Carbon nanomaterials as efficient catalysts for organic reactions

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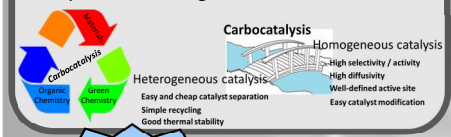
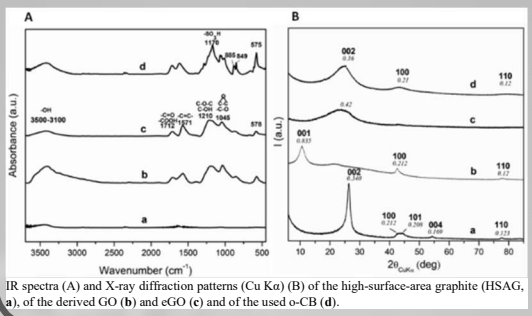
Introduction

The application of metal free catalysts has recently attracted growing attention due to the increasing need of sustainability in organic synthesis. In this context, the use of carbon nanomaterials as cheap catalysts (**carbocatalysts**) is an intriguing challenge, thanks to their properties (physical stability, accessibility, recyclability, easy handling, etc.), above all when an important building block can be obtained.



Carbocatalysts: Preparation and analysis



IR spectra (A) and X-ray diffraction patterns (Cu Kα) (B) of the high-surface-area graphite (HSAG, **a**), of the derived GO (**b**) and eGO (**c**) and of the used o-CB (**d**).

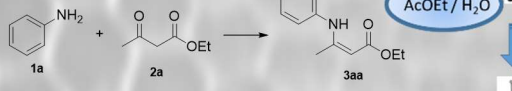
Table 1. Results of elemental analysis on the starting graphite and the derived oxidized samples.[a]

Sample	C (wt%)	H (wt%)	N (wt%)	O (wt%)	S (wt%)	O/C
Graphite	99.8	0.1	0.1	0.0	0.0	/
Carbon Black	97.8	0.3	0.1	1.8	0.0	0.02
GO	56.1	1.2	0.1	39.8	2.7	0.71
eGO	59.4	0.6	0.1	37.1	2.6	0.62
oCB[b]	50.3	2.3	0.1	41.7	5.7	0.83

[a] Elemental composition of the anhydrous samples: water contents of nearly 5 %wt. are evaluated by TGA for GO, eGO, and oCB. [b] The surface area of oxidized carbon black was 61 m^2/g

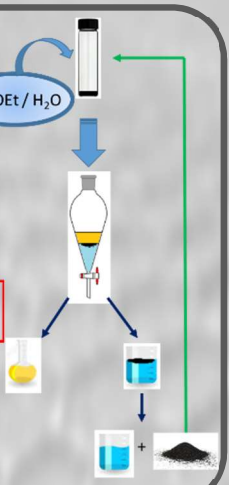
1 wt % (eGO or oCB) 5h/rt, solvent free

Reaction optimization



Entry	Catalyst (wt%) [a]	Time(hrs)	Yield (%)
1	-	3.5	29
2	eGO (5)	3.5	98
3	eGO (1)	5	96
4	oCB (1)	5	93
5	eGO (0.1)	24	88
6	oCB (0.1)	24	89
7[b]	oCB (1)	5	98

