

Liquid Phase Oxidation of Toluene to Benzaldehyde with Molecular Oxygen over Copper-Based Heterogeneous Catalysts

Feng Wang, Jie Xu,* Xiaoqiang Li, Jin Gao, Lipeng Zhou, Ryuichiro Ohnishi

State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Graduate School of the Chinese Academy of Sciences, Chinese Academy of Science, Zhongshan Road 457, P. O. Box 110, Dalian, 116023, People's Republic of China
Fax: (+86)-411-8437-9245, e-mail: xujie@dicp.ac.cn

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Abstract: We conducted the liquid phase oxidation of toluene with molecular oxygen over heterogeneous catalysts of copper-based binary metal oxides. Among the copper-based binary metal oxides, iron-copper binary oxide (Fe/Cu = 0.3 atomic ratio) was found to be the best catalyst. In the presence of pyridine, overoxidation of benzaldehyde to benzoic acid was partially prevented. As a result, highly selective formation of benzaldehyde (86% selectivity) was observed after 2 h of reaction (7% conversion of toluene) at 463 K and 1.0 MPa of oxygen atmosphere in the presence of pyridine. These catalytic performances were similar or better than those in the gas phase oxidation of toluene at reaction temperatures higher than 473 K and under 0.5–2.5 MPa. It was suggested from competi-

tive adsorption measurements that pyridine could reduce the adsorption of benzaldehyde. At a long reaction time of 4 h, the conversion increased to 25% and benzoic acid became the predominant reaction product (72% selectivity) in the absence of pyridine. The yield of benzoic acid was higher than that in the Snia-Viscosa process, which requires corrosive halogen ions and acidic solvents in the homogeneous reaction media. The catalyst was easily recycled by simple filtration and reusable after washing and drying.

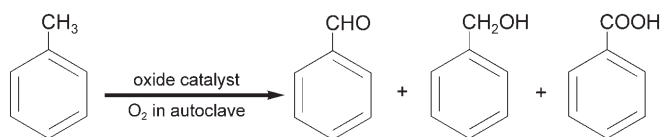
Keywords: benzaldehyde; C–H bond activation; heterogeneous catalysis; liquid phase; molecular oxygen; toluene

Introduction

Selective oxidation of sp^3 hybridized carbon of inactive hydrocarbons to industrially important intermediates still remains a major challenge.^[1–5] For example, toluene can be converted into oxidation products such as benzyl alcohol, benzaldehyde and benzoic acid. Among these products, benzaldehyde is the most desirable and value-added product. However, benzaldehyde is easily overoxidized to benzoic acid. Due to rather poor performance of direct oxidation, various substituted aromatic aldehydes are still manufactured in the traditional way of organic chemistry. Traditionally, benzaldehyde is produced by side-chain chlorination of toluene and saponification of the resulting dichloromethyl group to form the aldehyde group. The product, still containing the chlorinated impurities, does not meet food and drug grade specifications. Besides, these processes produce much waste causing environmental problems and, additionally, the efficiencies of these routes are not so high. There are some reports on vapor phase oxidation of toluene with oxygen. However, the common reaction conditions ($T > 473$ K and under 0.5–2.5 MPa pressure^[6–9]) seem too harsh for improving the selectivity

for benzaldehyde. Generally, the conversion has to be kept at less than 4% to attain 70% selectivity of benzaldehyde and to avoid the formation of carboxylic acids, phenols and decomposition to carbon oxides (CO_2 and CO) and tar.^[10–12]

The liquid phase oxidation of toluene with homogeneous metal salt catalysts was industrially realized in the Rhodia, Dow and Snia-Viscosa processes using oxygen or peroxides as oxidants.^[13–16] For example, the Snia-Viscosa process operates at 165 °C and under 10 atm of air in the presence of a homogeneous cobalt catalyst in acetic acid. At the optimal conditions, benzoic acid as the target product is produced with 90% selectivity, and benzaldehyde as a minor by-product is obtained in 3% selectivity at 15% conversion of toluene. In these processes, however, halogen ions and acidic solvents are indispensable, and they easily cause erosion of the facility. The formation of benzoic acid *via* toluene oxidation was also reported in supercritical CO_2 and ionic liquids as solvents.^[17,18] In the latter report, the maximum conversion of toluene was only 4.7% after 48 h. Toluene oxidation by the use of cobalt tetraphenylporphyrin as catalyst has also reported recently.^[19]



Scheme 1. Liquid phase oxidation of toluene with molecular oxygen over Cu-based heterogeneous catalysts.

