

Tuning Photocatalytic Activity of Carbon-Based Assemblies by their Morphology and Surface Functionalization

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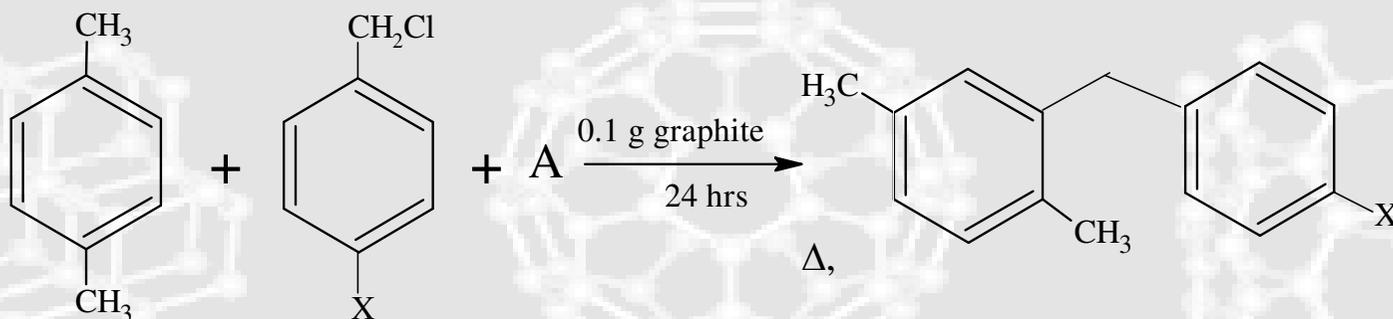
Outline

- Alkylation on commercial graphite and inactivity of purified carbons**
- Magnetite nanoparticles grown on carboxylated graphite as a catalyst for alkylation**
- Cyclohexene as promoter of benzylic oxidation and photooxidation on graphite**
- Morphology of carbonaceous materials and their photocatalytic activity**
- Tuning photocatalytic activity of graphite by modification with magnetite or silica nanoparticles**
- Linkers for non-destructive functionalization of carbons**

graphite

(10,10) tube

Commercial graphite catalyzes alkylation of *p*-xylene by *p*-substituted benzyl chloride which was sensitive to additives and the substituent in the chloride



X	Solvent (5 ml)	A	Yield of product (%)
COOH	Chloro benzene	---	No reaction
-CH ₃	Chloro benzene	---	83
-CH ₃	<i>p</i> -xylene	---	100
OCH ₃	Chloro benzene	---	37 (crude)
OCH ₃	<i>p</i> -xylene	---	47
NO ₂	Chloro benzene	---	No reaction
-H	Chloro benzene	Benzoic acid	22
-H	Chloro benzene	Acetic acid	No reaction
COCH ₃	<i>p</i> -xylene	---	100
OOCH ₃	<i>p</i> -xylene	---	No reaction

0.1 g graphite per
2 mmol of substituted
benzyl chloride

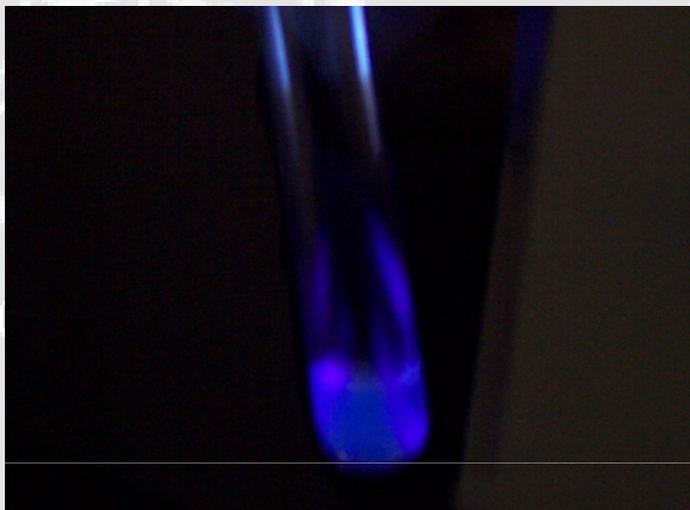
(Acid : substituted benzyl
chloride)

1 : 1

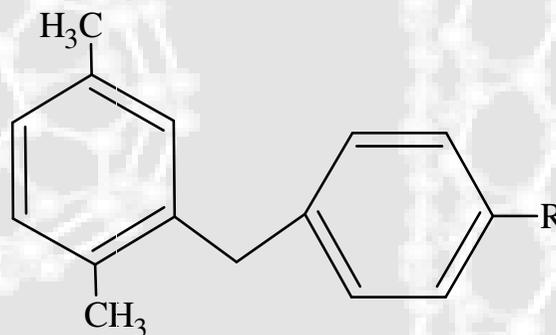
Sereda G.A. Alkylation on Graphite in the Absence of Lewis Acids. *T. Lett.*, **2004**, 45, 7265-7267.

Some of the alkylation products were able to detect explosives

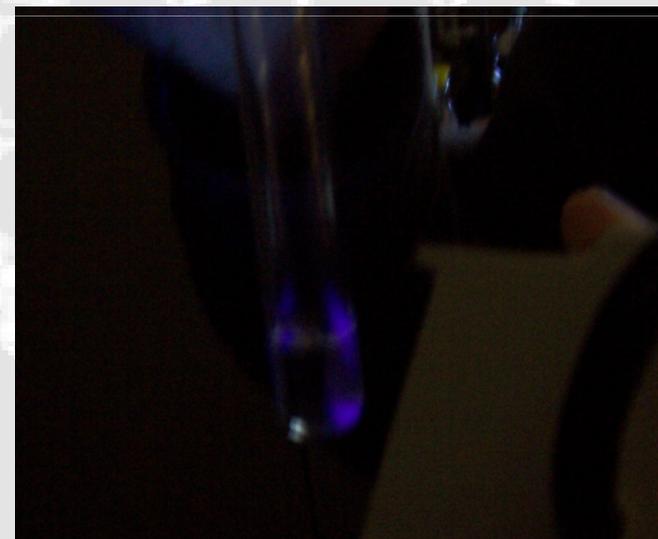
Synthesized compounds



R = -CH₃, -OH, -H, -OCOCH₃



After adding DNT (solution)



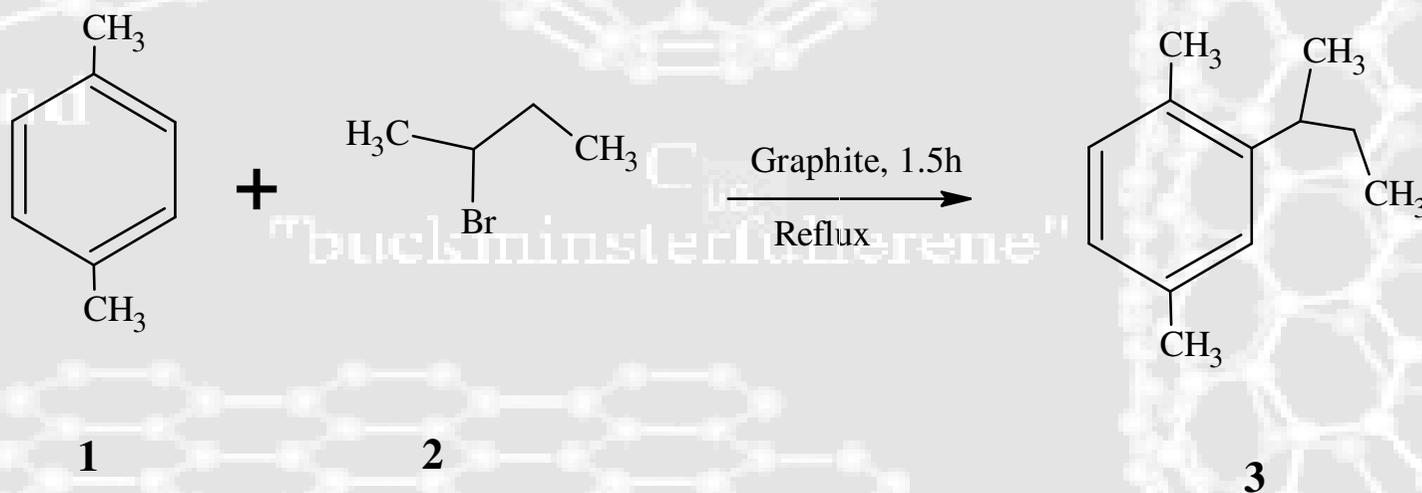
Fluorescent excitation at 365 nm for
2-(4-methyl benzyl), p-xylene

