

# Partially reduced iridium oxide clusters dispersed on titania as efficient catalyst for facile synthesis of dimethylformamide from CO<sub>2</sub>, H<sub>2</sub> and dimethylamine

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## Electronic Supplementary Information

### 1. Chemicals and materials

Dimethylamine (NHMe<sub>2</sub>, 40 wt% in H<sub>2</sub>O), diethylamine (NHEt<sub>2</sub>, >99.0 wt%), di-*n*-butylamine (NH(*n*-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>, 99.0 wt%), di-*n*-hexylamine (NH(*n*-C<sub>6</sub>H<sub>13</sub>)<sub>2</sub>, 99.0 wt%), diphenylamine (NHPh<sub>2</sub>, 99.0 wt%), *N*-methylaniline (NHMePh, 98.0 wt%), *n*-octane (*n*-C<sub>8</sub>H<sub>18</sub>, >99.0 wt%), 1,4-dioxane (C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>, 99.5 wt%), tetrabutyl titanate (C<sub>16</sub>H<sub>36</sub>O<sub>4</sub>Ti, 99.5 wt%), iridium chloride (H<sub>2</sub>IrCl<sub>6</sub>, Ir≥35.0 wt%), palladium chloride (PdCl<sub>2</sub>, Pd≥60 wt%), rhodium chloride hydrate (RhCl<sub>3</sub>·*x*H<sub>2</sub>O, Rh≥38.5 wt%), ruthenium chloride hydrate (RuCl<sub>3</sub>·*x*H<sub>2</sub>O, Ru≥37.5 wt%), copper nitrate hydrate (Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O) and zinc nitrate hydrate (Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O) were supplied by Alfa Aesar and used without further purification. P25 (TiO<sub>2</sub> with the specific surface area of 45 m<sup>2</sup> g<sup>-1</sup>, 70% anatase phase and 30% rutile phase), CeO<sub>2</sub> (Adnano 90) were donated from Evonik.

### 2. Catalyst characterization

**2.1 Elemental analysis:** The metal loadings of the catalysts were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a Thermo Electron IRIS Intrepid II XSP spectrometer.

**2.2 BET analysis:** The BET specific surface areas of the prepared catalysts were determined by adsorption–desorption of nitrogen at liquid nitrogen temperature, using a Micromeritics TriStar 3000 equipment. Sample degassing was carried out at 300 °C prior to acquiring the adsorption isotherm.

**2.3 X-ray diffraction (XRD) analysis:** The XRD information of the samples was carried out on a German Bruker D8 Avance X-ray diffractometer using nickel filtered Cu K $\alpha$  radiation at 40 kV and 40 mA.

**2.4 X-ray photoelectron spectroscopy (XPS):** XPS data were recorded with a Perkin Elmer PHI 5000C system equipped with a hemispherical electron energy analyzer. The spectrometer was operated at 15 kV and 20 mA, and a magnesium anode (Mg K $\alpha$ ,  $h\nu = 1253.6$  eV) was used. The C 1s line (284.6 eV) was used as the reference to calibrate the binding energies (BE).

**2.5 Transmission electron microscopy (TEM):** A JEOL 2011 microscope operating at 200 kV equipped with an EDX unit (Si(Li) detector) was used for the TEM investigations. The samples for electron microscopy were prepared by grinding and subsequent dispersing the powder in ethanol and applying a drop of very dilute suspension on carbon-coated grids. The mean Ir particle size in the samples was estimated from TEM micrographs by counting around 150–200 particles.

**2.6 Temperature-programmed reduction (TPR):** Prior to TPR test, the sample (50 mg) was pretreated at 200 °C for 2 h and cooled to 30 °C in flowing He. TPR experiment was carried out in 5 vol% H<sub>2</sub>/Ar flowing at 40 mL min<sup>-1</sup>, with a ramping rate of 5 °C min<sup>-1</sup> to a final temperature of ca. 600 °C. The signal was monitored using a TCD detector.

