

Communication

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Low Temperature Oxidation of Ethane to Oxygenates by Oxygen over Iridium-Cluster Catalysts

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Supporting Information Placeholder,

ABSTRACT: Directly selective oxidation of light alkanes, such as ethane, into value-added chemical products under mild reaction conditions remains a challenge in both industry and academia. Herein, the iridium cluster and atomically dispersed iridium catalysts have been successfully fabricated using nanodiamond as support. The obtained iridium cluster catalyst shows remarkable performance for selective oxidation of ethane under oxygen at 100°C, with an initial activity as high as 7.5 mol/mol/h and a selectivity to acetic acid higher than 70% after five *in-situ* recycles. The presence of CO in the reaction feed is pivotal for the excellent reaction performance. Based upon XPS analysis, the critical role of CO was revealed, which is to maintain the metallic state of reactive Ir species during the oxidation cycles.

With the continuous exploitation of petroleum resources, it is critically important to find a non-crude oil dependent approach for the fabrication of bulk and fine chemicals. Thus, the utilization of natural gas as a chemical feedstock has attracted more and more attention.¹ Ethane is the second most abundant component in natural gas and is difficult to be activated to obtain value-added chemicals.² In its direct catalytic activation, high temperature is always needed, and large amount of energy is required. Moreover, the target products (e.g., ethanol, acetaldehyde) are easier to be oxidized to CO_x than ethane itself under high temperature, leading to the difficulty in reaching high activity and high selectivity simultaneously.³

Direct selective oxidation of ethane at low temperatures is an alternative approach. However, due to the low reactivity of ethane, such a process usually requires expensive oxidants or corrosive reaction media that limits their applications.⁴ To pursue for sustainable chemical processes, the use of molecular oxygen to oxidize ethane under mild condition is preferred because of low cost and environmentally friendly characteristics of oxygen. In 1992, Sen group firstly reported an oxygen-based catalytic system for direct oxidation of ethane to acetic acid at 100°C. Although an acidic media was used, it was considered a breakthrough for lowtemperature oxidation of ethane.4a No further progress had been made along this direction over the following two decades. Until recently, the groups of Flytzani-Stephanopoulos^{5a} and Tao^{5b} reported independently that atomically dispersed rhodium species on the zeolite support could convert methane to acetic acid using O2 and CO in aqueous solutions at 150 °C by a CO insertion mechanism. Methanol can be the main products via an O-insertion mechanism, if the acidic site on the support was blocked or a nonacidic support was used. Both two routes showed a relatively low productivity to methanol. The TiO₂ supported Rh showed a 100% selectivity to methanol with a yield of 4.6 µmol in a three-hour test.5a

Herein, we report that the synthesis of nanodiamond (ND) supported iridium cluster (Ir_n/ND) and atomically dispersed Ir (Ir_1/ND) catalysts. We found that Ir_n/ND possessed high activity and stability for partial oxidization of ethane to valuable C_2 chemicals at 100 °C in the aqueous phase by O_2 in the presence of CO. The structure of the catalysts was investigated by TEM, XAFS and IR. Based on the *in-situ* XPS studies, it was confirmed that the oxidation state of iridium is critical for the efficient activation of ethane, and the role of CO added is to maintain the metallic state of the reactive Ir species.

The ND is a type of diamond-structured nano-carbon materials with a size of 5-10 nm (Figure S1). All ND supported metal

catalysts were prepared by an impregnation method. By controlling the loading amount of Ir, we could tune the dispersion of Ir to get two types of catalysts: Ir_1/ND (0.05 wt%) and Ir_n/ND (3.8 wt%).



Figure 1. (a) XRD patterns of bare ND and Ir/ND catalysts; (b) Ir L_3 -edge EXAFS of Ir/ND catalysts; WT analysis of Ir_n/ND (c) and Ir₁/ND (d).