We report here the liquid phase oxidation of toluene with molecular oxygen on copper-based binary metal oxide catalysts (see Scheme 1). To the best of our knowledge, no report is available on the heterogeneous catalytic oxidation of toluene to benzaldehyde with molecular oxygen in the liquid phase.

Results and Discussion

It can be seen from Table 1 that the blank run without catalyst gave no products. The support γ - Al_2O_3 itself gave minor conversion of 2%. Among the single component catalysts tested, only copper supported on γ - Al_2O_3 gave the best conversion of 2.5%, although it is still very low. GC-MS analyses of the post-reaction mixture showed that the main by-products were of the phenolic series and esters [(*o*-, *p*- and *m*-)cresols, benzoic acid methyl ester and formic acid benzyl ester], the products of ring-opening reactions (maleic anhydride), decarboxylation reactions (benzene and phenol) and coupling reactions (biphenyl, methyl-substituted biphenyl and 1,2-biphenylethane).

After screening several metal oxides, we focused our attention on copper-based binary metal oxide catalysts. The copper and cobalt binary oxide catalyst was tested first and gave a relatively low conversion of 0.7% (Table 2, entry 1). Among these catalysts, those of entries 2 and 4 have been reported to be highly selective (96% selectivity) and active (97% conversion) in the oxidation of cresols with oxygen to corresponding aldehydes at 348 K.^[20–22] However, both catalysts gave low conver-

sions in the oxidation of toluene. Only the copper-iron binary metal oxide catalyst (Table 2, entry 6) gave a promising activity of 7.4% and high selectivity (96.5%) of oxidized products at the benzylic position. At the long reaction time of 4 h, the conversion increased to 25.4% and benzoic acid became the predominant reaction product (71.6% selectivity). The yield of benzoic acid ($25 \times 72\% = 20\%$) was higher than that of the Snia-Viscosa process ($90 \times 15\% = 13.5\%$). Considering the indispensable usage of corrosive halogen ions and acidic solvents in the Snia-Viscosa process, this work could be judged to be the better system. The main product can be shifted from benzaldehyde to benzoic acid by prolonging the reaction time, as was expected.

The molar ratio of Fe to Cu was optimized to be 0.3:1, as presented in Figure 1. Yields of benzaldehyde and benzyl alcohol became maximal at Fe/Cu = 0.3 since the increases in benzaldehyde and benzyl alcohol selectivities were compensated with the decrease in the conversion, as the iron content increased. Magnesium and titanium(IV) oxide were employed as supports for iron-copper oxide (Fe/Cu = 0.3). Low conversions of below 2% were obtained on these catalysts, demonstrating that γ - Al_2O_3 is a suitable support for the oxidation of toluene. Although we do not know how the iron-copper metal oxide promotes the reaction, transition metal salts are known to pull hydrogen out from organic compounds forming radicals and/or to promote the decomposition of peroxide species.^[23,24]

A dramatic change in conversion and selectivity was observed when a small amount (1% of toluene) of polar organic additives was added to the reaction media. As shown in Table 3, NBS and 1,1,2,2-tetrabromoethane promoted the reaction while phenol retarded it. These results are typical for the case of a radical auto-oxidation reaction, where the former two additives act as initiators of the radical reaction by supplying bromine radical and phenol acts as a radical scavenger. A part of acetic acid was converted to benzyl acetate, which may be formed from a reaction of benzyl alcohol with acetic acid. The two bases, 3-methylpyridine and pyridine, were charac-

Table 1. Catalytic oxidation of toluene with single components catalysts.^[a]

Entry	Catalyst	Conversion ^[b] (mol %)	Product selectivities (%)			
			CHO ^[c]	CH ₂ OH ^[c]	COOH ^[c]	Others
1	No catalyst	0	–	–	–	–
2	γ - Al_2O_3	2.0	50.1	49.9	0	0
3	Fe/ Al_2O_3	1.1	95.7	4.3	0	0
4	Mn/ Al_2O_3	1.4	87.5	12.5	0	0
5	Zn/ Al_2O_3	1.8	88.5	11.5	0	0
6	Co/ Al_2O_3	2.0	77.8	20.6	0	1.6
7	Cu/ Al_2O_3	2.5	85.7	13.0	0	1.3

^[a] Toluene (50 mL, 0.47 mol) was oxidized in a 500-mL stirred autoclave at 463 K and 1.0 MPa O₂ for 2 h on 1.0 g catalyst

^[b] Conversion was calculated from GC measurement using 1,2,4,5-tetramethylbenzene (durene) as an internal standard.