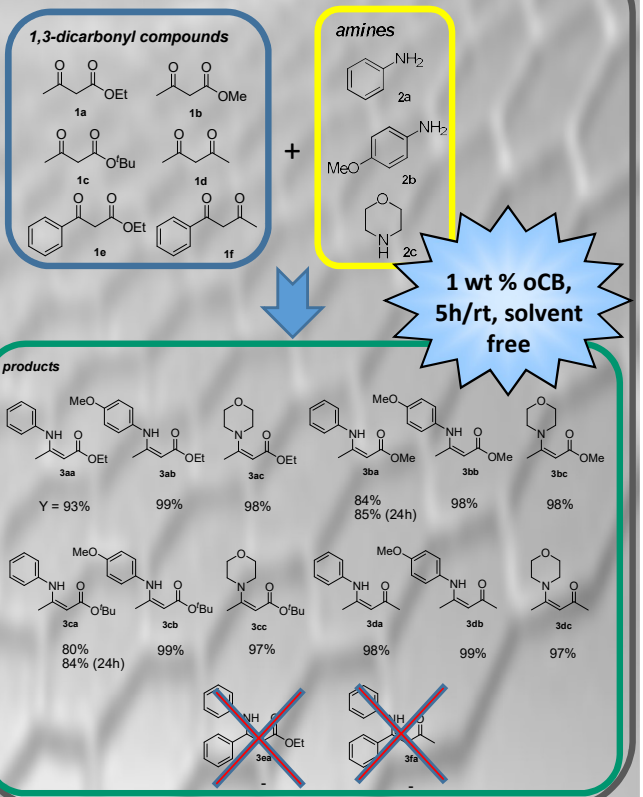
a) The wt% was calculated with respect to 1,3-dicarbonyl compound. b) The reaction was evaluated on a 10 times larger scale



Benefits:

- Extremely ecofriendly procedure (rt, solvent free, metal free, etc.)
- Small amounts of catalyst / High yields
- Very simple work up (H_2O/AcOEt)

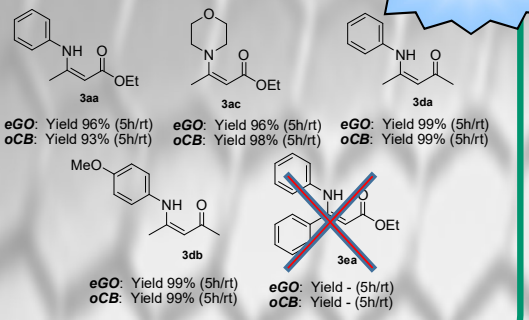
Substrate scope



1 wt % oCB, 5h/rt, solvent free

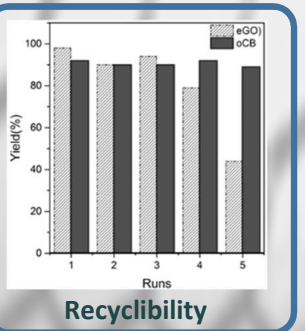
oCB VS eGO

1 wt % (eGO or oCB) 5h/rt, solvent free



Catalytic activity

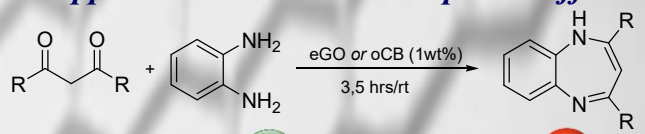
The reactions were very clean and the products were obtained in very good yields, in only 5hrs at room temperature. The yields were very high for aliphatic 1,3-dicarbonyl compounds but in the presence of aromatic substituents the reaction does not proceed at all also by prolonging the reaction time to 24h.



Recyclibility

While the eGO catalyst showed a drastically reduced activity after five runs, the oCB catalyst keeps its activity unchanged for all the cycles

An application: the benzodiazepine scaffold



R = alkyl ✓ R = aryl ✗

The elaborated methodology was conveniently exploited for the synthesis of the 1,5-benzodiazepine scaffold: in this case only 1wt% of oCB or eGO was sufficient to obtain the heterocyclic scaffold in quantitative yield at room temperature.

Conclusion & Future work

- eGO and oCB were effective catalysts for the synthesis of β-enamino-ketones and β-enamino-esters under very mild reaction conditions (low amounts of catalyst, room temperature, solvent free).
- An easy work up with AcOEt/H_2O was generally able to give pure products, so a very eco-friendly protocol is proposed.
- These heterogeneous catalysts can be recovered and recycled.
- The elaborated methodology was conveniently exploited for the synthesis of the 1,5-benzodiazepine scaffold.

New methodologies ??? New carbocatalysts ???

Ref.:
R. Villano, M. R. Acocella, G. Guerra *ChemistrySelect* **2017**, *2*, 10559