國立屏東大學
National Pingtung University

109年 培育產學合作教師計畫成果展暨分享會

主題：A reduced graphene oxide-supported iridium nanocatalyst for selective transformation of alcohols into carbonyl compounds via a green process

教師姓名： 陳存仁(Tsun-Ren Chen)

學院/系所： 理學院/應用化學系

計畫簡介

A nanocatalyst constructed from reduced graphene oxide and iridium atoms (RGOIrNc) showed high selectivity (99%–100%) and reliability for the transformation of aromatic alcohols into carbonyl compounds via ultrasonication without using harmful chemicals and solvents.

Experimental data including Fourier transform infrared spectroscopy, x-ray diffraction, spherical-aberration-corrected field emission transmission electron microscopy and Raman spectra confirmed the nanostructure of the RGOIrNc. Noticeably, the structural characteristics of this catalyst remained unchanged within 25 catalytic cycles and the activity and selectivity for the transformation of benzylic alcohols showed good stability. The average turnover frequency is greater than 9000 h−1, the total turnover number is more than 150 000 after 25 catalytic cycles and the productivity of carbonyl compounds reaches 376 048 molcarbonylcompoundkg−1 GO−Ircomplex, indicating that RGOIrNc catalyst has good durability and stability and high ‘greenness’.

研究方法

Preparation of graphene oxide:

Graphene oxide (GO) was synthesized from graphite powder following a modified Hummers method. The synthesized GO was dispersed in deionized (DI) water (0.5 mg ml−1) under ultrasonic treatment for 40 min, and then the solution was heated in an oil bath (90 ℃) for 60 min. The obtained GO was filtered through a nylon microporous membrane (0.22 μm) and dispersed in DI water.

Preparation of the graphene oxide-iridium complex:

A solution prepared by dissolving 1.5 g of IrCl3 in 250 ml of mixed solvent (ethyl ethanol:water, 3:1 v/v) was added to 500 ml of GO solution (2 mg ml−1). The mixture was stirred at room temperature for 0.5 h and ultrasonicated for 0.5 h, and then the mixture was refluxed for 96 h under argon. The obtained GO–iridium complex (GOIr complex) dispersion was purified by filtration and washing with DI water and ethanol and then re-dispersed in ethanol.

Preparation of RGOIrNc:

A solution prepared by dissolving 1.0 g of sodium borohydride in 50 ml of ethanol was added to the 100 ml of GOIr solution (15 mg ml−1). The mixture was stirred at room temperature for 48 h. The obtained reduced graphene–iridium composite dispersion was purified by filtration and washing with DI water and ethanol and then re-dispersed in ethanol.

Catalytic activity of catalysts:

The reaction temperature was well controlled in a water bath under a constant temperature (±1 ℃). For the catalytic reaction, 0.05–1 g of aromatic alcohol, 0.0005–0.01 g of RGOIrNc and 3 ml of toluene were mixed in a reaction flask irradiated with ultrasound, and the progress of the reaction was monitored by high-performance liquid chromatography (HPLC) and gas chromatography–mass spectrometry (GC-MS) to identify the composition of the product.

Catalyst reuse studies:

To check the catalytic activity of reused RGOIrNc, 2 g of aromatic alcohol, 0.0005 of RGOIrNc and 3 ml of toluene were mixed in a reaction flask irradiated with ultrasound. After a reaction time of 1 h the reaction mixture was centrifuged to separate out the catalyst and the residual clean supernatant was analyzed by HPLC and GC-MS to identify the composition of the product. Then, 1 g of aromatic alcohol and 3 ml of ethanol were added to a flask containing the recovered RGOIrNc for the next catalytic cycle. The RGOIrNc was recovered and used again 25 times without any evident loss of catalytic activity.

成果與成效

Substrate	Product	Transformation (%)[a,b]	Selectivity (%)[a,c]	Yield (%)[a,d]	Atomic efficiency (%)[e]	TOF (h^{-1})[f]
Benzyl alcohol	Benzaldehyde (almond oil)	92.53	97.61	90.31	98.15	9623
4-Methybenzyl alcohol	4-Methylbenzaldehyde (cherry scent oil)	94.93	99.36	94.89	98.36	9874
4-Methoxybenzyl alcohol	4-Methoxybenzaldehyde (anise oil)	88.65	99.58	88.59	98.55	9217
4-Chlorobenzyl alcohol	4-Chlorobenzaldehyde (plant growth regulators)	95.99	99.61	95.95	98.59	9982
1-Phenyl-2-propanol	Benzylacetone (flowery smell of cocoa)	85.17	100	85.17	98.53	8861

[a]0.15 M aromatic alcohols in toluene with 0.01 g RGOIrNc.
[b]Transformation percentage for alcohol.
[c]Selectivity for the transformation of alcohol into carbonyl compounds.
[d]Production yield for carbonyl compounds.
[e]Atomic efficiency for the transformation of alcohols into carbonyl compounds without considering the molecular weight of oxygen from the air.
[f]3.03 M aromatic alcohols in toluene with 0.0005 g RGOIrNc, TOF (h^{-1}) to carbonyl compound.