^[c] CHO, CH₂OH and COOH refer to benzaldehyde, benzyl alcohol and benzoic acid, respectively, unless otherwise noted.

Table 2. Catalytic oxidation of toluene with binary oxides catalysts.^[a]

Entry	Catalyst ^[b]	Conversion (%)	Product selectivities (%)			
			CHO	CH ₂ OH	COOH	Others
1	CuCo [1:0.3] (10)	0.7	12.4	36.7	29.9	21.0
2	CoCu/C [1:0.8] (10)	1.1	57.0	28.0	0	15.0
3	CuZn [1:0.3] (10)	1.1	86.6	13.4	0	0
4	CuMn/C [1:0.2] (7)	1.4	71.7	28.3	0	0
5	CuMn [1:0.3] (10)	1.9	74.9	19.1	3.2	2.8
6	CuFe [1:0.3] (10)	7.4	45.6	23.8	27.1	3.5
7	CuFe ^[c] [1:0.3] (10)	25.4	27.4	1.0	71.6	0
8	CuFe[1:0.3]/MgO	1.2	41.5	44.4	0	14.1
9	CuFe[1:0.3]/TiO ₂	1.8	27.2	37.9	5.2	29.7

^[a] Toluene (50 mL, 0.47 mol) was oxidized in a 500-mL stirred autoclave at 463 K and 1.0 MPa O₂ for 2 h on 1.0 g catalyst, which was supported on γ -Al₂O₃ unless otherwise noted.

^[b] Numbers in square brackets and parentheses are the molar ratios of two metals and the weight % of metal to support.

^[c] Reaction time 4 h.

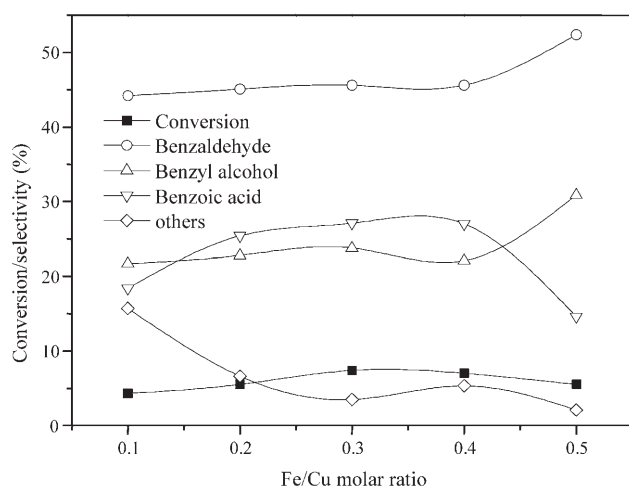


Figure 1. The effect of the Fe/Cu molar ratio. *Reaction conditions:* toluene 50 mL; catalyst 1.0 g; reaction temperature 463 K; reaction pressure 1.0 MPa O₂; reaction time 2 h.

terized by high selectivity for benzaldehyde + benzyl alcohol (>92%) and low selectivity for benzoic acid (<8%). In particular, pyridine promoted the reaction with 86% selectivity for benzaldehyde after 2 h of reaction at 7.3% conversion of toluene, which is the same as the original activity (7.4%). These catalytic performances were similar to or better than those obtained in the gas phase oxidation of toluene.

