

Electronic Supplementary Information (ESI) for Additive-free *N*-Methylation of Amines with Methanol over Supported Iridium Catalyst

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1. Materials

Chemical reagents used for catalyst preparation were sourced as follows. Alumina oxide (99.99% metals basis, γ phase, 20 nm), silicon oxide (99.5% metals basis, 15 nm), rhodium chloride hydrate ($\text{RhCl}_3 \cdot x\text{H}_2\text{O}$) and palladium chloride (PdCl_2) were purchased from Aladdin Bio-Chem Technology Co., Ltd.. Zirconia oxide (99.99% metals basis, 50 nm) and magnesium oxide (99.9% metals basis, 50 nm spherical) were supplied from Shanghai Macklin Biochemical Co., Ltd.. Titanium dioxide (P25, 50 m^2/g) were purchased from Evonik. Hexachloroplatinic acid hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) and ruthenium chloride hydrate ($\text{RuCl}_3 \cdot x\text{H}_2\text{O}$) were supplied by Shanghai Sinopharm Chemical Reagent Co., Ltd.. Dihydrogen hexachloroiridate (IV) hydrate ($\text{H}_2\text{IrCl}_6 \cdot x\text{H}_2\text{O}$) was purchased from Alfa Aesar (China) Chemical Co., Ltd. Unless otherwise noted, all organic chemicals used in this study were commercially available and used as received.

2. Catalyst characterizations

The Ir leaching test of the 0.3 wt% Ir/ZnO catalyst was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a Agilent 720ES spectrometer. The specific surface areas (SSA) of catalysts were measured by static N_2 physisorption at liquid nitrogen temperature (Quantachrome Autosorb iQ3) according to the Brunauer-Emmett-Teller (BET) methods. Before measurement, each sample (ca. 100 mg) was outgassed at 200 °C for 6 h. The X-ray diffraction (XRD) patterns of catalysts were recorded on Bruker D8 Advance X-ray diffractometer using the Ni-filtered Cu $K\alpha$ radiation source at 40 kV and 40 mA. The metal states of catalysts were measured by X-ray photoelectron spectroscopy (XPS, Thermo Scientific ESCALAB 250XI) and the binding energies refer to C1s at 284.8 eV. High resolution transmission electron microscopy (HRTEM) images were taken by a JEM-2100F microscope equipped with an EDX unit (Si (Li) detector) operating at 200 kV. The samples for characterization were prepared by grinding and subsequently dispersing the powder in ethanol and applying a drop of very dilute suspension on carbon-coated grids. The size distribution of the metal nanoclusters was determined by measuring more than 200 random particles in the images. The NH_3 - or CH_3OH -temperature-programmed desorption (NH_3 - or CH_3OH -TPD) for different catalysts using an BELCAT II (MICROTRAC MRB) equipped with a BEL mass. Generally, the loaded sample (100 mg) was pre-treated with high-purity Ar at 700 °C for 1 h. After cooling to the room temperature, NH_3 adsorption was performed by switching the Ar flow to a NH_3 gas until adsorption saturation. The gas-phase (and/or weakly adsorbed) NH_3 , was purged by Ar at the same temperature. NH_3 -TPD was then performed in the Ar flow by raising the temperature from 50 °C to 700 °C at a rate of 10 °C/ min^{-1} in pure He. The CH_3OH -TPD was performed by using a similar procedure.

3. Procedures for preparation of catalysts

(1) Preparation of ZnO. ZnO was synthesized via a chemical precipitation method.^[S1] Briefly, both an aqueous solution (120 mL H_2O) of $\text{Zn}(\text{SO}_4)_2 \cdot 7\text{H}_2\text{O}$ (60 mmol) and aqueous solution (120 mL H_2O) of NH_4HCO_3 (120 mmol) were fed dropwise into a blank beaker under agitation. A white slurry was then formed and stirred at room temperature for another 24 h. The precipitate was subsequently filtered and washed extensively with water (approximately 2 L). The precursor was dried in an oven at 100 °C for 12 h, and further calcinated at 500 °C for 2 h in a muffle furnace under air atmosphere with a rate of 5 °C/ min to obtain the ZnO. The specific surface area of resulted ZnO was 26 m^2/g .

(2) Preparation of Ir/ZnO with different Ir loadings. Series of Ir/ZnO catalysts with 0.1, 0.3, 0.5, 1.0 or 2.0 wt% Ir loadings were prepared by an incipient-wetness impregnation method. In a typical preparation, 0.99 g of ZnO (SSA: 26 m^2/g) was firstly added into 10 mL of an aqueous solution containing necessary amounts of $\text{H}_2\text{IrCl}_6 \cdot x\text{H}_2\text{O}$ (e.g. 3 mg Ir for 0.3 wt% Ir/ZnO). After a perfect mixing of the corresponding slurries, the resulting mixture was evaporated at 80 °C for 2 h and followed by drying at 100 °C for 5 h. Subsequently, the solid was treated in 10 vol % H_2/Ar at 400 °C with a heating rate of 5 °C/ min for 2 h to obtain the Ir/ZnO catalyst. The specific surface area of the optimized 0.3 wt% Ir/ZnO was 22 m^2/g . The

morphology and mean particle size distributions of 0.1, 0.3, 0.5, 1.0 and 2.0 wt% Ir/ZnO catalysts were measured by HRTEM.

(3) Preparation of 0.1 wt% Ir/Mg₄AlO. 0.1 wt% Ir/Mg₄AlO catalyst was prepared according our previous work.^[S2] Mg₄AlO was firstly synthesized via a coprecipitation-calcination method. A mixed aqueous solution (100 mL H₂O) containing Mg(NO₃)₂ · 6H₂O (80 mmol) and Al(NO₃)₃ · 9H₂O (20 mmol) were fed dropwisely into an equal volume of aqueous solution containing Na₂CO₃ (40 mmol) and NaOH (200 mmol) in around 2 h under vigorous stirring at room temperature. The formed slurry was aged at 65 °C for 18 h, after which the white precipitate was filtered and washed extensively with water (approximately 2 L) to avoid the residual Na species. The solid was dried in an oven at 100 °C for 12 h to obtain the hydrotalcite precursors, which was further calcinated at 500 °C for 4 h in a muffle furnace under air atmosphere with a rate of 5 °C/min to yield the Mg₄AlO. Subsequently, 2.0 g of obtained Mg₄AlO was introduced into an aqueous solution (10 mL) containing appropriate amounts of H₂IrCl₆ · 6H₂O (2 mg Ir). After a perfect mixing of the corresponding slurries, the resulting mixture was then evaporated at 80 °C, followed by drying at 100 °C for 5 h and then treated in 10 vol % H₂/Ar at 400 °C for 2 h to obtain the 0.1 wt% Ir/Mg₄AlO catalyst.

(4) Preparation of Supported Ir Catalysts with different supports. Supported Ir catalysts with different supports (including TiO, Al₂O₃, MgO, SiO₂ and ZrO₂) were prepared by a similar incipient-wetness impregnation method. 0.99 g of oxides was firstly added into a 10 mL aqueous solution of H₂IrCl₆ · xH₂O (containing 10 mg Ir). After a perfect mixing of the corresponding slurries, the resulting mixture was evaporated at 80 °C, followed by drying at 100 °C for 5 h and treating in 10 vol % H₂/Ar at 400 °C with a heating rate of 5 °C/min for 2 h to obtain the 1 wt% Ir/TiO₂, 1 wt% Ir/Al₂O₃, 1 wt% Ir/MgO, 1 wt% Ir/SiO₂ and 1 wt% Ir/ZrO₂, respectively. The morphology and mean particle size distributions of the catalysts were measured by HRTEM.

(5) Preparation of ZnO-supported Pd, Ru, Rh, and Pt catalysts. 1 wt% Pd/ZnO, 1 wt% Ru/ZnO, 1 wt% Rh/ZnO and 1 wt% Pt/ZnO catalysts were prepared by a similar incipient-wetness impregnation method. 0.99 g of ZnO was firstly introduced into a 10 mL of aqueous solution containing appropriate amounts of PdCl₂, RuCl₃ · xH₂O, RhCl₃ · xH₂O or H₂PtCl₆ · 6H₂O. After a perfect mixing, the corresponding slurries were evaporated at 80 °C, followed by drying at 100 °C for 5 h and then treated in 10 vol % H₂/Ar at 400 °C for 2 h or 300 °C for 2h. The morphology and mean particle size distributions of the catalysts were measured by HRTEM.

4. Catalytic activity measurements

4.1. General procedure A for catalytic activity tests using various catalysts and different under different reaction conditions. A mixture of aniline **1a** (0.5 mmol), methanol (1.0-7.0 mL), and catalyst (2 or 0.5 mol % metal based on **1a**) was charged into an autoclave (25 mL capacity, Anhui Kemi Machinery Technology Co., Ltd.). After sealing, the reactor was charged with N₂ (0.1-1 MPa) and heated at 100-150 °C with vigorous stirring (700 rpm with a magnetic stir bar) for 4 h. After the completion of the reaction, the autoclave was cooled to room temperature and the catalyst was filtered. The filtrate analyzed by GC and GC-mass using n-dodecane as the internal standard.

4.2. General procedure B for the synthesis of N,N-dimethylamines. A mixture of amines (0.5 mmol), methanol (5.0 mL) and 0.3 wt% Ir/ZnO (2 mol % Ir based on amine) was charged into an autoclave (25 mL capacity). After sealing, the reactor was charged with 0.5 MPa N₂ and heated at 150 °C with vigorous stirring (700 rpm with a magnetic stir bar) for given reaction time. After the completion of the reaction, the autoclave was cooled to room temperature and catalyst was filtered. The filtrate was firstly analyzed by GC and GC-mass using n-dodecane as the internal standard.

