

Water Oxidation Catalysts

Heterogenized Water Oxidation Catalysts Prepared by Immobilizing Kläui-Type Organometallic Precursors

Gabriele Pastori,^[a] Khaja Wahab,^[b] Alberto Bucci,^[a] Gianfranco Bellachioma,^[a] Cristiano Zuccaccia,^[a] Jordi Llorca,^[c] Hicham Idriss,^{*,[b]} and Alceo Macchioni^{*,[a]}

Abstract: An efficient heterogenized water oxidation catalyst (2_TiO_2) has been synthesized by immobilizing the Kläui-type organometallic precursor $[Cp^*Ir\{P(O)(OH)_2\}_3]Na$ (**2**, $Cp^* = 1,2,3,4,5$ -pentamethylcyclopentadienyl ligand) onto rutile TiO_2 . Iridium is homogeneously distributed at the molecular and atomic/small cluster level in 2_TiO_2 and $2'_TiO_2$ (solid catalyst recovered after the first catalytic run), respectively, as indicated by STEM-HAADF (scanning transmission electron microscopy - high angle annular dark field) studies. $2'_TiO_2$ exhibits TOF values up to 23.7 min^{-1} in the oxidation of water to O_2 driven by $NaIO_4$ at nearly neutral pH, and a TON only limited by the amount of $NaIO_4$ used, as indicated by multiple run experiments. Furthermore, while roughly 40% leaching is observed during the first catalytic run, $2'_TiO_2$ does not undergo any further leaching even when in contact with strongly basic solutions and completely maintains its activity for thousands of cycles. NMR studies, in combination with ICP-OES (inductively coupled plasma optical emission spectrometry), indicate that the activation of 2_TiO_2 occurs through the initial oxidative dissociation of PO_4^{3-} , ultimately leading to active centers in which a 1:1 P/Ir ratio is present (derived from the removal of two PO_4^{3-} units) likely missing the Cp^* ligand.

The development of an efficient catalytic pool for the oxidation of water,^[1–2] aimed at generating electrons and protons^[3] for the photosynthesis of renewable fuels,^[4] is one of the most

difficult challenges that the scientific community is facing today.

Molecular^[1] and material-based^[2] water oxidation catalysts (WOCs) with remarkable performances have been reported in recent years. Furthermore, it has been shown that anchoring a properly tailored homogeneous catalyst onto solid supports, thus, obtaining heterogenized WOCs, is a promising strategy to combine the best of two worlds.^[5–8] This allows for a fine modulation of the electron density and geometry of WOCs, whereas grafting the latter on solid supports is poised to enhance stability and facilitate the catalyst recovery.^[5] At the same time, the exploitation of metals can be minimized in heterogenized catalysts, due to the increased amount of active centers that are, in principle, not very different than their homogeneous analogues.^[5]

Kläui-type compounds (KTCs) $[(C_5R_5)M\{P(O)R'R''\}_3]^-$ ($R = H, Me$; $M = Co, Rh$; R' and $R'' = \text{alkyl, aryl, or } O\text{-alkyl}$)^[9] attracted our attention as precursors for fabricating heterogenized WOCs because three $P(O)(OH)_2$ moieties, which are particularly suitable for immobilizing the metal center onto properly selected functional materials, can be easily generated by their hydrolysis.^[10]

KTCs have been widely used as monoanionic terdentate ligands to stabilize coordination complexes and organometallics of almost all metals of the periodic table.^[11] The derived compounds have found applications in several fields, including homogeneous catalysis, lithium-selective transportation across membranes,^[12] and extraction of alkali metals, magnesium, and calcium ions.^[13] Attempts have been made to anchor KTCs onto solid supports with the main aim of generating novel exchange materials and heterogenized catalysts.^[14] In all cases, KTCs have been used as ligands and no investigation has been carried out to explore the possible catalytic activity of the metal center (M). This could be related to the fact that KTCs are 18-electron saturated compounds and therefore are expected to have little propensity to coordinate and activate a substrate. Nevertheless, we thought that such a possible drawback could be circumvented in the water oxidation, because a coordinative position might be generated by the oxidative elimination of metaphosphoric acid $P(O)_2(OH)$ (see below) or by the oxidative transformation of the C_5R_5 ligand.^[15]

