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Short Communication

Copper mediated epoxidation of high oleic natural oils with a cumene–O_2 system

Nicola Scotti [a], Nicoletta Ravasio [a,*], Rinaldo Psaro [a], Claudio Evangelisti [a], Sylwia Dworakowska [b], Dariusz Bogdal [b], Federica Zaccheria [a]

[a] CNR Istituto di Scienze e Tecnologie Molecolari, Via Golgi 19, 20133 Milan, Italy
[b] Department of Biotechnology and Physical Chemistry, Faculty of Chemical Engineering and Technology, Cracow University of Technology, Warszawska 24, 31-155 Cracow, Poland

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ABSTRACT

The epoxidation of methyl oleate or high oleic FAMEs from different vegetable oils was carried out in a one-pot reaction over supported copper catalysts by using cumene as oxygen carrier. Cumene firstly reacts with O_2 generating cumene hydroperoxide, that by reaction with methyl oleate forms the epoxide. By using 8% Cu catalysts supported on alumina or on a polymer yields up to 87% could be obtained in a single pot at 100 °C.

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1. Introduction

The growing demand for sustainable and biodegradable products, coupled with restrictions on the use of existing ones, are increasing the importance of oleochemicals in various segments of the chemical industry, notably polymers, lubricants and surfactants. The global oleochemicals market was estimated at 14 million tonnes in 2013 and it is expected to grow at 6%/year over the next five years to reach 18 million tonnes in 2018 [1].

This is strongly fostering innovation in this area, particularly as far as greener processes are concerned. One of the oleochemical industry processes requiring a more environmentally friendly approach is epoxidation. This reaction can lead to very important intermediates for large-scale application such as stabilizers and plasticizers in polymers, additives in lubricants, building blocks in plastics and in polyurethane foams but also as precursors of a wide series of high added-value compounds. However, the synthesis of epoxidized vegetable oils still relies on the use of in situ generated peracids. The reaction is highly exothermic and is normally performed in several steps, since too high temperature peaks cause the degradation of the formed oxirane ring. Moreover, a neutralization step is necessary to eliminate the excess of acid and to lower the excess of hydrogen peroxide [2].

Grafted Ti mesoporous silica materials were found to be very active catalysts for the selective epoxidation of C18 unsaturated fatty acid methyl esters with *tert*-butyl-hydroperoxide (TBHP) as oxidant under acid-free conditions [3] while Nb containing ones showed good activity and selectivity in the presence of aqueous hydrogen peroxide [4]. However, also Ti on silica catalysts are active in the presence of hydrogen peroxide [5,6] and as long as the oxidant is added dropwise yields up to 91% can be obtained in the epoxidation of methyl oleate [7].

Although the Ti and Nb based systems are very good alternatives to the peracid based reaction they still rely on the use of organic hydroperoxides or concentrated hydrogen peroxide solutions. A catalytic system able to in situ generate the active oxidant species would be very interesting from the safety point of view in order to avoid storage and handling of hazardous hydroperoxides.

Some of us recently reported on the epoxidation of olefins by using a CuO/Al_2O_3 catalyst and cumene in the presence of O_2. According to our protocol, as in the Sumitomo process for propylene oxide production, O_2 and cumene first react together to give cumyl hydroperoxide which is the active epoxidation species. Yield in epoxide as high as 95% in the case of activated substrates such as β-methylstyrene could be obtained in very short times [8].

Here we wish to report that a similar approach can be conveniently used in the epoxidation of fatty acid methyl esters, thus paving the way

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* Corresponding author.
E-mail address: n.ravasio@istm.cnr.it (N. Ravasio).

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to the epoxidation of these strategic intermediates under more sustainable conditions.

2. Experimental

CuO/γ-Al_2O_3 and CuO/PVPy (PVPy = polyvinylpyridine) catalysts, with an 8% metal loading, were prepared by chemisorption–hydrolysis [9]. The support (γ-Al_2O_3 or PVPy, 10 g) was added to a $[Cu(NH_3)_4]^{2+}$ solution obtained by the addition of NH_4OH to a $Cu(NO_3)_2 \cdot H_2O$ water solution (4 g in 20 ml) until pH 9. After 20 min under stirring, the slurry, held in an ice bath at 0 °C, was slowly diluted in order to allow hydrolysis of the copper complex and deposition of the finely dispersed product to occur. The solid was separated by filtration, washed with 0.5 l of water, dried in oven overnight at 120 °C. Finally, CuO/Al_2O_3 was calcined in static in air at 350 °C for 4 h, while CuO/PVPy was not treated at high temperature, in order to preserve the polymer.

