

Partially reduced iridium oxide clusters dispersed on titania as efficient catalysts for facile synthesis of dimethylformamide from CO₂, H₂ and dimethylamine†

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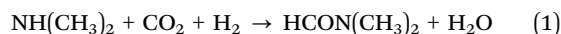
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A novel bifunctional catalyst based on partially reduced iridium oxide supported on TiO₂ was found to be exceedingly efficient for the organic-solvent-free synthesis of dimethylformamide from CO₂, H₂ and dimethylamine.

The use of CO₂ as a renewable and environmentally friendly C₁ source for the synthesis of fuels or value-added chemicals is a topic of current interest.¹ The high thermodynamic stability of CO₂ clearly calls for highly efficient activation which must be coupled with a strong thermodynamic driving force to ensure irreversible fixation.² One promising approach to overcoming the low reactivity of CO₂ is its activation by catalytic hydrogenation to form formic acid or its derivatives.³ This transformation offers direct access to chemical products based on waste material from the energetic use of fossil fuels, opens a possible route to convert CO₂ into CO, and is discussed as a potential option for the development of new chemical processes that utilize renewable resources.⁴ The industrial implementation of such advanced CO₂-utilization concepts faces a number of ecological, economic and technical challenges.⁵ On the most fundamental level, it is essential to develop a new, innovative and highly effective catalytic method which can allow facile reductive activation of CO₂ under favorable conditions to yield a range of key chemical compounds.^{1,2,5}

Dimethylformamide (DMF) is an important primary product, and has the high performance as a solvent, being particularly used in manufacture of polyurethane leatherette and polyacrylonitrile fiber.⁶ Currently, this compound is produced in industry from carbonylation of dimethylamine (NHMe₂) employing toxic CO as the C₁ feedstock.⁷ Although the hydrogenation of CO₂ in the presence of various amine substrates has been broadly investigated, the direct formation of DMF using CO₂ as a C₁ source in a highly facile and quantitative manner remains presently elusive.^{8,9} A very recent report describes the use of a Cu–ZnO nanocomposite as the

catalyst for the high yield (*ca.* 97%) synthesis of DMF employing high pressure CO₂–H₂ mixtures (total pressure up to 12 MPa).¹⁰ However, besides the inherent limitations associated with the handling problems, this system requires the use of ridiculously expensive dimethylammonium dimethylcarbamate (DIMCARB) as the amine source.¹⁰ Thus, the development of an efficient catalytic process for practical DMF synthesis based on CO₂ reduction (eqn (1)) using a cost-effective amine source under mild conditions is highly desirable.



From a synthetic point of view, it appears that a multifunctional catalyst with excellent capacity to activate CO₂ as well as H₂ would be a better candidate for this particular transformation. Ir-containing catalysts have been extensively employed in the past years for the reduction of nitric oxide, decomposition of hydrazine hydrate or ammonia and synthesis of quinolines.¹¹ Moreover, it is also established that Ir complexes including Ir(II) and Ir(III) are very active for a number of carboxylation or hydrogenation of CO₂.¹² Given the high efficiency of specifically designed Ir complexes for both CO₂ and H₂ activation, we were motivated to explore the possibility of using Ir-based heterogeneous catalysts for improved DMF synthesis *via* CO₂ hydrogenation in the presence of NHMe₂. Herein, we report an efficient titania supported Ir catalyst for straightforward synthesis of DMF from CO₂, H₂ and aqueous NHMe₂ under mild, practical and organic-solvent-free conditions. The key to the successful application of the catalyst was the favorable creation of partially reduced iridium oxide (Ir/IrO_x) clusters enabling facile reductive activation of CO₂ under an H₂ atmosphere. These findings not only provide a new catalytic system for the production of DMF, but also add another important example of heterogeneous Ir-catalyzed reactions.