The preferential desorption of adsorbed benzaldehyde by pyridine could be responsible for the selectivity increase for benzaldehyde. Accordingly, we conducted competitive adsorption experiments with benzaldehyde, pyridine, and a mixture of both on the catalyst surface in toluene solution. As shown in Figure 2, the adsorbed amount of pyridine was almost two times more than that of benzaldehyde when they were adsorbed separately. On competitive adsorption, however, pyridine

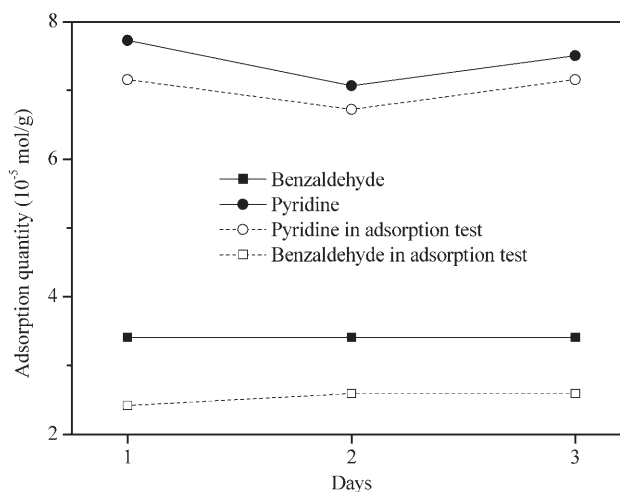


Figure 2. The competition tests.

was preferentially adsorbed on the catalyst over benzaldehyde. The amount of pyridine adsorbed did not vary while that of benzaldehyde decreased to 30% of that in the single component experiment. It can be concluded from the above experiments that the weakly bonded benzaldehyde on the catalyst surface is expelled by pyridine, which is more strongly held on the catalyst surface. 3-Methylpyridine ($pK_a=5.80$) is more basic than pyridine ($pK_a=5.67$) and thus expected to adsorb more strongly.

In Figure 3 are shown the time courses of the reaction catalyzed by a 10 wt % CuFe (1:0.3)/ γ -Al₂O₃ (lower), and its homogeneous counterpart of a copper and iron nitrate mixture (1:0.3 in mole) (upper). Benzyl hydroperoxide was not detected by iodometry in the heterogeneous reaction media at the early stages of reaction although it is reported in the literature on the homogeneous catalysis reaction.^[25] Because of the preferential formation of unidentified products as detected by GC, the

Table 3. The effect of different additives.^[a]

Additives ^[b]	Conversion (%)	Product distribution (%)			
		CHO	CH ₂ OH	COOH	Others
None	7.4	45.6	23.8	27.1	3.5
Phenol	0.34	83.5	0	0	16.5
3-Methylpyridine	2.0	63.7	36.3	0	0
Acetic Acid	5.6	25.8	33.1 (27.6) ^[c]	41.0	0
Pyridine	7.3	85.9	6.1	8.1	0
1,1,2,2-Tetrabromoethane	9.2	18.8	14.5	60.9	5.8
NBS ^[d]	31.0	18.7	9.1	61.2	11.0

^[a] Reaction conditions are the same as those of Table 1.

^[b] Molar ratio of toluene to additive is 100.

^[c] The number in the parentheses is the selectivity of benzyl acetate.

^[d] *N*-Bromosuccinimide.