**2.7 CO<sub>2</sub> temperature-programmed desorption (CO<sub>2</sub>-TPD):** The ability of CO<sub>2</sub> adsorption for the catalyst was measured by CO<sub>2</sub>-TPD experiment. Prior to adsorption of CO<sub>2</sub>, the sample (100 mg) was pretreated at 200 °C for 30 min and cooled to 80 °C in flowing He. At this temperature, sufficient CO<sub>2</sub> was injected until adsorption saturation, followed by purging with He (30 mL min<sup>-1</sup>) for about 2 h. The temperature was then raised from 80 °C to 800 °C at a ramp rate of 5 °C min<sup>-1</sup> to desorb CO<sub>2</sub>. The desorbed CO<sub>2</sub> was detected by on-line gas chromatography with a TCD detector.

### 3. Catalyst preparation

**3.1 Preparation of HSA-TiO<sub>2</sub> support:** HSA-TiO<sub>2</sub> (specific surface area: 124 m<sup>2</sup> g<sup>-1</sup>) powders predominantly in the anatase phase were prepared by the hydrolysis of tetrabutyl titanate (C<sub>16</sub>H<sub>36</sub>O<sub>4</sub>Ti). Briefly, 10.0 g C<sub>16</sub>H<sub>36</sub>O<sub>4</sub>Ti was dropwise added to 200 mL deionized water under vigorous stirring at 25 °C, and then the mixture was further stirred for 2 h. The precipitate obtained was filtered and washed with deionized water. The resultant powder was dried at 100 °C for 12 h and then calcined in air at 400 °C for 4 h with a ramp rate of 5 °C min<sup>-1</sup>.

**3.2 Preparation of Ir/HSA-TiO<sub>2</sub> and Ir/HSA-TiO<sub>2</sub>-A:** These catalysts were prepared using the deposition-precipitation (DP) method as described elsewhere.<sup>S1</sup> Briefly, 1.0 g HSA-TiO<sub>2</sub> support was dispersed in appropriate amount of aqueous solution of H<sub>2</sub>IrCl<sub>6</sub> (200 mL, 0.26 mM), the pH of which was adjusted to 8.0 using an aqueous solution of 0.1 M NaOH and kept stirring for 2 h. The dispersion was aged at 25 °C for 1 h and was extensively washed with deionized water until it was free of chloride ions. The solid sample was dried under vacuum at 25 °C for 12 h and then treated in 5 vol% H<sub>2</sub>/Ar denoted as Ir/HSA-TiO<sub>2</sub> or in air denoted as Ir/HSA-TiO<sub>2</sub>-A at 400 °C for 2 h with a ramp rate of 5 °C min<sup>-1</sup>, respectively. The actual Ir loading of 0.5 wt% was determined by ICP-AES analysis for both catalysts.

**3.3 Preparation of Ir/HSA-TiO<sub>2</sub>-IM:** Ir/HSA-TiO<sub>2</sub>-IM sample was prepared by a conventional incipient wetness impregnation (IM) method. Briefly, 1.0 g of HSA-TiO<sub>2</sub> support was added to 1 mL of an aqueous solution containing appropriate amount of H<sub>2</sub>IrCl<sub>6</sub> to prepare the 0.5 wt% Ir/HSA-TiO<sub>2</sub>-IM. After a perfect mixing of the slurry, sample was dried at 80 °C for 6 h and then treated in 5 vol% H<sub>2</sub>/Ar at 400 °C for 2 h with a ramp rate of 5 °C min<sup>-1</sup>.

**3.4 Preparation of Cu/ZnO-CP:** The Cu/ZnO-CP catalyst was prepared with the co-precipitation (CP) method as described elsewhere.<sup>S2</sup> Briefly, 4.4 g Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O and 3.6 g Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O were dissolved in 500 mL of deionized water. Then an aqueous solution of Na<sub>2</sub>CO<sub>3</sub> (0.25 M) was added dropwise under vigorous stirring at 80 °C until pH = 7. The resulting precipitate was aged for 4 h. The suspension was filtered and washed several times with deionized water. The solid was dried at 100 °C overnight, and then treated in air at 350 °C for 12 h. Prior to use, the catalyst was reduced in 5 vol% H<sub>2</sub>/Ar at 300 °C for 3 h with a ramp rate of 5 °C min<sup>-1</sup>. The Cu loading was controlled to be ca. 50 wt%.

