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Greener iodination of arenes using sulphated ceria-zirconia catalysts in polyethylene glycol†

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An environmentally benign method for the selective monoiodination of diverse aromatic compounds has been developed using reusable sulphated ceria–zirconia under mild conditions. The protocol provides moderate to good yields and selectively introduces iodine at the *para/ortho* position in monosubstituted arenes. $SO_4^{2-}/Ce_{0.07}Zr_{0.93}O_2$ was found to be the best choice for the synthesis of aryl iodides in high yield, presumably due to the maximum number of acid sites (4.23 mmol g⁻¹) among the various compositions of the catalyst system.

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Halogen derivatives of hydrocarbons form an important class of intermediates, as they can be converted efficiently into other functionalities by simple chemical transformations. Halogenated arenes and alkanes are precursors for organometallic reagents¹ and are widely used as intermediates for the synthesis of biologically active molecules, including drugs (*e.g.* galanthamine), fine chemicals (*e.g.*, iso-vanillyl sweeteners), pesticides and fungicides.^{2–5} The iodoarene moiety is an important structural motif in biologically active molecules (*e.g.*, thyroid hormone) and a synthetic intermediate for a variety of fine chemicals. The suitability of iodoarenes as synthetic intermediates is partly due to the fact that the iodo substituent can undergo a multitude of transition metal catalyzed cross-coupling reactions.

Numerous Pd coupling reactions including the Heck,⁶ Stille,⁷ Suzuki,⁸ and Sonogashira⁹ reactions require aromatic halides as precursors to prepare more complex targets and aromatic iodides are among the most versatile building blocks in this category. Although there are numerous examples (direct or indirect synthesis), where electrophilic aromatic substitution is used to replace an aryl hydrogen atom with a halogen group, iodination still remains a difficult transformation to facilitate.¹⁰ Iodo compounds are often synthesized *via* the reduction of nitroarenes followed by the Sandmeyer reaction. Bromination and chlorination easily proceed with, or sometimes without, Lewis acid catalysts, but iodination is usually more difficult owing to the low electrophilicity of iodide. Hence, efforts are being made towards the development of efficient, selective and mild methods for the direct introduction of iodine into organic compounds. Besides the use of volatile organic solvents as reaction media, most of the methods studied used harsh reaction conditions, such as the extensive use of strong acids or the use of heavy metal salts and the need for oxidants as activators for iodine;¹¹ this requires special safety precautions in experimental handling and generates serious concerns regarding environmental and health issues.

PEG is a non-toxic, inexpensive, and non-volatile solvent, employed in synthetic chemistry for various organic transformations.¹² It also has good thermal stability, and is miscible with a number of organic solvents.

The development of mild, cost effective and environmentally benign catalytic procedures for the iodination of aromatic compounds is a fertile area of research. Previously, heterogeneous metal oxides and sulfate catalysts have been deployed as acid or oxidative catalysts for iodination chemistry.¹³

Recently, we have found that ceria–zirconia mixed oxides can act as an efficient bifunctional catalyst system for the sequential epoxidation–aminolysis of styrenes.¹⁴ The sulphated form of these mixed oxides has been found to be a good catalyst for the modified Ritter reaction.¹⁵ In a continuation of research activities on the development of benign protocols using heterogeneous catalysts,^{16–18} we have now explored the catalytic activity of these oxides for the iodination of arenes. Herein, we report a mild and experimentally simple catalytic method for the synthesis of iodoarenes using sulphated ceria–zirconia as a heterogeneous, inexpensive and recyclable catalyst. The method does not require the addition of any oxidant or activator, such as heavy metals (lead, mercury and chromium). The

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Scheme 1 Synthesis of iodoarenes catalysed by sulphated ceriazirconia as a catalyst in PEG-200.

mild reaction conditions and the use of PEG-200 as a green solvent make the process environmentally benign and hazardfree (Scheme 1).

Results and discussion

To develop a suitable catalytic protocol for the synthesis of iodoarenes, iodination of aniline in the presence of several surface modified metal oxides and mixed metal oxides using I_2 and PEG-200 as reaction medium was chosen as the test reaction (Scheme 2 and Table 1).

Among the various catalysts tested in the study, $SO_4^{2-}/Ce_xZr_{1-x}O_2$ gave the maximum yield (97%) with preferential *para* selectivity. In the absence of a catalyst only a 25% yield of



Scheme 2 Synthesis of 4-iodoaniline in PEG-200 at 30 °C.

4-iodoaniline was obtained even after 24 h under the present reaction conditions (Table 1, entry 1).