4.3. General procedure C for the synthesis of N-monomethylamines. A mixture of amines (0.5 mmol), methanol (0.5-5.0 mL), mesitylene (0-6 mL) and 0.3 wt% Ir/ZnO (Ir: 0.5 mol % based on amines) was charged into an autoclave (25 mL capacity). After sealing, the reactor was charged with 0.5 MPa N₂ and

heated at 150 °C with vigorous stirring (700 rpm with a magnetic stir bar) for given reaction time. After the completion of the reaction, the autoclave was cooled to room temperature and catalyst was filtered. The filtrate was firstly analyzed by GC and GC-mass using n-dodecane as the internal standard.

4.4. Flow reaction for the synthesis of *N,N*-dimethylamines (recycle mode). A solution of amines (0.5 mmol) in methanol (2.0-6.0 mL) was circulated through a heated column (4.6 × 50 mm) packed with 0.3 wt% Ir/ZnO (0.64 g, 2 mol%) at 150 °C with 0.125 - 0.5 mL/min flow rate under a back pressure of 1.5 MPa. After the completion of the reaction, the products were analyzed by GC and GC-mass using n-dodecane as the internal standard.

4.5 Recovery and reuse of 0.3 wt% Ir/ZnO catalyst without any treatment. First, fresh 0.3 wt% Ir/ZnO catalyst (2 mol % Ir based on aniline) was used in a mixture containing aniline (0.5 mmol), methanol (5.0 mL). The reaction was performed according to general procedure A. After the reaction, the catalyst was collected after filtration, washed with acetone three times and then then dried in vacuum for 12 h to obtain the first reused catalyst. Second, the first reused catalyst was then added for the next reaction with a mixture containing aniline (0.5 mmol), methanol (5.0 mL), with reaction following general procedure A. Repeating the recovery process and catalytic test process yields the second, third and fourth reused catalysts. After five runs, the the activity of the 0.3 wt% Ir/ZnO catalyst decreased gradually due to the slightly increasing of Ir NPs on the catalyst.

4.6 Recovery and reuse of 0.3 wt% Ir/ZnO catalyst with a treatment. First, fresh 0.3 wt% Ir/ZnO catalyst (2 mol % Ir based on aniline) was used in a mixture containing aniline (0.5 mmol), methanol (5.0 mL). The reaction was performed according to general procedure A. After the reaction, the catalyst was collected after filtration, washed with acetone three times and then then dried in vacuum for 12 h to obtain the first reused catalyst. Second, the first reused catalyst was calcinated at 400 °C for 0.5 h in the air and then reduced at 400 °C for 0.5 h under 10 vol% H₂/Ar before using it for the next reaction and then was used in a mixture containing aniline (0.5 mmol), methanol (5.0 mL), with reaction following general procedure A. Repeating the recovery process and catalytic test process yields the second, third and fourth reused catalysts. After five runs, the 0.3 wt% Ir/ZnO catalyst still remained highly active (Table 1, entry 18). Further reusing the catalysts to ten runs, the activity of the 0.3 wt% Ir/ZnO catalyst decreased gradually due to the increasing of Ir NPs on the catalyst.

4.7 Control experiments

(1) The reaction between *p*-toluidine and methanol: A mixture of *p*-toluidine (0.5 mmol), methanol (5.0 mL), and IrO₂ (2.2 mg), ZnO (640mg) or mixture of IrO₂ (2.2 mg) and ZnO (640mg) were placed into an autoclave (25 mL capacity). After sealing, the reactor was charged with 0.5 MPa N₂ and heated at 150 °C under vigorously stirred (700 rpm with a magnetic stir bar) for 2 h. After the reaction, the autoclave was cooled to room temperature and catalyst was filtered. The conversions and yields of the reactions were determined by GC analysis using n-dodecane as the internal standard..

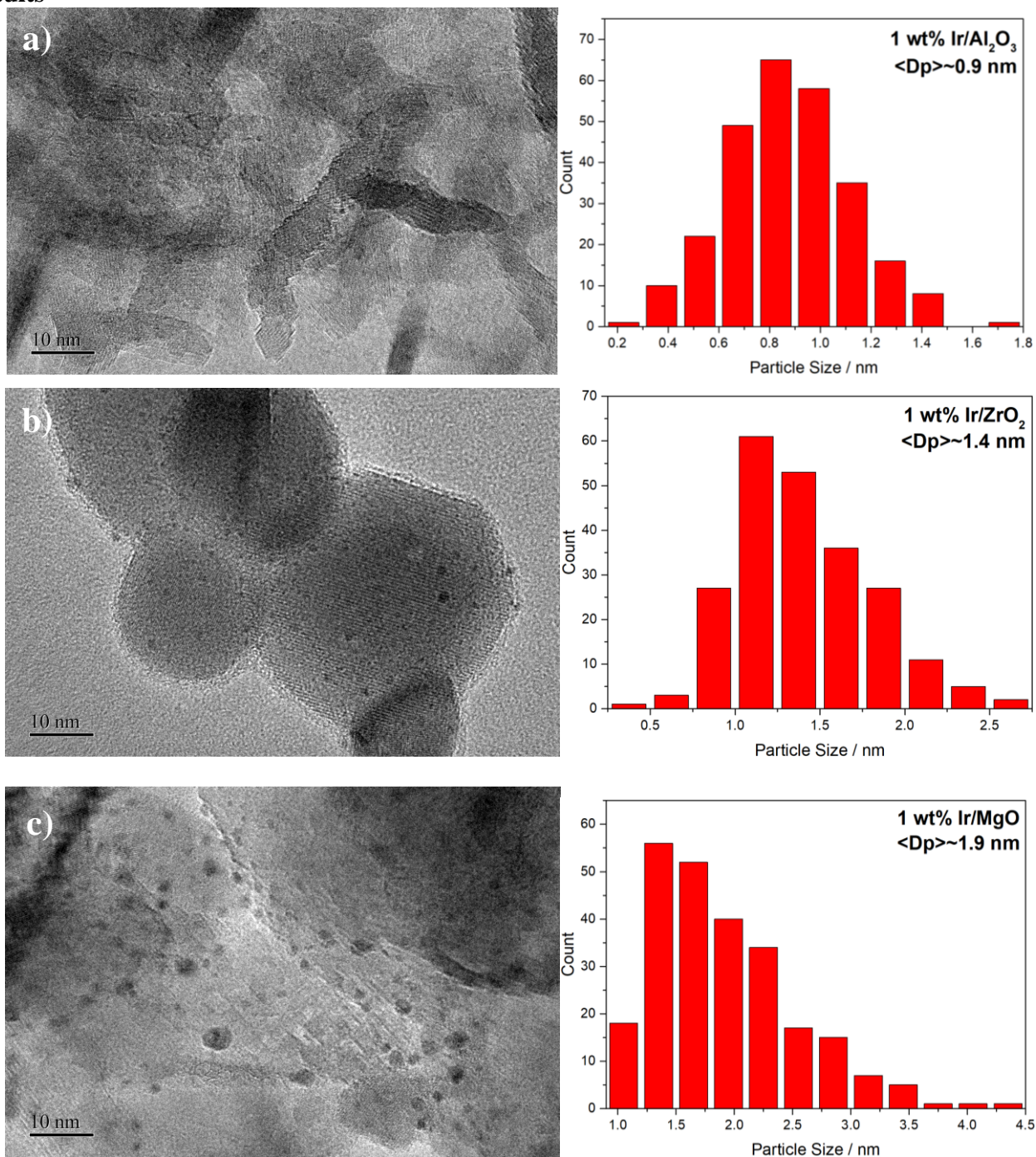
(2) The reaction of *p*-toluidine and formaldehyde: A mixture of *p*-toluidine (0.5 mmol), formaldehyde (10 mmol) and methanol (5.0 mL) were placed into a 25 mL autoclave and then conducted at room temperature (25 °C) in the air with vigorous stirring (700 rpm with a magnetic stir bar) for 5 min. The mixture was analysed by GC analysis using n-dodecane as the internal standard.