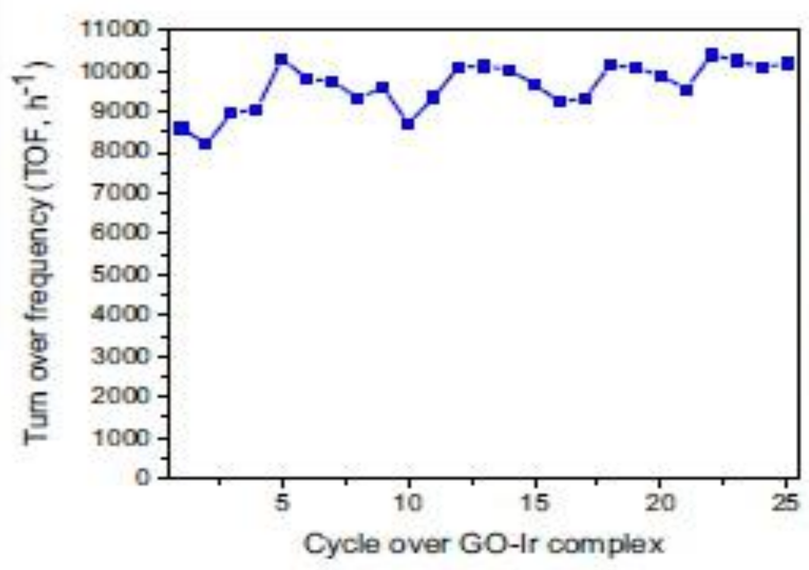

Figure 11. The TOF of the catalytic cycles for the transformation of benzyl alcohol into benzaldehyde, showing that the catalytic capability of RGOIrNc for the selective transformation of alcohol is quite steady.

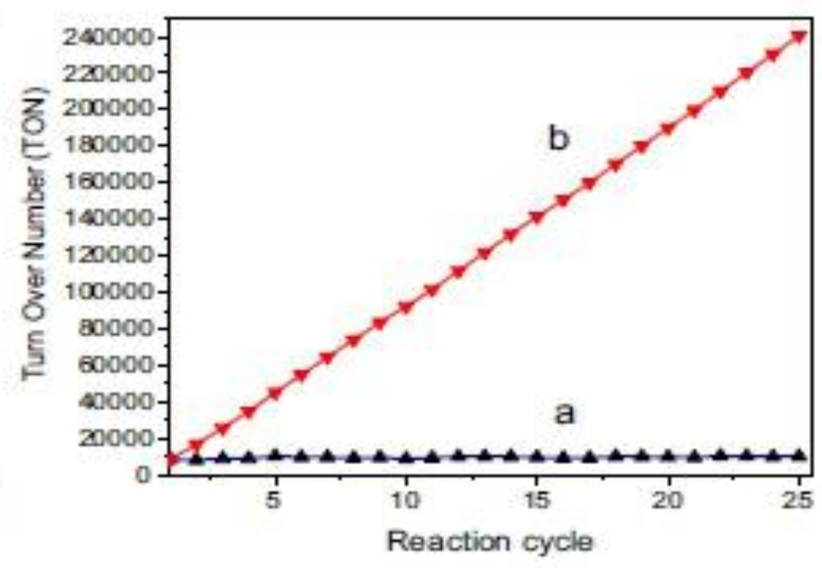

Figure 12. The TON of the catalytic cycles for the transformation of benzyl alcohol into benzaldehyde: (a) TON of each cycle, (b) accumulated TON.