From XRD patterns (Figure 1a), no diffractions associated with Ir were observed on the Ir₁/ND and Ir_n/ND catalysts, proving that the Ir species were highly dispersed on the two catalysts. The X-ray absorption fine structure (XAFS) results further provided evidence to determine the dispersion of Ir species on ND. Fouriertransformed k³-weighted extended X-ray-absorption fine-structure (EXAFS) analysis are shown in Figures 1b and S2. For Ir_n/ND, the Ir-Ir scattering is the major peak, with the coordination number of 9.7 (Table S1). For Ir₁/ND, Ir-O/C coordination peak at 1.96 Å is the dominant one, while the Ir-Ir scattering is significantly weakened. The Ir-Ir coordination number reduces to 1.8, and the Ir-O/C coordination number is 4.9. These findings imply that highly dispersed iridium species are the dominant structure in Ir₁/ND catalyst. Wavelet transform (WT) of Ir L₃edge EXAFS further revealed the dispersion nature of Ir species in the catalysts. Figure 1c shows a maximum of the WT plots at 2.5 Å that corresponds to the Ir-Ir scattering in Ir_n/ND . For Ir_1/ND , a maximum at 1.6Å in Figure 1d is correlated with the Ir-O/C contribution (WT analysis of Ir and IrO2 are shown in Figure S3 for comparison). To investigate the dispersion of Ir, aberrationcorrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) was employed (Figure 2). For Ir_n/ND, ultrafine Ir clusters with a size of 1-2 nm were clearly observed, along with a small amount of atomically dispersed Ir species. Of note, for Ir₁/ND, Ir species were atomically dispersed on the support predominantly, together with few small nanoclusters.



Figure 2. (a, b) HAADF-STEM images of Ir_n/ND; (c-g) HAADF-STEM images of Ir₁/ND.

The structural nature of the two Ir/ND catalysts was further studied by CO adsorption via infrared spectroscopy. Ir_n/ND exhibited multiple overlapped IR peaks (Figure 3a) between 2100 and 1800 cm⁻¹. The strongest absorption peak at 2037 cm⁻¹ is assigned to the atop binding of CO on Ir clusters, and the broad band centered at 1935 cm⁻¹ is contributed by bridged CO species, which indicate the existence of Ir clusters or nanoparticles.⁶ Two additional features are at 2065 and 1985 cm⁻¹, which may be attributed to dicarbonyl species (Ir(CO)₂).⁷ Of note, dicarbonyl species can only be formed on isolated species.^{5a, 8} The atop and bridged CO species and dicarbonyl species exist in Ir_n/ND, suggesting that Ir species have a relatively broad distribution. As expected, for Ir₁/ND, the absorption peaks at 2065 and 1985 cm⁻¹ are dominated, which should be derived from the dicarbonyl species. A small amount of atop CO was observed, which could be contributed by small Ir nanoclusters in the catalyst. The infrared spectra confirmed the structural feature of Ir species in both catalysts, which is consistence of both TEM and XAFS results: Ir on Ir_n/ND are small clusters whereas on Ir₁/ND are mainly atomically dispersed with very few clusters.

Different metal/ND catalysts were prepared for the oxidation of ethane by oxygen at 100°C. The results are summarized in Table 1. The nanodiamond support cannot catalyze the ethane activation (Table 1, entry 1). Clearly, Ag/ND is nearly inactive for ethane oxidation (Table 1, entry 2), and so does Au/ND (Table 1, entry 3). For Pd/ND, the productivities towards ethanol, acetaldehyde, acetic acid and ethene increased simultaneously, which agrees well with previous report.4a The activity of Pt/ND reaches to 2.6 mol/mol/h, which is even higher than Pd/ND. Among these catalysts, iridium cluster catalyst (Ir_n/ND) exhibited the highest activity (7.5 mol/mol/h, see Entry 6 of Table 1 and Figure S4). This is the best activity that has been reached (Table S3) so far. Significantly, only water was used as solvent in our case, in contrast to the use of acid (HCl or CF₃COOH) as co-catalyst in previous reports.^{4a, 9} Here, the main products are ethanol, acetaldehyde, and acetic acid, accompanied by a small amount of methanol, ethylene, and propionic acid (CO_2 is not included). When the dispersion of Ir species was reduced from Ir clusters to

atomically dispersed Ir species (Ir_1/ND), the activity still kept at 3.5 mol/mol/h and acetaldehyde is the only product(Table 1, Entry 7). This finding indicates that iridium is indeed active for ethanol oxidation, and the dispersion of Ir has significant impact on the

product distribution. Moreover, the Ir_n/ND catalyst is very stable, no visible deactivation was observed even after five reaction cycles (Figures 3b and S5).