Metal loadings were determined by ICP-OES (ICAP6300 Duo purchased from Thermo Fisher Scientific) and an external calibration methodology, after microwave digestion of fresh and used catalysts in HNO_3.

High-resolution transmission electron microscopy (HRTEM) analysis of CuO/PVPy was operated at 200 kV with a LIBRA 200FE analytical transmission electron microscope, equipped with FEG source and purchased from Zeiss. Samples were deposited on holey carbon-coated grids from alcohol suspensions. Samples, in the form of powders, were ultrasonically dispersed in isopropyl alcohol, and a drop of the suspension was deposited on a holey carbon film grid (300 mesh). Histograms of the metal particle size distribution for the Cu samples were obtained by counting at least 300 particles onto different high resolution micrographs; the mean particle diameter (d_m) was calculated by using the formula $d_m = \Sigma d_i n_i / \Sigma n_i$ where n_i was the number of particles of diameter d_i.

Reactions were performed at 100 °C and under stirring (1250 rpm) in a 50 ml glass flask provided of a condenser, operating at atmospheric pressure, without the use of radical initiators, by bubbling molecular oxygen (30–35 ml/min), in the presence of cumene as both solvent and reactant, and eventually a co-solvent (cumene + co-solvent = 20 ml, olefin 10 or 5 mmol, catalyst 250 mg). All the products were analyzed by GC–MS HP-5890 series, equipped with HP5 (5% phenyl)-methyl-polysiloxane capillary column, length 30 m (initial temperature = 60 °C and 3 min hold, then 15 °C/min to 280 °C and 20 min hold). Conversion was calculated by using the following equation: $C\,(\%) = \frac{\text{mol MO reacted}}{\text{Starting mol MO}} \cdot 100$, while selectivity was calculated as $C\,(\%) = \frac{\text{mol MO reacted}}{\text{Starting mol MO}} \cdot 100$.

X-ray powder diffraction patterns were recorded within the range of 10° to 70° 2θ, with a step of 0.02° 2θ and counting time 1 or 4 s/step on Philips PW-3020 powder diffractometer Ni-filtered Cu Kα radiation. The peak of CuO (111) at 2θ = 35.5° was used for line-broadening determinations.

Copper leaching was measured after a sulfonitric digestion of a sample of 100 mg of the reaction mixture, after catalyst filtration at the end of the reaction.

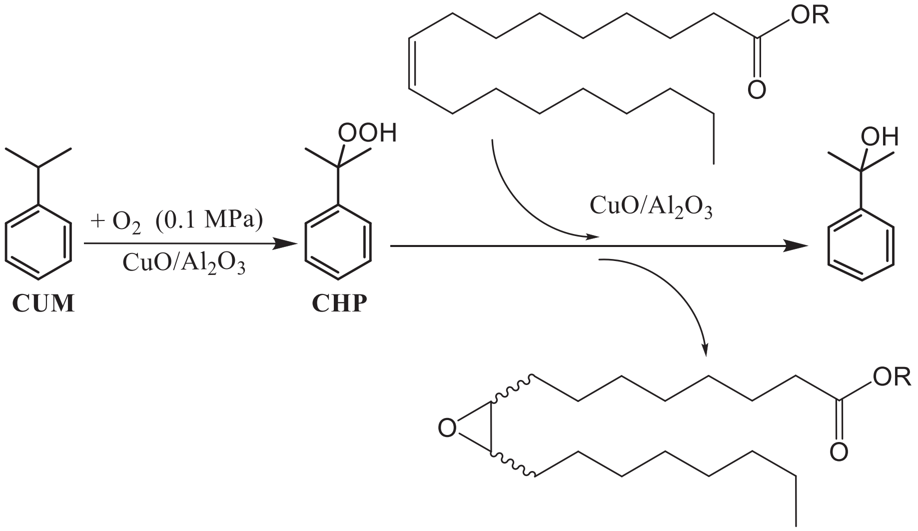
3. Results and discussion

CuO/γ-Al_2O_3 catalyst shows very high catalytic performances in the epoxidation of methyl oleate (MO). The one-pot transformation, as represented in Scheme 1, starts with the copper catalyst promoted oxidation of cumene into cumyl hydroperoxide by oxygen. The oxidant species thus formed allows the epoxidation of the substrate again mediated by CuO/Al_2O_3.