We began our study by examining the direct hydrogenation of CO₂ in the presence of commercially available aqueous NHMe₂ (40 wt%) at 140 °C, as this is expected to represent the easiest scheme for DMF production from CO₂. First of all, we have studied several potential noble-metal-based catalysts prepared by a conventional impregnation technique in the presence of 60 bar H₂/CO₂ (see ESI†). Prior to use, all catalysts were pretreated in an H₂ atmosphere to ensure all metal species were reduced to their metallic state (see ESI†).

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Table 1 Activity of various catalysts for DMF synthesis from CO₂, H₂ and aqueous NHMe₂^a

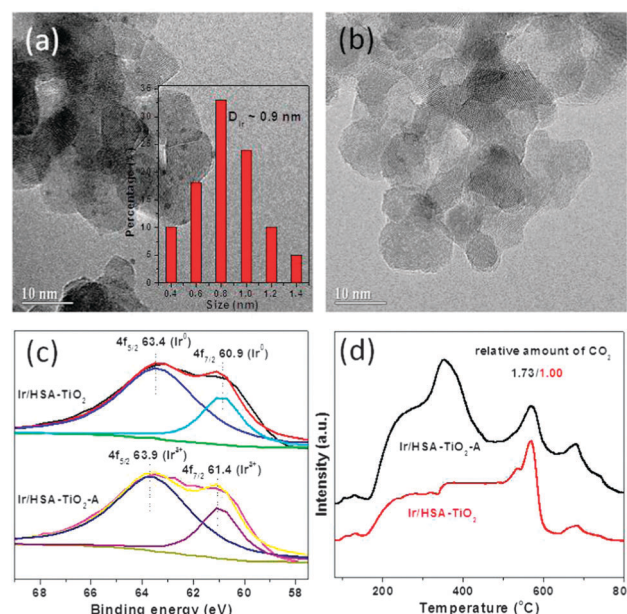
Entry	Catalyst	Time (h)	Yield ^b (%)	DMF productivity (mmol g _{Metal} ⁻¹ h ⁻¹)
1	Pd/P25-IM	10	9.9	150
2	Ru/P25-IM	10	9.2	139
3	Rh/P25-IM	10	3.4	51
4	Pd/ZrO ₂ -IM	10	8.7	132
5	Ru/ZrO ₂ -IM	10	6.3	95
6	Ir/P25-IM	10	16.8	255
7	Ir/ZrO ₂ -IM	10	13.1	198
8	Ir/Al ₂ O ₃ -IM	10	12.4	187
9	Ir/ZnO-IM	10	10.4	157
10	Ir/CeO ₂ -IM	10	12.2	184
11	Ir/MgO-IM	10	7.1	108
12 ^c	Cu/ZnO-CP	14	5.1	0.6
13	Ir/HSA-TiO ₂ -IM	10	25.6	388

^a All noble-metal-based catalysts were prepared by the impregnation method and the metal loading was 0.5 wt%. Reaction conditions: 200 mg catalyst, 15.1 mmol NHMe₂, P_{CO₂} = P_{H₂} = 30 bar at 25 °C, 140 °C, 1,4-dioxane as the internal standard. ^b Based on the NHMe₂ feed. ^c Prepared *via* conventional the co-precipitation method.

While palladium, ruthenium, and rhodium displayed very poor performances for DMF synthesis with the yield lower than 10% (Table 1, entries 1–5), only catalysts based on Ir can deliver notable activity with appreciable DMF yields (entries 6–11). Note that the previously reported co-precipitation-derived Cu/ZnO catalyst was nearly inactive under the present reaction conditions, probably due to its inherent weak water-tolerance (entry 12). Of the Ir catalysts tested, the use of TiO₂, especially high surface area TiO₂ (HSA-TiO₂, Fig. S1, ESI†), as a support can afford much higher activity with a moderate DMF yield of *ca.* 26% (entry 13). This corresponds to a DMF productivity of *ca.* 388 mmol g_{Ir}⁻¹ h⁻¹. Already, this result represents the best catalyst productivity ever reported for DMF synthesis *via* CO₂ hydrogenation in the presence of NHMe₂.^{8,10}

