

Fullerene-based ruthenium catalysts in cinnamaldehyde hydrogenation

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Ruthenium on fullerenes and ruthenium and palladium on activated carbon were compared for their catalytic activity and selectivity in cinnamaldehyde hydrogenation. The fullerene support had a marked effect on the selectivity, even though the fullerenes themselves showed no catalytic activity.

Keywords: fullerenes, ruthenium, cinnamaldehyde, cinnamylalcohol, hydrocinnamaldehyde, hydrogenation

1. Introduction

Fullerenes have recently been reported to act as hydrogen shuttles, and have been proposed as catalysts for hydrogenation [1–3]. Fullerene–alkali-metal compounds have been found to possess catalytic properties resembling those of platinum and palladium, which are common metals in hydrogenation catalysts [4]. The organometallic polymer $C_{60}Pd_n$, prepared by Nagashima and co-workers [5], was active in the catalytic hydrogenation of olefins and acetylene [6]. The properties and catalytic potential of ruthenium–fullerene compounds as hydrogenation catalysts have been discussed by Wohlers and co-workers [7]. The insoluble ruthenium/nanotube catalyst, which contains fullerenes, proved active in liquid-phase cinnamaldehyde hydrogenation [8].

The catalytic properties of fullerenes have also been studied in reactions other than hydrogenation. Lohen et al. [9] report that fullerenes catalyse the oxidation of organic solvents, and Claridge et al. [10] have developed a new catalyst with fullerenes as a ligand for the hydroformylation of alkenes.

In this work, we present measurements describing the “activity and selectivity” of fullerenes and ruthenium–fullerene catalysts in cinnamaldehyde hydrogenation. The properties are compared with those of commercial ruthenium and palladium catalysts under various reaction conditions. Because fullerenes and ruthenium–fullerene catalysts partially dissolve [11–13] in the conditions of the test reaction, we also measured the solubility of fullerenes and the ruthenium–fullerene catalysts in cinnamaldehyde alone and in cinnamaldehyde with various solvents.

2. Experimental

Ruthenium on fullerene catalysts were prepared by the impregnation of fullerenes (C_{60} ultra-pure, Materials and Electrochemical Research (MER) Corporation, AZ, USA) with solutions of ruthenium(III) acetylacetonate (Strem, Inc.) and bis(cyclopentadienyl) ruthenium (Strem, Inc.) in ethanol with a known ruthenium concentration. After the impregnation, the samples were dried at 373 K. These catalysts, the commercial ruthenium supported on activated carbon catalyst (5% Ru/C, Strem, Inc.) and catalysts obtained from Helsinki University of Technology (4% Ru/C and 5% Pd/C) were reduced at 537 K (fullerene-based catalysts) and 673 K (others) under flowing H_2 . A temperature-programmed reduction (TPR) analysis was made to determine optimal reduction temperature. Metal contents of the catalysts were measured by neutron-activation analysis before and after the test reaction. Metal concentrations were also measured for some of the reaction products.

Cinnamaldehyde (Merck, purity 99%), solvent and catalyst were loaded into a 138 cm³ autoclave under inert atmosphere. The reaction was performed at 333–393 K under 1–40 bar H_2 pressure and at stirring speed of 750 rpm. The reaction mixture was cooled in liquid nitrogen to prevent further hydrogenation, and the samples were removed. The reaction mixture was separated from the catalyst by centrifugation. Reactant and products were analysed with a gas chromatograph (Hewlett-Packard 5890) equipped with a temperature program, a flame-ionization detector and an integrator. The GC column was SE-30 with 25 m length and 0.32 mm diameter. Response factors were determined for cinnamaldehyde, ethanol and all hydrogenation products. One response factor was used for the two acetals. Naphthalene was used as internal standard. The response factors were found to be linear at the concentration levels studied.

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The conversions in hydrogenation were calculated from the concentration of hydrogenation products (acetals excluded). Total conversions were calculated from the amount of reacted cinnamaldehyde. Selectivities were calculated from the expression $S_i = n_i / \sum n_i$, where n_i is the mol amount of the substance and $\sum n_i$ the total mol amount of the products formed.

Solubilities of fullerenes and 5% Ru/C₆₀ catalysts were measured by gravimetric and absorbency methods. The absorbency measurements were carried out with a UV spectrophotometer. The solubility was calculated from the absorbency values at 328 nm [11].