**3.5 Preparation of other supported metal catalysts:** The samples Pd/P25-IM, Ru/P25-IM, Rh/P25-IM, Pd/ZrO<sub>2</sub>-IM, Ru/ZrO<sub>2</sub>-IM, Ir/P25-IM, Ir/ZrO<sub>2</sub>-IM, Ir/Al<sub>2</sub>O<sub>3</sub>-IM, Ir/ZnO-IM, Ir/CeO<sub>2</sub>-IM, Ir/MgO-IM were prepared by IM method as described in Section 3.3. H<sub>2</sub>IrCl<sub>6</sub>, PdCl<sub>2</sub>, RhCl<sub>3</sub>·xH<sub>2</sub>O and RuCl<sub>3</sub>·xH<sub>2</sub>O precursors were used to impregnate the corresponding metal oxide supports. The metal loadings were controlled to be ca. 0.5 wt%.

## 4. Catalytic activity measurement

**4.1 General procedure for the direct synthesis of DMF from CO<sub>2</sub>, H<sub>2</sub> and aqueous NHMe<sub>2</sub>:** The experiments were carried out in high-pressure stainless steel autoclave mini-reactor (25 mL). Typically, 15.1

mmol  $\text{NHMe}_2$  solution and a known amount of catalyst were placed in the autoclave. Then the autoclave was sealed, and  $\text{CO}_2$  and  $\text{H}_2$  gaseous mixtures were charged into it after internal air being degassed completely using  $\text{N}_2$  at 25 °C. The stirrer (800 rpm) was started until the desired temperature was reached. After a certain time, the autoclave was placed in cool water and the gas was carefully released. The gaseous mixture was analyzed using a gas chromatograph Agilent 6820 equipped with a TDX-01 column connected to a thermal conductivity detector. A known amount of internal standard 1,4-dioxane was added into the aqueous product in autoclave. The reaction mixture was transferred into a centrifuge tube and the solid catalyst was separated by centrifugation. The product solution was quantitatively analyzed using a gas chromatograph Agilent 7820 A equipped with a HP-WAX capillary column (0.25 mm  $\times$  30 m) connected to a flame ionization detector. Identification of the products was performed by using a GC-MS spectrometer. For the catalyst recycling experiment, the centrifuged catalysts were collected and washed with deionized water several times, followed by drying under vacuum at room temperature for 12 h.

**4.2 Direct synthesis of other formamide from  $\text{CO}_2$ ,  $\text{H}_2$  and the corresponding amine:** The synthesis experiments were carried out in high-pressure stainless steel autoclave mini-reactor (25 mL). Typically, 5 mmol amine, 2 mL *n*-octane and 100 mg Ir/HSA-TiO<sub>2</sub>-A catalyst were placed in the autoclave. Then the autoclave was sealed and 30 bar  $\text{CO}_2$  and 30 bar  $\text{H}_2$  were charged into it after internal air being degassed completely using  $\text{N}_2$  at 25 °C. The stirrer (800 rpm) was started until the desired temperature of 140 °C was reached. After 10 h, the autoclave was placed in cool water and the gas was carefully released. The gaseous mixture was analyzed using a gas chromatograph Agilent 6820 equipped with a TDX-01 column connected to a thermal conductivity detector. A known amount of internal standard 1,4-dioxane was added into the aqueous product in autoclave. The reaction mixture was transferred into a centrifuge tube and the solid catalyst was separated by centrifugation. The product solution was quantitatively analyzed using a gas chromatograph Agilent 7820 A equipped with a HP-WAX capillary column (0.25 mm  $\times$  30 m) connected to a flame ionization detector. Identification of the products was performed by using a GC-MS spectrometer.