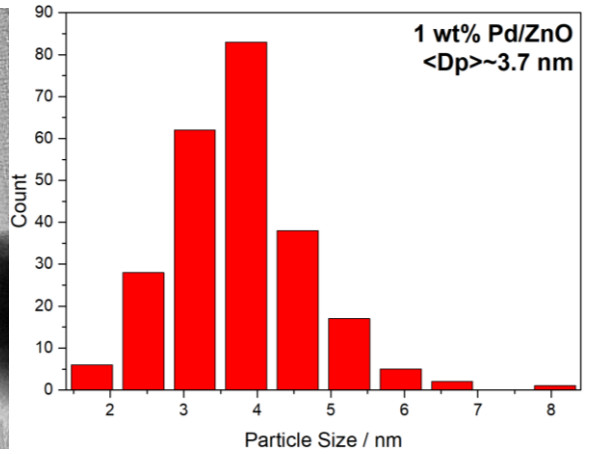
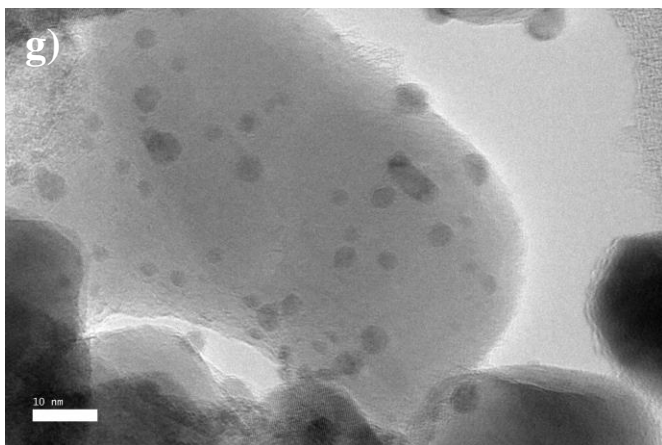
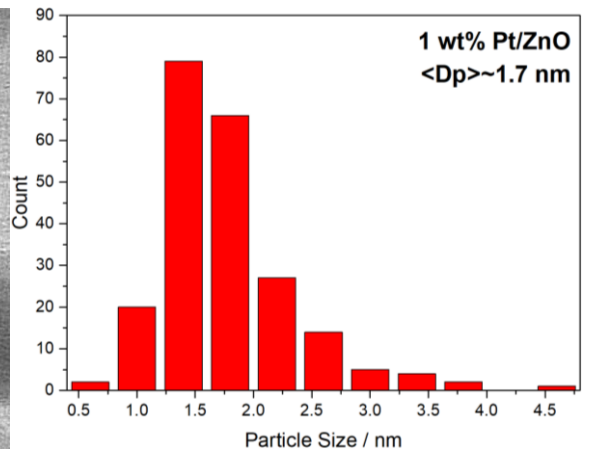
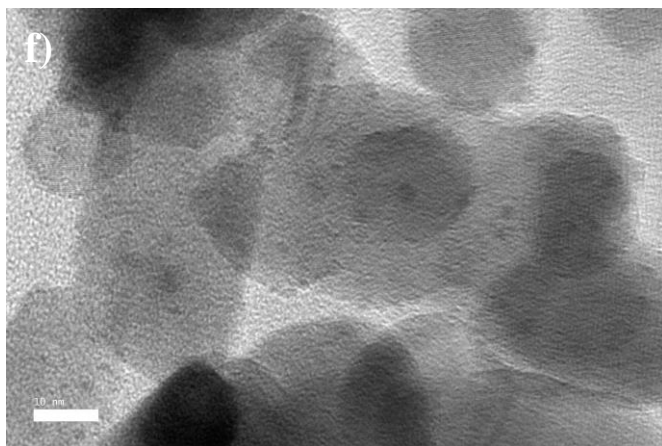
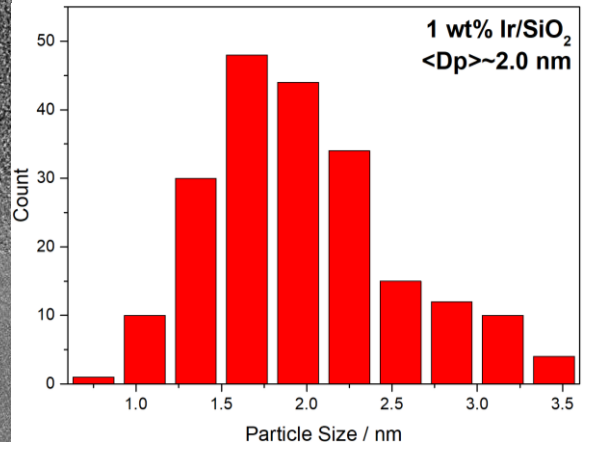
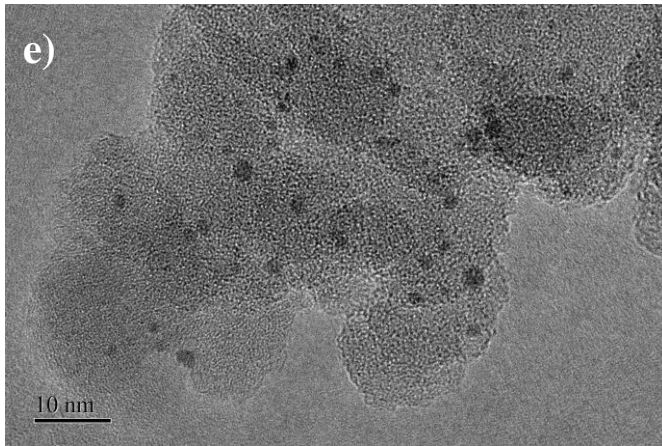
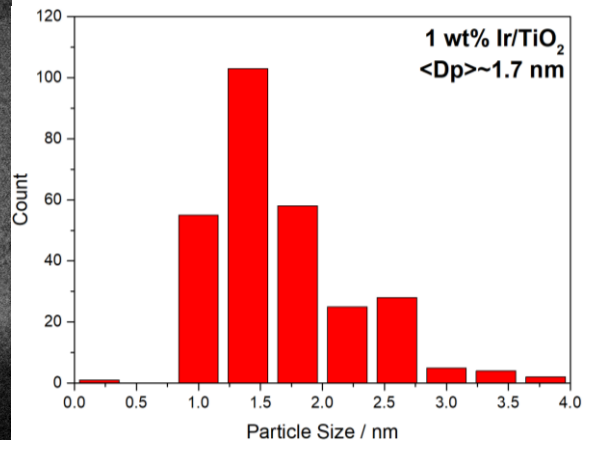
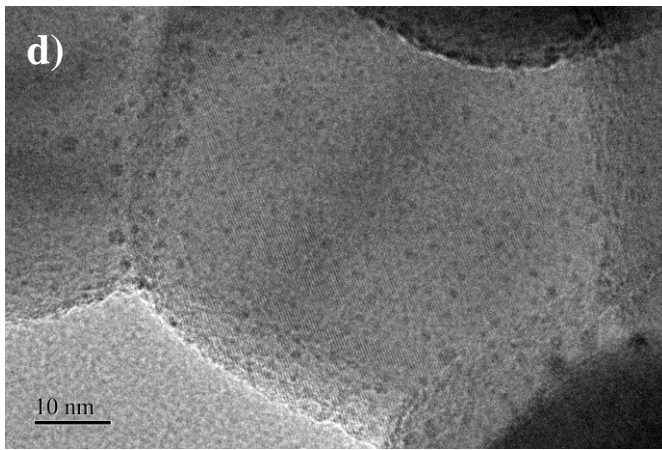
(3) The reaction of *p*-toluidine and formaldehyde with catalyst in the H₂: A mixture of *p*-toluidine (0.5 mmol), formaldehyde (10 mmol) and mesitylene (3.0 mL), were placed into a 25 mL autoclave and then conducted at room temperature (25 °C) in the air with vigorous stirring (700 rpm with a magnetic stir bar) for 5 min. Then 0.3 wt% Ir/ZnO (2 mol% Ir based on *p*-toluidine) was placed into an autoclave (25 mL capacity). After sealing, the reactor was charged with 1 bar H₂ and heated at 150 °C under vigorously stirred (700 rpm with a magnetic stir bar) for 2 h. After the reaction, the autoclave was cooled to room temperature and

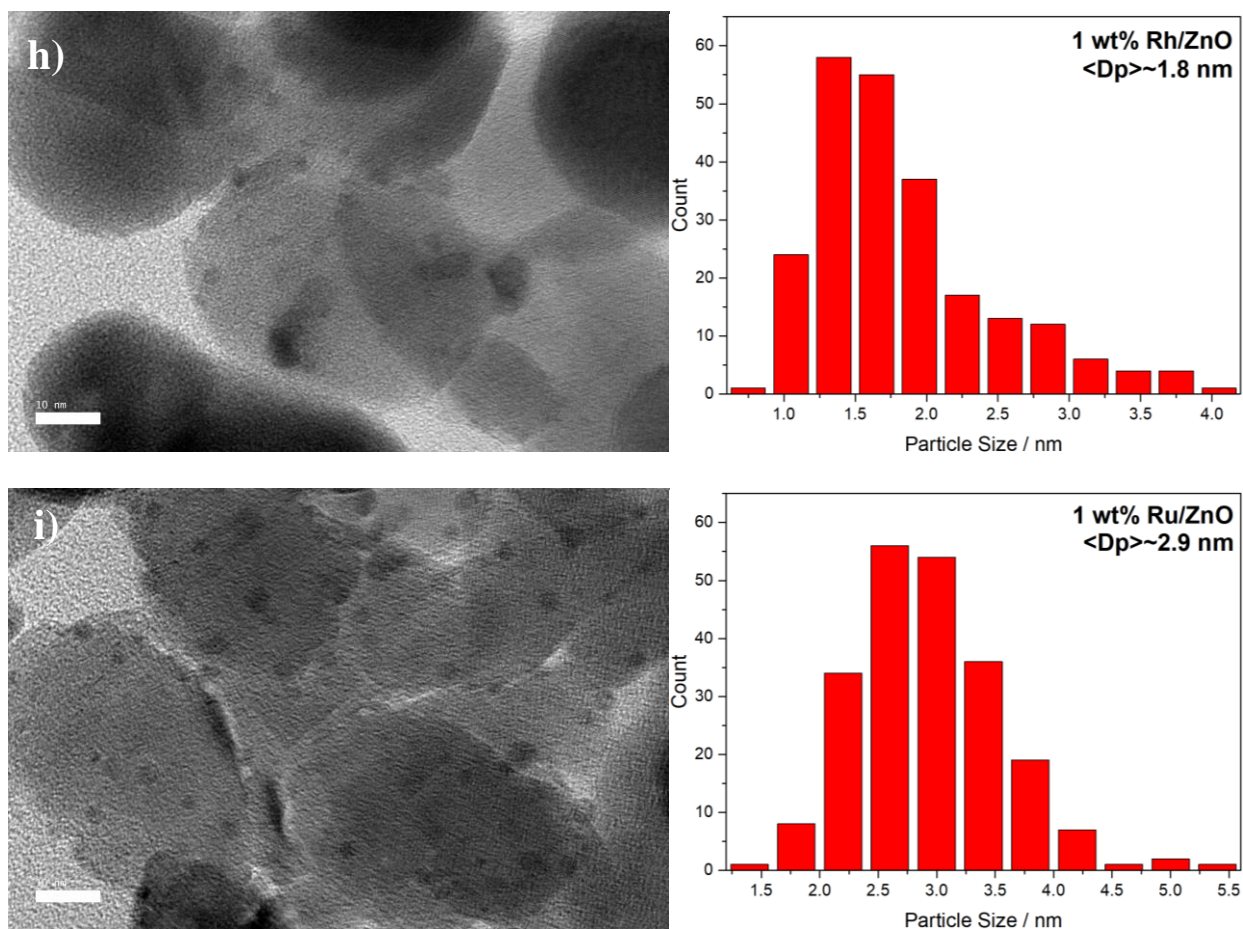
catalyst was filtered. The conversions and yields of the reactions were determined by GC and GC-MS analysis.

