

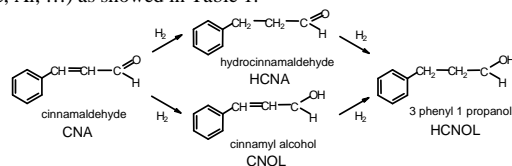
# Promoted Cobalt Supported Over Carbon Nanotubes For the Cinnamaldehyde Hydrogenation

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## Introduction

Carbonaceous supports, such as graphites or activated carbons; have been successively used for years by our team for the cinnamaldehyde hydrogenation [1] and for other hydrogenation or oxidation reactions. Only few works have been published on the cinnamaldehyde hydrogenation (Fig. 1) reaction using carbon nanotubes (CNT) as catalyst support [2,3]. In these cases, noble metals were used as active sites and the authors noted that the use of CNT produced selectively the unsaturated aldehyde (HCNA). In order to change the reaction selectivity we decided to use modified cobalt supported CNT as catalysts. We present, in this abstract, the results obtained using three supports containing various amount of promoters (Fe, Al, ...) as showed in Table 1.



**Figure 1.** Reaction scheme for cinnamaldehyde hydrogenation

From a fundamental point of view, the hydrogenation of an unsaturated carbonyl compound generally produces a saturated carbonyl compound; an important challenge is to obtain the unsaturated alcohol with high selectivity. Such reactions are currently catalyzed by systems involving supported noble metals, such as Pt, Pd, Ru. However, noble metals are expensive and predominantly hydrogenate the C=C bond rather than the C=O group.

## Materials and Methods

The catalysts were prepared by an incipient wetness impregnation of Co nitrate on different carbonaceous supports (CNT, graphite, activated carbon or carbon fiber). Before test the catalyst was pre-reduced under hydrogen flow at 350°C. The catalytic reaction was carried out at atmospheric pressure in a batch reactor under a hydrogen flow (1 L h<sup>-1</sup>) at 140°C, using 1 mL of cinnamaldehyde, 0.5 g of catalyst dispersed in 25 mL of propylene carbonate. The reactants and products were analyzed by a GPC and a CPSIL 8 CB capillary column.

## Results and Discussion

Table 1 shows that, as described earlier by the teams of B. Coq [3] and M. Ledoux [2], the use of Pd supported on CNT leads to the selective formation of HCNA, which is not

the target product. On the other hand, when cobalt is supported over carbon material, the selectivity is greatly changed and two main tendencies can be underlined.

**Table 1. Catalytic properties of Co and Pd supported CNTs or other carbon phases.**

Catalyst	Time (h)	TTG (%)	Selectivity (%)					Initial speed mol. h <sup>-1</sup> .g <sup>-1</sup>
			HCNA	HCNOL	CNOL	Condensed products	Others	
Pd/B	0.6	98.9	93.1	12.7	0.0	0.0	0.0	2.3 x 10 <sup>-1</sup>
Co/Graphite	2.0	78.1	27.5	30.4	18.4	0.0	23.7	9.5 x 10 <sup>-3</sup>
Co/AC	2.5	81.7	33.1	31.4	4.4	0.0	31.2	7.9 x 10 <sup>-3</sup>
Co/CF	9.7	83.8	38.6	26.4	6.2	0.0	28.9	2.2 x 10 <sup>-3</sup>
Co/A	2.0	84.3	16.9	27.4	17.8	10.4	27.5	1.1 x 10 <sup>-2</sup>
Co/B	4.1	96.0	2.1	12.2	4.8	19.4	61.6	5.6 x 10 <sup>-3</sup>
Co/C	8.5	98.3	9.1	35.3	1.1	10.1	44.4	5.9 x 10 <sup>-3</sup>

A: CNT without promoters; B: CNT with 2 wt % Fe and 2.35 wt % Al; C: CNT with 1.4 wt % Fe, AC: Activated Carbon and CF: Carbon Fiber. Metal content : 5wt% Pd and 7 wt% Co.

Firstly, the use of CNT as support of Co (compared to other carbonaceous supports) for the hydrogenation of cinnamaldehyde clearly changes the selectivity of the reaction and unfavors the HCNA formation and the main primary product is CNOL which is further hydrogenated to HCNOL. Secondly, these catalysts, when they are promoted by Fe and Al, favor the formation of condensed products [4] and "other products" which were assigned by GC-MS to the reaction of HCNOL with propylene carbonate (solvent). The proportion of these by products (1-phenylpropan propan-2 ol carbonate and 1-phenylpropan 2-methylethanol carbonate) depends of the amount of promoters added in the CNT. We suggest for that new reaction a bifunctional mechanism occurring over metal particles inside the CNT (confinement effect) for the hydrogenation and over the acid sites closed to the metal particles for the carbonate formation. The detailed results as well as the characterizations of the catalysts will be also discussed.

## Significance

The results evidence that modified cobalt CNT catalysts produce unsaturated alcohol and that this alcohol reacts further to form a new carbonate compound. A bifunctional mechanism over metal particles and acid sites should occur inside the channels of the CNT.

## References

- Barrault, J., Derouault, A., Martin, O., and Promier, S. ; *C.R. Acad. Sci. Paris, série IIc* p.507 (1999).
- Tessonier, J-P., Pesant, L., Ehret, G., Ledoux, M. J., and Pham-Huu, C. *Appl. Catal. A: General* 288, 203 (2005).
- Planeix, J. M., Coustel, N., Coq, B., Brotons, V., Kumbhar, P. S., Dutartre, R., Geneste, P., Bernier, P., and Ajayan, P. M. *J. Am. Chem. Soc.* 116, 7935 (1994).
- Barrault, J., Derouault, A., Courtois, G., Maissant, J.M., Dupin, J.C., Guimon, C., Martinez, H., and Dimitriu, E. *Appl. Catal. A: General* 262, 43 (2004).