## 5. Results

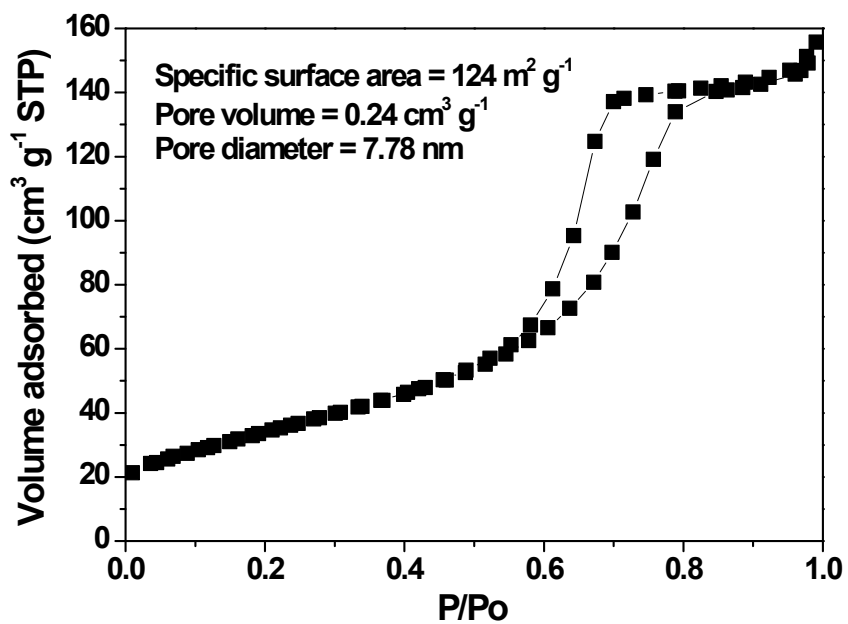


Fig. S1  $\text{N}_2$  adsorption-desorption data of HSA- $\text{TiO}_2$ .

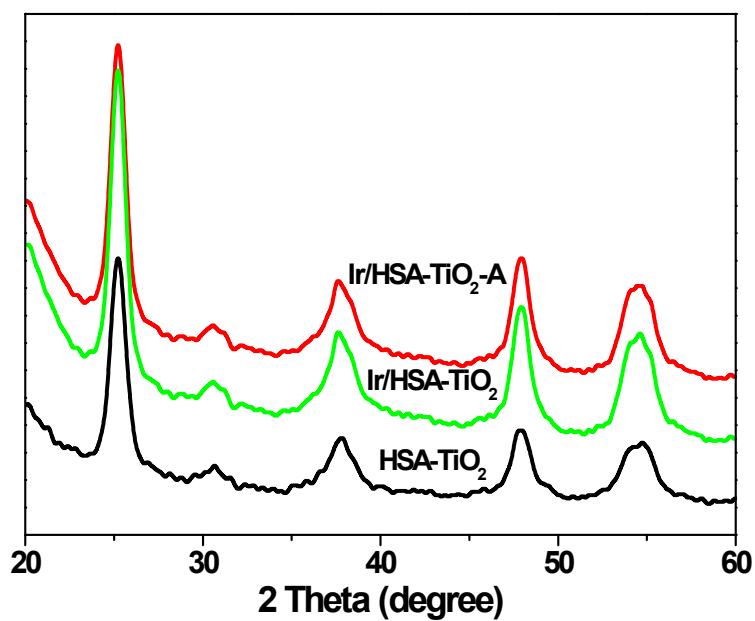


Fig. S2 XRD patterns of HSA- $\text{TiO}_2$ , Ir/HSA- $\text{TiO}_2$ -A, and Ir/HSA- $\text{TiO}_2$  samples.