Fluorescence intensity :

-CH₃ > -OH > -H > -OCOCH₃

Graphite is a much more environmentally friendly alkylation catalyst, than traditional Lewis acids, which let us improve teaching green chemistry

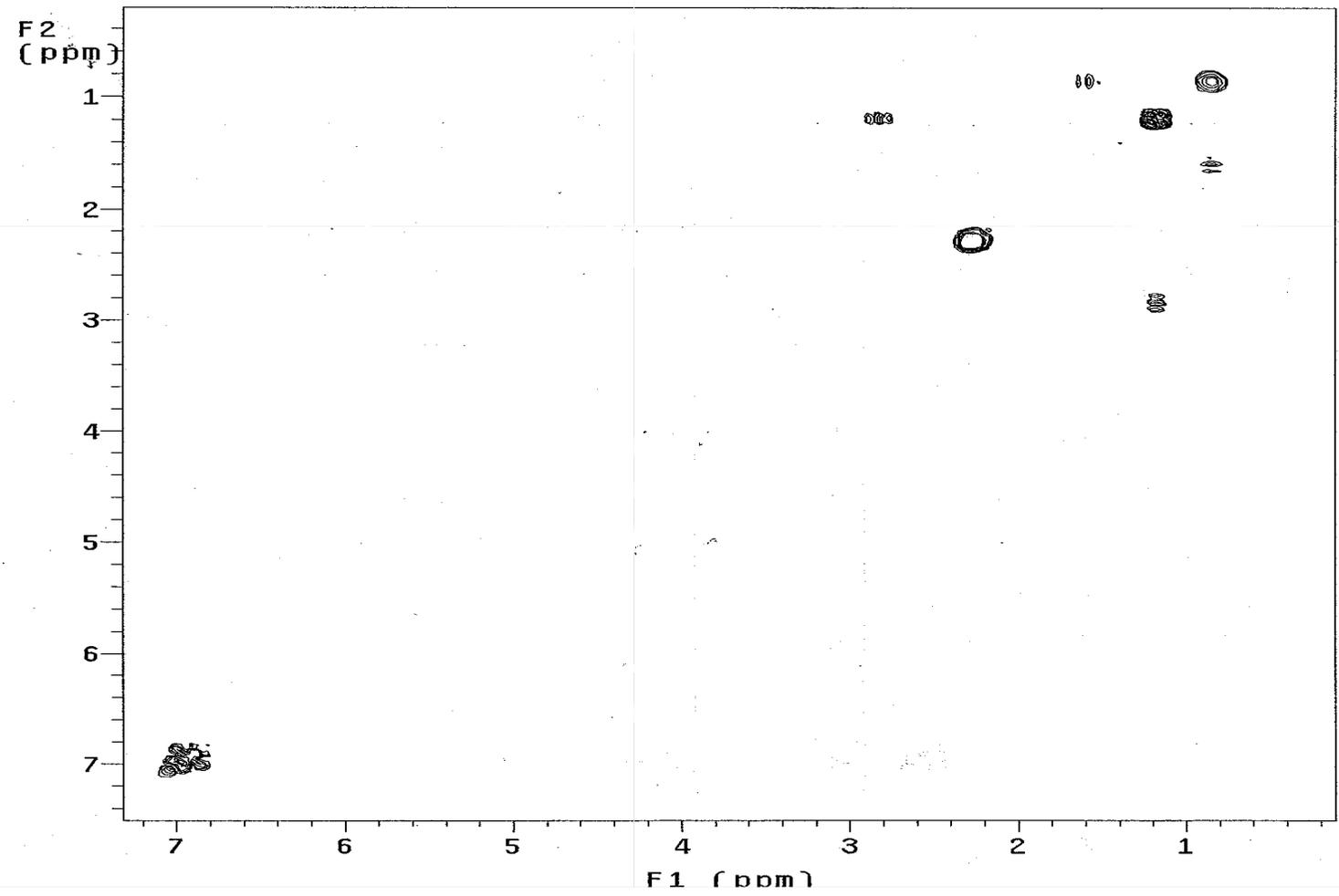
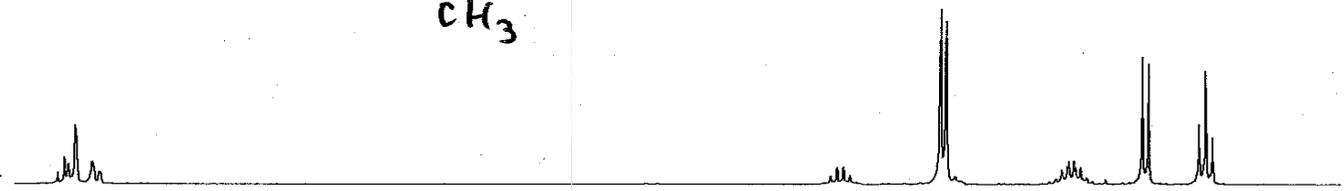
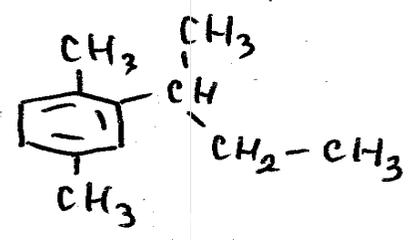
We suggested a simple laboratory experiment that introduces organic chemistry students to the basic principles of green technologies, such as lack of toxic or bulk by-products, non-toxicity, and reusability of the catalyst.



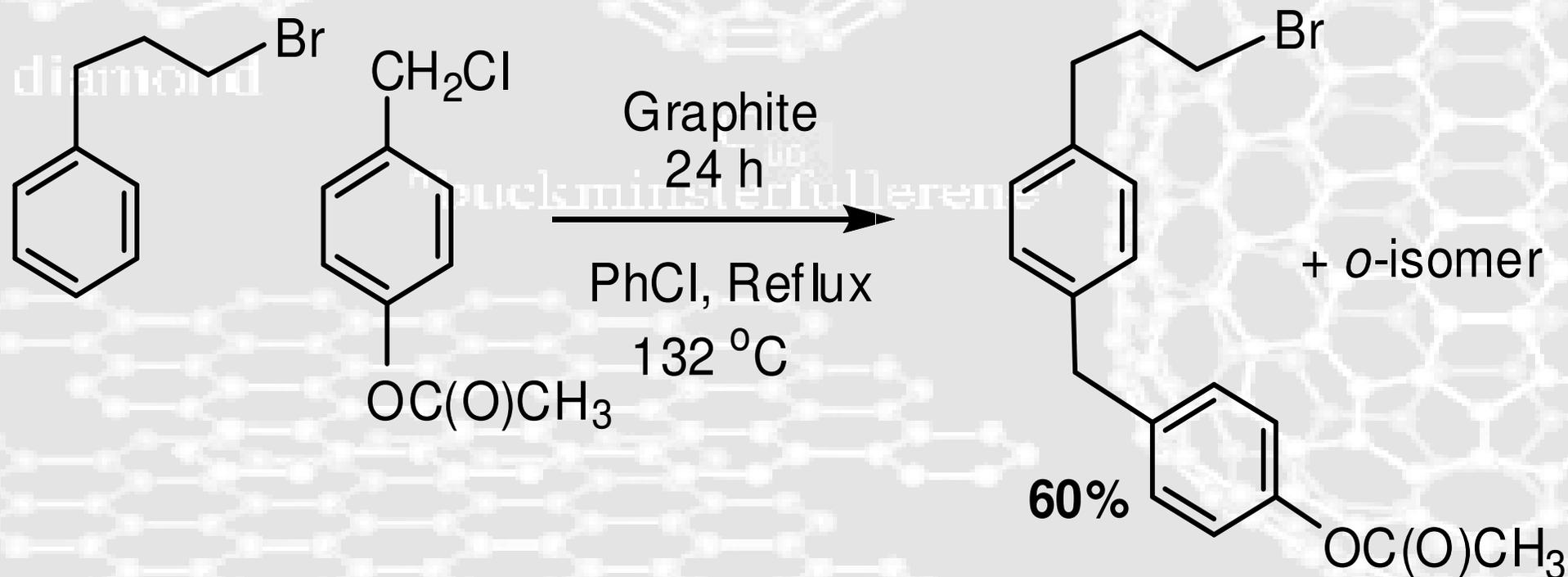
The 2D-NMR spectrum of one of the products was an excellent example to teach NMR spectroscopy

Reda G.A., Rajpara, V.B. A Green Alternative to Aluminum Chloride Alkylation of Xylene J. Chem. Educ., 2007, 84, 692-693..

