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POLYOXOANION MEDIATED METHANE ACTIVATION AND FUNCTIONALIZATION: MOLECULAR DESIGN OF NEW HOMOGENEOUS AND NEW SOLID STATE/HETEROGENEOUS CATALYSTS

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ANNUAL PROGRESS REPORT FOR THE PERIOD

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PROGRESS REPORT

Project Goals

The overall goal of our DOE-funded research is to develop a chemical paradigm for polyoxoanion-supported transition-metal catalysis, with an emphasis on small molecule (H_2, O_2, CH_4) catalytic activation and functionalization (CH_4, RH). Sub-goals or sub-projects include solution (i.e. homogeneous) catalysis studies, and then the preparation and study where warranted of a new class of novel, polyoxoanion-based solid-state (heterogeneous) catalysts. Kinetic and mechanistic studies are an integral part of this work, since they provide both the best and fastest way to reliably establish the strengths and weaknesses of this previously unknown class of catalytic materials.

At this writing, it has been 1 year and 8 months since our DOE-funded research began. Our research has gone extremely well as documented below, the addition of DOE support having proven to be the needed "catalyst" to our efforts beginning almost 10 years ago in this challenging and exciting area.

Catalytic and Mechanistic Studies of First H_2 Activation and Then O_2, CH_4 and Other Alkane Activations

Recently, in a communication acknowledging our DOE support, we reported the *first* example of a polyoxoanion-*supported* catalyst.[1] That work, which examines H_2 activation and olefin reductions, takes advantage of our molecularly designed and molecularly engineered, second-generation, *optimized* catalyst precursor,[2] $(1,5\text{-COD})Ir{\bullet}P_2W_{15}Nb_3O_{62}^{8-}$ (1). Preliminary mechanistic data were also reported in one[1] of these two, back-to-back communications, results which establish the crucial result that the iridium *remains supported in the true catalyst*. Work necessary for two full papers is essentially done, one paper describing the

challenging synthesis and characterization and a second paper describing the non-trivial kinetic and mechanistic studies we have done. The two full papers are presently nearing completion.

These papers plus our recent communications[1,2] meet our ten year old research goal of establishing a paradigm for polyoxoanion-supported catalysis. As such, we anticipate that they will become classics papers in a this new sub-area of catalysis, one created with the help of our DOE support.

O_2 Activation and Catalytic Oxidations Using (1,5-COD)Ir•$P_2W_{15}Nb_3O_{62}^{8-}$ (1)

Polyoxoanion-based systems like 1 are all inorganic and thus represent a new class of oxidation resistant and robust catalysts. Hence one of the especially significant and thus exciting applications of the unprecedented 1 is in oxidation chemistry.

We are pleased to report that our DOE support has allowed us to develop and communicate the first example of a polyoxoanion-supported *oxidation* catalysts based on (1,5-COD)Ir•$P_2W_{15}Nb_3O_{62}^{8-}$ (1).[3,4] This catalyst, which uses the cheapest and environmentally most desirable of all terminal oxidants, *molecular* O_2, is also just the second polyoxoanion-*supported* catalyst ever described. Further studies are needed (and are in progress) to define the range of substrates, the scope of the reaction, and the key aspects of the reaction mechanism.

Alkane, Olefin and Arene Hydroxylations by $P_2W_{17}O_{61}Mn^{III}O_{61}^{7-}$ and PhIO

This work was began more than five years ago, but remained unfinished due to the lack of manpower until our DOE support arrived. With just part time effort of David Lyon (who recently completed his Ph.D), this work has been completed and two full papers are almost ready for submission. This work is the

best and most complete in a area that has only ca. five papers. In particular, we will report: (a) the best characterized such polyoxoanion catalyst systems; (b) the second generation, more optimum $P_2W_{17}MnO_{61}^{7-}$ catalyst (more optimum in terms of its catalytic properties or the ability to characterize and study it by NMR, for example); (c) a wider range of substrate studies than previously examined; and (d) internal controls and comparisons to some of the best Mn(porphyrin) catalysts. These controls are necessary to connect our work to the large body of information examining metalloporphyrin catalysts, but such crucial controls and comparisons have not been previously reported.

Summary

It is probably apparent that our 1 year and 8 month old DOE-funded research is progressing very well, perhaps remarkably so given that our DOE grant funds just two students. This is precisely the effect I anticipated, when I wrote and submitted our DOE proposal, since this area and our initial results continue to be ripe for further advances.

References

1. Lyon, D. K; Finke, R. G. *Inorg. Chem. 1990*, *29*, 1787-1789.
2. Finke, R. G.; Lyon, D. K.; Nomiya, K.; Sur, S.; Mizuno, N. *Inorg. Chem.* **1990**, *29*, 1784-1787.
3. Mizuno, N.; Lyon, D. K.; Finke, R. G. *J. Catalysis*, **1990**, *127*, 0000 (in press).
4. A patent application on the work with O_2 is under construction.

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