4.8 Flow system for the *N*-methylation of aniline or *p*-toluidine with methanol in gram scale. A solution of aniline or *p*-toluidine (10 mmol) in methanol (60 mL) was circulated through a heated column ($\Phi 1.0 \times 5.0$ cm) packed with 0.3 wt% Ir/ZnO (3.2 g) at 150 °C with 1.25 mL/min flow rate under a back pressure of 1.5 MPa. After the completion of the reaction (24 h), the products were analyzed by GC and GC-mass using *n*-dodecane as the internal standard.

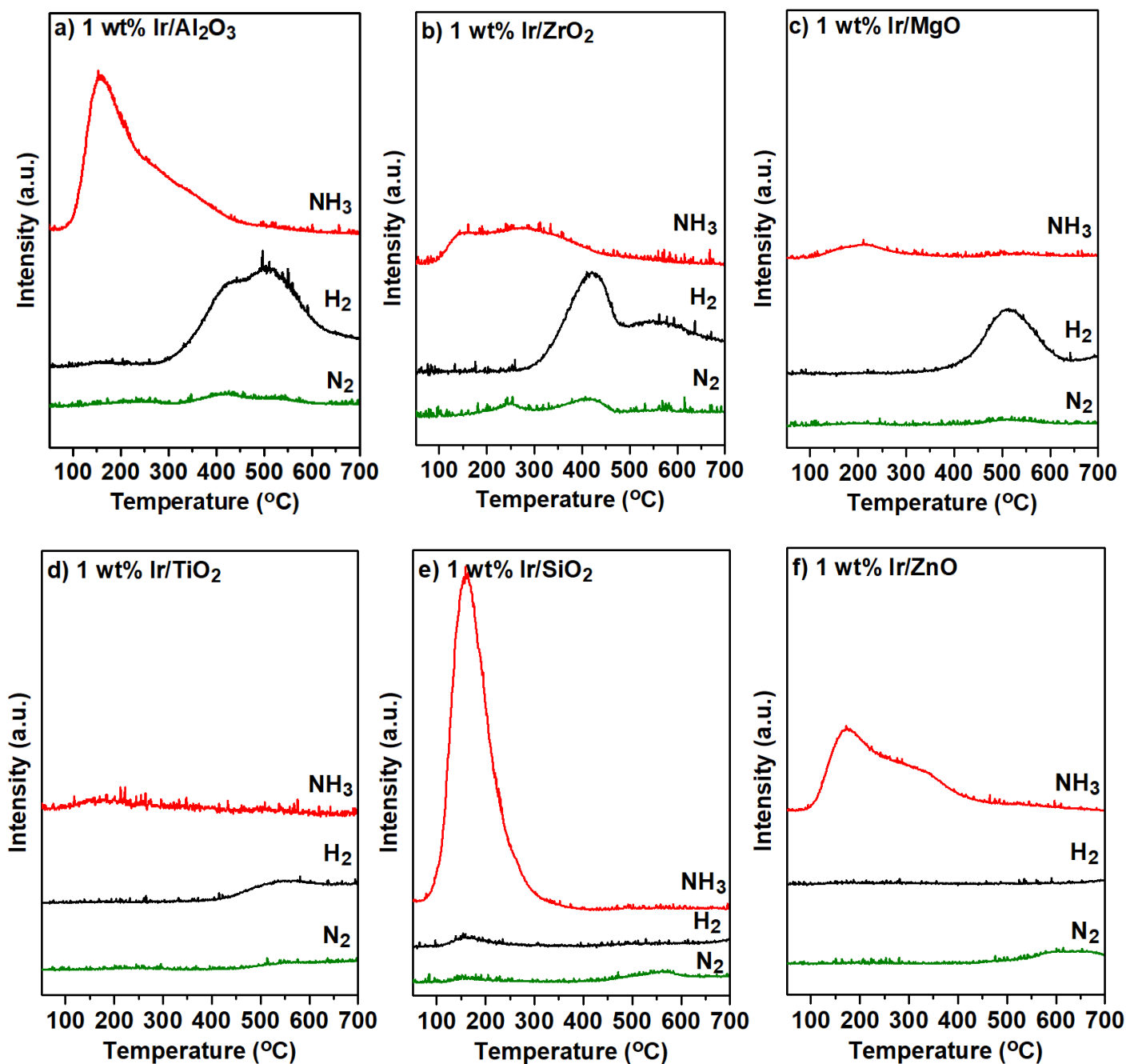
5. Results





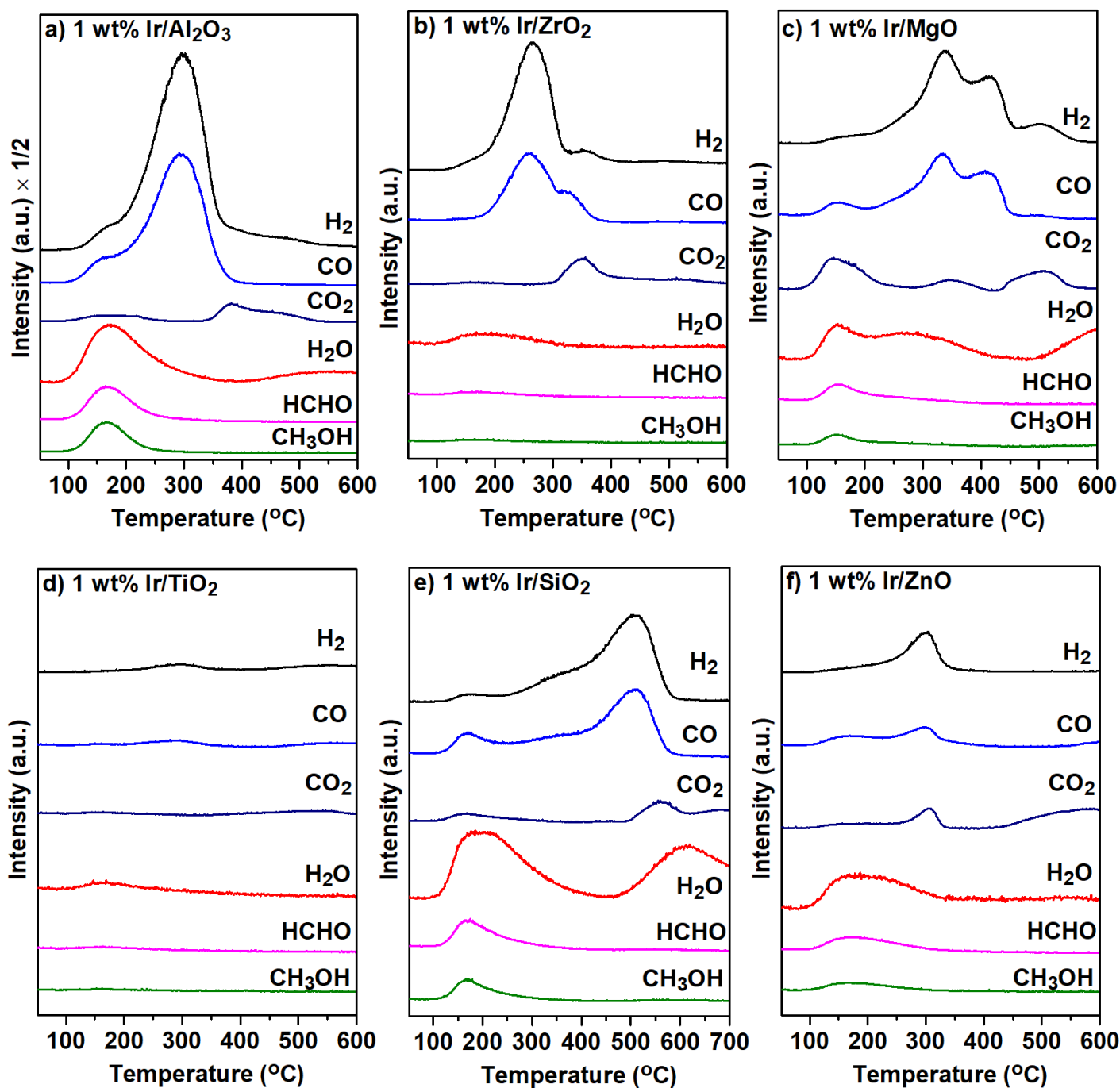


5.1 Figure S1. HRTEM images and metal particle size distribution of (a) 1 wt% Ir/Al₂O₃; (b) 1 wt% Ir/ZrO₂; (c) 1 wt% Ir/MgO; (d) 1 wt% Ir/TiO₂; (e) 1 wt% Ir/SiO₂; (f) 1 wt% Pt/ZnO; (g) 1 wt% Pd/ZnO; (h) 1 wt% Rh/ZnO; (i) 1 wt% Ru/ZnO. Scale bar: 10 nm.



5.2 Figure S2. NH₃-TPD results of (a) 1 wt% Ir/Al₂O₃; (b) 1 wt% Ir/ZrO₂; (c) 1 wt% Ir/MgO; (d) 1 wt% Ir/TiO₂; (e) 1 wt% Ir/SiO₂; (f) 1 wt% Ir/ZnO.

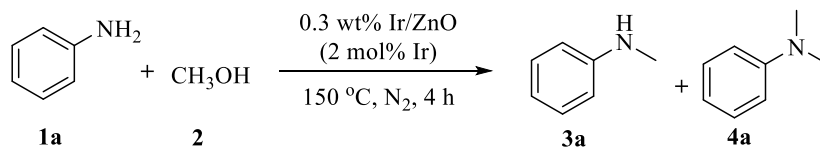
Note: The observation of H₂ and N₂ was due to the decomposition of NH₃ on Ir catalysts. 1 wt% Ir/ZnO absorbed a medium concentration of NH₃. Higher concentrations of absorbed NH₃ was observed on 1 wt% Ir/Al₂O₃ and 1 wt% Ir/SiO₂. Lower concentrations of NH₃ was detected on 1 wt% Ir/ZrO₂, 1 wt% Ir/MgO and 1 wt% Ir/TiO₂. While strong absorptions (even higher than 400 °C) were also observed on 1 wt% Ir/Al₂O₃, 1 wt% Ir/ZrO₂ and 1 wt% Ir/MgO. Due to both the absorption of anilines and desorption of *N*-methylated amines were occurred during the *N*-methylation reaction, a relatively weak and medium concentration of NH₃ absorption was crucial to obtain a high reactivity.