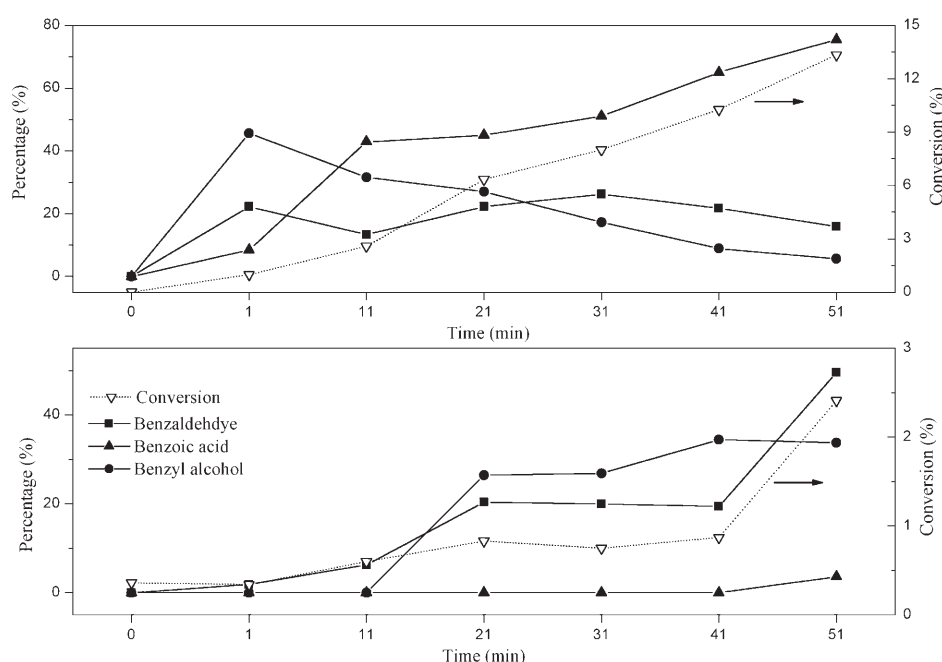


Figure 3. Time-course of reactions over CuFe/γ-Al₂O₃ (lower) and a homogeneous catalyst (upper). Reaction conditions: toluene 50 mL; CuFe (1:0.3)/γ-Al₂O₃ 1.0 g; reaction temperature 463 K; reaction pressure 1.0 MPa O₂; reaction time 2 h.

sum of selectivities was almost zero at the early stage of the reaction. As the reaction proceeded, the amount of unidentified products decreased and oxidation products at the benzylic position were produced. The product distribution among the oxidation products in the heterogeneous reaction was quite different from that in the homogeneous reaction. Adsorption of the reaction products on the heterogeneous catalyst may account for this difference. Compounds having an acidic proton such as benzyl alcohol and benzoic acid should be strongly held on the heterogeneous catalyst, as compared with benzaldehyde. Consequently, benzaldehyde was observed at the early stage of reaction while benzyl alcohol and benzoic acid were not. It should be noted

that the rate of reaction (slope of conversion vs. time) increased with time in the case of the heterogeneous reaction although it was constant in the homogeneous case. This result suggests that the reaction intermediates are accumulating on the heterogeneous catalyst. The accumulating intermediates will surely speed up the reaction rate through enhancing the extent of desorption of benzaldehyde.

In Figure 4 are shown the reusability tests of catalyst. In the reusability test, a used catalyst was washed with ethanol and deionized water, and then employed for another reaction. After the catalyst was used for four times, the conversion of toluene and the selectivity for benzaldehyde (column 4 in Figure 4) still remained compara-

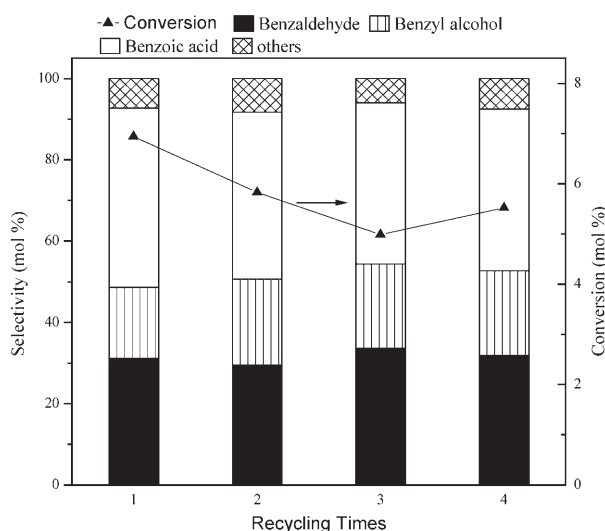


Figure 4. Catalyst reusability tests. *Reaction conditions:* toluene 50 mL; CuFe (1:0.3)/ γ -Al₂O₃ 1.0 g; reaction temperature 463 K; reaction pressure 1.0 MPa O₂; reaction time 2 h.

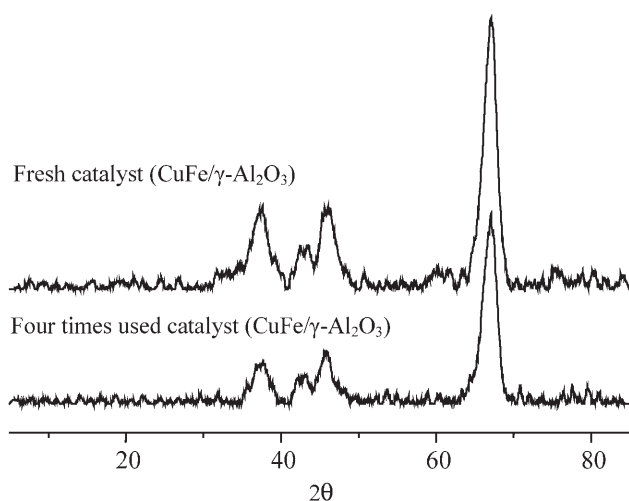


Figure 5. The XRD spectra of fresh catalyst and four times used catalyst.

ble to the values of the first run (column 1 in Figure 4). Figure 5 shows the recorded XRD spectrum, which indicates that the main characteristics of the catalyst were preserved during recycling and reuse.

