and volatility (TGA Noack) – were evaluated according to ASTM standards (Table 2). We also explored the structure–property relationship by studying a number of different analogues with varying functionality around the cyclohexane core. A steady increase in the VI of **4b** through **4g** (Table 2, entries 1–6 and Fig. 1) indicates that the viscosity change with temperature decreases as the length of the linear alkyl substitution increases. Higher analogues of this series of compounds (C_{33+} , **4e–g**) possessed an excellent VI compared to that of petroleum-derived C_{30} PAO (entry 14). In general, the measured kinematic viscosities of cyclic alkanes at reference temperatures (40 °C and 100 °C) are higher than those of the corresponding acyclic, branched alkanes (entries 3 vs. 14). The viscous nature of the cyclic compounds is highly evident when the alkyl side chain of **4** contains additional cyclohexane functionalities (**4h**, entry 7). However, the presence of the cyclohexane core improved the pour points of most analogues to <-60 °C. We also found that longer alkyl chain substitution in **4g** resulted in a poor pour point due to alkyl chain stacking, similar to that found in waxes. While the oxidation stabilities of the cyclic lubricants are comparable to each other and to that of commercial C_{30} PAO, the volatilities are inversely proportional to the molecular weights within the subset of **4b–g** (Table 2, entries 1–6 and Fig. 1). **4g** turned out to be the least volatile lubricant and exhibited a high VI; however, the pour point for this compound was also quite high. Of all the compounds analyzed, **4e** and **4f** contained the best overall lubricant properties consistent with those currently used in the transportation sector.

The branched alkyl substituted cyclohexane **4i** exhibited higher viscosities but a lower VI than that of the corresponding linear alkyl substituted isomer **4e** (entries 4 vs. 8). This is a consequence of the high dependence of viscosity on temperature attributable to excessive branching of the molecular structure. Notably, the volatility of **4i** is exceptionally high (~10 fold) compared to that of **4e** due to decreased intermolecular interactions caused by increased branching. The properties of the structurally similar lubricants **4b**, **4c** and **4j**, **4k** derived from alkyl and furanic precursors, respectively, were compar-

able (entries 1, 2 and 9, 10). Due to the high viscosities associated with 2-methylfuran-derived lubricant, **4l** may be better suited for industrial applications such as in wind turbines and compressors, rather than for automotive use. Aromatic C_{30} -lubricant **3b** and the corresponding cyclohexane analogue **5b** have good viscosity indices, pour points and oxidation stabilities, but poor volatilities compared to those of commercial C_{30} PAO (entries 12–14). A comparison of volatilities of various C_{30} base-oils (entries 3, 7, and 12–14) suggests that this property does not depend on the molecular weight alone but involves other functionalities present in the molecular structure.

In conclusion, we have developed a strategy for the highly selective trimerization of methyl ketones to produce bio-lubricants. The alkyl and furan-containing ketones required for this process can be conveniently obtained from biomass and the metal oxide catalysts employed are non-corrosive solids (e.g., $MgAlO$). The cyclic alkane lubricants derived from this method possess excellent pour points, viscosity indices, and oxidation stabilities which are comparable to those of conventional synthetic lubricants. A systematic structure–property relationship study indicated that the viscosity index of these materials increases steadily with length of alkyl side chain. Conversely, the volatility of these compounds exhibits an inverse dependence on alkyl chain length. Such relationships are valuable for directing future research aimed at developing renewable lubricants.

Experimental

General procedure for $MgAlO$ -catalyzed self-condensation of ketones: a solution of **1** (20 g) in toluene (200 mL) was added with $MgAlO$ (20 g) in a 500 mL round bottom flask equipped with a magnetic spin bar. The flask was then attached to the Dean–Stark apparatus and refluxed with stirring (800 rpm) in a pre-heated oil bath at conditions A given in Table 1. A collection of by-product water was observed in the side-arm of the apparatus during the course of the reaction. The product mixture was then cooled to room temperature and filtered through a fritted funnel by washing the catalyst using ethyl acetate (3×100 mL). The products (**2**) in the filtrate were recovered after evaporation of the solvents and used for the next step without further purification.