Catalyst	Conversion (%)	Selectivity (%)	TOF (h^{-1})	Runs	TON per run	TON (total)	Ref.
Meso-Co_3O_4	93.6	98.2	0.23	5	1.84	9.2	[63]
OMS-2	93	88	25.5	8	204	1632	[64]
Au/CuO	99	96	35.64	4	71	285	[65]
P123-stabilized Pd nanoclusters	99	100	5.5	12	49	594	[66]
ZnS-Ni_xS_y (2)	49.3	80.4	7.1	4	21	84	[67]
ZnS-Ni_xS_y (3)	42.1	90.5	6.4	4	19	76	[67]
Pd/$H_2Ti_3O_7$	89	68.9	1459	5	8754	43 770	[61]
$H_2Ti_3O_7$	2.2	89.2	54	5	216	1080	[61]
Pd/TiO_2 (P25)	49.5	76	1217	5	4868	24 340	[61]
20% PMo_{11}/Al_2O_3	21	91	46	3	1109	3327	[68]
Au/$MgAl_2O_4$	94	31	494	1	2470	2470	[69]
Au–Pd/TiO_2	71.7	95.8	589	7	3534	24 738	[70]
$Fe(DS)_3$	100	100	32.4	4	194	777	[71]
RGOIrNc	92.5	97.6	9623	25	9623	245 091	this work

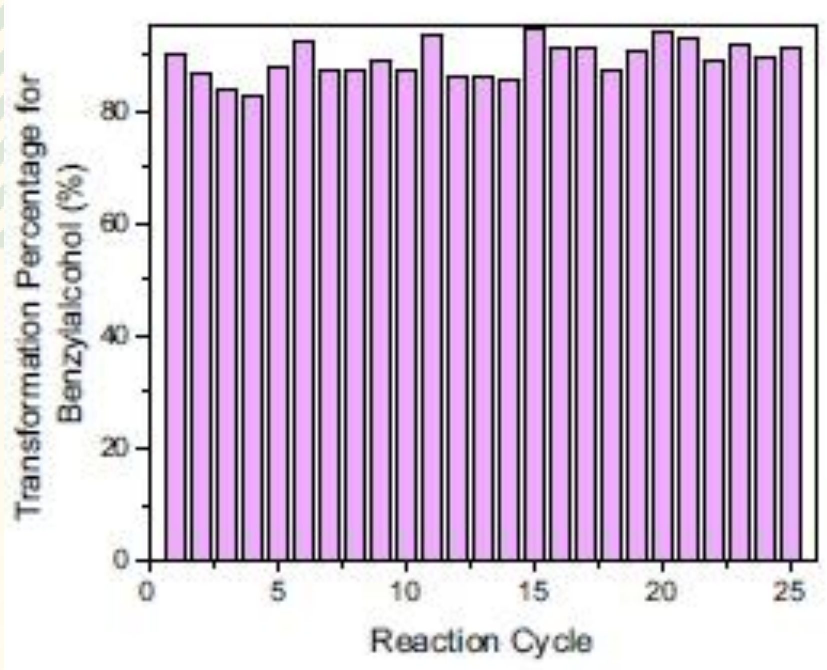

Figure 13. Transformation percentage for each catalytic cycle, showing that most of the benzyl alcohol was transformed.

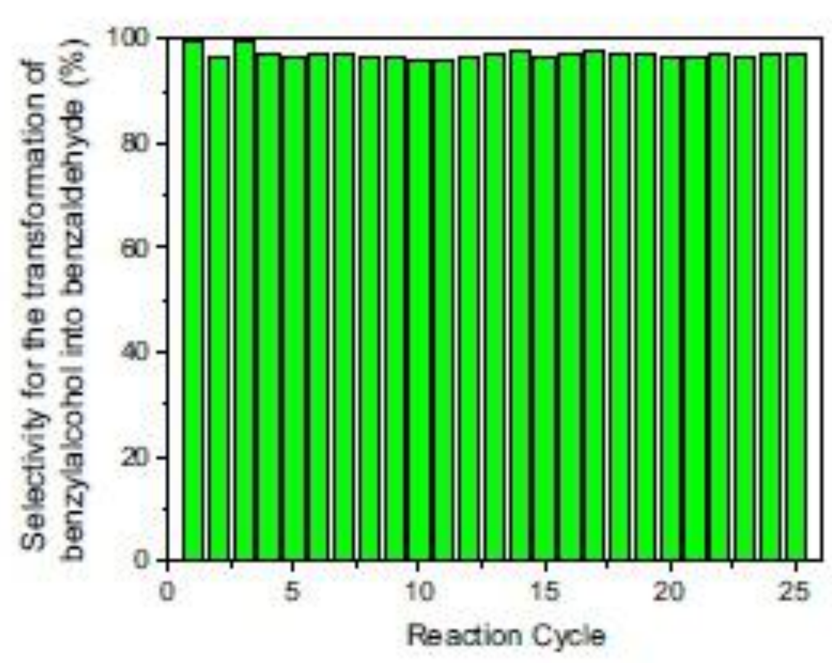

Figure 14. The selectivity of each catalytic cycle: all the catalytic cycles show high selectivity for the transformation of benzyl alcohol into benzaldehyde.

主辦單位:研究發展處技術合作組