Conclusion

In summary, following conclusions are drawn from these studies:

- An activity of 7.4% and more than 90% selectivity of oxidized products at the benzylic position were obtained in liquid phase oxidation of toluene on a copper-iron binary metal oxide catalyst at 463 K

and 1.0 MPa of oxygen pressure for 2 h. At the long reaction time of 4 h, the conversion increased to 25.4% and benzoic acid became the predominant reaction product at 71.6%.

- A small amount of polar additives caused a dramatic change in conversion and selectivity. Pyridine improved the selectivity for benzaldehyde to 86% while conversion retained at 7.3% for 2 h. It was found that pyridine was more strongly held on the catalyst surface than benzaldehyde and thus prevented further oxidation of benzaldehyde.
- The catalyst was reusable after washing and drying. After the catalyst had been used four times, about 95% conversion of toluene and 97% selectivity for benzaldehyde are still maintained with respect to their original values.

Although further researches will be required for applications of the copper-oxide based catalyst system in synthesizing benzaldehyde, such an impressive activity and selectivity, as we have showed here, opens a new possibility for activating *sp*³ hybridized carbon atoms of inactive hydrocarbons to synthesize the corresponding aldehydes through heterogeneous catalysis with molecular oxygen in the liquid phase.

Experimental Section

Catalyst Preparation and Characterization

The γ -alumina support was impregnated with an aqueous solution of metal nitrate(s) according to the metal-to-metal ratio and metal weight %, as listed in Table 1, using the incipient wetness method. After impregnation, the samples were dried at 393 K and then calcined at 823 K for 3 h in a quartz tube for transformation to the oxides.

X-ray powder diffraction patterns of the catalysts were recorded on a Rigaku Miniflex with CuK α radiation ($\alpha = 0.1542$ nm) at 30 kV and 15 mA. The pore diameter and the BET surface area were characterized using a Micromeritics ASAP 2000 Physi/Chemisorption apparatus. The γ -Al₂O₃-supported catalysts have a mean pore diameter of 66 Å and a specific surface area of 233 m²/g (BET).

Catalytic Reaction

The oxidation reactions were carried out in a 500-mL stirred autoclave at 463 K and 1.0 MPa of oxygen atmosphere. In a typical reaction, toluene (50 mL, 0.47 mol) and catalyst (1.0 g) were charged into the reactor. The autoclave was heated up to a set temperature in a nitrogen atmosphere. At the set temperature, nitrogen was replaced with oxygen and the reaction started. After a certain reaction time interval, products were analyzed by an HP-4890 gas chromatograph and quantified using the internal standard 1,2,4,5-tetramethylbenzene (durene). The internal standard was added to samples before injection into GC.

The data of saturated vapor pressure and explosive limits for toluene in air and oxygen atmosphere were carefully calculated before we launched the reaction. The explosive limit for toluene is 1.27–7.75% (volume ratio). Equation (1) used for this purpose is as follows with y standing for the saturated vapor pressure and x for the temperature ($^{\circ}\text{C}$):

$$y = -1.00256 + \frac{202159.14701}{152.60722 \times \sqrt{\frac{\pi}{2}}} e^{-\frac{(x-275.50787)^2}{152.60722^2}} \quad (1)$$

Based on the calculated data, the toluene oxidation reaction under 10 atm oxygen or air pressure at 190°C will fall into the lower explosive limit zone and thus is a safe reaction in the laboratory.

Competitive Absorption

Amount of absorption was determined using three stock solutions of benzaldehyde (4.8 mM), pyridine (6.2 mM), and a mixture of benzaldehyde and pyridine (4.8 and 6.2 mM, respectively), in toluene solution with an internal standard of durenene (10.7 mM). Catalyst (0.5 g) was added to 10 mL of the stock solutions, and the concentration of each component was monitored by GC at a time intervals of 1, 2 and 3 days.

Acknowledgements

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