COSY NMR (In CDCl₃)



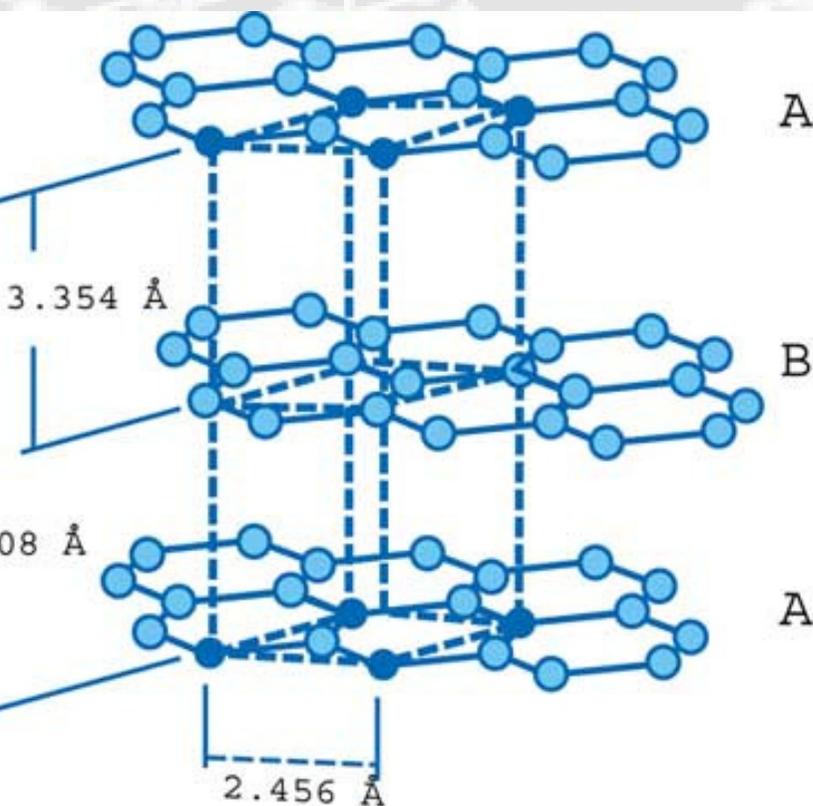
Activity of the graphite-catalyzed alkylation was demonstrated by a reaction that is available for the traditional conditions of strong Lewis acid – catalyzed alkylation:



a G., Rajpara, V., Slaba R. The Synthetic Potential of Graphite-Catalyzed Alkylation Tetrahedron, 2007, 63, 34, 8351-8357.

Secondary alkyl bromides exhibit the unique activity toward alkylation: chlorides, iodides and sulfates are not active at all. Possible reason – inclusion of bromine between graphite layers.

opens possibility for the design of new alkylation catalysts by varying morphology of carbonaceous materials



A

B

A

Ultrapure graphite did not exhibit catalytic activity, which must be linked to the iron contained in commercial graphite. Does it present in the form of magnetite nanoparticles?

of anions: Cl⁻ 0.99 Å; Br⁻ 1.98 Å; I⁻ 2.16 Å

(10,10) tube

G., Rajpara, V., Slaba R. The Synthetic Potential of Graphite-Catalyzed Alkylation Tetrahedron, 2007, 63, 34, 8351-

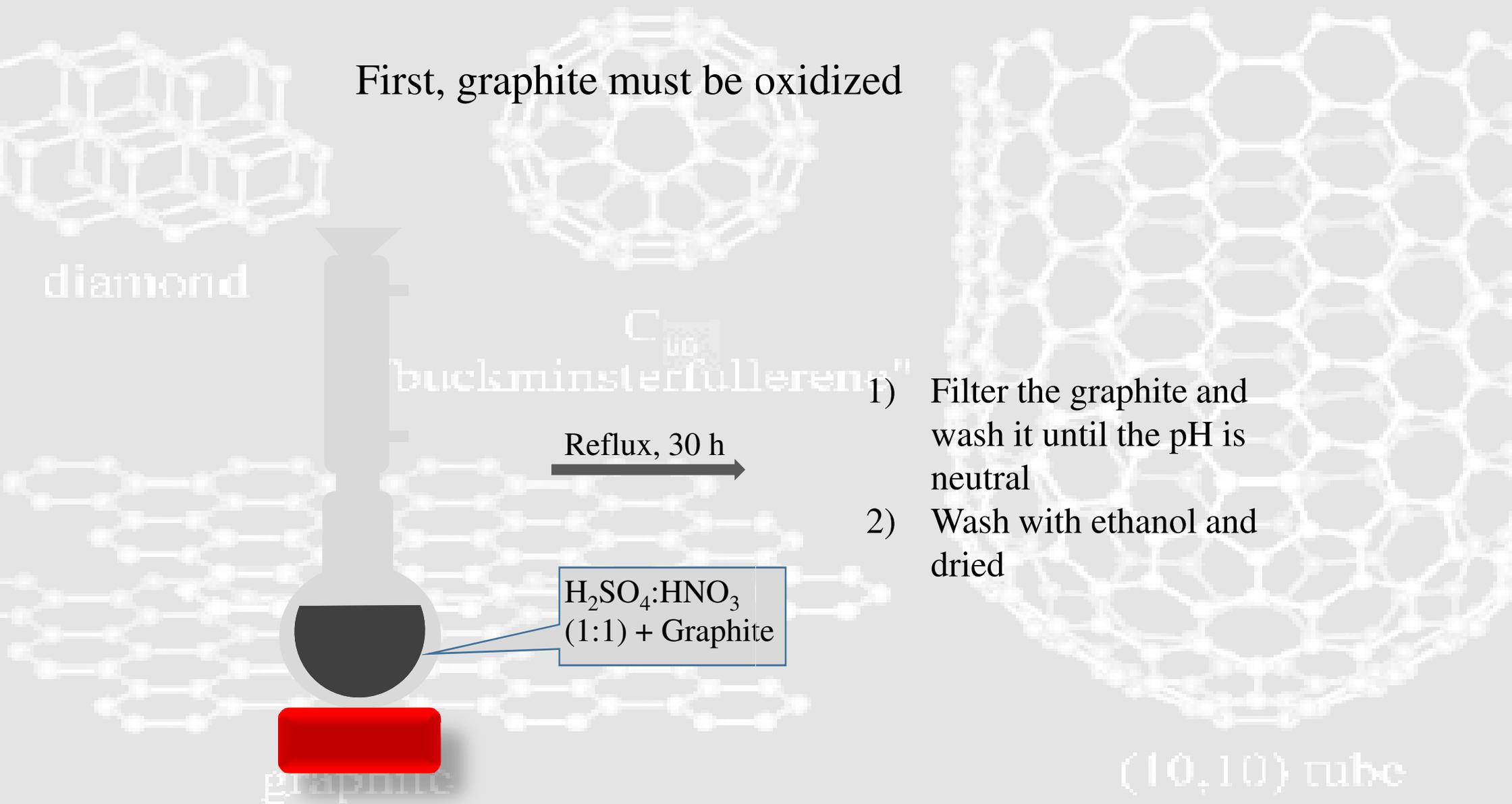
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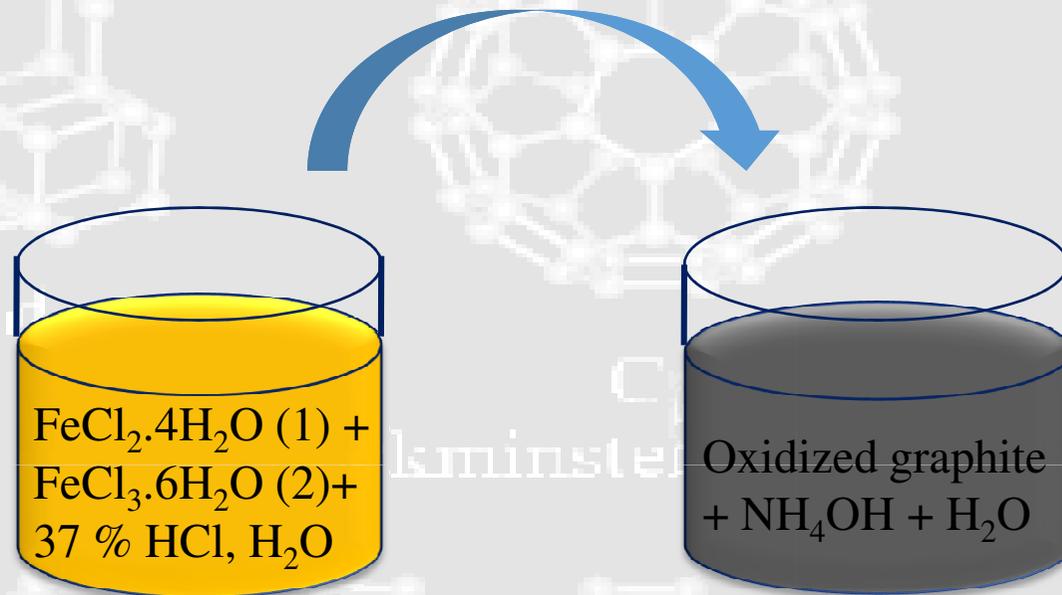
graphite

