

Effects of Ligand Composition on the Activity of Rh(III) for the Oxidative Carbonylation of Toluene to p-Toluic Acid

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Introduction

Rh-based catalysts are known to activate C-H bonds for the oxidative carbonylation of toluene to form p-toluic acid in the presence of carbon monoxide [1-2]. The reaction is thought to proceed through an electrophilic mechanism [3], which is consistent with the observation that the oxidative carbonylation of various hydrocarbons proceeds faster in the presence of trifluoroacetic acid than in the presence of acetic acid [4-5]. The superior performance of trifluoroacetic acid to acetic acid has been attributed to the higher electrophilicity that it imparts to the metal cation [6-7]. The principle objective of the present study was to develop a systematic understanding of the effects of ligand composition on Rh catalysts for the oxidative carbonylation of toluene to p-toluic acid, especially why methanesulfonic acid derivatives are not effective.

Materials and Methods

Reactions were conducted in stirred, 50 mL Parr autoclaves made of Hastelloy C. During typical reactions, anhydrous toluene, the designated acid, either $\text{CF}_3\text{SO}_2\text{OH}$, $\text{CH}_3\text{SO}_2\text{OH}$, $\text{CF}_3\text{CF}_2\text{COOH}$, CF_3COOH , CClF_2COOH , CCl_3COOH , CCl_2HCOOH , CClH_2COOH , or CH_3COOH , the corresponding anhydride, $\text{Rh}(\text{acac})_3$, and NH_4VO_3 were placed into the autoclave, which was sealed and purged with helium. After purging, the reactor was pressurized with O_2 and CO and heated to 353K for four hours. Upon completion, the reactors were quenched with ice water. Deionized water was added to work-up the reactor contents. The concentration of toluic acid was determined by gas chromatography.

Theoretical calculations were performed in Q-Chem with the B3LYP density functional. Structure optimization, including transition state searches were performed at the 6-31G* level, the energetics were refined at the 6-311G** level, and the LANL2DZ pseudopotential was employed for rhodium. The Growing String Method [8] was used to generate initial guesses at TS structures connecting reactant and product configurations. Finally, Energy Decomposition Analysis [9] was employed to further understand the trends in toluene binding energy.

Results and Discussion

Figure 1 indicates the effect of acid pKa on the number of turnovers obtained for Rh(III) catalysts during a 4-h period. Only acids with pKa's between -2 and 3 were effective for the reaction, and the most effective acids were those with pKa's between 0 and 0.5. CClF_2COOH yielded the highest activity for all times ranging from 0 to 12h. Theoretical calculations indicate that the observed pattern is attributable to two effects. First, the ligand must be a sufficiently weak base to enhance the electrophilicity of the Rh metal center to facilitate toluene coordination. Second, the ligand must be sufficiently basic to abstract a proton from the benzene ring. The balance between these two factors cause the trend observed

in Figure 1. Differences in the geometry and electronics of the sulfonate-containing anions compared to the carboxylate-containing anions resulted in higher energies for toluene coordination, which contributed to the low activity observed when the sulfonate-containing anions were used.

Significance

A detailed understanding of the influence of ligand composition on the activity of Rh(III) complexes for the oxidative carbonylation of toluene to toluic acid has been established. This work demonstrates that by altering ligand composition the activity of the catalyst can be tuned to achieve an optimum. The optimum activity results from a balancing of the heat of toluene coordination and the activation barrier for activation of the C-H bond on the benzene ring at the para position.

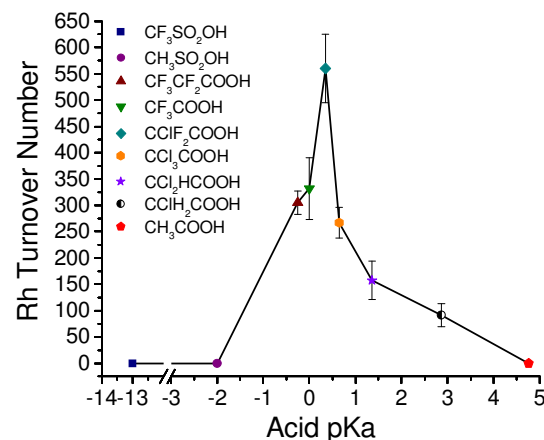


Figure 1. Effect of acid pKa on Rh(III) activity for the oxidative carbonylation of toluene to p-toluic acid.

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