3. Results and discussion

3.1. Metal determination

Before the test reaction, the ruthenium content of the prepared fullerene catalysts 5% Ru/C₆₀ was the same as that of the commercial catalyst 5% Ru/C, but after the hydrogenation, the ruthenium content of the 5% Ru/C₆₀ was increased to about 10%. The increase was probably due to the partial dissolving of fullerenes during the reaction (see section 3.3), or the support C₆₀ might be hydrogenated. When the 5% Ru/C and 5% Ru/C₆₀ catalysts were used in the catalysis experiments, the ruthenium concentration in the reaction mixture after separation of the catalyst by filtration and centrifugation were 5.5 and 11.5 ppm, respectively. This corresponds to 1 and 2% of the catalyst ruthenium used in the experiment. When the 5% Pd/C catalyst was used, the concentration of palladium in the reaction

mixture was less than 2 ppm corresponding to less than 0.5% of the palladium used.

3.2. Reduction of the catalysts

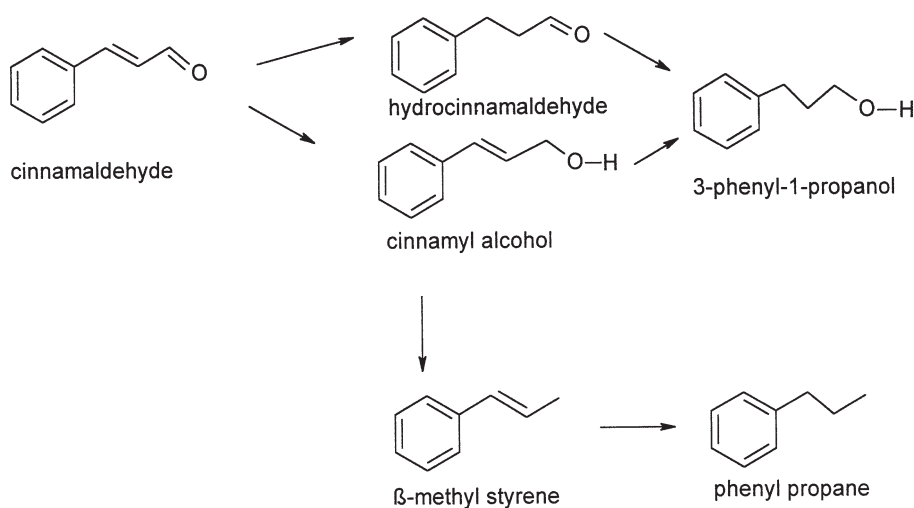
After the impregnation and drying, the ruthenium complexes ruthenium(III) acetylacetonate and bis(cyclopentadienyl) ruthenium on fullerene were reduced with hydrogen at 573 K. Both complexes and, also, the fullerenes alone are relatively volatile. The bis(cyclopentadienyl) ruthenium was found to sublime before and during the reduction. If the reduction temperature was under 573 K, the amount of ruthenium reduced was insignificant. The ruthenium(III) acetylacetonate on the fullerene was reduced with hydrogen at 573 K, and this catalyst was used for the further investigations.

Temperature-programmed reduction (TPR) analysis showed 673 K to be best reduction temperature for the 5% Ru/C catalyst, and 673 K was also used in the reduction of the other catalysts on activated carbon (4% Ru/C, 5% Pd/C).

3.3. Solubility of fullerenes and of ruthenium on fullerenes

Fullerenes dissolve in most organic solvents. We used gravimetry and absorbency measurements to determine the solubilities of fullerene and 5% Ru/C₆₀ catalyst in cinnamaldehyde and selected solvents (table 1). For fullerene solubility in toluene, the value obtained from absorbency measurements (2.9 mg/g) agrees well with the value given in the literature (2.8 mg/ml) [14]. Ajie et al. [12] report similar values for the solubility of a mixture of C₆₀

(a) Cinnamaldehyde hydrogenation by using Ru/C and Ru/C₆₀ catalysts



(1)

(b) Cinnamaldehyde hydrogenation by using Pd/C catalyst



Table 1

Solubilities of fullerenes measured by gravimetry and absorbance method.

