

# Use of Field-Induced Surface-Organometallic Interactions to Control Selectivity in Rhodium-Catalyzed Organic Reaction

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## Abstract:

A major challenge facing chemists is to control the selectivity of chemical reactions. The common response is to focus entirely on catalyst design to improve yields of desired products. Electric fields generated at the interface of an electrode and electrolyte solution have shown promise as an additional method to control chemical reactions. In previous work, our group showed that Lewis acid-catalyzed rearrangements of epoxides favor different products when subjected to interfacial electric fields [1]. It was also established that interfacial electric fields can induce surface-organometallic interactions that can change product ratios in a rhodium-catalyzed carbene reaction more than 100-fold [2]. In this work, we exploited a field-induced  $\text{TiO}_2$ -rhodium porphyrin interaction to change the site selectivity of a C-H insertion reaction (Figure 1). Depending on the interfacial charge density, the product ratio in the rhodium porphyrin-catalyzed reaction of 1-diazo-3-(3-methoxyphenyl)propan-2-one (1) to 5-methoxy-1*H*-inden-2(3*H*)-one (2) and 4-methoxy-1*H*-inden-2(3*H*)-one (3) changes 16-fold, with a 3.6-fold increase in conversion of the starting material. We also investigated alternative  $\text{HfO}_2$  and  $\text{Ta}_2\text{O}_5$  dielectrics, which showed similar field-induced selectivity effects.

## Introduction:

Chemists can exert substantial control over the selectivity of many reactions by changing the steric and electronic properties of the relevant catalyst, but very little is known about the impact of certain environmental factors on catalytic selectivity. Specifically, the application of an electric field has the potential to affect selectivity in chemical reactions by stabilizing aligned transition-state dipolar species, lowering the activation barrier towards—and altering selectivity in favor of—the associated product. In the model reaction cell outlined in Figure 2, an applied potential induces the formation of an electric field at the interface between a charged dielectric surface and the contiguous electrolyte solution.

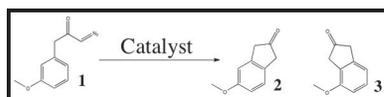


Figure 1: Reaction scheme for conversion of 1-diazo-3-(3-methoxyphenyl)propan-2-one (1) to 5-methoxy-1*H*-inden-2(3*H*)-one (2) and 4-methoxy-1*H*-inden-2(3*H*)-one (3).

Using a catalyst fixed to the dielectric surface by intermolecular forces, previous work by our group has shown two interesting results. First, electric fields can change the selectivity of certain chemical reactions. Second—in the case of a rhodium porphyrin-catalyzed carbene reaction—an electric field can induce an interaction between the catalyst and a titanium dioxide ( $\text{TiO}_2$ ) dielectric. This result is interesting because the selectivity change was in the opposite direction to that shown on an aluminum oxide ( $\text{Al}_2\text{O}_3$ ) dielectric under otherwise identical conditions. This and other experiments conducted in the same study indicated an electric field-induced interaction between a  $\text{TiO}_2$  dielectric surface and the rhodium porphyrin catalyst that could potentially be used to control selectivity in other reactions [2].

The purpose of this study is to further investigate this electric field-induced catalyst-dielectric interaction by examining a carbene insertion reaction (Figure 1) using a rhodium porphyrin catalyst on aluminum oxide, titanium oxide, and other dielectric surfaces.

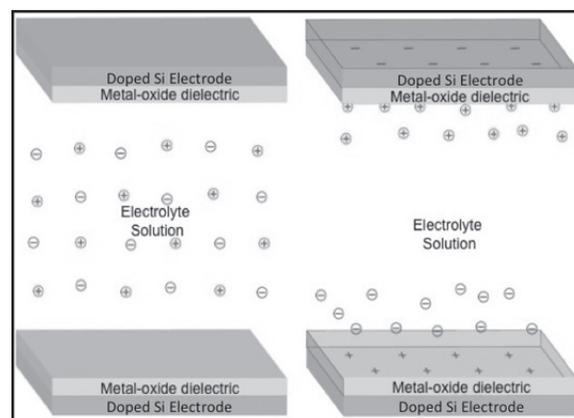


Figure 2: Model of the reaction cell used in this study. Left: a neutral reaction cell. Right: a reaction cell with applied potential, forming a localized electric field at each dielectric surface.