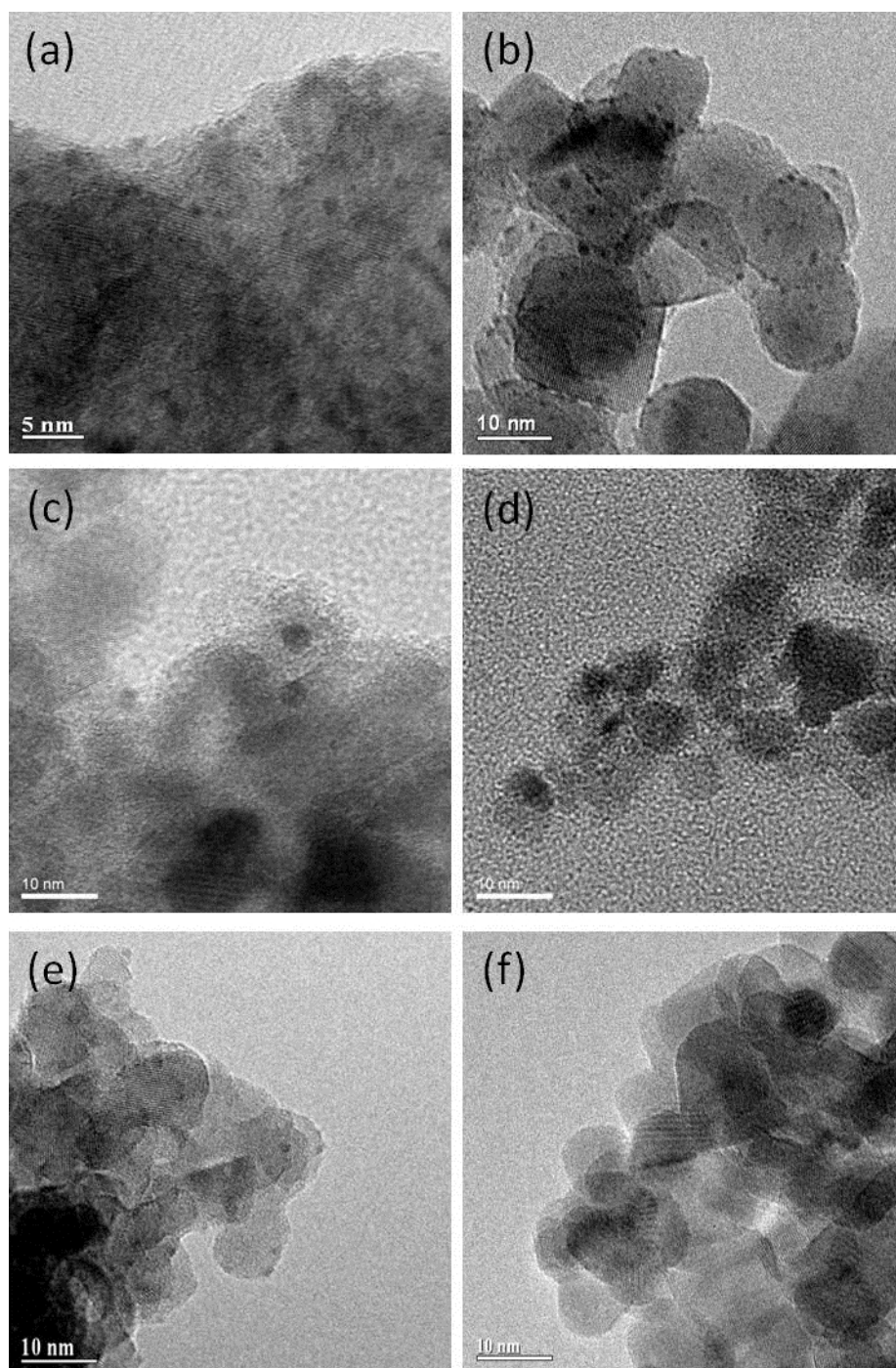


Fig. S3 TEM images of (a) Ir/ZrO<sub>2</sub>-IM, (b) Ir/P25-IM, (c) Ir/HSA-TiO<sub>2</sub>-IM, (d) Ir/CeO<sub>2</sub>-IM, (e) Ir/HSA-TiO<sub>2</sub>-A-H and (f) Ir/HSA-TiO<sub>2</sub>-H-A.