Catalyst	Solvent ^a	Solubility ($\mu\text{g/g}$)	
		gravimetry	absorbance
C ₆₀	Toluene	4833	2917
C ₆₀	CAL	1670	2019
C ₆₀	Ethanol	324	55
C ₆₀	CAL : ETH (1 : 1)	3412	2990
5% Ru/C ₆₀ (after test reaction)	CAL : ETH (1 : 1)	5272	8245
5% Ru/C ₆₀ (after test reaction)	CAL : THF (1 : 3)	4595	4871

^a CAL = cinnamaldehyde, ETH = ethanol, THF = tetrahydrofuran. Density of CAL : ETH (1 : 1) = 0.9263 g/cm³. Density of CAL : THF (1 : 3) = 0.9359 g/cm³.

and C₇₀ in benzene (about 5 mg/ml at 25 °C). Meier and Selegue [13] employed toluene solutions saturated with fullerenes, and they report a concentration of ca. 0.6–8 mg/ml. We found the solubility of fullerenes to be lower in ethanol than in cinnamaldehyde, but a mixture of cinnamaldehyde and ethanol dissolved more fullerenes than cinnamaldehyde alone. Probably the acetals formed in the reaction (see equation (2)) also dissolved fullerene.

The amount of fullerenes dissolved was also measured after the reactions. A greater amount of fullerenes was dissolved after than before the reaction, evidently due to (a) hydrogenated products that also dissolve fullerene, (b) high pressure (40 bar, other solubility measurements at 1 bar), and (c) high temperature (60 °C, other measurements at 25 °C). We note, however, that in the investigation of Ruoff et al. [14] the solubility maximum was near room temperature (about 280 K) for all solvents studied.

Krätschmer et al. [15] have shown that fullerenes do not dissolve in ether. An ether with high boiling point would thus be eminently suitable as a solvent. Unfortunately,

fullerene also dissolved in a mixture of cinnamaldehyde and tetrahydrofuran. Although in our experiments the ratio of cinnamaldehyde to tetrahydrofuran (1 : 3) was higher than that of cinnamaldehyde to ethanol (1 : 1), the solubilities were in the same range. Thus, tetrahydrofuran offered no help.

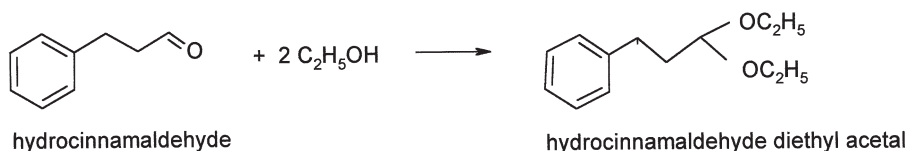
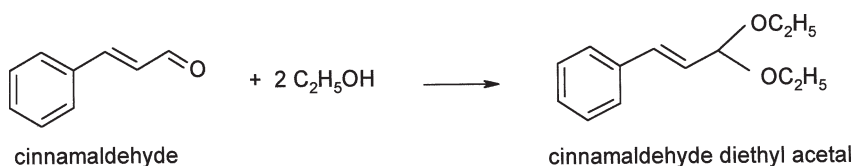
3.4. Reaction of cinnamaldehyde

The following products were formed when Ru/C catalysts were used in the hydrogenation of cinnamaldehyde: hydrocinnamaldehyde, cinnamyl alcohol, methyl styrene, phenyl propane, and 3-phenyl-1-propanol. In addition, when ethanol was used as the solvent, two acetals, hydrocinnamaldehyde diethylacetal and cinnamaldehyde diethylacetal were present. With 5% Pd/C and ethanol, only hydrocinnamaldehyde and hydrocinnamaldehyde diethylacetal were formed. The products formed in the hydrogenation of cinnamaldehyde with 5% Ru/C₆₀ catalyst were the same as those formed with Ru/C catalyst. Fullerenes alone showed no catalytic activity for cinnamaldehyde hydrogenation.