Table 1. Catalytic performance of ethane oxidation reaction with different catalysts

Entry	Catalysts	Feed gas	Reaction time (h)	Productivity (mmol / mol _{metal} / h)						Activity	Total amount of
				СН ₃ ОН	CH ₃ CH ₂ OH	СН ₃ СНО	СН ₃ СООН	C_2H_4	CH ₃ CH ₂ COOH	(mol/mol/h)	products (μ mol)
1	ND	$C_2H_6 + CO + O_2$	3	/	/	/	/	/	1	/	0
2	Ag/ND	$C_2H_6 + CO + O_2$	3	0	8	8	0	0	0	0.016	0.2
3	Au/ND	$C_2H_6 + CO + O_2$	3	0	42	17	0	0	0	0.059	0.7
4	Pd/ND	$C_2H_6 + CO + O_2$	3	0	358	476	125	383	0	1.3	16
5	Pt/ND	$C_2H_6 + CO + O_2$	3	25	483	642	308	600	500	2.6	30.7
6	Ir _n /ND	$C_2H_6 + CO + O_2$	3	75	1150	3575	2233	117	417	7.5	90.8
7	Ir ₁ /ND	$C_2H_6 + CO + O_2$	6	0	0	3483	0	0	0	3.5	1.1
8	Ir _n /ND	$CO + O_2$	3	0	0	0	0	0	0	0	0
9	Ir _n /ND	$C_2H_6 + O_2$	3	0	0	0	0	0	0	0	0

Typical reaction conditions: 20 mg catalyst, 15 mL water, feeds ($C_2H_6 / CO / O_2 / He / Ar / N_2 = 35 / 8 / 2.5 / 1 / 1 / 52.5$), 3MPa, 100 °C. The productivities were normalized over metal dosage. Activities were calculated based on the amount of converted C_2H_6 over metal dosage (two CH₃OH molecules were considered to originate from one C_2H_6 molecule).



Figure 3. (a) Infrared spectra of CO adsorbed on Ir/ND catalysts; (b) Stability of Ir_n/ND catalyst in ethane oxidation reaction; (c) XPS studies of Ir_n/ND catalyst under different reaction atmospheres.

Interestingly, we found that CO played a critical role in ethane oxidation. When C_2H_6 is absent, no C_{2+} products were observed (see Table 1, Entry 8). Understandably, C_{2+} products are derived from ethane. If the reactants are ethane and oxygen but without CO, the formation of C_{2+} products is also prohibited (Table 1, Entry 9).

Although it has been reported that the involvement of CO is pivotal for this system, no solid evidence has been given regarding the role of CO. Flytzani-Stephanopoulos has smartly speculated that CO can regenerate the low valence state of Rh (Rh⁺) in the Rh-ZSM-5 catalyst for methane oxidation.^{5a}

Following this speculation, we designed *in-situ* XPS experiments to analyze the critical role of CO in this process on Ir_n/ND . The characteristic peaks of Ir_n/ND after preactivation in H₂ (Figure 3c) are centered at approximately 60.7 eV (Ir $4f_{7/2}$) and 63.7 eV (Ir $4f_{5/2}$), which can be assigned to metallic Ir species.¹⁰ Subsequently, the sample was treated in the mixture of C₂H₆, O₂ and water vapor at 100°C for 3h. Clearly, the binding energy of Ir $4f_{7/2}$ shifted to 62.0 eV, implying the formation of iridium oxide (Ir⁴⁺) species.¹¹ Thus, for the reaction without CO, Ir species

could be easily over-oxidized to a high-valence state, which is considerably unable to adsorb the alkane at low temperature and consequently showed no activity for ethane oxidation (Table 1, entry 9).¹² After the sample was treated in a mixture of CO and water vapor at 100°C for 3 hours, the binding energy of Ir $4f_{7/2}$ shifted to 61 eV. This demonstrated that the Ir cluster species were reduced by CO to a metallic state. The role of CO is to reduce Ir clusters and make it stay in a low-valance state (close to metallic state). Indeed, for the catalyst after real catalytic reaction, we can clearly see that Ir clusters was slightly oxidized, but could still maintain its low-valence state, implying the importance of CO in the catalytic reaction of Ir cluster catalyst.

In summary, we discovered a highly active nanodiamond supported iridium clusters to catalyze the direct oxidation of ethane to oxygenates in the presence of oxygen and carbon monoxide at 100°C in the aqueous phase. The activity of Ir clusters/nanoparticles is higher than atomically dispersed Ir. The critical role of CO was clearly demonstrated by *in-situ* XPS experiments, CO maintains the low-valance state (metallic state) of Ir that is required for ethane adsorption during the reaction. This work provides a basis for the investigation of new Ir catalysts

for the direct oxidation of ethane by oxygen under mild conditions, and offers new insights to design efficient catalysts for low temperature alkane activation in the future.

ASSOCIATED CONTENT

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The Supporting Information is available free of charge on the ACS Publications website.

Detailed experimental procedures, characterization methods and additional tables and figures (PDF)

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The authors declare no competing financial interest.

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A highly active iridium catalyst is investigated for partially oxidizing ethane to valuable oxygenates by O₂ in the presence of CO at 100°C in water.