Bearing in mind that the particle size has proven to be especially influential for supported Ir catalysts, we envisioned that dispersed Ir nanoclusters (NCs) with improved metal dispersion could be more effective for the direct synthesis of DMF from CO₂ and aqueous NHMe₂. To explore this possibility, a new heterogeneous Ir catalyst sample composed of ultra-small Ir NCs finely dispersed on HSA-TiO₂ (denoted as Ir/HSA-TiO₂) was prepared by a deposition-precipitation (DP) method (Fig. 1a, for details see ESI†). To our delight, this catalyst gave much higher activity: 43.4% yield and 657 mmol g_{Ir}⁻¹ h⁻¹ productivity (Table 2, entry 1). Of yet further interest is that the Ir/HSA-TiO₂-A sample prepared under otherwise identical conditions without H₂ pretreatment can deliver a much higher efficiency toward DMF synthesis (entry 2). More relevant is that an even higher yield of *ca.* 93.5% can be obtained over Ir/HSA-TiO₂-A and extended reaction time under 60 bar and 140 °C (entry 3). Particularly noteworthy is that this iridium catalyst gave an exceptional productivity up to 955 mmol g_{Ir}⁻¹ h⁻¹ (entry 4). This is the best value reported so far for DMF synthesis from CO₂, H₂ and NHMe₂.^{8,10}

The outstanding efficiency for DMF synthesis over Ir/HSA-TiO₂-A under the conditions mentioned above clearly reflects the fast surface kinetics as a result of the creation of favorable

**Fig. 1** TEM images of (a) Ir/HSA-TiO₂ and (b) Ir/HSA-TiO₂-A, and (c) XPS data and (d) CO₂-TPD profiles of both catalysts.

catalytic active species enabling facile activation of both CO₂ and H₂. While TEM measurements have confirmed that the DP method can result in the formation of smaller Ir domains (Fig. 1a) with higher metal dispersion than its impregnation-derived analogue (Fig. S3, ESI†), XPS analysis reveals the presence of both metallic and oxidized Ir species on the surface of the used Ir/HSA-TiO₂-A sample (Fig. S5, ESI†). Moreover, it was confirmed in two separate experiments that whereas the air-pretreated Ir/HSA-TiO₂ sample showed a prominent increase in its activity, a drastic activity decrease was identified for the H₂-pretreated Ir/HSA-TiO₂-A sample (Table 2, entries 5 and 6). To better understand the superior performance of Ir/HSA-TiO₂-A, both catalysts were characterized with CO₂-temperature-programmed desorption (CO₂-TPD). The fact that Ir/HSA-TiO₂-A exhibited much higher CO₂ adsorption capacity than Ir/HSA-TiO₂ (Fig. 1d) indicates that the CO₂ molecule can be activated much more readily on the surface of the oxidized Ir species.

Table 2 DMF synthesis from CO₂, H₂ and aqueous NHMe₂ over different DP-derived TiO₂ supported Ir catalysts^a

Entry	Catalyst	Time (h)	Yield ^b (%)	DMF productivity (mmol g _{Ir} ⁻¹ h ⁻¹)
1	Ir/HSA-TiO ₂	10	43.4	657
2	Ir/HSA-TiO ₂ -A	10	60.6	918
3	Ir/HSA-TiO ₂ -A	16	93.5	882
4 ^c	Ir/HSA-TiO ₂ -A	10	31.6	955
5 ^d	Ir/HSA-TiO ₂ -A-H	10	36.7	555
6 ^e	Ir/HSA-TiO ₂ -H-A	10	62.6	946

^a Ir loading was 0.5 wt%. Reaction conditions: 200 mg catalyst, 15.1 mmol NHMe₂, P_{CO₂} = P_{H₂} = 30 bar at 25 °C, 140 °C, 1,4-dioxane as the internal standard. ^b Based on the NHMe₂ feed. ^c 100 mg catalyst. ^d Ir/HSA-TiO₂-A-H denotes the sample obtained by a further treatment of the Ir/HSA-TiO₂-A catalyst in 5 vol% H₂/Ar at 400 °C for 2 h. ^e Ir/HSA-TiO₂-H-A denotes the sample obtained by further calcination of the Ir/HSA-TiO₂ material in air at 400 °C for 2 h.