Herein we report the synthesis and characterization of a novel KTC $[Cp^*Ir\{P(O)(OH)_2\}_3]Na$ (**2**, $Cp^* = 1,2,3,4,5$ -pentamethylcyclopentadienyl ligand) and show that it is a competent WOC and, more importantly, a particularly suitable precursor to be anchored onto a stable metal oxide, such as TiO_2 , provid-

[a] Dr. G. Pastori, Dr. A. Bucci, Prof. G. Bellachioma, Prof. Dr. C. Zuccaccia, Prof. Dr. A. Macchioni
Department of Chemistry, Biology and Biotechnology and CIRCC
University of Perugia, Via Elce di Sotto 8, 06123 Perugia (Italy)
E-mail: alceo.macchioni@unipg.it

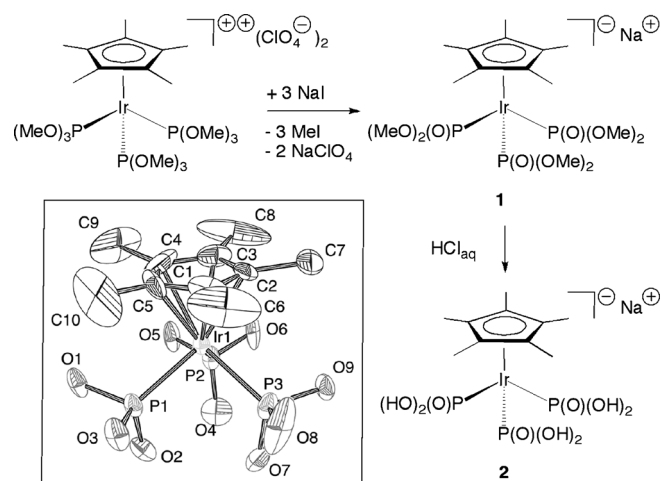
[b] K. Wahab, Prof. Dr. H. Idriss
Corporate Research and Development (CRD) Centre at SABIC-KAUST P.O.
Box 4545-4700, Thuwal 23955 (Saudi Arabia)
E-mail: IdrissH@SABIC.com

[c] Prof. Dr. J. Llorca
Institute of Energy Technologies and
Centre for Research in Nanoengineering
Universitat Politècnica de Catalunya
Diagonal 647, 08028 Barcelona (Spain)

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ing a heterogenized WOC with remarkable activity and robustness.

Complex **2** was synthesized by the hydrolysis of $[\text{Cp}^*\text{Ir}\{\text{P}(\text{O})(\text{OMe})_2\}_3]\text{Na}$ (**1**), prepared by a reported procedure,^[16] with 3 M HCl (Scheme 1, for details see Supporting Information). The



solid structure of **2** was determined by single-crystal X-ray diffraction. The intramolecular structure (Scheme 1) does not reveal any particular feature with the exception of a rather long Ir–Cp* distance (1.935 Å). This indicates that the three $\text{P}(\text{O})(\text{OH})_2^-$ ligands provide a high electron density at the metal center that makes the Cp* coordination weaker than usual. Consistently, the CMe quaternary carbons resonate at a rather high chemical shift (101.9 ppm) in the ^{13}C NMR spectrum.^[17]

The intermolecular structure exhibits an alternation of hydrophobic and hydrophilic layers constituted by the Cp* and Ir– $\text{P}(\text{O})(\text{OH})_2$ moieties, respectively (see Supporting Information).

Compound **2** was heterogenized by dispersing rutile TiO_2 (1 g) in roughly 5 mL of an aqueous solution of **2** ($3\text{--}4 \cdot 10^{-3}$ M) with subsequent stirring at room temperature for 24 h. The extent of heterogenization was followed by monitoring the intensity decrease of the ^{31}P NMR resonance of **2**. The resulting **2**_ TiO_2 material was washed with water, aqueous 0.1 M HNO_3 , acetonitrile, and dichloromethane, and finally dried under vacuum. The loading of iridium, as evaluated by ICP-OES (inductively coupled plasma optical emission spectrometry), was $8.54 \mu\text{mol g}^{-1}$. Compound **2**_ TiO_2 was structurally characterized by solid-state NMR spectroscopy and STEM-HAADF (scanning transmission electron microscopy-high angle annular dark field) (see Supporting Information). Figure 1 shows a comparison between the ^{31}P and ^{13}C CPMAS (cross-polarization magic angle spinning) NMR spectra of the precursor **2**, **2**_ TiO_2 , and a sample recovered after the first catalytic run (**2'**_ TiO_2). Consistently with the literature, the heterogenization of **2** onto TiO_2 causes a shift of the carbon and phosphorous resonances to