By using 20 ml of cumene and 10 mmol of MO (3 g) after 6 h we obtained a conversion of 87%, but selectivity was only 63%. On the other hand, by using toluene as co-solvent, selectivity raised to 81% in 6 h, likely due to the decrease in oxidant species concentration. A further decrease in cumene and solvent amount (5 ml of cumene + 5 ml of toluene) led to a little worsening in the performances (conv. = 80%, sel. = 75%, t = 6 h), while optimum results were obtained by lowering the amount of substrate (Table 1, entry 4).

A mixture of *cis* and *trans* isomers is obtained, thus suggesting that a radical mechanism is involved [10]. We already reported [8] that the first step of the reaction, namely cumene oxidation, follows a radical pathway: both cumyl-hydroperoxide (CHP) and cumene hydroperoxide radical are supposed to be the epoxidating species. Therefore, assuming a pathway similar to the one reported by Köckritz at al. for the epoxidation of MO in the presence of aldehyde/azobisisobutyronitrile, the hydroperoxide radical should be responsible for the formation of *trans*-epoxystearate, while only *cis* isomer derives from CHP [11].

The reaction of methyl elaidate (the *trans* isomer) is very much slower, the difference in activity being comparable with that observed in the presence of Ti grafted on non-porous, non-ordered silica and *tert*-butyl hydroperoxide [10]. The better reactivity of



Scheme 1. One-pot epoxidation of MO over bifunctional CuO/Al_2O_3, through in-situ formation of CHP by reaction between cumene and O_2.

Table 1
One-pot epoxidation of MO on CuO/Al_2O_3.[a]

Entry	MO	Solvent (ml)	Time (h)	Conv. (%)	Sel. (%)
1	10 mmol, *cis*	CUM = 20	6	87	63
2	10 mmol, *cis*	CUM = 10 HEP = 10	6	77	70
3	10 mmol, *cis*	CUM = 10 TOL = 10	6	84	81
4	5 mmol, *cis*	CUM = 10 TOL = 10	6	98	86
5	5 mmol, *trans*	CUM = 10 TOL = 10	9	36	71
6[b]	5 mmol, *cis*	CUM = 10 TOL = 10	8	99	88

[a] T = 100 °C, O_2 = 30–35 ml/min, cat. = 250 mg, CUM = cumene, TOL = toluene, HEP = heptane.
[b] CuO/PVPy as the catalyst.

oleate is ascribable to steric effects, since the approach to the catalyst surface for *cis* C═C bonds is much less hindered than for *trans* C═C bonds.

As far as the support effect is concerned, a copper catalyst prepared by using a polymer, namely polyvinylpyridine (PVPy), showed good catalytic activity (Table 1, entry 6) and selectivity slightly higher than CuO/Al_2O_3, as shown by conversion and selectivity profiles reported in Fig. 1a–b.

Cu catalysts supported on polymers are used in organic synthesis but they are usually prepared by anchoring Cu salts or Cu complexes [12–14] this is a rare example of a polymer supported CuO catalyst prepared by chemisorption. The presence of CuO is well evident in XRD spectra (Fig. S1) from which a particle size of 11 nm ± 3 can be estimated. Transmission electron micrographs and particle size distribution of the CuO/PVPy system are reported in Fig. 2. TEM images at low magnification (see Fig. 2A and B) showed CuO particles held together by the amorphous polyvinylpyridine phase making very difficult to discriminate individual crystalline particles in order to measure them. Images at higher magnifications (see as example Fig. 2C–F) pointed out the presence of crystalline CuO nanoparticles with irregular shape with lattice planes extended to the whole nanoparticle and an amorphous phase bonded to their surface. Copper nanoparticles are present with a size distribution ranging from 3 to 18 nm and an average diameter close to 9 nm (Fig. 3). The particles appeared to be well dispersed and covered by an amorphous phase which can be ascribed to the PVPy resin. Lattice fringe analysis of the Cu nanoparticles exhibits spots in the FT pattern at 2.5 Å in agreement with the (002) lattice spacing of Cu(II) oxide [15]. This evidence shows that on PVPy big CuO aggregates survive exposure to the electron beam thus showing to be hardly reducible.