When the same reaction was carried out in the presence of other reported catalysts such as H_2SO_4 , $ZrSO_4$, low yields and poor regioselectivity were observed (Table 1, entries 2 and 3). Also, with single component oxides – CeO_2 or ZrO_2 , only a 35–48% yield of 4-iodoaniline was obtained (Table 1, entries 4 and 5). However, upon sulphation, the yield of 4-iodoaniline increased to 43–77% (Table 1, entries 6 and 7) with improved selectivity. A physical mixture of SO_4^{2-}/CeO_2 and SO_4^{2-}/ZrO_2 (10 wt% of each) gives a 55% yield, with poor regioselectivity towards 4-iodoaniline (Table 1, entry 8). The investigation was further extended to several compositions of sulphated ceria-zirconia and sulphated yttria-zirconia system gave better yields/regioselectivity for the synthesis of iodoanilne compared to sulphated yttria-zirconia catalysts (Table 1, entry 10–21).

As the cerium content in $SO_4^{2-}/Ce_xZr_{1-x}O_2$ was increased from 0.02–0.07 mol%, the total acidity and surface area of the catalysts were also found to increase. A further increase in cerium content resulted in a decrease in both total acidity and surface area (see ESI[†]), which was also manifested in the activity and selectivity of the reaction.

When the reaction was carried out with $SO_4^{2-}/Ce_{0.07}Zr_{0.93}O_2$ catalyst, 97% yield with 100% selectivity for 4-iodoaniline was obtained, which is the highest among the various compositions of $SO_4^{2-}/Ce_xZr_{1-x}O_2$ studied (Table 1, entry 11). This could be due to the maximum value in the number of acid sites (4.23 mmol g⁻¹) and acid strength as determined by potentiometric titration using *n*-butylamine.¹⁹ In this method, the initial electrode potential (*E*_i) indicates the strength of the acid sites and

Table 1 Synthesis of iodoanilne using sulphated ceria-zirconia solid acid catalysts^a

Entry	Catalyst	BET Surface area $(m^2 g^{-1})$	Acidity $(\text{mmol } \text{g}^{-1})^b$	$E_{i} (mV)^{c}$	Conversion $(\%)^d$	Selectivity $(\%)^e$	Yield (%) ^f
1^g					30	80/20	25
2	H_2SO_4	_	—	_	70	85/15	54
3	$ZrSO_4$	—	—	—	45	67/33	27
4	ZrO_2	12	0.8	55	60	93/7	48
5	CeO ₂	10	0.3	27	45	91/9	35
6	SO ₄ ²⁻ /ZrO ₂	37	2.07	168	84	96/4	77
7	SO ₄ ²⁻ /CeO ₂	23	1.22	154	54	85/15	43
8	Ce _{0.07} Zr _{0.93} O ₂	17	1.54	157	43	100	38
9^h	SO ₄ ²⁻ /CeO ₂ + SO ₄ ²⁻ /ZrO ₂	—	_	—	65	88/12	55
10	SO4 ²⁻ /Ce _{0.02} Zr _{0.98} O ₂	22	3.17	440	80	100	76
11	SO4 ²⁻ /Ce _{0.07} Zr _{0.93} O ₂	53	4.23	560	100	100	97
12	$SO_4^{2-}/Ce_{0.10}Zr_{0.90}O_2$	28	3.52	450	82	100	75
13	SO4 ²⁻ /Ce _{0.15} Zr _{0.85} O ₂	14	3.50	460	62	98/2	55
14	$SO_4^{2-}/Ce_{0.20}Zr_{0.80}O_2$	12	2.97	248	57	95/5	49
15	$SO_4^{2-}/Ce_{0.25}Zr_{0.75}O_2$	10	2.17	197	53	95/5	44
16	$SO_4^{2-}/Y_{0.04}Zr_{0.96}O_2$	34	1.23	148	56	92/8	46
17	$SO_4^{2-}/Y_{0.08}Zr_{0.92}O_2$	43	1.64	195	54	90/10	48
18	$SO_4^{2-}/Y_{0.12}Zr_{0.88}O_2$	52	1.93	310	68	90/10	57
19	$SO_4^{2-}/Y_{0.16}Zr_{0.84}O_2$	75	4.19	530	92	94/6	86
20	SO4 ²⁻ /Y0.20Zr0.80O2	35	2.91	330	69	99/1	65
21	$SO_4^{2-}/Y_{0.24}Zr_{0.76}O_2$	29	2.65	248	60	100	56