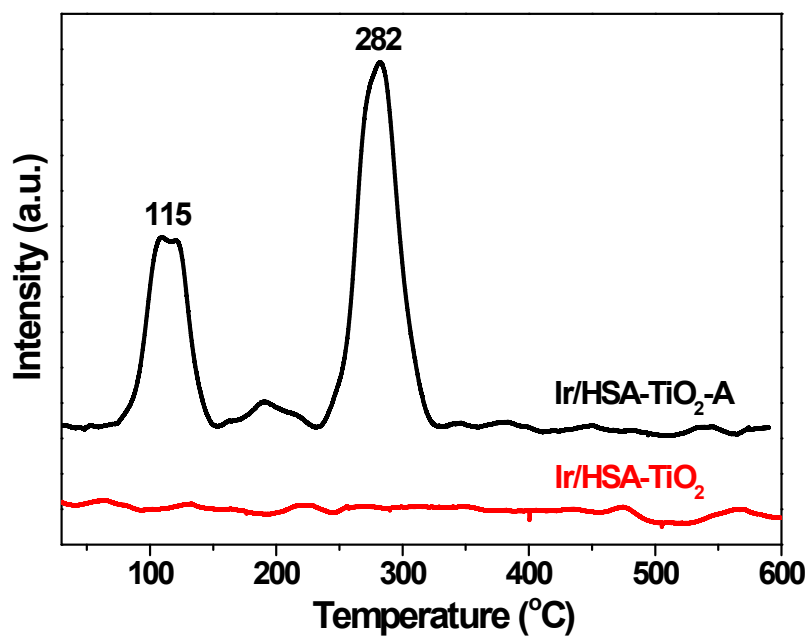


Fig. S4 TPR profiles of Ir/HSA-TiO<sub>2</sub>-A and Ir/HSA-TiO<sub>2</sub> catalysts. For the Ir/HSA-TiO<sub>2</sub>-A sample, the peak at 115 °C ascribed to the reduction of highly dispersed iridium oxide species, and the peak at 282 °C attributed to the reduction of bulk IrO<sub>x</sub>.<sup>S3</sup>

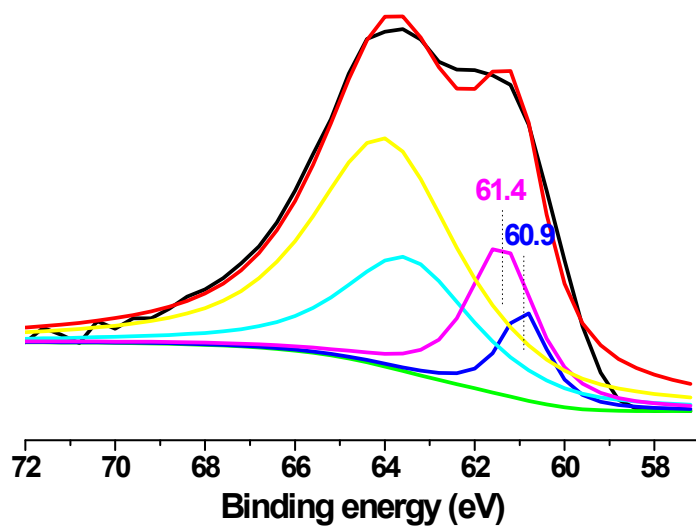
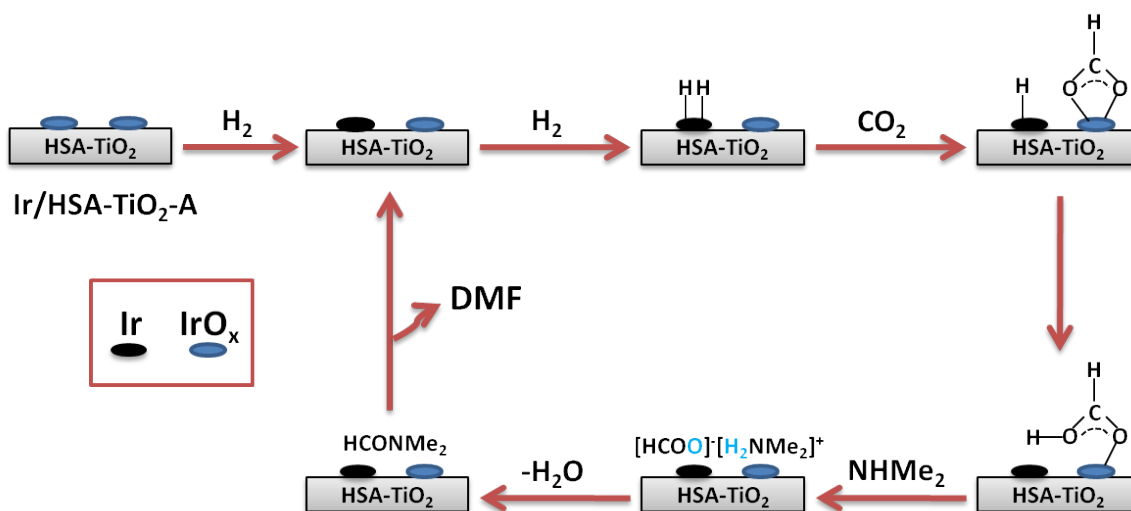


Fig. S5 XPS data of the used Ir/HSA-TiO<sub>2</sub>-A catalyst. The surface molar ratio of Ir(0)/Ir(<sup>δ+</sup>) for the used Ir/HSA-TiO<sub>2</sub>-A catalyst was calculated to be 3/7 according to the XPS peak areas of 4f<sub>7/2</sub>.