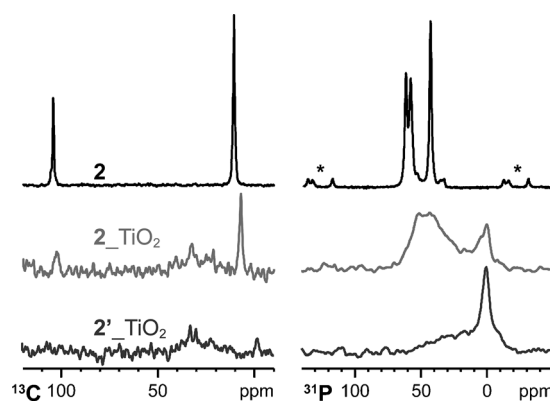


Figure 1. $^{13}\text{C}\{^1\text{H}\}$ (left) and $^{31}\text{P}\{^1\text{H}\}$ (right) CPMAS (cross-polarization magic angle spinning) NMR spectra of **2** (black), **2**_ TiO_2 (light grey), and **2'** (grey). Asterisks denote spinning side bands.

lower frequencies.^[18] Furthermore, a remarkable broadening of the ^{31}P resonance is observed, likely due to the different binding modalities of the Ir– $\text{P}(\text{O})(\text{OH})_2$ moieties and the typologies of the TiO_2 superficial sites. A sharper resonance is present at -0.8 ppm, reasonably due to the oxidative detachment of a phosphate group that binds in a monodentate fashion to TiO_2 .^[19] Such a resonance is also present with a higher intensity in **2'**_ TiO_2 , whereas the intensities of the broader resonances are substantially reduced. Also the ^{13}C NMR resonances have a dramatically lower intensity in the spectrum of **2'**_ TiO_2 compared with that of **2**_ TiO_2 . The reasons of these observations are discussed below after having reported the catalytic results.

STEM-HAADF studies of **2**_ TiO_2 indicate that the sample contains TiO_2 particles that are very well dispersed and quite homogeneous in size (ca. 20×40 nm). A general view of the sample is depicted in Figure 2. At high levels of magnification only the TiO_2 support crystallites are visible, (Figure 2a,c), sug-

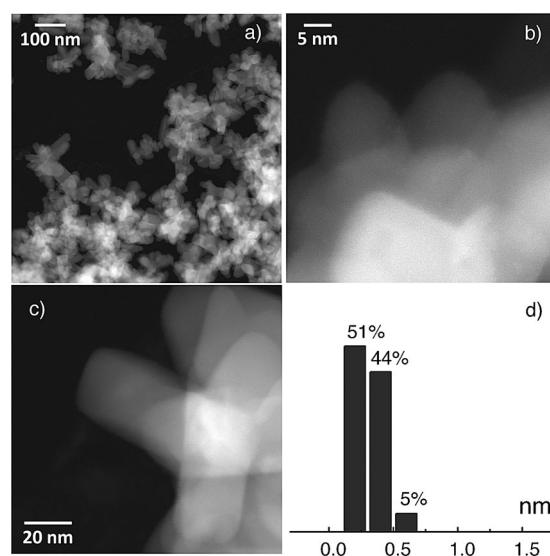


Figure 2. a) and c) STEM-HAADF (scanning transmission electron microscopy-high-angle annular dark-field imaging) images of **2**_ TiO_2 at different levels of magnification. b) A STEM-HAADF image of **2'**_ TiO_2 at the maximum level of magnification. d) Size distribution of the Ir particles in **2**_ TiO_2 .

gesting that **2** is homogeneously dispersed onto TiO₂ at a molecular (subnanometric) level. STEM-HAADF studies of 2'_TiO₂ show extremely small Ir clusters (at the limit of the microscope sensitivity), ranging from 0.2 to 0.4 nm (Figure 2b,d). Assuming a Gaussian particle-size distribution, even smaller clusters, which escape STEM detection, should be present. In the STEM-HAADF images, the clusters can hardly be seen as brighter spots on the TiO₂ crystallites. All these findings seem to indicate that Ir is atomically distributed or forms very small clusters in 2'_TiO₂. Given the small particle size, no EDS (energy-dispersive X-ray spectroscopy) analysis was reliable. It is important to note that these metallic clusters are not formed upon electron beam exposure, therefore, they are not the result of electron damage to the sample. This has been carefully checked by using different electron beam intensities during the TEM experiments.