(10,10) tube

Alkylation on Graphite – Iron Oxide Nanoparticle hybrid catalyst (GIONP)



Growing iron oxide nanoparticles on carboxylated graphite



- 1) Shaken overnight
- 2) Washed well with water and ethanol – dried

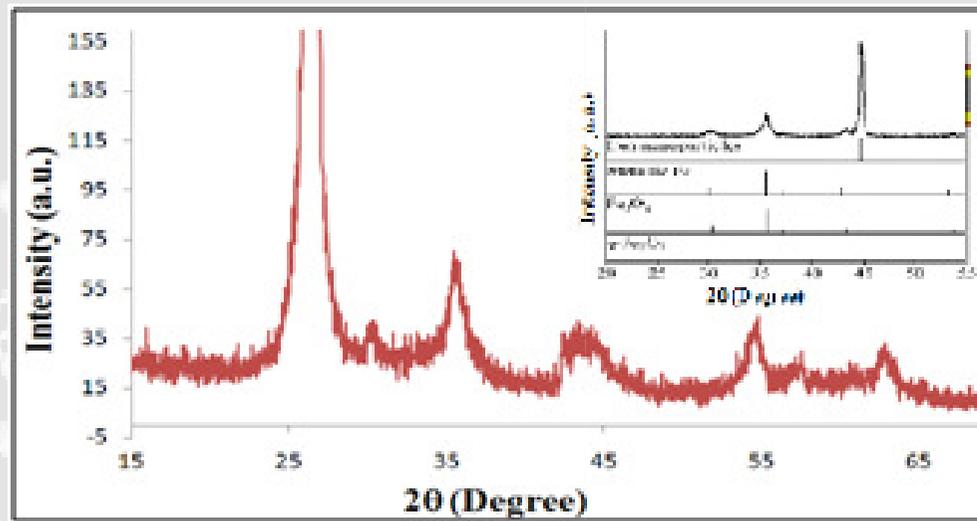
After the reaction is complete, the catalyst can be easily removed by a magnet

graphite

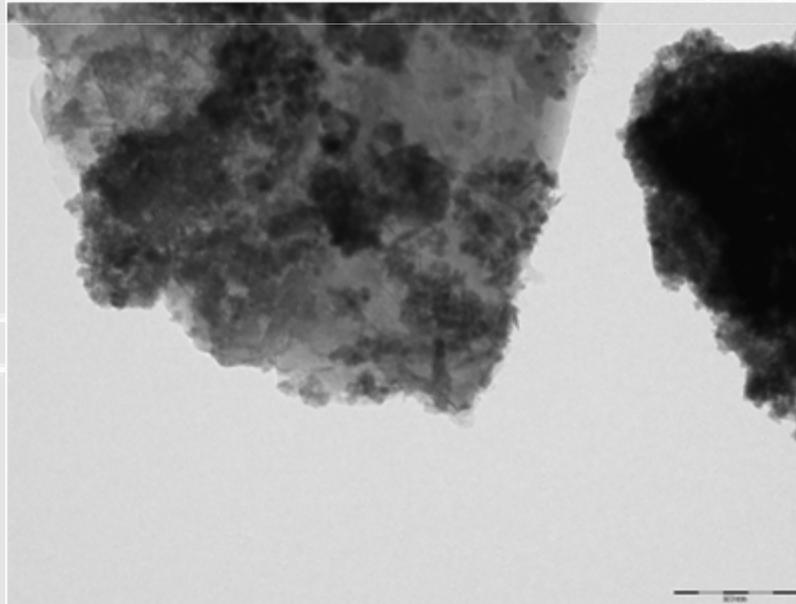
(10,10) tube



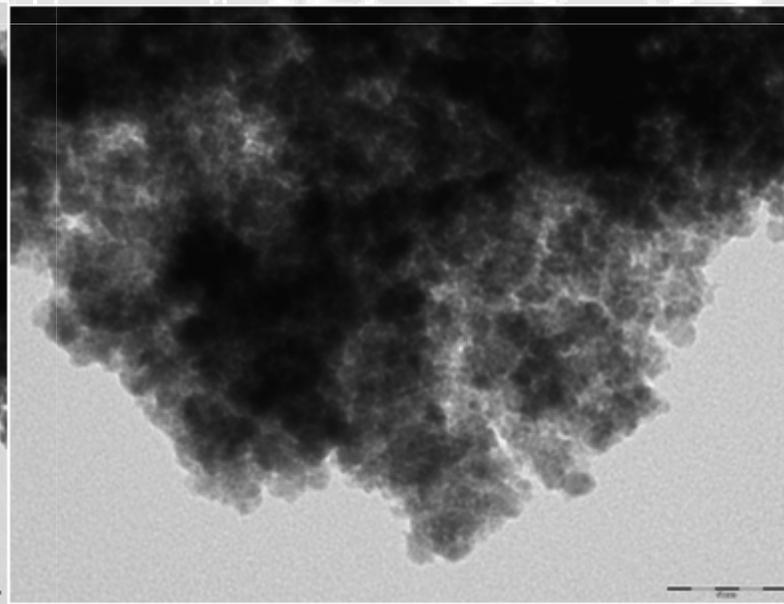
diamond



XRD of GIONP



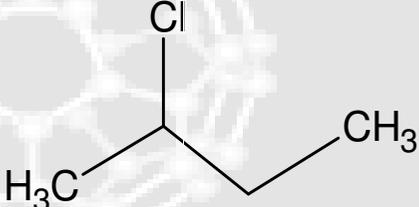
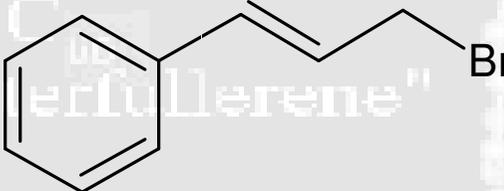
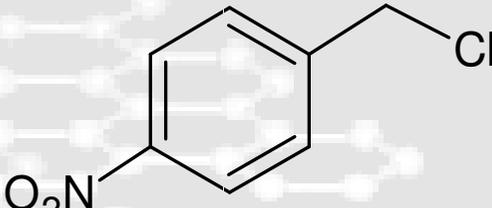
graphene