Scheme S1 Possible reaction pathway for DMF synthesis from H<sub>2</sub>, CO<sub>2</sub> and aqueous NHMe<sub>2</sub> over Ir/HSA-TiO<sub>2</sub>-A catalyst.

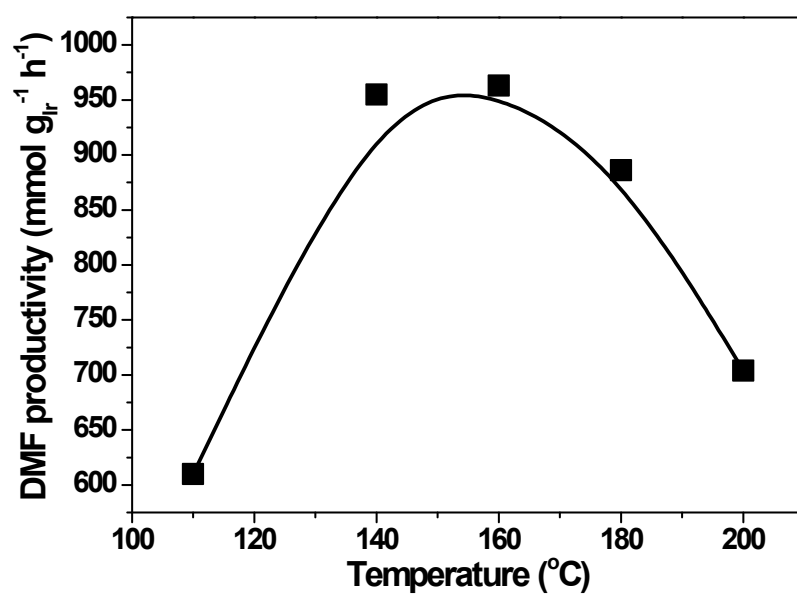


Fig. S6 DMF productivity as a function of reaction temperature over Ir/HSA-TiO<sub>2</sub>-A. Reaction conditions: 100 mg catalyst, 15.1 mmol NHMe<sub>2</sub>, P<sub>CO<sub>2</sub></sub> = P<sub>H<sub>2</sub></sub> = 30 bar at 25 °C, 10 h.



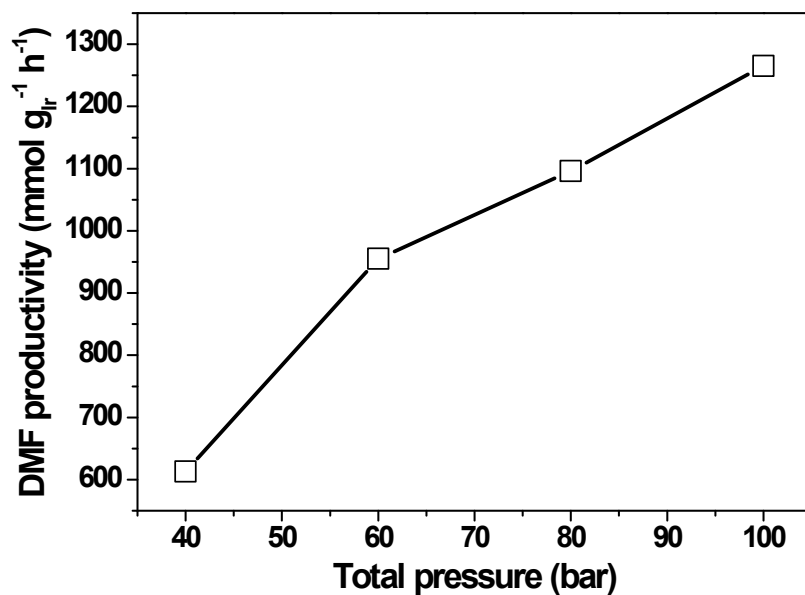


Fig. S7 DMF productivity as a function of total pressure over Ir/HSA-TiO<sub>2</sub>-A. Reaction conditions: 100 mg catalyst, 15.1 mmol NHMe<sub>2</sub>, P<sub>CO<sub>2</sub></sub> = P<sub>H<sub>2</sub></sub> at 25 °C, 140 °C, 10 h.