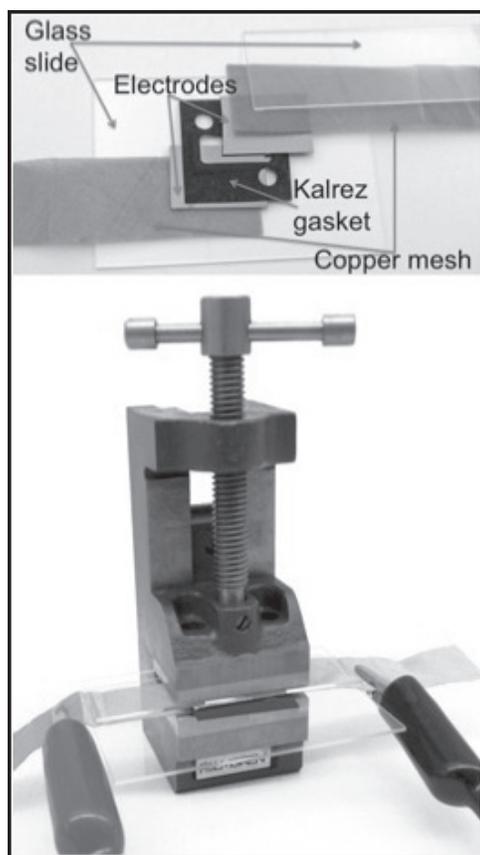


Figure 3: The parallel plate cell.

### Experimental Procedure:

Using atomic layer deposition (ALD), 50 Å of metal oxide were deposited on highly doped silicon wafers. The wafers were then sliced into smaller pieces and used to assemble multiple parallel plate cells (Figure 3). A reaction solution consisting of 5 millimolar (mM) substrate **1**, 500 micromolar ( $\mu\text{M}$ ) tetrabutylammonium hexafluorophosphate (TBA PF<sub>6</sub>) electrolyte, and 10  $\mu\text{M}$  rhodium tetraphenylporphyrin iodide (RhTPPI) catalyst in dichloromethane solvent was added to the cell via pipette. The cell was then compressed in a vice and a potential difference applied to the copper mesh contacts. The reaction was allowed to run overnight then stopped. The cell was opened and the reaction solution examined by high pressure liquid chromatography to determine total product conversion and product ratio.

### Results and Conclusions:

When using an aluminum oxide dielectric in our parallel plate cell, we found that we could not alter the selectivity in this reaction by applying a potential difference. As can be seen in Figure 4, the product ratio **2:3** remains at about 10:1 for both a 0 volt (V) and a 4.5 V potential. However, when a titanium

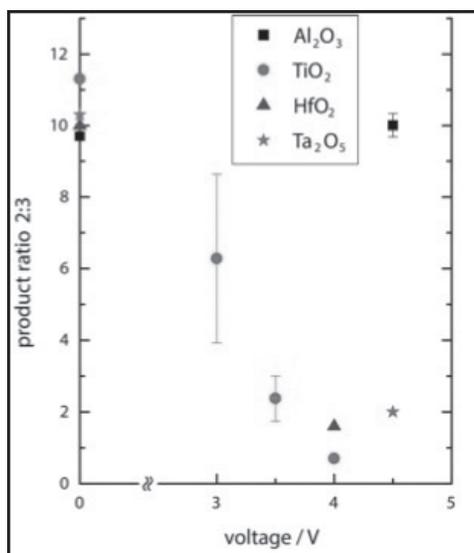


Figure 4: Product ratio **2:3** as a function of applied voltage on Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, HfO<sub>2</sub>, and Ta<sub>2</sub>O<sub>5</sub> dielectrics.

oxide dielectric was used, we found that the **2:3** ratio was 11.3:1 at 0 V, but fell to 0.7:1 at 4 V. We also observed electric field-induced selectivity changes when using hafnium oxide and tantalum oxide dielectrics. These results are all shown in Figure 4, which displays product ratio **2:3** as a function of voltage applied to the plate cell for each of the four dielectrics used.

These results support our earlier hypothesis that there exists an electric field-induced interaction between a TiO<sub>2</sub> dielectric and rhodium porphyrin catalyst, which can be used to control selectivity in a chemical reaction. This phenomenon is seen with both HfO<sub>2</sub> and Ta<sub>2</sub>O<sub>5</sub> dielectrics, but not with an Al<sub>2</sub>O<sub>3</sub> dielectric.

### Future Work:

This as-yet untapped phenomenon in catalysis has huge potential as a future tool in industrial and academic chemistry, but several challenges remain before it can be effectively exploited. These include elucidating the mechanism of the selectivity change, developing a method to increase the scale of the reaction cell (the experiments in this study were run on a 75 microliter scale), and determining the applicability to industrially relevant chemical syntheses.

### Acknowledgements:

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### References:

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- [2] Gorin, C., Beh, E., Kanan, M.; "Interfacial Electric Field Effects on a Carbene Reaction Catalyzed by Rh Porphyrins"; *Journal of the American Chemical Society*, 135, p 11257-11265 (2013).