5.3 Figure S3. CH₃OH-TPD results of (a) 1 wt% Ir/Al₂O₃; (b) 1 wt% Ir/ZrO₂; (c) 1 wt% Ir/MgO; (d) 1 wt% Ir/TiO₂; (e) 1 wt% Ir/SiO₂; (f) 1 wt% Ir/ZnO.

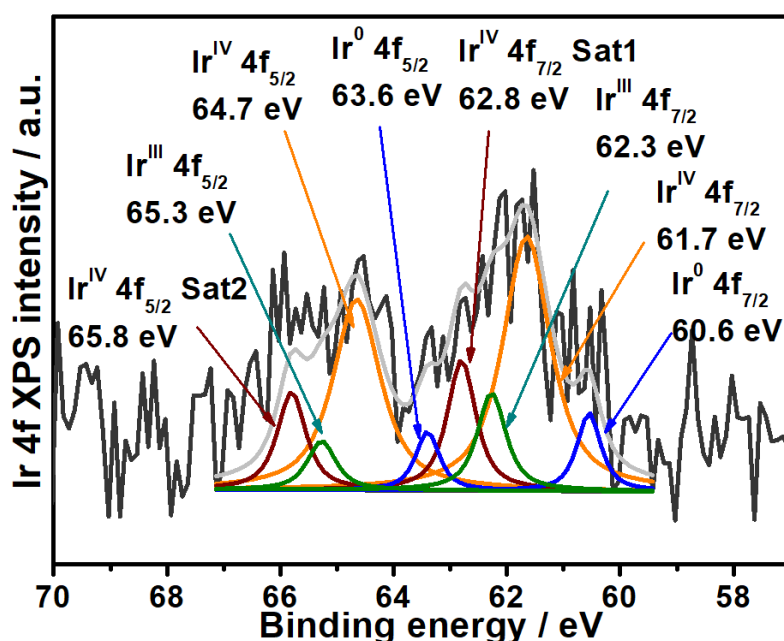
Note: the mass signal of CH₃OH, HCHO, CO₂, CO, H₂O and H₂ indicated the absorption of methanol and further reaction on the surface of the catalyst. On the 1 wt% Ir/Al₂O₃, 1 wt% Ir/MgO, 1 wt% Ir/SiO₂ and 1 wt% Ir/ZnO catalysts, the dehydrogenation of methanol could occur at 150 °C (the temperature used in *N*-methylation reaction). While on the 1 wt% Ir/Al₂O₃, 1 wt% Ir/MgO or 1 wt% Ir/SiO₂, the absorption of methanol was much stronger and the concentration was much higher than on the 1 wt% Ir/ZnO. There was almost no methanol dehydrogenation occurred on the 1 wt% Ir/ZrO₂ or 1 wt% Ir/TiO₂. Combining the above NH₃-TPD results and catalytic performances, it might suggest that a relatively moderate absorption of the substrates (including anilines and methanol) and the capability of dehydrogenation of methanol were the key factor to promote the reaction well.

5.4 Table S1. Methylation of aniline with methanol under different reaction conditions.^a

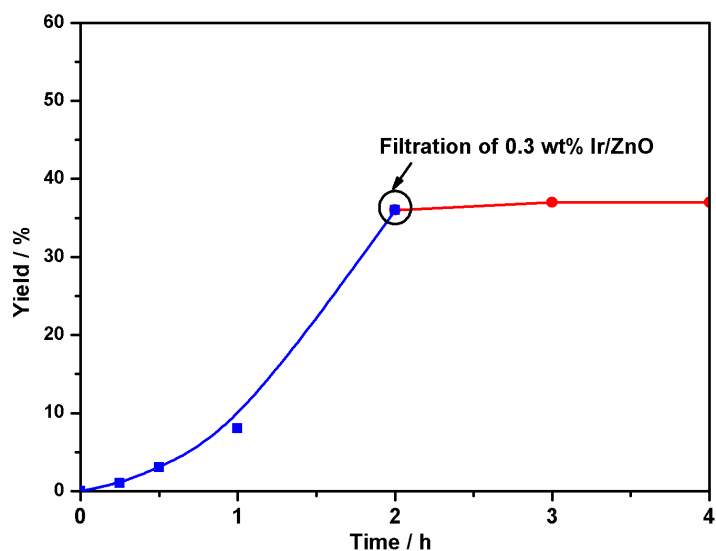


Entry	CH ₃ OH (mL)	H ₂ O (mL)	N ₂ Pressure (MPa)	T (°C)	Conv. (%) ^b	Yield (%) ^b		
						3a	4a	Others ^c
1	3	-	0.1	150	94	1	80	13
2	3	-	0.5	150	99	5	89	5
3	3	-	1	150	91	3	85	3
4	1	-	0.5	150	31	28	2	0
5	5	-	0.5	150	99	0	93	6
6	7	-	0.5	150	96	24	73	0
7	5	-	0.5	140	99	12	87	0
8	5	-	0.5	130	80	41	37	3
9	5	-	0.5	120	75	43	32	1
10	5	-	0.5	100	43	36	7	0
11	5	0.1	0.5	120	47	36	9	1
12	5	0.3	0.5	120	47	34	10	3
13	5	0.5	0.5	120	50	37	12	2

^a Reaction conditions: aniline (0.5 mmol), 0.3 wt% Ir/ZnO (2 mol % Ir based on **1a**), methanol, N₂. ^b Conversion and yield were determined by GC analysis based on **1a** consumption. ^c The main byproducts were 4-methyl-*N,N*-dimethylaniline and/or 4,4'-methylenebis(*N,N*-dimethylaniline).

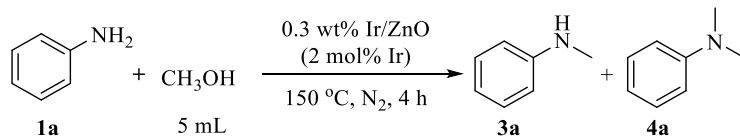


5.5 Figure S4. XPS results of 0.1% Ir/ZnO with a larger intensity scale.



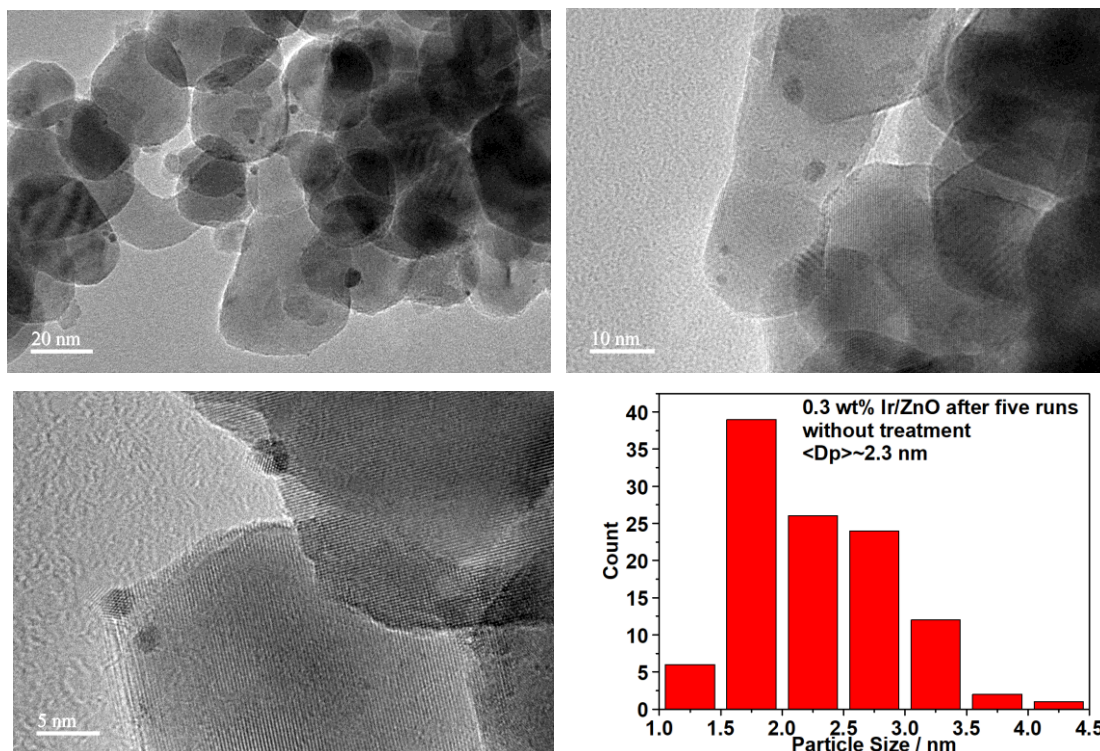
5.6 Figure S5. *N,N*-dimethylamine yield as a function of time in the hot filtration test. Reaction conditions: aniline (0.5 mmol), 0.3 wt% Ir/ZnO (2 mol% Ir based on **1a**), methanol (5.0 mL), 0.5 MPa N₂.

5.7 Table S2. Recycle results of the 0.3 wt% Ir/ZnO catalyst without any treatment in the reaction of aniline with methanol.



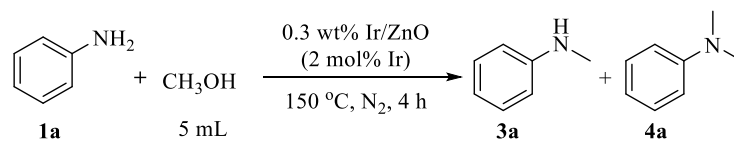
Run	Conv. (%) ^b	Yield (%) ^b		
		3a	4a	Others ^c
1	99	0	93	6
2	100	0	95	0
3	99	13	86	0
4	98	19	79	0
5	98	22	76	0

^a Reaction conditions: aniline (0.5 mmol), 0.3% Ir/ZnO (2 mol % Ir based on **1b**), CH₃OH (5 mL), 0.5 MPa N₂, 150 °C, 4 h. ^b Conversion and yield were based on GC analysis. ^c The main by-products were 4-methyl-*N,N*-dimethylaniline and/or 4,4'-methylenebis(*N,N*-dimethylaniline).