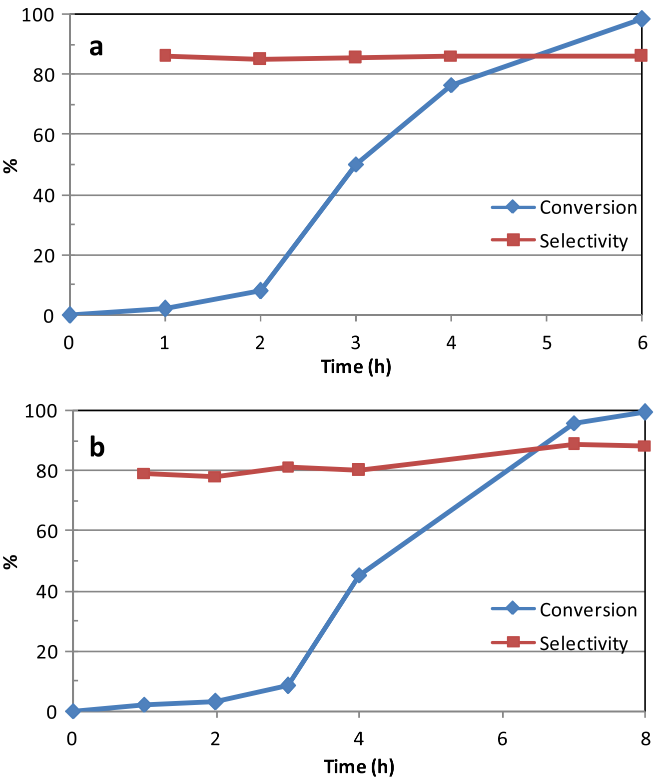


Fig. 1. Conversion and selectivity profiles of MO epoxidation: a) CuO/Al_2O_3, see Table 1, entry 4; b) CuO/PVPy, see Table 1, entry 6.

The presence of CuO on the alumina surface is also witnessed by XRD (Fig. S2) and TEM that put in light the presence of CuO particles with an average 4 nm diameters [8]. The CuO/Al_2O_3 catalyst already showed to be resistant to reduction, particularly in the liquid phase [16]. This suggests that for the epoxidation reaction bigger, less easily reducible CuO aggregates are required instead of small ones giving very easily well formed, three-dimensional Cu crystallites as in the case of hydrogenation reactions. Thus, CuO/SiO_2, very easily reducible to very small, three-dimensional cuboctahedral particles [17] is the most performant hydrogenation system but does not show any activity in epoxidation [8]. Work is in progress to better characterize, through FT IR spectroscopy of adsorbed CO, the morphology of CuO particles on alumina and PVP, as it was already shown that bidimensional particles are the most effective ones in the oxidative polymerization of 2,6-dimethyl-phenol [18].

Comparison of these results with those reported in the literature puts in light the originality and the effectiveness of the Cu promoted epoxidation. Thus, the epoxidation of methyl oleate with O_2 has been reported only in the presence of an aldehyde and a radical initiator [19]. Yields up to 99% without the need of a metal catalyst but a high pressure of O_2 in organic solvents was used. The use of TBHP as an oxidant gave 75% yield at 70 °C in the presence of Co oxides [20], while Ti grafted catalysts gave yields up to 91% at 90 °C for long reaction times [10,21–24].

Only hydrogen peroxide as an oxidant allowed one to obtain yield higher than 85%. Thus, Ti grafted on a mesoporous silica (MCM41) gave >91% yield at 85 °C due to high conversion and selectivity [7]. Methyl esters epoxidation has been recently reported also over immobilized peroxometalates and peroxophosphotungstate [25,26], one-dimensional MoO/bipyridinedicarboxylate hybrid [27] and also over metal complexes based on Ru and Mo [28,29] always in the presence of TBHP or H_2O_2 obtaining yields and reaction times (3–24 h) comparable to those reported in the present paper.