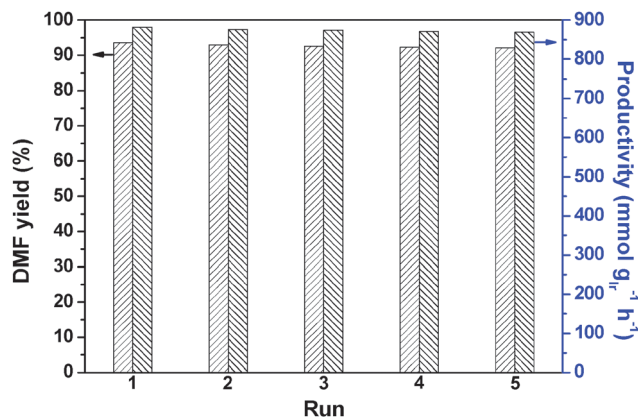


Fig. 2 Recycling of Ir/HSA-TiO₂-A for DMF synthesis from CO₂, H₂ and aqueous NHMe₂. Reaction conditions: 200 mg catalyst, 15.1 mmol NHMe₂, $P_{\text{CO}_2} = P_{\text{H}_2} = 30$ bar at 25 °C, 140 °C, 16 h.

These data, together with the catalytic results shown in Table 2, strongly suggest that the unique bifunctional character of partially reduced iridium oxide species is essential to greatly facilitate the desired DMF synthesis.

On the basis of the above results and the relevant literature,¹⁰ a possible reaction pathway for DMF synthesis involving formate intermediate formation *via* synergistic-cooperative combination of Ir and IrO_x species over Ir/HSA-TiO₂-A was proposed (Scheme S1, ESI†). Further investigation into the effect of reaction parameters on the performance of the Ir/HSA-TiO₂-A catalyst revealed that a temperature of 140 °C is optimal for this reaction. Higher temperatures (*e.g.* > 180 °C) can lead to appreciable generation of toxic CO gas as a result of the undesirable reverse water-gas shift (RWGS) reaction, thus poisoning the Ir-based catalyst and decreasing the DMF productivity (Fig. S6, ESI†). The increase of total pressure is in favor of reaction proceeding (Fig. S7, ESI†), and the reaction at an equivalent molar ratio of CO₂ to H₂ is most suitable (Fig. S8, ESI†). To confirm whether the Ir-catalyzed reaction occurs on the solid surface of Ir/HSA-TiO₂-A, it was removed by filtration from the reaction mixture after reaction. Continuous treatment of the resulting filtrate under similar reaction conditions did not afford any products. In addition, inductively coupled plasma (ICP) analysis showed the absence of Ir species in the filtrate (detection limit of 0.1 ppm), revealing that no leaching occurred during the reaction. Compared with the fresh Ir/HSA-TiO₂-A sample, there was no significant change of morphology and no aggregation of particles for the used Ir catalyst (Fig. S9, ESI†). The recovered Ir/HSA-TiO₂-A sample was reusable for a subsequent reaction and exhibited a high product yield and specific productivity after the 5th reuse (Fig. 2).

In conclusion, we have demonstrated that partially reduced iridium oxide clusters dispersed on TiO₂ exhibited superior performance for efficient and practical synthesis of DMF from CO₂, H₂ and NHMe₂ under mild aqueous conditions. A preliminary study using other amine substrates showed that the present Ir-catalyzed protocol is not limited to the DMF synthesis *via* CO₂ hydrogenation (Table S1, ESI†). The catalytic system present here, in which the unique characteristics of bifunctional Ir/IrO_x clusters can enable a facile reductive activation of CO₂ in a cooperative manner, may

contribute to the design of more efficient catalytic systems and may provide a new strategy for the development of green organic transformations using CO₂ as the renewable resource.

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