^{*a*} Reaction conditions: aniline (2 mmol), I_2 (2 mmol), PEG-200 (2 ml), 12 h, RT, catalyst (15 wt% w.r.t. aniline). ^{*b*} Surface acidity values determined using the *n*-butylamine potentiometric titration method. ^{*c*} E_i initial electrode potential (mV). ^{*d*} Conversion determined using GC analysis. ^{*f*} Selectivity determined using GC analysis. ^{*f*} Isolated yields. ^{*g*} 24 h. ^{*h*} 7.5 (wt%) of each w.r.t. aniline.

the end point of the titration is related to the number of acidic sites (mmol g⁻¹). For comparison, a test reaction was also carried out with non-sulphated $Ce_{0.07}Zr_{0.93}O_2$, which gave a 38% yield of 4-iodoaniline (Table 1, entry 8). We also explored the effect of surface ratio of (Ce/Zr) and surface density of sulphation. The highest surface sulphate ratio of Ce/Zr (0.075) was obtained with $SO_4^{2-}/Ce_{0.07}Zr_{0.93}O_2$, which was also found to have maximum acid sites (ESI Table 2†).

The effect of various reaction parameters such as catalyst loading, solvent system *etc.* was also investigated for the model reaction. An increase in initial catalyst loading, up to 15 wt%, results in an increased yield of the product while further increase has no profound effect (Table 2, entry 1–5).

The solvent plays a key role in catalyst activity and thus choice of the proper solvent is crucial (Table 3). The synthesis of iodoanilne under solvent-free conditions gave a 35% yield of the desired product (Table 3, entry 1). It was observed that non-polar solvents like 1,4 dioxane, *n*-hexane and mildly polar solvents like chloroform, ethyl acetate, tetrahydrofuran, dichloromethane, and dichloroethane gave good to moderate yields of the product (Table 3, entries 2–8). Polar solvents such as methanol, acetonitrile and ethanol, were found to be better reaction media for iodination (Table 3, entries 9–11). Interestingly, when the reaction was carried out in acetone (Table 3,

Table 2	Effect of catalyst loading on the yield of iodoaniline ^a			
Entry	Catalyst loading (wt%)	Yield $(\%)^b$		
1	5	61		
2	10	74		
3	15	97		
4	20	97		
5	25	97		

^{*a*} Reaction conditions: aniline (2 mmol), I_2 (2 mmol), PEG-200 (2 ml), 12 h, RT, $SO_4^{2-}/Ce_{0.07}Zr_{0.93}O_2$ catalyst (wt% w.r.t. aniline). ^{*b*} Isolated yields.

 Table 3
 Effect of solvent on the iodination of aniline^a

Entry	Solvent	Yield $(\%)^b$	
1	_	35	
2	1,4 Dioxane	49	
3	<i>n</i> -Hexane	54	
4	Chloroform	60	
5	Ethyl acetate	65	
6	Tetrahydrofuran	67	
7	Dichloromethane	78	
8	Dichloroethane	80	
9	Methanol	83	
10	Acetonitrile	85	
11	Ethanol	87	
12	Acetone	0	
13	PEG-200	97	
14	PEG-400	85	
15	PEG-600	79	

 a Reaction conditions: aniline (2 mmol), I₂ (2 mmol), solvent (2 ml), 12 h, RT, SO₄ $^{2-}/Ce_{0.07}Zr_{0.93}O_2$ catalyst (15 wt% w.r.t. aniline). b Isolated yields.

entry 12), it reacted with aniline to form 2,2,4-trimethyl-1,2-dihydroquinoline as the exclusive product.

As the primary goal of this study was to develop a process that is 'green' and environmentally viable, the iodination reaction was conducted in polyethylene glycol (PEG); (Table 3, entries 13–15) PEG-200 gave the highest yield (97%) of 4iodoaniline (Table 3, entry 13). Hayase *et al.* have studied the interaction of molecular iodine with PEG and proposed that the interatomic distance in the iodine molecule slightly increased when the concentration of PEG was larger than a limiting concentration, C_1 . It was observed that C_1 decreased with an increase in the molecular weight of PEG in the case of molecular weights below 300 and was unaffected for higher molecular weights of PEG.²⁰

In the iodination reaction, an increase in the interatomic distance would result in weakening of the I–I bond in molecular iodine, which in turn would favour the electrophilic aromatic substitution reaction. See ESI for UV-Vis spectra of I₂+PEG-200-600.† λ_{max} = 360 nm corresponds to diatomic I₂, which is slightly shifted by interaction with the solvent (PEG).²⁰

Interestingly, when the iodination reaction was carried out with ICl, poor regioselectivity was observed as evidenced by the presence of polyiodination products of aniline shown by GC and GC-MS analysis (m/z (%) = 345 (100%) M⁺) (Scheme 3 and Fig. 7 ESI†).

