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Chromium(0) Nanoparticles as Effective Catalyst for the Conversion of Glucose into 5-Hydroxymethylfurfural

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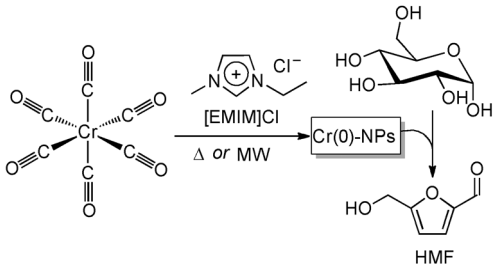
In 2007, a seminal work by Zhang et al. revealed that glucose can be converted into 5-hydroxymethylfurfural (HMF) in good yields by using a catalyst system based on divalent $CrCl_2$ in ionic liquids (ILs), particularly 1-ethyl-3-methylimidazolium chloride ([EMIM]Cl).[1] This work is significant because (i) glucose, derived from hydrolysis of cellulosic biomass, is a renewable source of HMF and a more desirable feedstock than the food-based fructose previously employed for HMF production; and (ii) the main product of the process, HMF, is a versatile, key biorefining building block for sustainable chemicals, materials, and liquid fuels.[2] Currently major efforts are directed at developing economically viable pathways to convert nonfood biomass into biofuels and/or feedstock chemicals,[3] and the glucose/cellulose-to-HMF conversion process holds great potential to meet this goal. However, the challenge has been how to advance the catalyst system so that it becomes technologically and economically competitive, compared to petroleum refineries. Since the discovery of the $CrCl_2$/IL catalyst system, a large number of effective metal catalyst systems have been reported for this common goal of glucose/cellulose-to-HMF conversion in ILs; they are mostly halide,[4] but also a few alkoxide,[5] complexes of metals, but *all at +n oxidation states* and, to the best of our knowledge, *no catalyst system based on metal nanoparticles* (M-NPs) has been reported for this process.

We reasoned that the currently unexplored zero-valent metal carbonyl complexes could be especially attractive for the glucose-to-HMF conversion in ILs for several reasons. (i) They are known to be excellent precursors to well-defined M^0-NPs under microwave irradiation[6a] or thermal decomposition (thermolysis)[6b] conditions in ILs, thereby offering an interesting opportunity to explore new nanocatalysis for this process. (ii) They are typically less expensive than the corresponding halide complexes (e.g., the cost of the air-stable, zero-valent $Cr(CO)_6$ is about half that of the air-sensitive, divalent $CrCl_2$). (iii) Because small M^0-NPs are considered strong Lewis acids, which is the main reason they typically require stabilization, with stabilizers ranging from donor polymers or solvents to anions,[7] they could promote efficient catalysis for the glucose-to-HMF conversion following the general catalysis scheme proposed for other Lewis acids such as $CrCl_x$ ($x=2,3$), that is, acid-catalyzed isomerization of glucose to fructose followed by dehydration to HMF.[1,4] (iv) As homogenous biomass conversion systems use ILs as solvent, the IL solvent can also function as the stabilizer for M^0-NPs.[8]

In this Communication, we present several lines of evidence that suggest that Cr^0-NPs, either preformed or generated in situ, serve as the true catalyst for the conversion of glucose to HMF in ILs employing $Cr(CO)_6$ (Scheme 1). Also reported is



Scheme 1. General scheme for the conversion of glucose into HMF by Cr^0-NPs.

evidence for the presence of Cr-NPs even in glucose conversions that employ divalent $CrCl_2$ in ILs or in DMF, although detailed investigations indicated that the dominant catalysis in the $CrCl_2$/IL system is not brought about by these Cr-NPs.