(10,10) carbon

TEM images of GIONP

The GIONP hybrid catalyst has superior performance comparing with its components

Entry	Catalyst	Alkyl halide	Yield (%)
1a	Graphite		0
1b	IONP		60
1c	GIONP		85
1d	OG		0
2a	Graphite		0
2b	IONP		30*
2c	GIONP		98*
2d	OG		0
3a	Graphite		0
3b	IONP		80
3c	GIONP		98
3d	OG		0

* Reaction was performed for 30 minutes at 60°C

Parra, V.; Banerjee, S.; Sereda, G. Iron Oxide Nanoparticles Grown on Carboxy-Functionalized Graphite: An Efficient and Recyclable Catalyst for Alkylation of Arenes. Synthesis, 2010, 16, 2835-2840.

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Linkers for non-destructive functionalization of carbons

graphite

(10,10) tube

Graphite catalyzes benzylic oxidation of *p*-xylene by air in the presence of cyclohexene as cocatalyst. Formation of an ester in the dark is intriguing and is not a result of esterification

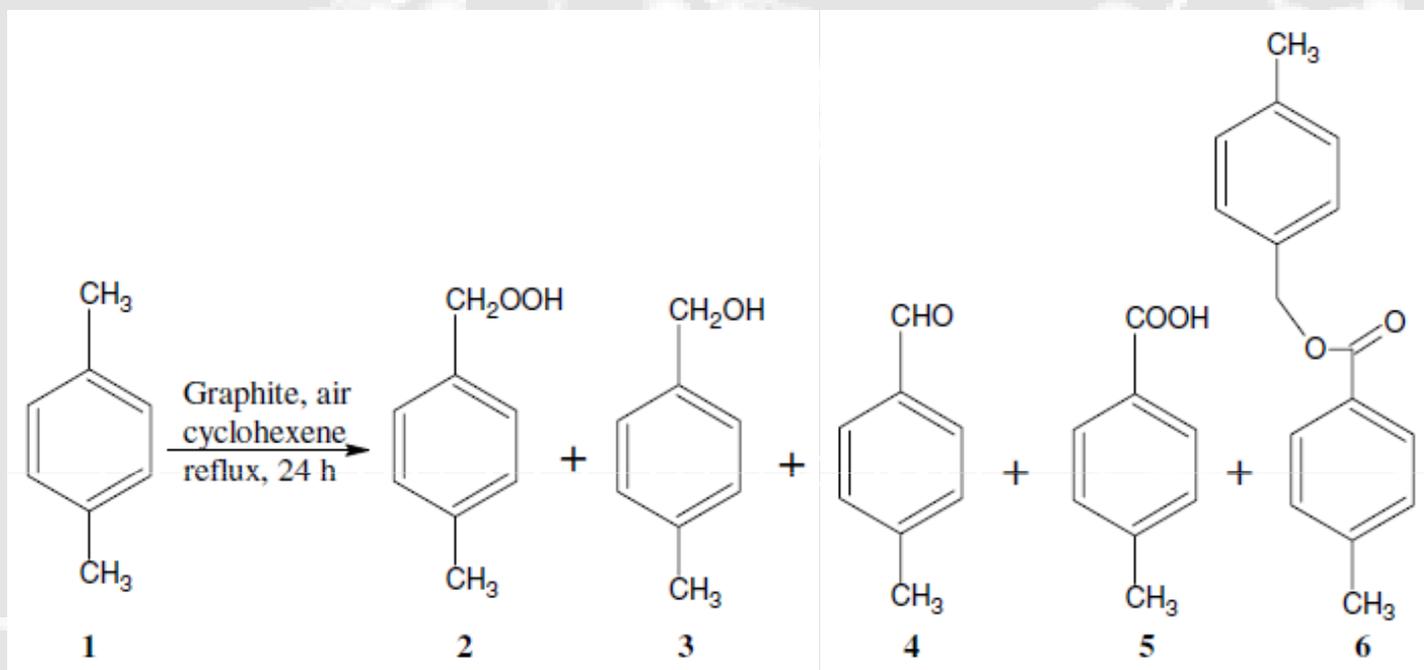


Table 1. Oxidation of *p*-xylene in the presence of cyclohexene

Catalyst	Light protection	Peroxide	Alcohol	Aldehyde	Acid	Ester	Total yield (g)	Entry
None	No	0	0	0	0	0	0	1
Graphite	Yes	0	1	1	1.7	1.7	0.23	2
	No	4.5	1.5	1	1.5	0	0.23	3

Ma G., Rajpara, V. Benzylic Oxidation and Photooxidation by Air in the Presence of Graphite and Cyclohexene Tetrahedron Letters, 2006, 48, 3417-3421.

Table 1. Oxidation of *p*-xylene in the presence of cyclohexene

Catalyst	Light protection	Peroxide	Alcohol	Aldehyde	Acid	Ester	Total yield (g)	Entry
None	No	0	0	0	0	0	0	1
Graphite	Yes	0	1	1	1.7	1.7	0.23	2
	No	4.5	1.5	1	1.5	0	0.23	3

In the dark, ester was the major product and the peroxide was not found. In the presence of ambient light, peroxide was the major product and the ester was not found. In the presence of only cyclohexene and ambient light, no products were formed.

We believe that in the dark, the hydroperoxylated surface of the catalyst plays an enhanced role in the reaction, which leads to dimerization of adsorbed intermediates.

Table 2. Oxidation of *p*-xylene (24 h, no light protection)

Catalyst	Peroxide	Alcohol	Aldehyde	Acid	Ester	Phenolic products	Total yield (g)
None	0	0	0	0	0	0	0
Graphite	0.5	0.5	1	0.5	0	2	0.06 ^a

^a Substantial amounts of unidentified products were formed.

Presence of both graphite and cyclohexene is necessary to yield the product.

In the presence of cyclohexene, graphite shuts down oxidation of ethylbenzene and suppresses oxidation of cumene in the dark, perhaps, by adsorption of polar intermediates (radicals or hydroperoxides), which leads to their deactivation rather than dimerization.

Table 4. Oxidation of ethylbenzene and cumene in the presence of cyclohexene

Catalyst	Substrate	Light protection	Peroxide	Alcohol	PhAc	Phenolic products	Total yield (g)	Entry
None	Ethylbenzene	Yes	1	1	1	0	0.13	1
		No	20	1	1	0	0.1	2
	Cumene	Yes	0.3	1.8	1	0	0.97	3
		No	0	0.7	1	0.1	1.84	4
Graphite	Ethylbenzene	Yes	0	0	0	0	0	5
		No	0.06	0.3	1	0.1	0.79	6
	Cumene	Yes	—	—	—	—	0.09 ^a	7
		No	0	0.3	1	0	2.20	8

^a Only unidentified products were formed.

Vereda G., Rajpara, V. *Benzylic Oxidation and Photooxidation by Air in the Presence of Graphite and Cyclohexene* Tetrahedron Letters, **2007**, 48, 3417-3421.