When different iodine sources were used for the synthesis of 4-iodoaniline, it was observed that molecular iodine gave better yield and selectivity over iodine monochloride and *N*-iodo-succinimide under similar experimental conditions (Table 4, entries 1–3).

To evaluate the applicability of the $SO_4^{2-}/Ce_{0.07}Zr_{0.93}O_2$ catalytic system for iodination, the reactions of structurally varied and electronically diverse amines and phenols were carried out with I_2 and PEG-200 as a reaction medium; the results are summarized in Table 5. Iodination of aniline preferably takes place at the *para* position, with a high yield (97%)



Scheme 3 Reaction of aniline with ICl in PEG-200 at 30 °C.

Table 4	lodination of aniline with various iodine sources ^a			
Entry	Iodinating source	Yield $(\%)^b$		
1	I ₂	97		
2 3	NIS ICl	74 65 $(60/40)^c$		
		· · ·		

 a Reaction conditions: aniline (2 mmol), iodinating source (2 mmol), PEG-200 (2 ml), 12 h, RT, SO₄ $^{2-}/Ce_{0.07}Zr_{0.93}O_2$ catalyst (15 wt% w.r.t. aniline). b Isolated yields. c Polyiodination of aniline was observed.

Table 5 Iodination of arenes with I2 using sulphated ceria-zirconia^a

Entry	Substrate	Product	Time (h)	Yield $(\%)^b$
1	NH ₂	NH ₂	12	97
2	NH ₂	NH ₂	12	95
3	NH ₂ NO ₂	NH ₂ NO ₂	12	52
4	NH ₂ NO ₂	NH ₂ NO ₂	12	70
5	NH ₂	NH ₂ NO ₂	12	61
6	NH ₂	NH ₂	12	95
7	NH ₂	NH ₂ Cl	12	60
8			12	85
9		~o-~ı	12	35
10	N	N I	12	99

Entry	Substrate	Product	Time (h)	Yield $(\%)^b$
11	NH ₂	NH ₂ CH ₃	12	96
12			12	85
13	OCH ₃	OCH ₃	12	95
14	OH	OH	12	82
15	OH	OH	12	75
16	OH	OH	15	75
17	СНООН	СНООН	15	70
18	OH	OH CI	15	45



^{*a*} Reaction conditions: Arene (2 mmol), I₂ (2 mmol), PEG-200 (2 ml), RT, SO₄²⁻/Ce_{0.07}Zr_{0.93}O₂ catalyst (15 wt% w.r.t. arene). ^{*b*} Isolated yields, NR – no reaction.

of the product (Table 5, entry 1). When reaction of 4-iodoaniline was carried out with I2, 2,4-diiodoaniline was obtained also with an excellent yield of 95% (Table 5, entry 2). The iodination reaction of various arenes exhibited a strong dependency on the electron withdrawing and donating nature of the substituents present in the aromatic ring. Reactions of substituted anilines containing a strong electron withdrawing nitro group (-NO₂) at the ortho, meta and para positions gave moderate yield of the products (Table 5, entries 3-5). 3-Chloroaniline, gave 4-iodo-3chloroaniline in an excellent yield, whereas with 4-chloroaniline under the same reaction conditions, only a moderate yield of 2-iodo-4-chloroaniline was obtained (Table 5, entries 6 and 7). Interestingly, it was found that when the reaction of diphenylamine and diphenyl ether was carried out with two equivalents of I₂, only monoiodination occurred at one of the aromatic rings (Table 5, entries 8 and 9). The present reaction system was also applicable for the iodination of N,N-dimethylaniline, 4-methylaniline, 3-methoxyanisole and anisole (Table 5, entries 10-13).

To further expand the generality of the protocol, iodination of several phenols were carried out under the optimized reaction conditions (Table 5, entries 14–19). The reaction of phenol gave good yields of 4-iodophenol (Table 5, entry 14). The presence of electron donating and withdrawing substituents such as $-CH_3$, $-C(CH_3)_3$, -CHO and -Cl (*ortho* and *ortho*, *para*), which strongly influence the substitution reaction gave moderate to good yields of the products (Table 5, entries 15–19). Iodination of benzene and benzoic acid did not take place even when the reaction was conducted for 24 h (Table 5, entries 20 and 21). This indicates that the present process requires the presence of an electron donating group on the aromatic ring to facilitate the electrophilic aromatic substitution reaction.