Following our continuous interest in developing chemical processes relevant to the biorefinery scenario, we applied this epoxidation method

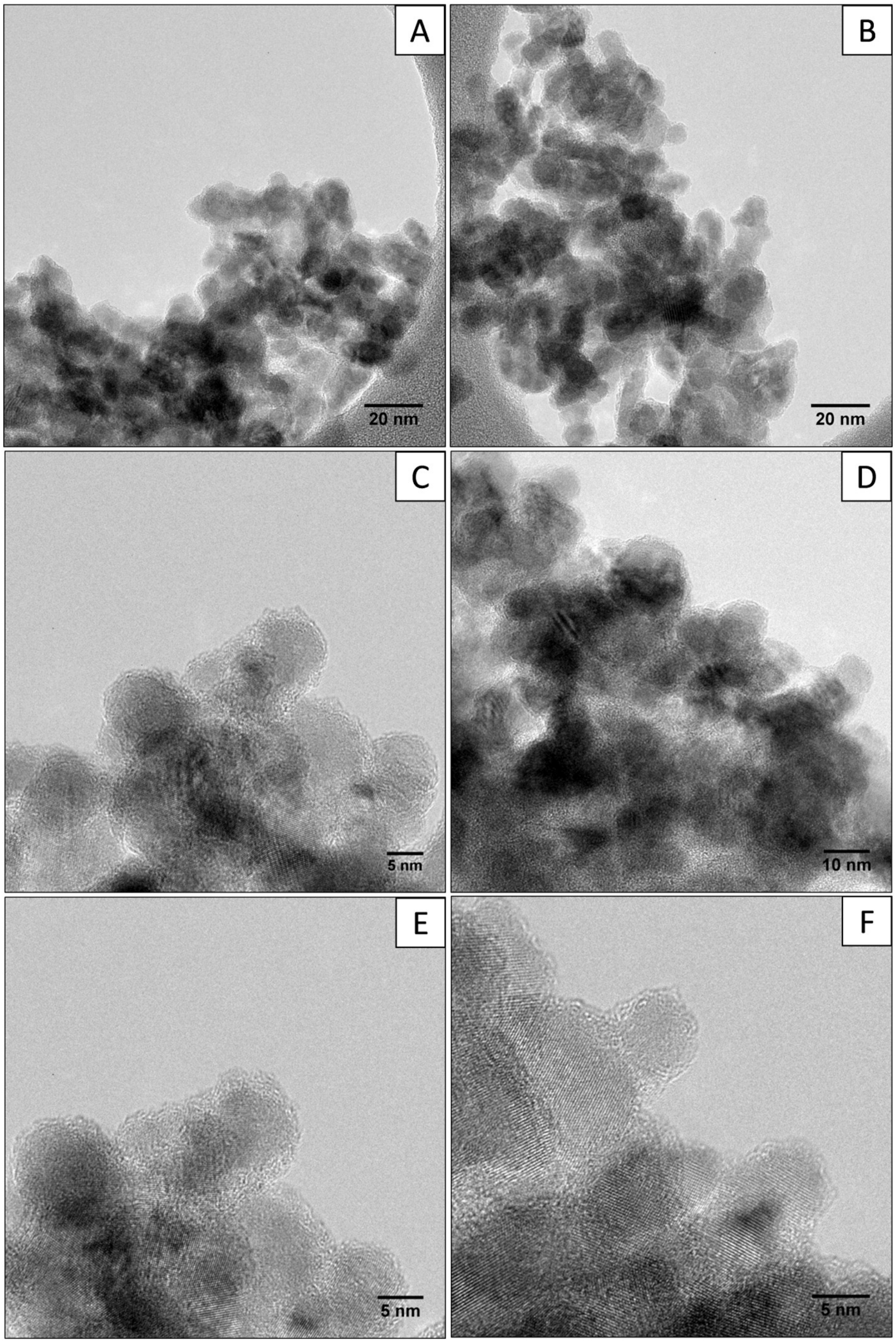


Fig. 2. HRTEM of CuO/PVPy at different magnification.

to methylester mixtures obtained from natural oils. In particular we tested high-oleic sunflower oil fatty acid methyl-esters (FAMEs) and "stabilized" rapeseed and soybean oil FAMEs. We already reported on a versatile protocol for the selective hydrogenation of many polyunsaturated oils [30–32]. This method, useful not only to improve the oxidative stability but also to standardize the composition of very different oils in order to have in hand a raw material with uniform chemical composition, relies on the use of a supported Cu catalyst under mild hydrogenation conditions. The catalyst is selective for the hydrogenation of polyenes to monoenes thus granting not only an improved stability towards oxidation, but also to preserve acceptable cold properties as the stearic acid content keeps unchanged during the process. In the particular case of rapeseed and soybean oil methylester hydrogenation, very high amount of monounsaturated component can be obtained (Table 2).