Under the standard conditions employed in this study (i.e., 0.50 g [EMIM]Cl, 10 mol% precatalyst relative to glucose, $T=120\,^{\circ}C$), the $CrCl_2$-based benchmark catalyst system gave a HMF yield of 45% in 6 h or 50% in 24 h (Table S1).[9] In comparison, the HMF yield from glucose conversion using $Cr(CO)_6$ was 49% in 6 h or 41% in 24 h, indicating that $Cr(CO)_6$ was more effective than $CrCl_2$ in the shorter-time run (6 h). However, other group 6 metal (Mo and W) carbonyl complexes were much less effective (Table S1). A benzene derivative prepared by replacing three carbonyl ligands in $Cr(CO)_6$ with one η^6-benzene ligand, giving $(\eta^6\text{-}C_6H_6)Cr(CO)_3$, proved a poor precatalyst for the glucose conversion, affording HMF in low yields of $\leq$14% under various reaction conditions (Table S1). Under the current conditions, group 8 iron carbonyl complexes, $Fe(CO)_5$ and $Fe_2(CO)_9$, were not capable of catalyzing this conversion, nor were carbonyl complexes of groups 7 and 9, $Mn_2(CO)_{10}$ and $Co_2(CO)_8$. Focusing on the best-performing carbonyl complex of this series, $Cr(CO)_6$, we investigated the effects of reaction temperature and time, catalyst loading, IL structure, and additives on the glucose conversion. Figure S3 summarizes the effects of reaction temperature and time on the HMF yield. When the conversion was carried out at $T=100\,^{\circ}C$, the HMF yield increased gradually and reached a maximum of 47% after 42 h, but the yield dropped sharply to only 4.5% after 48 h. On the other hand, at $T=120\,^{\circ}C$ the reaction reached the

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maximum yield of ca. 50% much more quickly (6 h), and maintained this yield level during up to 12 h of reaction, after which the yield began to decline (41% after 24 h). A much lower HMF yield achieved for the reaction after extended time is likely due to gradual degradation of HMF at high temperatures.[4f,5a]

Several interesting initial observations on the $Cr(CO)_6$ system revealed its unique catalytic behavior. Firstly, unlike for the $CrCl_2$ system, the HMF yield achieved by $Cr(CO)_6$ was insensitive to the precatalyst loading. Specifically, using the conditions that gave the best HMF yield ($T=120\,^{\circ}C$, $t=6$–12 h), we varied the $Cr(CO)_6$ loading from 10 mol% to 1.25 mol% and observed a nearly constant HMF yield of 50 ± 3% (Figure S4). Secondly, replacing the IL solvent [EMIM]Cl by polar organic solvents such as DMSO and DMF prohibited the catalysis, which is in drastic contrast to the $CrCl_2$ system, which gave comparable yields of HMF in [EMIM]Cl and the above polar organic solvents.[4l] Thirdly, the addition of one equivalent (relative to Cr) of an N-heterocyclic carbene (NHC) ligand, 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes), completely shut down the catalysis. This result is again in sharp contrast to the $CrCl_2$ system, for which an enhanced HFM yield upon addition of an NHC ligand has been reported,[4l] but is consistent with catalysis by M^0-NPs considering the NHC ligand as a potent M^0-NP poison.[10] Finally, performing the conversion in the common ammonium salt Et_4NCl, which is known to be an effective stabilizer of M-NPs,[11] was as effective as [EMIM]Cl, requiring either a longer reaction time (45% yield at $T=120\,^{\circ}C$ for 24 h) or higher temperature (49% yield at $T=130\,^{\circ}C$ for 9 h).

Because the results described above are consistent with the catalysis behavior of M^0-NPs, we sought direct evidence for the presence of Cr^0-NPs in the glucose conversion system that employed $Cr(CO)_6$ as the source of catalyst. Specifically, we analyzed samples withdrawn from the solution at the end of the conversion reactions by transmission electron microscopy (TEM).[9] Indeed, TEM images of these post-reaction samples clearly revealed the presence of small, monodisperse Cr^0-NPs with an average size of NP(100) of 2.3 ± 0.4 nm (Figure 1). Cautioned by a report that some M-NPs can be formed from metal salts in ILs under accelerated electron-beam irradiation,[12] we carried out a control experiment to examine the alternative hypothesis that the formation of Cr^0-NPs was induced by the TEM beam. Specifically, a sample of $Cr(CO)_6$ in a room-temperature IL, 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF_4), which received neither microwave irradiation nor thermolysis pretreatment, was imaged using TEM conditions identical to those used to image the NPs shown in Figure 1. We did not observe NPs under these conditions. When the TEM electron beam was focused on a small area with increased beam current density, some much larger NPs were formed (34.5 ± 6.6 nm; Figure S7). Notably, the smaller NPs formed under the real reaction conditions (i.e., the NPs shown in Figure 1) did not change during such focusing steps.