Experimental

All commercial reagents were used as received unless otherwise mentioned. For analytical and preparative thin-layer chromatography, Merck (0.2 mm) and Kieselgel GF 254 (0.5 mm) precoated plates were used. The catalysts were characterized using XRD, FT-IR, TGA-DSC, BET surface area, total acidity by *n*-butylamine potentiometric titration method and SEM/EDAX. XRD patterns of the catalysts were recorded using a Bruker AXS diffractometer with Cu–K α radiation ($\lambda = 1.540562$ Å) over a 2θ range of 0-80°. SEM-EDAX data were obtained using a Tungsten source and a JEOL (model JSM-6390) instrument. Thermograms were recorded on an SDT Q 600V 8.2 Build 100 model from TA instruments. Potentiometric titrations were carried out using an Equiptronics digital potentiometer (EQ-614A) instrument fitted with a double junction electrode. The percentage conversion, selectivity and relative yields of the final products were determined using a Thermofisher gas chromatograph (GC-1000) fitted with a capillary column (30 m \times 0.32 mm ID – 0.25 µm BP-10) and FID detector. The products were identified by GC-MS using a Shimadzu (GCMS-QP 2010) E.I. mode instrument with high purity helium as the carrier gas. All the products obtained and discussed in this work have been previously reported and representative products were characterized by suitable technique such as GC and GC-MS (Shimadzu QP 2010) analysis.

Reusability of SO₄²⁻/Ce_{0.07}Zr_{0.93}O₂

A set of experiments were carried out to examine the reusability of the $SO_4^{2-}/Ce_{0.07}Zr_{0.93}O_2$ catalyst in the iodination reaction. The catalyst was separated after each run by filtration, washed



Fig. 1 Reusability of $SO_4^{2-}/Ce_{0.07}Zr_{0.93}O_2$ for iodination of aniline. *Reaction conditions*: aniline (10 mmol), I₂ (10 mmol), PEG-200 (10 ml), 12 h, 30 °C, $SO_4^{2-}/Ce_{0.07}Zr_{0.93}O_2$ catalyst: 15 wt% w.r.t. aniline, isolated yield.

with acetone and dried at 100 °C for 2 h in an oven before use in the next catalytic cycle. The $SO_4^{2-}/Ce_{0.07}Zr_{0.93}O_2$ catalyst was found to be reusable for five times without any significant loss in activity (Fig. 1).

Catalyst preparation

All chemicals of analytical grade were used without any further purification. A series of $SO_4^{2-}/Ce_xZr_{1-x}O_2$ catalysts were prepared by the method described by Lee *et al.*^{21,22} A precipitate of Zr(OH)₄ was obtained by adding aqueous ammonia to 0.25 M solution of zirconium oxychloride at room temperature with vigorous stirring until the pH reached 8.0. To this, an acidic aqueous solution of cerium sulphate, $Ce(SO_4)_2 \cdot 4H_2O$, was added and the ensuing precipitate was dried at 110 °C for 24 h and calcined at 650 °C for 2 h. A series of catalysts were prepared by varying the mol % of cerium (0.02–0.25) added.

General procedure for the iodination reaction

In a typical reaction procedure, 2 mmol of aniline and 2 mmol of molecular iodine were taken in a 25 ml round bottom flask. $SO_4^{2-}/Ce_xZr_{(1-x)} O_2$ (15 wt%) with 2 ml PEG-200 were added to the flask and the reaction mixture was stirred for 12 h at room temperature (30 °C). The reaction was continuously monitored by TLC and gas chromatography. After completion of the reaction, 10 ml of ethyl acetate was added to the reaction mixture and the catalyst was separated by simple filtration. The resulting reaction mass was treated with Na₂S₂O₃ solution (10 ml) and extracted with ethyl acetate (10 ml). It was then passed through a bed of anhydrous Na₂SO₄. Evaporation of the solvent yielded the iodo compound, which was purified by column chromatography on silica gel using a mixture of hexane–EtOAc (80 : 20) as the eluent. All the reaction products were compared with known samples and confirmed by GC-MS.

Conclusion

Sulphated ceria-zirconia was successfully employed as a heterogeneous catalyst with good activity for the synthesis of aryl iodides using molecular iodine in PEG-200 as a solvent. Various electron donating and withdrawing substituents on both aniline and phenol gave good to excellent yields with high regioselectivity. Among the various compositions studied, $SO_4^{2-}/Ce_{0.07}Zr_{0.93}O_2$ was found to be the best candidate in terms of activity, selectivity and reusability. Salient features such as an easy workup procedure, avoiding the use of an oxidant, an environmentally viable solvent and a recyclable catalyst renders the protocol environmentally benign.

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