General procedure for hydrodeoxygenation of condensates: a solution of **2** (5 mmol) was added with respective hydrogenation catalysts (metal loadings are calculated with respect to **2**) in a 25 mL Parr reactor vessel. Octane (5 mL) was added to reduce the viscosity and ensure good mixing in the Parr reactor during the reaction. The reactor was sealed, flushed with nitrogen gas (2 $\times$), hydrogen gas (3 $\times$) and subsequently charged with the required pressure of hydrogen gas. The Parr reactor was stirred at 500 rpm and subjected to respective conditions mentioned in Table 1, conditions B. The reaction mixture was cooled to room temperature and filtered through a fritted funnel using hexanes as a washing solvent (3×20 mL) to remove the catalyst. The filtrate was concentrated under reduced pressure to recover cyclic alkanes **4**.

Fig. 1 Variations in the properties of lubricant base-oils depending on the number of carbon atoms in the linear side chains **4b–g**.

Acknowledgements

This work was funded by the Energy Biosciences Institute. The authors would like to thank the analytical team as well as the technology team of BP Castrol for evaluating the lubricant properties of the compounds synthesized.

Notes and references

- 1 R. Buckhalt, in *Society of Tribologists and Lubrication Engineers*, 2014.
- 2 S. Boyde, *Green Chem.*, 2002, **4**, 293–307.
- 3 L. R. Rudnick, *Synthetics, Mineral Oils, and Bio-Based Lubricants: Chemistry and Technology*, Taylor & Francis, 2nd edn, 2013.
- 4 S. Ray, P. V. C. Rao and N. V. Choudary, *Lubr. Sci.*, 2012, **24**, 23–44.
- 5 P. Wasserscheid, S. Grimm, R. D. Köhn and M. Haufe, *Adv. Synth. Catal.*, 2001, **343**, 814–818.
- 6 G. D. Yadav and N. S. Doshi, *Green Chem.*, 2002, **4**, 528–540.
- 7 F. Mo and G. Dong, *Science*, 2014, **345**, 68–72.
- 8 Y.-F. Wang, Y.-R. Gao, S. Mao, Y.-L. Zhang, D.-D. Guo, Z.-L. Yan, S.-H. Guo and Y.-Q. Wang, *Org. Lett.*, 2014, **16**, 1610–1613.
- 9 A. Acosta-Ramirez, M. Bertoli, D. G. Gusev and M. Schlaf, *Green Chem.*, 2012, **14**, 1178–1188.
- 10 J. T. Kozlowski and R. J. Davis, *ACS Catal.*, 2013, **3**, 1588–1600.
- 11 P. Anbarasan, Z. C. Baer, S. Sreekumar, E. Gross, J. B. Binder, H. W. Blanch, D. S. Clark and F. D. Toste, *Nature*, 2012, **491**, 235–239.
- 12 E.-B. Goh, E. E. K. Baidoo, J. D. Keasling and H. R. Beller, *Appl. Environ. Microbiol.*, 2012, **78**, 70–80.
- 13 M. Balakrishnan, E. R. Sacia, S. Sreekumar, G. Gunbas, A. A. Gokhale, C. D. Scown, F. D. Toste and A. T. Bell, *Proc. Natl. Acad. Sci. U. S. A.*, 2015, **112**, 7645–7649.
- 14 E. R. Sacia, M. Balakrishnan, M. H. Deaner, K. A. Goulas, F. D. Toste and A. T. Bell, *ChemSusChem*, 2015, **8**, 1726–1736.
- 15 H.-J. Chae, T.-W. Kim, Y.-K. Moon, H.-K. Kim, K.-E. Jeong, C.-U. Kim and S.-Y. Jeong, *Appl. Catal., B*, 2014, **150–151**, 596–604.
- 16 W. Xu, Q. Xia, Y. Zhang, Y. Guo, Y. Wang and G. Lu, *ChemSusChem*, 2011, **4**, 1758–1761.