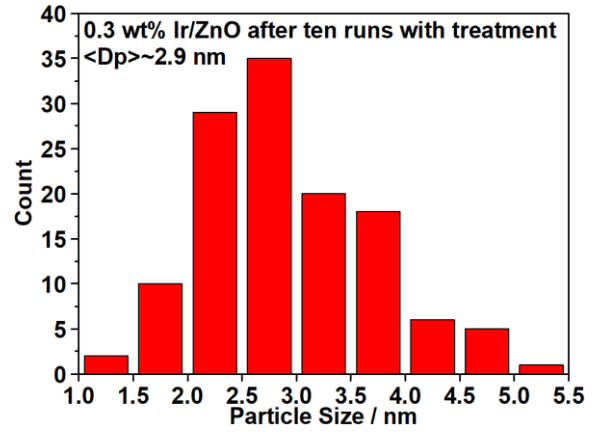
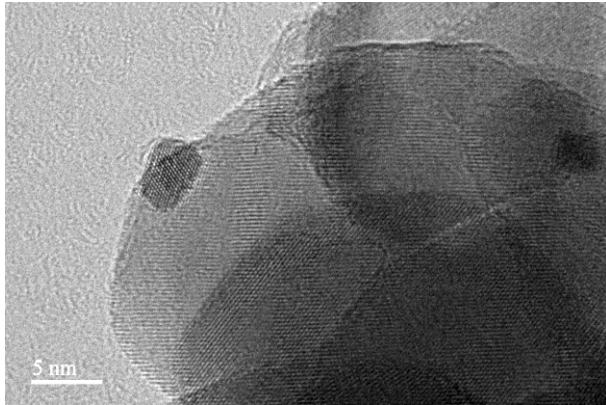
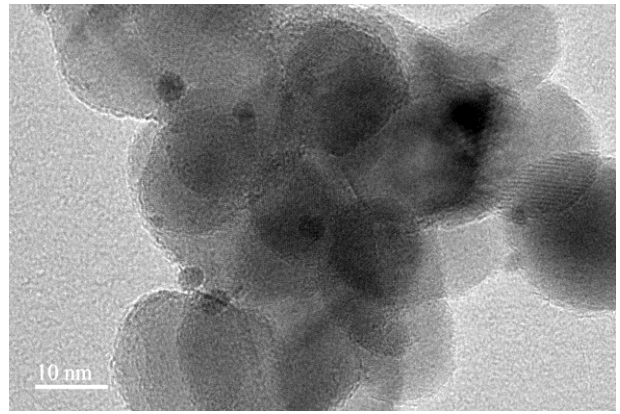
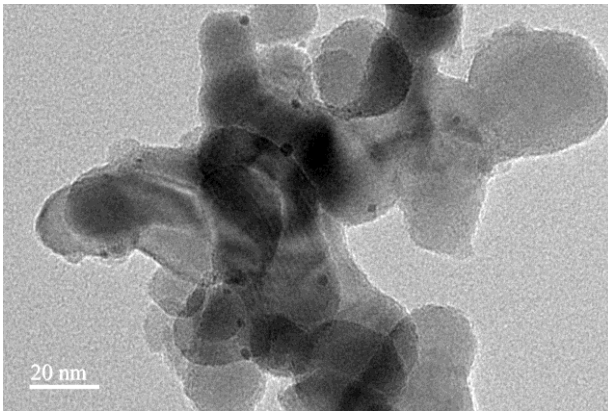
5.8 Figure S6. HRTEM images and metal particle size distribution of 0.3% Ir/ZnO after five runs without any treatment.

5.9 Table S3. Recycle results of the 0.3 wt% Ir/ZnO catalyst with a calcination-reduction treatment (details see section 4.5 in ESI) in the reaction of aniline with methanol.



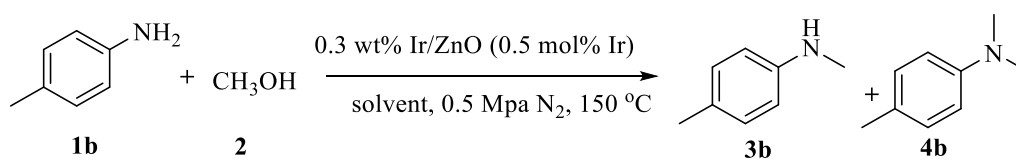
Run	Conv. (%) ^b	Yield (%) ^b		
		3a	4a	Others ^c
1	99	0	93	6
2	100	2	98	0
3	100	0	96	4
4	100	0	97	3
5	100	0	96	4
6	98	11	87	0
7	87	25	62	0
8	88	27	54	2
9	82	35	47	0
10	81	37	44	0

^a Reaction conditions: aniline (0.5 mmol), 0.3% Ir/ZnO (2 mol % Ir based on **1b**), CH₃OH (5 mL), 0.5 MPa N₂, 150 °C, 4 h. ^b Conversion and yield were based on GC analysis. ^c The main by-products were 4-methyl-*N,N*-dimethylaniline and/or 4,4'-methylenebis(*N,N*-dimethylaniline).



5.10 Figure S7. HRTEM images and metal particle size distribution of 0.3% Ir/ZnO after ten runs with calcination-reduction treatment.

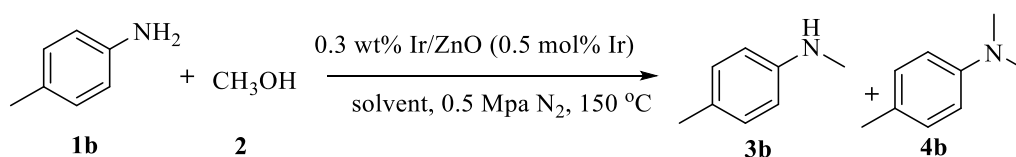
5.11 Table S4. *N*-monomethylation of *p*-toluidine with methanol catalyzed by 0.3 wt% Ir/ZnO in different solvents^a



Entry	Solvent	Conv. (%) ^b	Yield (%) ^b		
			3b	4b	Others
1 ^c	-	66	45	21	0
2	H ₂ O	40	33	7	0
3	CH ₃ CN	8	1	0	7
4	THF	20	20	0	0
5	<i>tert</i> -butanol	41	37	4	0
6	toluene	13	13	0	0
7	hexane	45	40	2	0
8	<i>o</i> -xylene	32	24	0	5
9	<i>m</i> -xylene	58	53	5	0
10	<i>p</i> -xylene	59	3	36	20
11	mesitylene	57	54	3	0

^a Reaction conditions: *p*-toluidine (0.5 mmol), 0.3% Ir/ZnO (0.5 mol % Ir based on **1b**), solvent (3 mL), CH₃OH (1 mL), 0.5 MPa N₂, 150 °C, 4 h. ^b Conversion and yield were based on GC analysis. ^c CH₃OH 5 mL.

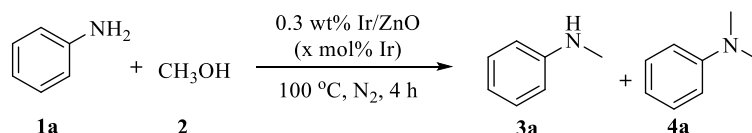
5.12 Table S5. Effect of solvent volume for the 0.3 wt% Ir/ZnO catalyzed *N*-methylation of *p*-toluidine with methanol.^a



Entry	V _{mesitylene} (mL)	V _{CH₃OH} (mL)	t (h)	Conv. (%) ^b	Yield (%) ^b		
					3b	4b	Others
1	3	1	4	57	54	3	0
2	3	1	7	77	61	16	0
3	3	1	9	95	77	18	0
4	6	1	6	44	43	1	0
5	6	1	12	87	81	5	1
6	6	0.5	7	50	48	2	0
7	6	0.5	15	95	83	12	0

^a Reaction conditions: *p*-toluidine (0.5 mmol), 0.3% Ir/ZnO (0.5 mol% Ir based on **1b**), 0.5 MPa N₂, 150 °C, 4 h. ^b Conversion and yield were based on GC analysis.

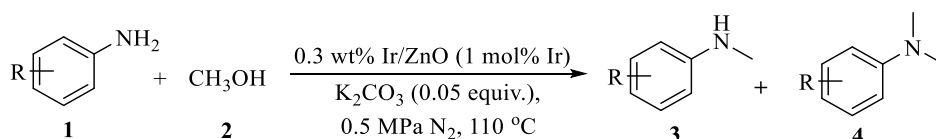
5.13 Table S6. Methylation of aniline with methanol in the presence of different bases.^a



Entry	Base	Ir (x mol%)	Temperature (°C)	t (h)	Conv. (%) ^b	Yield (%) ^b		
						3a	4a	Others ^c
1	-	2	100	4	43	36	7	0
2	NaOMe (0.1 equiv.)	2	100	4	34	31	2	1
3	KO ^t Bu (0.1 equiv.)	2	100	4	32	31	2	0
4	NaOH (0.1 equiv.)	2	100	4	28	26	1	1
5	Cs ₂ CO ₃ (0.1 equiv.)	2	100	4	29	29	0	0
6	Na ₂ CO ₃ (0.1 equiv.)	2	100	4	35	34	1	0
7	Na ₂ CO ₃ (1 equiv.)	2	100	4	23	23	0	0
8	K ₂ CO ₃ (0.1 equiv.)	2	100	4	39	38	1	0
9	K ₂ CO ₃ (1 equiv.)	2	100	4	9	9	0	0
10	K ₂ CO ₃ (0.1 equiv.)	1	100	4	26	26	0	0
11	K ₂ CO ₃ (0.1 equiv.)	1	100	24	39	38	1	0
12	K ₂ CO ₃ (0.05 equiv.)	1	100	24	54	52	2	0
13	K ₂ CO ₃ (0.05 equiv.)	1	110	24	90	84	6	0