3.5. Conversion of cinnamaldehyde

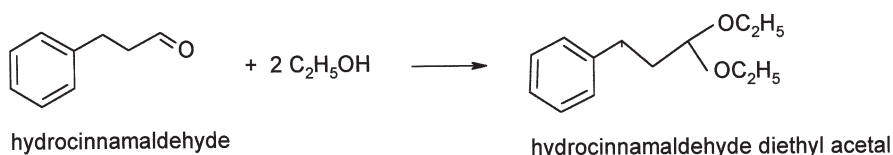
Cinnamaldehyde was hydrogenated at temperatures 313–373 K and pressures 1–100 bar in order to find the reaction conditions supporting conversions of 5–30%. This conversion range was chosen for comparison of the activity of the catalysts because (a) at low conversion level, the error in the GC analysis is relatively large, (b) at lower conversion level, the conversion due to the acetal formation (non-catalytic reaction) is greater than the conversion due to hydrogenation, (c) at higher conversion level, the differences in the conversions are small and it is difficult to control the temperature of the exothermic reaction. We found that 40 bar and 60 °C

(a) Acetal formation by using Ru/C and Ru/C₆₀ catalysts



(2)

(b) Acetal formation by using Pd/C catalyst



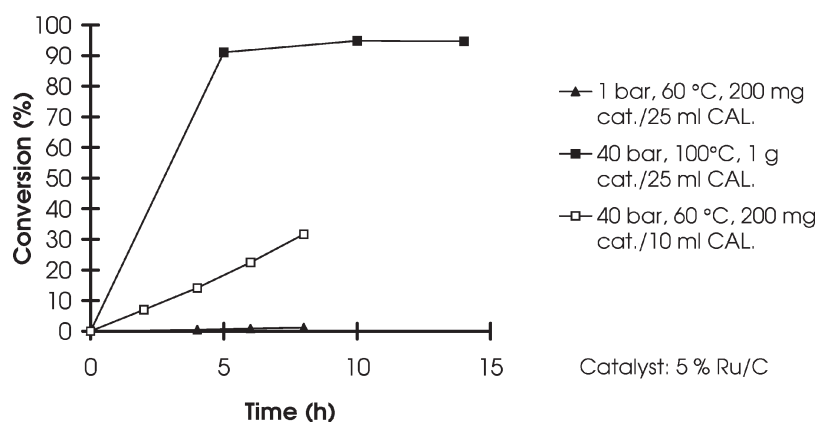


Figure 1. Conversion of cinnamaldehyde with the 5% Ru/C catalyst under various reaction conditions.

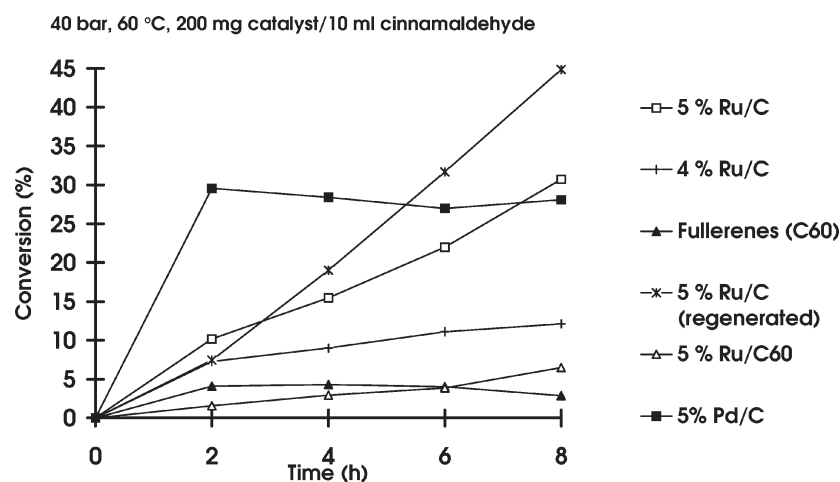


Figure 2. Conversion of cinnamaldehyde as a function of time with various catalysts.

are suitable conditions for the comparison of the catalysts when the catalyst to cinnamaldehyde ratio is 0.02. Under these conditions, the conversions were 5–30% (figure 1).

The conversions of cinnamaldehyde in hydrogenation with different catalysts are shown in figure 2. Conversion in the cinnamaldehyde hydrogenation catalysed by the prepared 5% Ru/C₆₀ catalyst was low, but could probably be improved through the optimization of the reducing conditions.

When fresh catalysts were used, the 5% Ru/C catalyst was more active than the 4% Ru/C catalyst. Moreover, when reusing the catalyst a second time, the regenerated 5% Ru/C catalyst converted more cinnamaldehyde than the fresh one, probably because the catalyst thus was twice reduced.