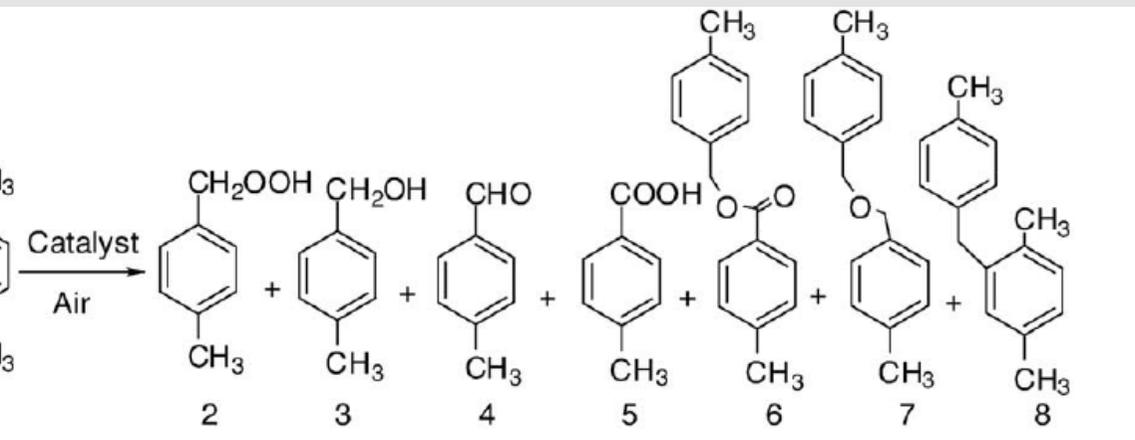
(10,10) tube

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graphite

(10,10) tube



Catalytic and photocatalytic activity and selectivity of carbons significantly depend on their morphology. Oxidation of p-xylene on the surface deactivates graphite and MWCNT.

Table 1
Oxidation of p-xylene catalyzed by carbonaceous materials.

Entry	Catalyst	Surface area m ² /g (Aver. pore size, Å)	Light	Molar ratio			Phenols	Total yield (g)	Turnover frequency (h ⁻¹ nm ⁻²)				
				2	3	4				5	6	7	8
1	Graphite	5.9 (19.6)	No	0	0	0	0	0	0				
2 ⁷			Yes	0.5	0.5	1	0.5	0	0	0	2	0.06 ^a	56
3	CB	80 (289)	No	4.7	2	1	1.8	0	0	0	0	0.41	28
4			Yes	1	0.1	0	0.05	0	0	0	0.35	0.05	3
5	GNF	19 (1.4)	No	0	0.42	1	0.38	0.07	0	0	0	0.19	54
6			Yes	0	0.75	1	2.8	0.75	0	0	0	0.50	142
7	UPG	30	No	0	0.65	1	1.05	0.03	0	0	0	0.18	32
8			Yes	19	2.7	1	2.5	0	0	0	11.5	0.15	27
9	MWCNT	99 (261)	No	0	0.4	1	0.55	0.45	0.1	0.5	0.25	0.07	4
10			Yes	0.2	0.35	1	0.7	0.7	0.13	0.7	0.5	0.07	4
11	C ₆₀	1629 (calcd)	No	0	0	0	0	0	0	0	0	0	0
12			Yes	4.2	1.8	1	2.3	0	0	0	0	0.007	0.02
13	OG	13	No	0	0	0	0	0	0	0	0	0	0
14			Yes	0	0	0	0	0	0	0	0	0	0
15	OMWCNT	132	No	0	0	0	0	0	0	0	0	0	0
16			Yes	0	0	0	0	0	0	0	0	0	0
17 ^b	SWCNT	281	No	0.46	0.66	1	0.83	0	0.22	0.41	1	0.03	0.6
18 ^b			Yes	0.15	0.8	1	1.75	0	0	0	0	0.19	4

^aSubstantial amounts of unidentified products are formed.

^bSWCNT were treated with conc. HCl (24 h) to remove possible impurities of Fe, washed with water, dried, and sonicated with p-xylene.

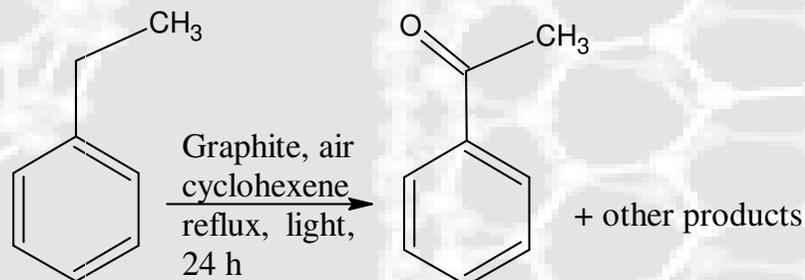
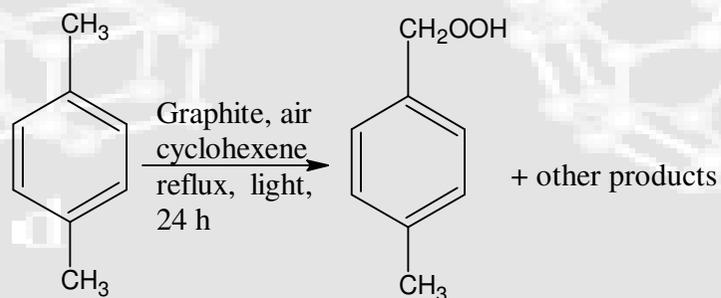
the presence of cyclohexene, activity of oxidized carbons comes back, but drops by 1/2 under ambient light.

Table 1. Oxidation of *p*-xylene in the presence of cyclohexene.

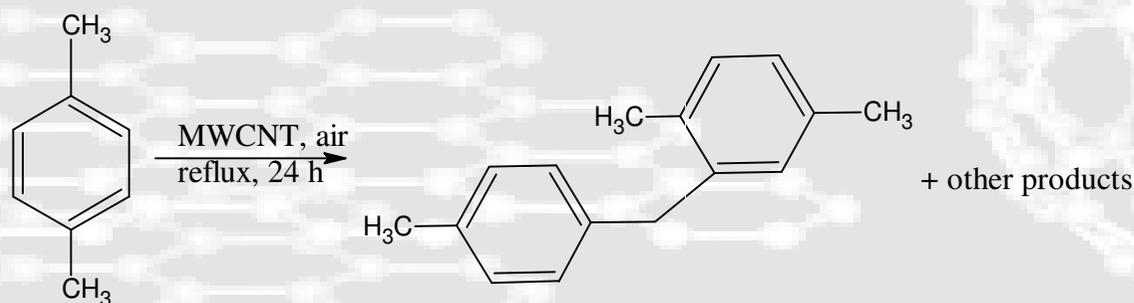
Entry	Catalyst	Surface area, m ² /g (average pore size, nm)	Light	Molar ratio							Total (g)
				1	7	8	2	9	10	11	
1	CB	80	No	0.8	1.5	1	2	0.25	0	0	0.4
2		(289)	Yes	33	2	1	0.3	0	0	0	0.0
3	OG	13	No	2.1	1.65	1	1	0	0	0	0.4
4		Yes	8	1.1	1	0.8	0	0	0	0.2	
5	UPG	30	No	2.2	1.8	1	0.72	0	0	0	0.2
6		Yes	12.5	1.5	1	1	0	0	0	0.2	
7	GNF	19	No	0	0.6	1	1.1	0.1	0	0	0.2
8		(1.4)	Yes	0	1	1	2.7	0.31	0	0	0.5
9	SWCNT	281	No	0	0.85	1	1.25	0.09	0	0	0.1
10		Yes	0	0.32	1	3	0	0	0	0.5	
11	MWCNT	99	No	0	0.7	1	0.7	0.7	0.14	0.34	0.1
12		(261)	Yes	0.3	0.2	1	0.5	0.7	0.14	0.5	0.1
13 ¹⁴	Graphite	5.9	No	0	1	1	0.7	0.7	0	0	0.2
14 ¹⁴		(19.6)	Yes	4.5	1.5	1	1.5	0	0	0	0.2

Other observations

Practical procedures for photooxidation of *p*-xylene to 4-methylbenzyl hydroperoxides and ethylbenzene to acetophenone have been developed



Only multiwall carbon nanotubes catalyze oxidative self-alkylation of *p*-xylene



Light is able to not only activate, but also suppress or even prevent oxidation (expected photopassivation)

Possible rationalization

Only carbon nanotubes catalyze formation of “coupled” products, probably, due to the presence of intermediates inside the tubes.