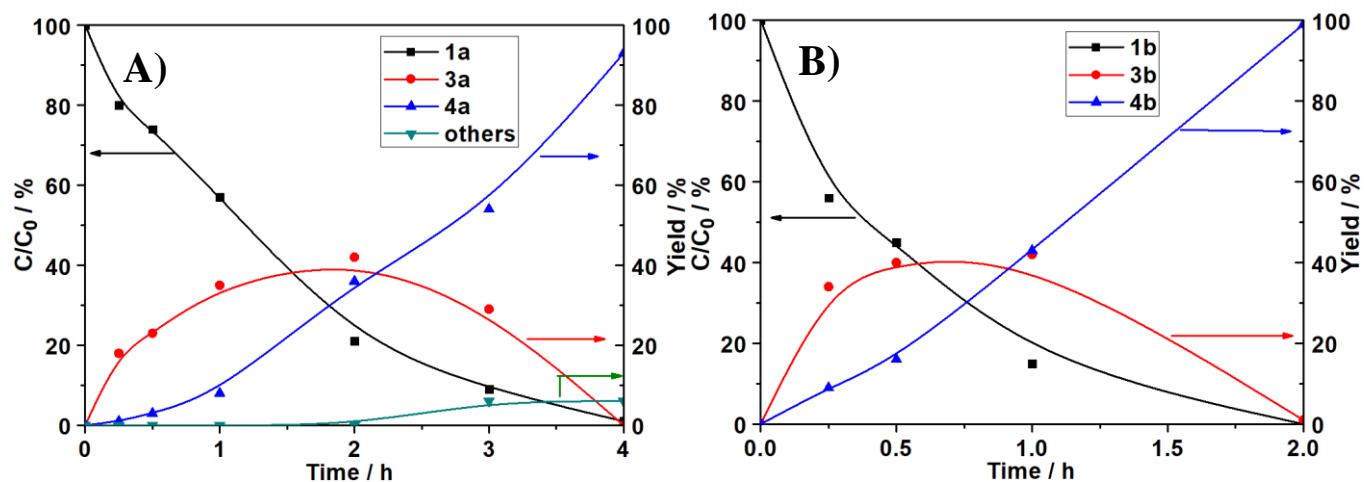
^a Reaction conditions: aniline (0.5 mmol), base (0.1-1 equiv.), 0.3 wt% Ir/ZnO (2 mol % Ir based on **1a**), methanol (5 mL), 100 °C, 0.5 Mpa N₂. ^b Conversion and yield were determined by GC analysis based on **1a** consumption.

5.14 Table S7. *N*-monomethylation of amines with methanol in the presence of K₂CO₃.^a

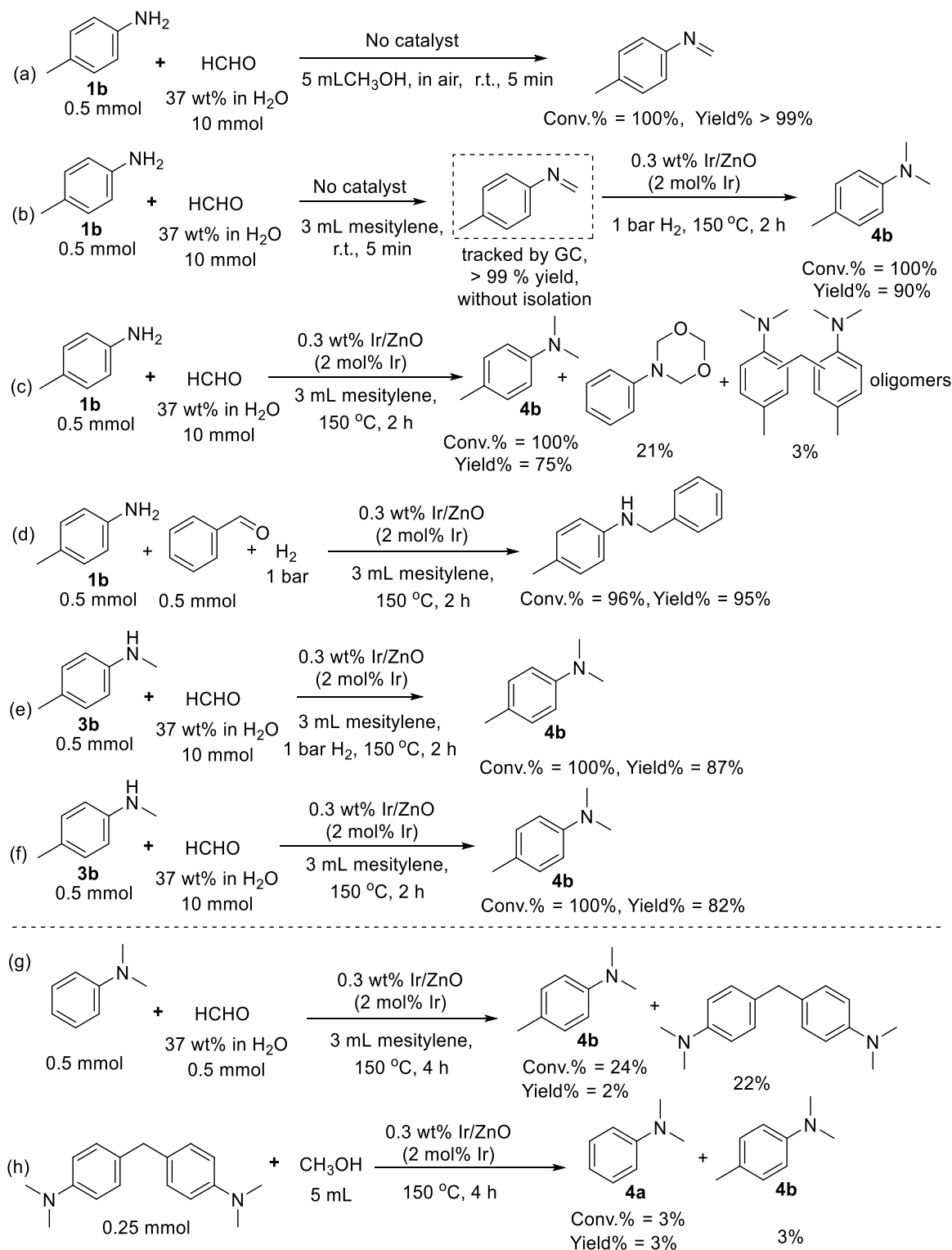


Entry	Substrate	t (h)	Conv. (%) ^b	Yield (%) ^b	
				3	4
1		24	90	84	6
2		16	87	78	9
3		24	93	87	6

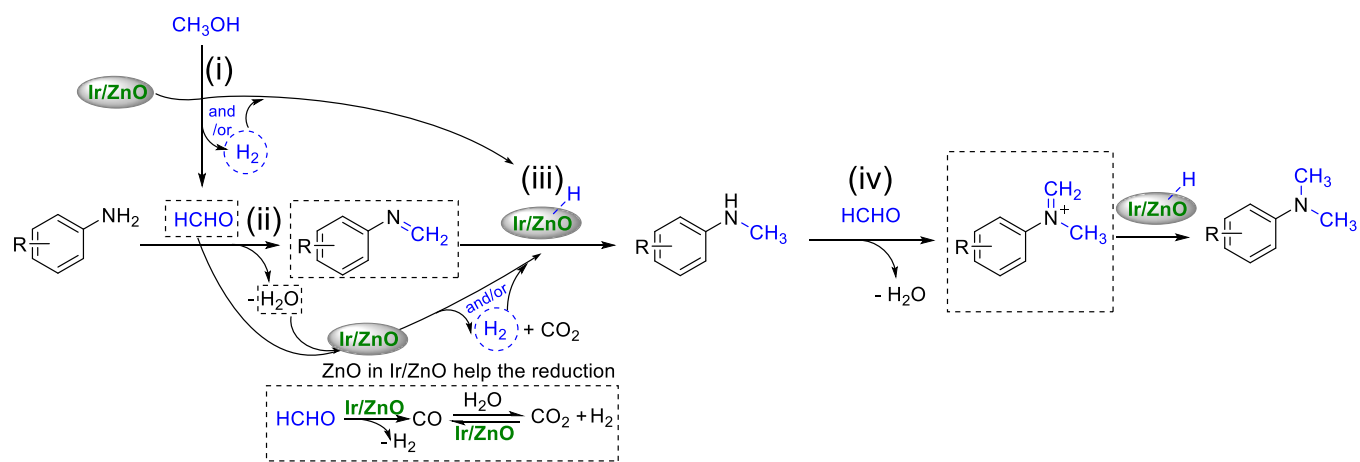
^a Reaction conditions: amine (0.5 mmol), 0.3 wt% Ir/ZnO (1 mol % Ir based on **1**), K₂CO₃ (0.05 equiv. based on **1**), 0.5 MPa N₂, methanol (5 mL), 100 °C. ^b Conversion and yield were determined by GC and GC-MS analysis based on **1** consumption.



5.15. Figure S8. A) Reaction profiles for **4a** synthesis from **1a-methanol** over 0.3 wt% Ir/ZnO. Reaction conditions: aniline (0.5 mmol), 0.3 wt% Ir/ZnO (1 mol% Ir based on **1a**), 5.0 mL methanol, 0.5 MPa N₂. 4-methyl-*N,N*-dimethylaniline and/or 4,4'-methylenebis(*N,N*-dimethylaniline) was identified as the main compound in the other by products determined by GC-MS. B) Reaction profiles for **4b** synthesis from **1b-methanol** over 0.3 wt% Ir/ZnO. Reaction conditions: 4-Methylaniline (0.5 mmol), 0.3 wt % Ir/ZnO (2 mol% Ir based on **1b**), 5.0 mL methanol, 0.5 MPa N₂. Concentration of the reactants and yield of the products were determined by GC.