With the Pd/C catalyst, the conversion of cinnamaldehyde increased during the two first hours to 30%, which was a conversion value much higher than that obtained by the Ru/C catalysts. After two hours, however, the Pd/C catalyst was no longer active, and after a further six hours, the conversion stayed constant and different from the Ru/C catalysts that stayed active to the end of the experiment by increasing the conversion to 45%.

When ethanol was used as solvent and no catalyst was added, the conversion (3–4%) was due to the reaction between cinnamaldehyde and ethanol. When fullerenes were tested as catalyst, the conversion was at the same level (3–4%) as when no catalyst was used. Acetals were formed at all pressures tested.

There were no significant differences between the ruthenium catalysts in the acetals formation: all seemed to

Table 2
Comparison of catalysts performance in cinnamaldehyde hydrogenation.
The conversions are for 8 h reaction time at 333 K and 40 bar.

Catalyst	Solvent	Conversion in hydrogenation (%)	Turnover number ^a $n_{\text{CAL}}/n_{\text{M}}$	Total conversion (%)
5% Ru/C ₆₀	Ethanol	6	47	7
5% Ru/C	Ethanol	32	252	34
5% Ru/C, after regeneration	Ethanol	42	331	45
4% Ru/C	Ethanol	10	99	12
5% Pd/C	Ethanol	17	141	28
5% Ru/C	—	12	95	12

^a Results are given in mole of cinnamaldehyde hydrogenated per mole of metal in the catalyst.

produce both cinnamaldehyde diethylacetal and hydrocinnamaldehyde diethylacetal. In contrast, with the Pd/C catalyst only hydrocinnamaldehyde diethylacetal seemed to be formed. The amount of acetal with the 5% Pd/C catalyst was, nevertheless, higher than the total amount of acetals with the Ru/C catalysts. The explanation for this different formation of acetals eludes us at the moment.

Hydrogenations of cinnamaldehyde performed in ethanol and without ethanol showed that ethanol increased the conversions of the hydrogenation. Table 2 summarizes the total conversions of cinnamaldehyde after 8 h reaction time with various catalysts and reaction conditions.

3.6. Selectivities of cinnamyl alcohol and hydrocinnamaldehyde

The selectivities for cinnamyl alcohol and hydrocinnamaldehyde were affected by the reaction conditions and the properties of the catalysts.

The selectivity of cinnamyl alcohol by using Ru catalysts varied with the conversion level, as can be seen from figure 3. When 5% Ru/C was used as catalyst, the maximum selectivity for the cinnamyl alcohol was 30%. Conversions were then 15–40%.

Comparison of the different catalysts showed both the support and the dramatically active metal to affect the selectivity. The selectivity of cinnamyl alcohol by using 5% Ru/C₆₀ was 60%, when the conversion was 7%. When other Ru/C catalysts were used, the cinnamyl alcohol selectivity was less than 30% on the same conversion. No cinnamyl alcohol was formed when 5% Pd/C catalyst was used.

Similar results were obtained by Plainex et al. [8]. They found ruthenium/nanotube catalyst, which contains fullerenes, to be highly selective for cinnamyl alcohol (up to 92%). Under the same conditions, and with the use of Ru/Al₂O₃ catalysts with similar-sized Ru particles, the selectivity was only 20–30%. The high selectivity for cin-

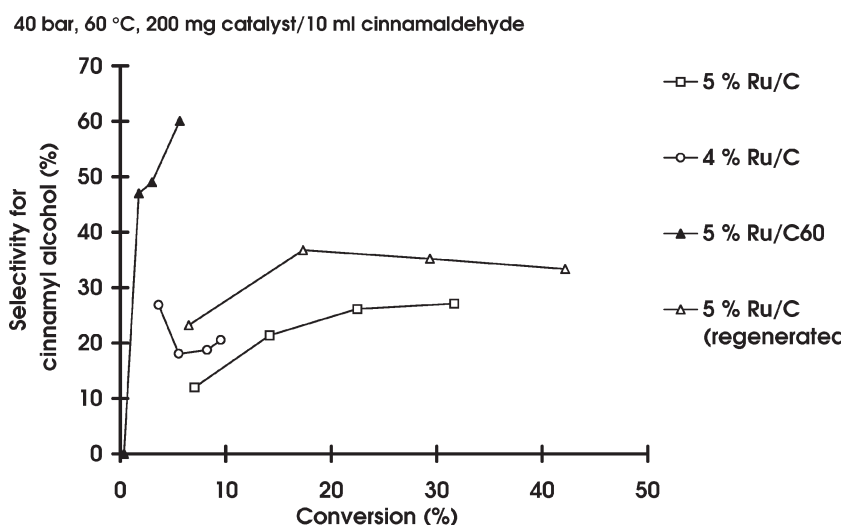


Figure 3. Selectivity for cinnamyl alcohol with the various catalysts, plotted as a function of the conversion. The conversion is calculated only from the hydrogenation.