Effect of light (activation or deactivation) was observed for all material with a significant G band Raman band (CB, OG, GNF) or high surface curvature (SWCNT, 1 nm OD), which points to the defects and edges as sole photocatalytic sites. C₆₀ (no defects or edges) and oxidized graphite (oxidized defects or edges) did not show any catalytic activity without cyclohexenone promoter.

Ambient light suppresses free radical oxidation on carbon black and oxidized graphite. This is always accompanied by a significant increase of the hydroperoxides production. The presence of hydroperoxides may block the catalytic site similarly to what we observed for acetophenone and benzoic acids in the reaction of alkylation.

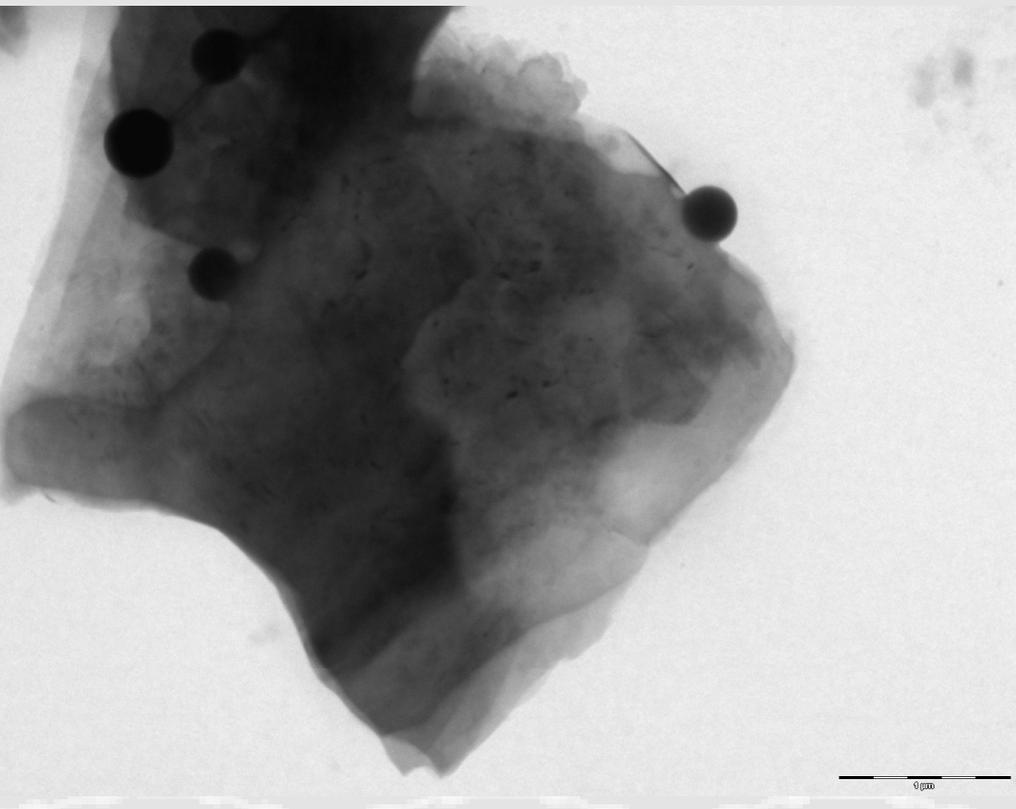
da, G.; Rajpara, V. Photoactivated and photopassivated benzylic oxidation catalyzed by pristine and oxidized carbons. Commun., 2011, 12, 669-672.

Outline

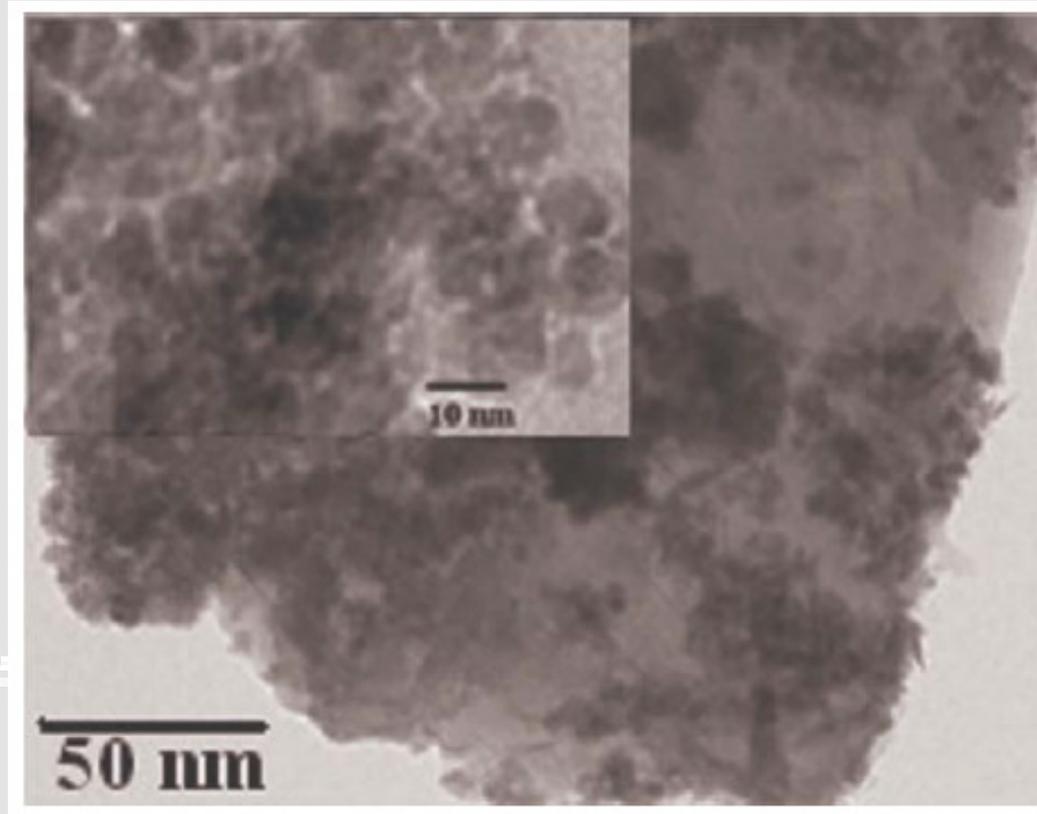
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graphite

(10,10) tube



SiO₂ nanoparticles attached to oxidized graphite. Scale bar = 1 μm



Fe₃O₄ nanoparticles grown on oxidized graphite

...tion of bulk SiO₂, bulk Al₂O₃ or covalent attachment of SiO₂ or Fe₃O₄ nanoparticles
...lized graphite shuts down its catalytic activity toward benzylic oxidation in the da
...ably, due to the scavenging of polar intermediates from the reaction mixture
...graphite (10,10) tube

Table 1: Catalytic oxidation and photooxidation of *p*-xylene.

Entry	Catalyst	Surface area, m ² /g (Average pore size, Å)	Surface area of the parent carbon (Average pore size, Å)	F ₃ O ₄ phase	Magnetic	Light	Molar Ratio					Total Yield (g)	Turnover frequency (h ⁻¹ nm ⁻²)
							2	3	4	5	6		
1	FeOGA	54 (138)	6 (19.6)	Yes	Yes	No	0	0	0	0	0	0	0
2						Yes	0.4	1.15	1	0.86	0.03	0.69	69
3	FeOUPGA	50 (150)	30	Yes	Yes	No	0	0	0	0	0	0	0
4						Yes	0	0.91	1	2.4	0	1.02	110
5	FeOCBA	89 (107)	80 (289)	Yes (traces)	No	No	0	0	0	0	0	0	0
6						Yes	0	0	0	0	0	0	0
7	FeOGB	19 (123)	6 (19.6)	No	No	No	0	0.65	1.0	1.13	0.18	0.31	88
8						Yes	9.5	1.1	1	0.3	0	0.20	57
9	FeOUPGB	57 (161)	30	No	No	No	0	0	0	0	0	0	0
10						Yes	0	0	0	0	0	0	0
11	FeOCBB	104 (108)	80 (289)	Yes (traces)	No	No	0	0	0	0	0	0	0
12						Yes	0	0	0	0	0	0	0
13	IONP	145	-	Yes	Yes	No	0	1.3	1	1.6	0	0.16	6
14						Yes	3	2	1	1	0	0.16	6
15	OG	13	6 (19.6)	-	-	No	2.1	1.65	1	0.8	0	0.42	175
16						Yes	8	1.1	1	1.6	0	0.21	87