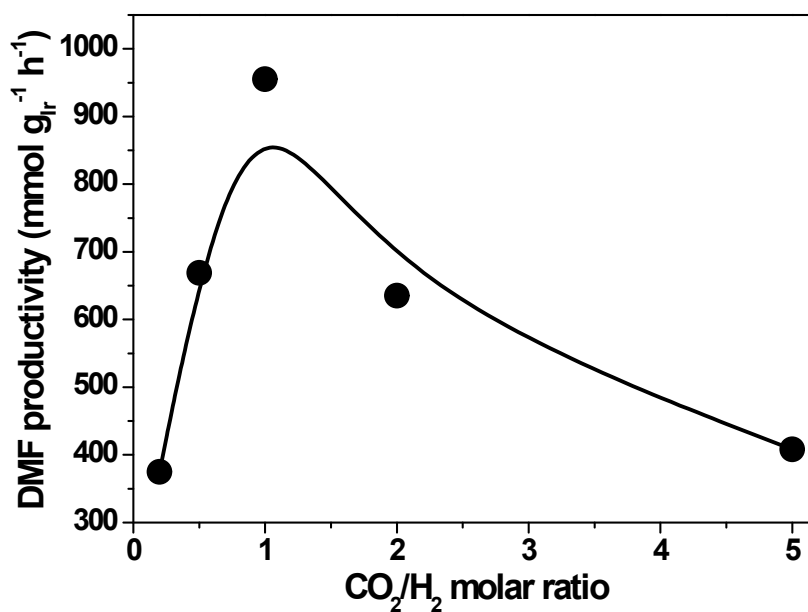


Fig. S8 DMF productivity as a function of CO<sub>2</sub>/H<sub>2</sub> molar ratio over Ir/HSA-TiO<sub>2</sub>-A. Reaction conditions: 100 mg catalyst, 15.1 mmol NHMe<sub>2</sub>, total pressure of 60 bar at 25 °C, 140 °C, 10 h.

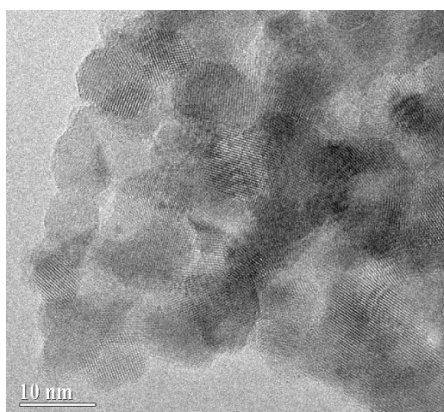


Fig. S9 TEM image of used Ir/HSA-TiO<sub>2</sub>-A catalyst.

Table S1 Ir/HSA-TiO<sub>2</sub>-A catalyzed formamide synthesis from CO<sub>2</sub>, H<sub>2</sub> and various amines.<sup>a</sup>

Entry	Amine	Yield <sup>b</sup> (%)	Formamide productivity (mmol g <sub>Ir</sub> <sup>-1</sup> h <sup>-1</sup> )
1	NHEt <sub>2</sub>	92	920
2	NH( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub>	86	860
3	NH( <i>n</i> -C <sub>6</sub> H <sub>13</sub> ) <sub>2</sub>	73	730
4	NHPh <sub>2</sub>	28	280
5	NHMePh	69	690

<sup>a</sup> Reaction conditions: 100 mg catalyst, 5 mmol amine, 2 mL *n*-octane, P<sub>CO<sub>2</sub></sub> = P<sub>H<sub>2</sub></sub> = 30 bar at 25 °C, 140 °C, 10 h, 1,4-dioxane as the internal standard. <sup>b</sup> Based on the amine feed.

## References

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