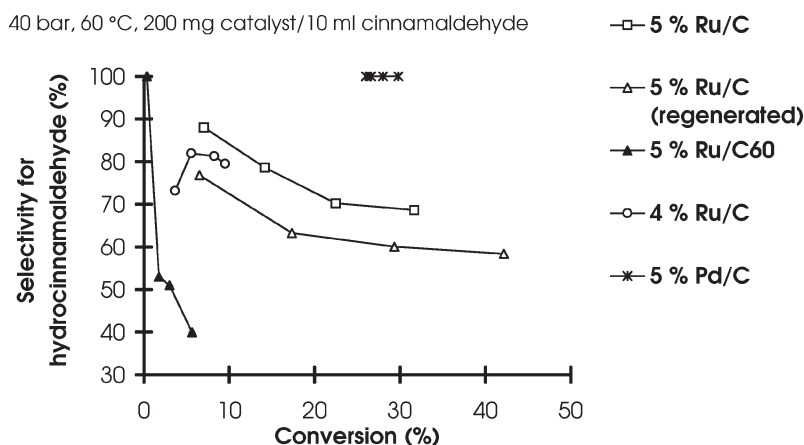


Figure 4. Selectivity for hydrocinnamaldehyde with various catalysts, plotted as a function of the conversion. The conversion is calculated only from the hydrogenation.

namyl alcohol with fullerene-based catalysts shows that fullerene favours the C=O bond hydrogenation. The types of π -conjugated carbon cages of C₆₀ (C=C bond) could explain this phenomenon. The metal cluster size of ruthenium on fullerenes and, also, the bond strength between ruthenium and C₆₀ affect the adsorption of cinnamaldehyde and the hydrogen.

The selectivities for hydrocinnamaldehyde obtained with different catalysts are compared in figure 4. At 7% conversion, the selectivity was 40% when 5% Ru/C₆₀ was used, and between 80% and 90% with the other ruthenium catalysts. The selectivity decreased with increasing conversion when ruthenium catalysts were used. The selectivity for hydrocinnamaldehyde at all measured conversions was 100% when 5% Pd/C provided the catalyst.

At low conversion level, the ratio of cinnamyl alcohol to hydrocinnamaldehyde increased with the conversion when ruthenium catalysts were used. This means that the hydrocinnamaldehyde was reacting to 3-phenyl-1-propanol and acetal faster than cinnamyl alcohol reacted to 3-phenyl-1-propanol and hydrocarbon products. At high conversion level, the ratio of the selectivity for cinnamyl alcohol to the selectivity for hydrocinnamaldehyde decreased and reached zero at the conversion level of 98%. This means that the cinnamyl alcohol reacted faster to 3-phenyl-1-propanol, methylstyrene and phenylpropane than did hydrocinnamaldehyde to 3-phenyl-1-propanol.

4. Conclusions

The fullerene-based ruthenium catalyst differed markedly from the other ruthenium catalysts in its selectivity in cinnamaldehyde hydrogenation. The fullerene-based ruthenium catalyst favoured hydrogenation of the C=O bond, while the activated carbon-based ruthenium catalysts mostly hydrogenated the C=C bond.

Likewise, the metal had a marked effect on selectivity in cinnamaldehyde hydrogenation. When ruthenium-based catalysts were used, both cinnamyl alcohol and hydrocinnamaldehyde were formed. With palladium catalyst, only hydrocinnamaldehyde was present in the products.

The fullerenes partially dissolved in cinnamaldehyde and the solvents tested. The solubility was lower in the ethanol than in cinnamaldehyde, but addition of solvent (ethanol or

tetrahydrofuran) to cinnamaldehyde increased the solubility. The solubility results obtained by gravimetry and by absorbency method were similar. Work is now in progress to prepare insoluble fullerene-based catalysts.

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