The epoxidation reaction proceeded with very high conversion and selectivity on all the natural mixtures, over both CuO/PVPy and CuO/γ-Al_2O_3 although results confirmed the higher activity of the γ-alumina supported catalyst (Table 3). It is interesting to note that performances of bioproducts derived from vegetable oils strongly depend on their unsaturation level. In particular, the quality of polyol esters to be used for casting and coating compositions is very much improved when very high oleic, low stearic vegetable oils are used as starting materials. Some of us recently reported on the higher quality of polyurethane foams obtained from hydrogenated rapeseed oil with respect to the analogs obtained from rapeseed

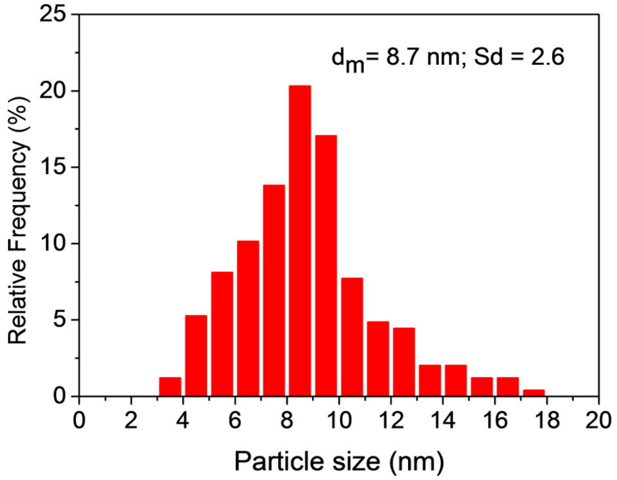


Fig. 3. Particle size distribution of CuO/PVPy.

Table 2
Starting composition (mol%) of stabilized FAMEs.

FAME	C16:0	C18:0	C18:1	C18:2	C18:3
Sunflower highly oleic	4.2	3.4	86.3	6.1	–
Stabilized rapeseed	4.5	1.9	89.6	2.3	1.7
Stabilized soybean	10.7	4.7	72.0	11.9	0.8

oil, particularly as far as compressive strength and elongation at break are concerned [33].

It is also worth noting that leaching of the metal is lower for the reaction of MO with respect to what observed with the previously studied olefins. In fact, in the case of methyl oleate and natural derived FAMEs leaching values less than 1% were measured (see Table S1), whereas in the case of stilbene and other simpler olefins, value around 4% was recorded [8].

4. Conclusions

In conclusion, we show that the cumene–O_2 system, promoted by supported copper catalysts is an effective and selective tool for the epoxidation of methyl oleate and high oleic FAMEs allowing one to obtain methyl-epoxy-stearate in high yield. Moreover, results obtained in the present work show that oils with a very high oleic content obtained by selective hydrogenation over Cu catalysts can be conveniently epoxidized over the same kind of catalysts, thus suggesting that a one pot-two step process can be envisaged to convert polyunsaturated oils into monoepoxides.

Table 3
One-pot epoxidation of MO and natural derived FAMEs.

Substrate	Cat.	Time (h)	Conv. (%)	Sel. (%)
Sunflower highly oleic	CuO/Al_2O_3	6	99	78
	CuO/PVPy	7	96	89
Stabilized soybean	CuO/Al_2O_3	6	98	79
	CuO/PVPy	9	81	80
Stabilized rapeseed	CuO/Al_2O_3	7	95	79
	CuO/PVPy	9	99	82

T = 100 °C, O_2 = 30–35 ml/min, olefin = 5 mmol, cat. = 250 mg, CUM = 10 ml, toluene = 10 ml.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.catcom.2015.02.008.

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