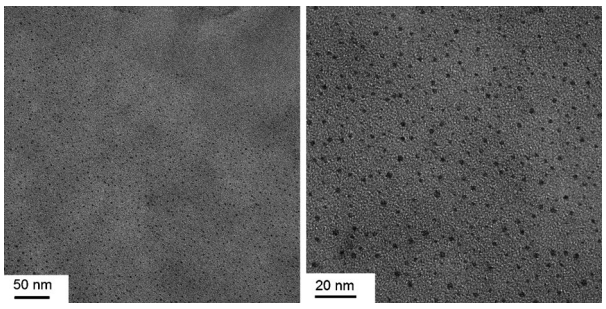

Figure 1. TEM images of Cr^0-NPs obtained at the end of the glucose conversion reaction in [EMIM]Cl, employing $Cr(CO)_6$ at 120 °C for 6 h. The average size of the NPs(100) is 2.3 ± 0.4 nm.

A critical question is whether or not the Cr^0-NPs formed during the reaction are responsible for the catalysis. To address this question, we preformed Cr^0-NPs via microwave irradiation of a dispersion of $Cr(CO)_6$ in [BMIM]BF_4.[6,9] TEM images shown in Figure S6 confirmed the formation of uniform NPs (3.6 ± 0.7 nm). Two experimental results that followed are significant. (i) Glucose conversion by using these preformed Cr^0-NPs gave a noticeably higher HMF yield (54%) than that achieved by directly employing $Cr(CO)_6$ (49%) under the current standard conditions. (ii) Catalysis using the preformed NPs reached the maximum HMF yield much sooner than the 6 h period typically observed for the reaction when employing the molecular precursor $Cr(CO)_6$. For example, after only 1 h, Cr^0-NPs derived from thermolysis by heating $Cr(CO)_6$ in DMF ($T=120\,^{\circ}C$ for 6 h), [EMIM]Cl ($T=120\,^{\circ}C$ for 6 h), [$T=$EMIM]Cl (230 °C for 12 h), and [$T=$BMIM]BF_4 (230 °C for 12 h) achieved a maximum HMF yield of 43%, 50%, 48%, and 49%, respectively, during glucose conversion carried out in [EMIM]Cl at $T=120\,^{\circ}C$. Overall, the above results based on the preformed Cr^0-NPs are consistent with the assertion that the NPs are responsible for the catalysis.

To further confirm that the Cr^0-NPs truly serve as catalyst, we performed quantitative poisoning experiments on the glucose-to-HMF catalysis in the presence of varied amounts of 1,10-phenathroline (PHEN). Amongst several common poisons investigated (e.g., Hg, CS_2), PHEN has been identified as the most suitable poison for distinguishing between a M-NP catalyst and a ligand-stabilized molecular or sub-nanometer cluster catalyst in a catalytic system operating in conditions $\geq100\,^{\circ}C$.[13] Figure 2 plots the relative HMF yield achieved by the preformed Cr^0-NPs via microwave irradiation versus the number of equivalents of PHEN (relative to Cr) subsequently added to the reaction mixture. Figure 2 clearly shows that a sub-stoichiometric amount of PHEN drastically suppressed the catalytic activity; the linear, extrapolated portion of the data yielded an intercept of 0.28, which can be considered as the calculated equivalent of PHEN (per metal) needed to halt the catalysis.[13] A similar poisoning experiment performed on a system with in situ generated Cr^0-NPs from thermolysis showed that the catalytic activity diminished to the background level (1–4% HMF yield in [EMIM]Cl, without any catalyst) in the presence of a fractional equivalent of PHEN,[9] and the linear, extrapolated portion of the data yielded an intercept of 0.20 (Figure S11), comparable to that of the microwave irradiation route. Overall, the above quantitative poisoning experi-

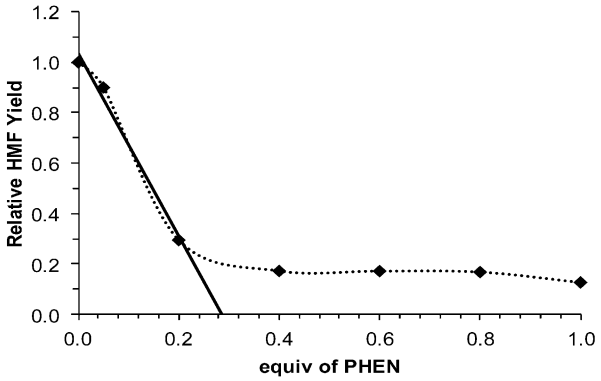

Figure 2. Plot of the relative HMF yield vs equiv of the poison PHEN added to the conversion system in [EMIM]Cl (120 °C, 6 h) by Cr^0-NPs derived from microwave irradiation.

ments showed that a sub-stoichiometric amount of PHEN (<0.3 equiv for both Cr-NP systems) can halt the catalysis, presenting very strong evidence for NP catalysis by the $Cr(CO)_6$/IL system.