1, **2**, and 2'_TiO₂ were tested as WOCs using cerium ammonium nitrate (CAN) and NaIO₄ as chemical sacrificial oxidants and monitoring the reaction by manometry and a Clark electrode. Selected results are reported in Table 1 (complete data set is given in the Supporting Information). Complex **1** is not active at all with CAN and exhibits a poor catalytic activity with NaIO₄, affording only 26 cycles with a TOF of 0.1 min⁻¹ (Table 1, entries 1,2). On the contrary, complex **2** is an efficient WOC with both oxidants, capable of completing almost all expected cycles (based on the concentration of the employed sacrificial oxidants) with TOFs up to 29.9 and 46.0 min⁻¹ with

CAN and NaIO₄, respectively (Table 1, entries 3–6). The catalytic activity of **2** was strongly affected by the pH of the reaction medium. This was demonstrated by adding an increased amount of KOH to the solution of **2** before the injection of a solution of NaIO₄ (see Supporting Information). The TOF of the oxygen production remains substantially the same (ca. 5–6 min⁻¹) when 1–4 equivalents of KOH were added (see Supporting Information), but it markedly increases up to 46.0 min⁻¹ when 16 equivalents of KOH were added (Table 1, entry 6). According to Meyer et al,^[20] a beneficial effect of increasing pH on the catalytic performance of **2** can be attributed to a concerted atom–proton transfer (APT) in the critical step of the O–O bond formation.

Also 2'_TiO₂ is an active WOC with both CAN and NaIO₄. However, an almost complete leaching of the catalyst occurs with CAN after the first catalytic run (see Supporting Information), as revealed by the marked reduction of the activity in the second run (Table 1, entries 7–9). This is likely due to the high tendency of KTCs to act as terdentate ligands for the oxophilic Ce⁴⁺.^[21]

With NaIO₄ as sacrificial oxidant, 2'_TiO₂ exhibited a catalytic activity similar to that of **2** (compare entries 10 and 5 in Table 1); it underwent a 34.5% leaching after the first catalytic run and, consequently, the supernatant was active (Table 1, entry 11). Nevertheless, the recovered solid 2'_TiO₂ (5.59 μmol g⁻¹ Ir according to ICP-OES measurements) was still active (Table 1, entry 12), with a TOF even higher than that of 2'_TiO₂. The recovered solid 2'_TiO₂ also did not leach any further, consistently with the complete inactivity of the second supernatant (Table 1, entry 13) and the almost identical activity of the second recovered solid (Table 1, entry 14). Apparently, 2'_TiO₂ contains less, but more active, metal centers that are also more strongly bound to the TiO₂ surface. Perhaps, (per)-iodate plays a role in enforcing the immobilization of the Ir active centers, as recently proposed by Sheehan and co-workers.^[8d]

The stability and recyclability of 2'_TiO₂ was further explored by performing ten catalytic runs, using the same batch of the powder (Table 1, entries 15–22, for details see Supporting Information). In the first one, 16 equivalents of KOH were added to 2'_TiO₂; an increase of the TOF from 2.8 min⁻¹ to 23.7 min⁻¹ (Table 1, entries 10 and 15) was observed in analogy to **2** with a slightly higher leaching (43.5%). The pH was measured for all steps of this catalytic experiment and changed from 5.10 to 4.41 when 2'_TiO₂ was dispersed in deionized water. The addition of KOH caused an increase of the pH up to 9.60, whereas the injection of NaIO₄ led to a pH of 6.32, which remained substantially unaltered until the end of the run. The observed acidification due to the NaIO₄ addition can be explained by the hydration of IO₄⁻ with two water molecules, leading to the weak acid H₄IO₆⁻.^[22]

Three successive runs were performed after washing 2'_TiO₂ with water (Table 1, entries 16–18); all expected cycles were completed and the TOF in the absence of KOH gradually decreased, but always remained higher than that of 2'_TiO₂.