Reda, G.; Horn, A.; Rajpara, V.; Koodali, R.; Urness, M.; Kruse, A.; Stewart, M.; Schloss, J.; Rodriguez, A.; Amundson, M.; Regmair, A.; Zimmerman, A.; Woodring, R.; McInerney, K. *Benzylic Photooxidation Catalyzed by Carbon-Supported Iron Oxides* J. Und. Chem. Res., **2011**, 10 (3), 81-84.

ambient light turns on catalytic activity of Fe_3O_4 nanoparticles on oxidized graphite while
activating oxidized graphite and having no effect on loose nanoparticles

oxidation proceeds all the way to the carboxylic acid, but still regioselective

trapure graphite is activated by iron oxide nanoparticles twice as efficiently as commercial
graphite while no activation was observed for carbon black

"buckminsterfullerene"

**How do the components of the photocatalyst (FeOGA) work together?
Does graphite photosensitizes iron oxide or vice versa?**

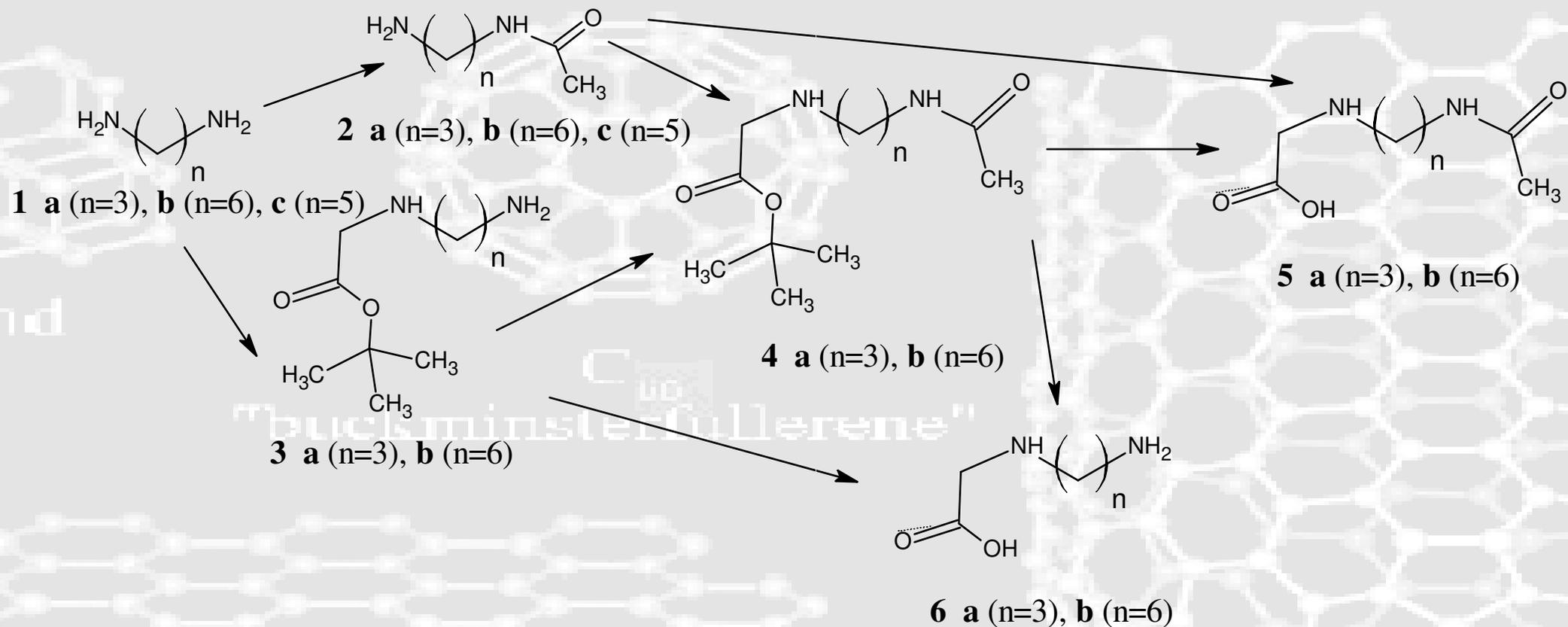
*Meda, G.; Horn, A.; Rajpara, V.; Koodali, R.; Urness, M.; Kruse, A.; Stewart, M.; Schloss, J.; Rodriguez, A.; Amundson, M.;
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graphite

(10,10) tube



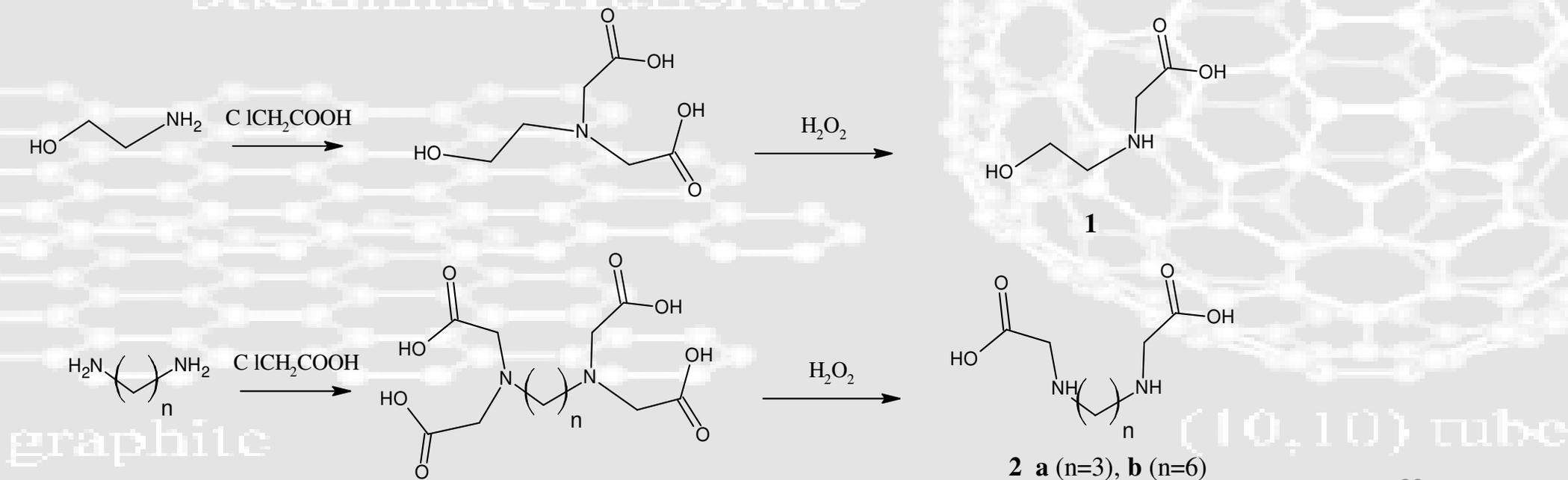
In order to introduce carboxy- and other functional groups to carbonaceous materials, we have prepared linkers of different lengths **5a,b** that are known to functionalize graphene and carbon nanotubes in the presence of formaldehyde by 1,3-dipolar addition.

graphite

(10,10) tube

have synthesized an alternative group of linkers, including bidentate ones, using a little known reaction of oxidation of bis-glycineamines **1**, **2a,b**.

Functionalization of carbonaceous materials with interacting surface groups (such as oppositely charged) will let us assemble them in bundles, other architectures and design biocatalytic sites and their environment. It opens the door for the improvement of carbon supported iron oxide and other catalysts known for the Fischer-Tropsch reaction, water splitting and other important industrial processes.



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