To probe the possibility that Cr-NPs could also be present in the glucose conversion system employing $CrCl_2$, we studied the $CrCl_2$ system in a similar manner as we did the $Cr(CO)_6$ system. Intriguingly, TEM images of post-reaction samples taken from the glucose conversion employing $CrCl_2$ in [EMIM]Cl or in DMF at $T=120$ °C for 6 h also revealed the presence of small, uniform NPs, with the average size of NPs(100) being 3.4 ± 0.6 nm for reactions in [EMIM]Cl (Figure S8) or 3.0 ± 0.4 nm for reactions in DMF (Figure S9).[14] A control experiment on a sample of $CrCl_2$ in $[BMIM]BF_4$ that was not subject to the reaction conditions revealed *no* formation of NPs although, with increased beam current density, some much larger NPs (24.7 ± 7.9 nm) were formed (Figure S10). Worth noting again is that the small NPs formed under the reaction conditions did not change upon such treatment. To determine if the catalysis demonstrated by the $CrCl_2$-based system was brought about by the presence of small NPs in the glucose conversion system, or by molecular complexes derived from $CrCl_2$ in the IL or DMF, we again performed quantitative poisoning experiments using PHEN. Behaving differently from the $Cr(CO)_6$ system, a super-stoichiometric amount of PHEN added to a preheated solution of $CrCl_2$ at $T=120$ °C for 3 h in [EMIM]Cl (to generate NPs or other types of active species) was required to substantially suppress the catalytic activity of the system. The linear, extrapolated portion of the data yielded an intercept of 5.0 (Figure S12), which represents the calculated equivalents of PHEN needed to halt the catalysis; remarkably, this value is identical to the reported 5 equiv of 2,2′-bipyridine needed to shut down catalysis by $CrCl_2$ in [EMIM]Cl.[1] The same poisoning experiment performed on the $CrCl_2$ system in DMF, which gave a HMF yield comparable to the conversion in [EMIM]Cl under the current conditions, yielded an intercept of 2.5 (Figure S13). Overall, the above results indicate that Cr-NPs and molecular active species co-exist in the $CrCl_2$-based catalyst system, but the quantitative poisoning experiment data seemed indicative of dominant catalysis by $CrCl_x$ or the corresponding metallate complex, but not the Cr-NPs present in the system.

In conclusion, the zero-valent $Cr(CO)_6$-based catalyst system proved more effective for the conversion of glucose to HMF under current conditions ([EMIM]Cl, $T=120$ °C) than the divalent $CrCl_2$-based benchmark catalyst system, especially at low catalyst loadings. Evidence from different sources, obtained by in situ, ex situ, and quantitative poisoning experiments, demonstrate for the first time that small, uniform Cr^0-NPs, either preformed via microwave irradiation (3.6 ± 0.7 nm) or generated in situ via thermolysis (2.3 ± 0.4) during the reaction, are active species responsible for the observed catalysis when using $Cr(CO)_6$ as the precatalyst. Being strong Lewis acids, such small Cr^0-NPs promote efficient catalysis, presumably following the general mechanism proposed for other Lewis acids such as $CrCl_x$. In view of some of the favorable characteristics of the $Cr(CO)_6$-derived NP catalyst system, including the relatively low cost and air-stability of the precatalyst as well as its ability to maintaining high efficiency levels at low catalyst loadings, the results reported herein should stimulate future efforts to develop more effective M-NP catalysts for glucose- or related biomass-conversion processes.

Experimental Section

The Supporting Information contains experimental details, as well as Tables (3), and Figures (13)referred to in the text.

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[14] It is not clear at present how a small amount of Cr^{II} is reduced to Cr^0 under the current reaction conditions (in IL or DMF, 120 °C, 6 h), but the presence of glucose (a reducing sugar) is critical for Cr^0-NP formation.

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