After four catalytic runs, alternating basic and neutral conditions, in which the performances remained substantially unal-

Table 1. Selected catalytic data for WOCs obtained by manometry.					
Entry	C _{cat} [μM]	C _{ox} [mM]	TOF [min ⁻¹]	TON	O ₂ yield [%]
cat. 1					
1	5.0	CAN/10.0	–	–	0
2	10.0	NaIO ₄ /10.0	0.1	26	5
cat. 2					
3	5.0	CAN/10.0	29.9	496	99
4	10.0	NaIO ₄ /10.0	9.6	3365	67
5	18.2	NaIO ₄ /9.1	3.0	230	92
6 ^[c]	5.0	NaIO ₄ /10.0	46.0	1000	100
cat. 2'_TiO ₂					
7 ^I _{solid}	20.0	CAN/10.0	63.8	93	74
8 ^I _{supernatant}	–	CAN/10.0	–	–	83
9 ^{II} _{solid}	–	CAN/10.0	–	–	18
10 ^I _{solid}	19.4	NaIO ₄ /9.1	2.9	200	85
11 ^I _{supernatant}	6.7	NaIO ₄ /9.1	5.2	373	55
12 ^{II} _{solid}	12.7	NaIO ₄ /9.1	4.3	212	90
13 ^{II} _{supernatant}	–	NaIO ₄ /9.1	–	–	0
14 ^{III} _{solid}	12.7	NaIO ₄ /9.1	3.6	308	86
15 ^I _{solid} ^[c]	19.1	NaIO ₄ /9.1	23.7	235	99
16 ^{II} _{solid}	10.8	NaIO ₄ /9.1	11.1	421	100
17 ^{III} _{solid}	10.8	NaIO ₄ /9.1	7.5	421	100
18 ^{IV} _{solid}	10.8	NaIO ₄ /9.1	7.0	420	99
19 ^{IX} _{solid} ^[a]	10.8	NaIO ₄ /9.1	10.1	380	90
20 ^{IX} _{supernatant}	–	NaIO ₄ /9.1	–	–	0
21 ^X _{solid} ^[b]	10.8	NaIO ₄ /9.1	11.7	416	99
22 ^X _{supernatant}	–	NaIO ₄ /9.1	–	–	0

[a] Run performed leaving the catalytic suspension at pH 10 for 24 h (catalytic data of V–VIII are reported in the Supporting Information). [b] Run performed after leaving the catalytic suspension at pH 14 for 24 h. [c] Reaction with 16 equiv KOH.

tered (see Supporting Information), two additional and more extreme runs were carried out. Compound **2'**-TiO₂ was dispersed in water at pH 10 (Table 1, entries 19–20) and pH 14 (Table 1, entries 21–22) for 24 h each, and tested after washing with water; the catalyst maintained its performances both in terms of TON and TOF and, importantly, the supernatants were not active at all, suggesting no leaching in both cases (see Supporting Information). These results suggest that **2**-TiO₂ is an efficient WOC that, after the first catalytic run, becomes extremely stable and capable to complete thousands of cycles without any sign of deactivation, even when subjected to harsh conditions.

In order to understand the modality of the activation of **2** and **2**-TiO₂ and the reason why **1**, contrary to **2**, exhibits a poor catalytic activity, preliminary NMR studies were performed. ¹H and ³¹P NMR spectra of 1–5 mM solutions of **1** were found to be substantially unaffected by the addition of up to 16 equivalents of KOH and several equivalents of NaIO₄ (see Supporting Information). On the contrary, ¹H and ³¹P NMR spectra of **2** showed a shift of the resonances to lower frequencies as increasing amounts of KOH were added, consistent with the gradual deprotonation of acidic functionalities (see Supporting Information). More importantly, the multiple addition of 0.25 equivalents of NaIO₄ nicely tracks with the quantitative appearance of the ³¹P NMR resonance assigned to PO₄³⁻ (see Supporting Information). In addition, the intensity of the ¹H NMR Cp* resonance of **2** (a quartet due the H–P scalar coupling with ³¹P) decreases and a singlet appears at 1.50 ppm, suggesting the elimination of all P-containing moieties. Oxidative transformation of Cp*, as indicated by the appearance of ¹H resonances of acetic and formic acids,^[23] initiate successively to the PO₄³⁻ elimination. It can be concluded that **2** easily transforms into a Cp*IrX₃ species (X = anionic species or water) by the oxidative elimination of PO₄³⁻, asking for the presence of a P–O–H functionality as illustrated in Scheme 2a. This might explain why **1** is not an active WOC.