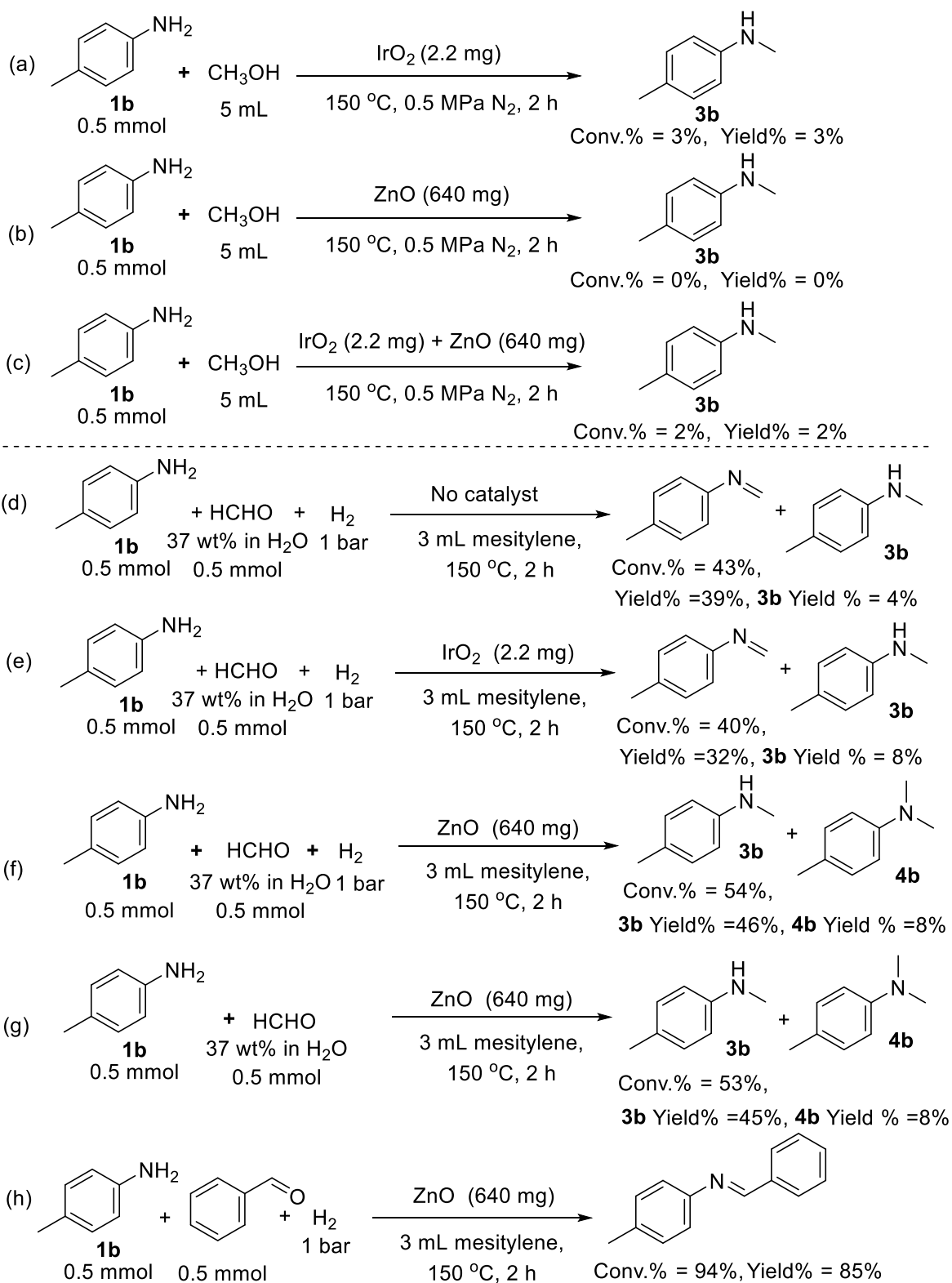
5.16. Scheme S1. Control experiments for the mechanism study.



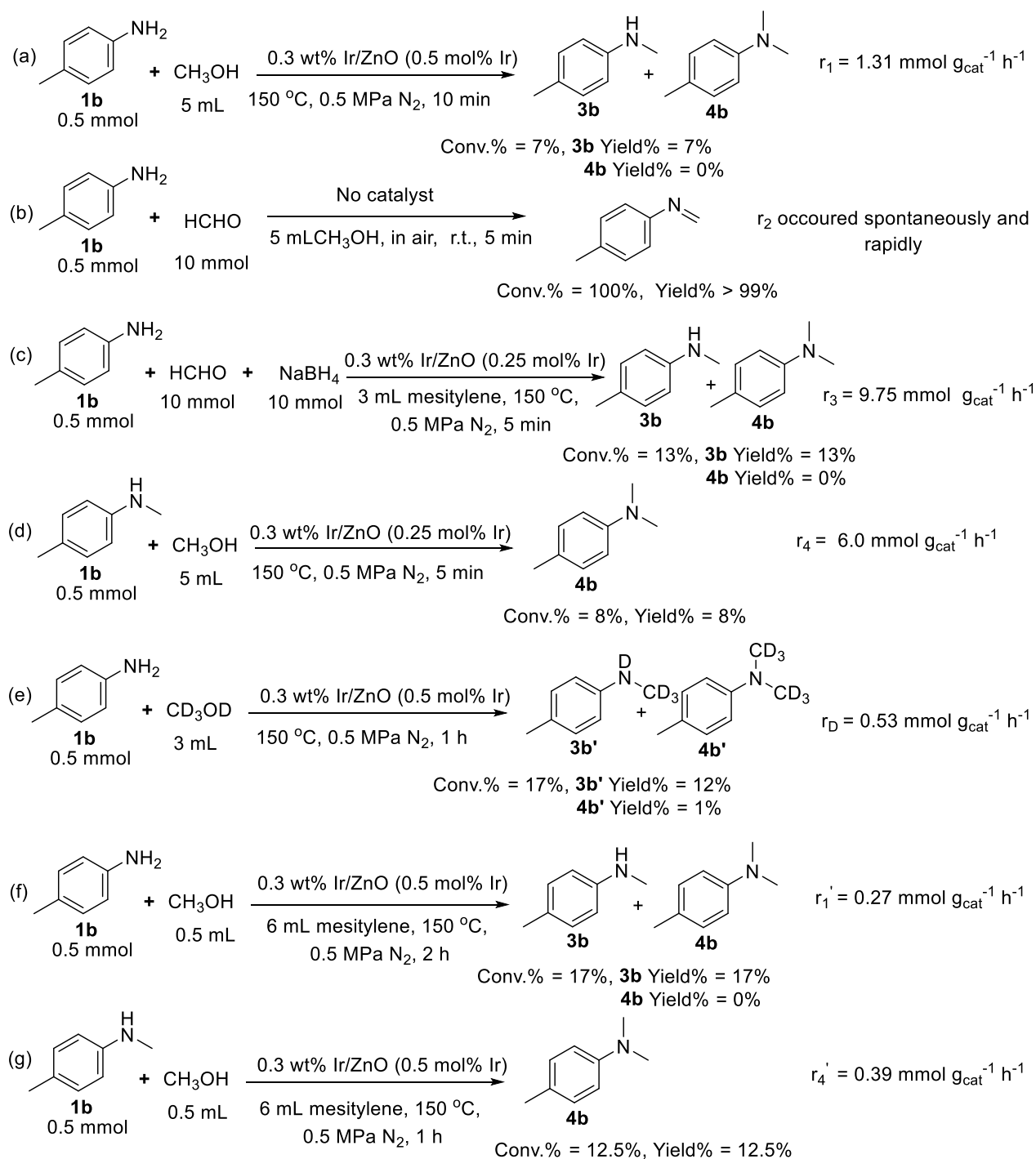
5.17. Scheme S2. Plausible mechanism for the *N*-methylation reaction.

5.18. Table S8. The amounts of Ir and ZnO employed in the reaction for different Ir/ZnO samples.

Entry	Samples	Amount (mg)	
		Ir	ZnO
1	2 wt% Ir/ZnO	1.9	94.1
2	1 wt% Ir/ZnO	1.9	190.1
3	0.5 wt% Ir/ZnO	1.9	382.1
4	0.3 wt% Ir/ZnO	1.9	638.1
5	0.1 wt% Ir/ZnO	1.9	1918

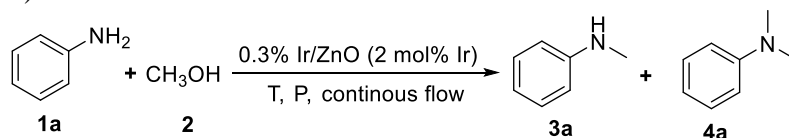


5.19. Scheme S3. Control experiments for the studies on roles of Ir and ZnO.



5.20. Scheme S4. Initial reaction rate for steps involved in the *N*-methylation reaction.

5.21. Table S9. 0.3 wt% Ir/ZnO catalyzed *N*-methylation of aniline with methanol under continuous flow conditions (recycle mode).^a



Entry	Flow rate (mL/min)	CH ₃ OH (mL)	Conv. (%) ^b	Yield (%) ^b		
				3a	4a	Others
1	0.125	6	87	18	69	0
2	0.25	6	97	13	87	0
3	0.5	6	91	46	45	1
4	1.0	6	55	41	12	2
5	1.5	6	54	41	12	1
6	0.25	4	98	8	89	2
7	0.25	3	100	5	95	0
8	0.25	2	100	1	99	0

^a Reaction conditions: a mixture of **1a** (0.5 mmol) and CH₃OH was circulated through a heated column packed with 0.3 wt% Ir/ZnO (0.64 g, 2 mol%), 150 °C, 2 h. The back pressure was 1.5 MPa under the temperature of reaction. ^b Conversion and yield were based on GC analysis.

6. References

[S1] C. Zhou, Y. Wang, L. Du, H. Yao, J. Wang and G. Luo, *Ind. Eng. Chem. Res.*, 2016, **55**, 11943.

[S2] W. Qiang, X. Liu and T.-P. Loh, *ACS Sustainable Chem. Eng.*, 2019, **7**, 8429.