Interestingly, a coordination vacancy appears to be necessary in order to initiate the oxidative transformation of Cp* and this is not the case in **1**, which cannot undergo the expulsion of a P(O)(OMe)₂ unit, according to the mechanism proposed in Scheme 2a.

Concerning the activation of **2**-TiO₂, ICP-OES measurements indicated that 43.5% of Ir leached out after the first catalytic run with 16 equivalents of KOH. In addition, the ³¹P NMR quan-

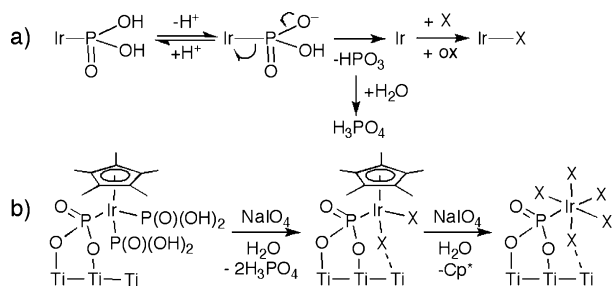
titative studies with the supernatant showed that exactly three equivalents of PO₄³⁻ were liberated with respect to the leached Ir. As a consequence, a 3:1 P/Ir ratio has to be present also in **2'**-TiO₂. The solid-state ³¹P NMR spectrum shows that small amounts of PO₄³⁻ are already present in **2**-TiO₂ before the catalysis, likely derived from the oxidative dissociation catalyzed by TiO₂, and are substantially increased in **2'**-TiO₂ after the first catalytic run (Figure 1). Nevertheless, a broad band centered at 24.7 ppm is also present, likely due to iridium centers missing the Cp* ligand but still containing a bonded phosphate. Deconvolution of the two bands led to a 1:2 Ir–P(O)(OTi)₂/PO₄³⁻ ratio (see Supporting Information) suggesting that all iridium centers still bear a phosphonate moiety (Scheme 2b). It can be hypothesized that the μ²-immobilized species remain anchored onto TiO₂ even after having expelled two PO₄³⁻ and Cp* moieties, providing more active and stable sites (Scheme 2b).

In conclusion, it has been demonstrated that KTCs, bearing P(O)(OH)₂ functionalities, are excellent precursors for the fabrication of heterogenized catalysts for water oxidation. The resulting iridium–TiO₂ hybrid materials exhibit remarkable TOF and TON performances in the oxidation of water driven by NaIO₄. This strategy appears to be rather general and many extensions can be envisioned. For example, the nature of the KTC metal center, especially considering earth abundant metals, and the support can be changed. At the same time, photochemical and electrochemical tests have to be performed. All these experiments are in progress in our laboratories and results will be reported in due time.

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Keywords: iridium · Kläui-type compounds · titanium dioxide · water oxidation · water splitting



Scheme 2. Modality of the activation of **2** (a) and **2**-TiO₂ (b) (X = anion or water, ox = oxidant).

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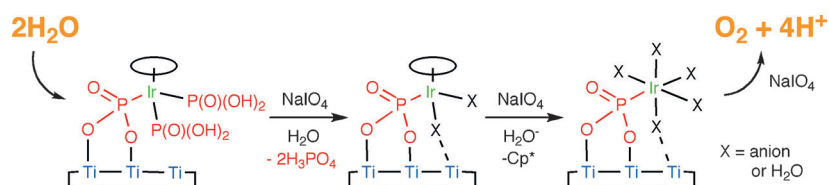
COMMUNICATION

Water Oxidation Catalysts

G. Pastori, K. Wahab, A. Bucci,
G. Bellachioma, C. Zuccaccia, J. Llorca,
H. Idriss,* A. Macchioni*



Heterogenized Water Oxidation Catalysts Prepared by Immobilizing Kläui-Type Organometallic Precursors



Highly stable water oxidation catalyst:

An efficient heterogenized water oxidation catalyst has been synthesized by immobilizing a new organo-iridium Kläui-type precursor onto rutile TiO₂. Iridium homogeneously distributes at

atomic/small cluster level and exhibits a high resistance to leaching after the first catalytic run and a remarkable activity, which was only limited by the amount of NaIO₄, and that persists for many thousands of cycles.