

C-O BOND ACTIVATION ON MULTIFUNCTIONAL HETEROGENEOUS CATALYSTS

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Abstract

Facile C-O bond scission is essential for optimal product selectivity in industrially important processes ranging from Fischer-Tropsch synthesis to biofuels production. A grand challenge is that the C-O scission rate is several orders of magnitude slower than C-C and C-H bond breaking, rendering monofunctional heterogeneous catalysts (e.g., precious metals or reducible metal oxides) either not selective or not very active (temperatures >350 °C needed). Multifunctional catalysts (Rh/ReO_x, Rh/MoO_x, Ir/ReO_x, Ru/RuO_x), developed recently, are capable of catalyzing selective C-O bond scission in oxygenates at moderate temperatures. Here, we elucidate the synergy of multiple active sites for C-O bond activation using a model reaction system: catalytic transfer hydrogenolysis of furfural on a Ru/RuO₂ catalyst using 2-propanol as a hydrogen donor. By combining density functional theory, microkinetic modeling, and electronic structure analysis, we gain insights into why neither Ru nor RuO₂ phase alone are capable of catalyzing C-O bond hydrogenolysis. We expose a trifunctional catalytic mechanism involving both Ru and RuO₂ sites that drives the high catalyst activity. The mechanism is in quantitative agreement with H/D tracing and kinetic isotope effect measurements, providing opportunities for reaction pathway and catalyst design.

Keywords

Multifunctional Catalysis, Furanics, Hydrodeoxygenation.

Introduction

Facile C-O bond scission is essential in various industrially important processes. For example, in Fischer-Tropsch synthesis, which experiences revival due to the revolution of shale gas, C-O bond activation can potentially govern the hydrocarbons-to-alcohols product ratio. Selective C-O cleavage is also crucial in production of biofuels, as efficient oxygen removal is necessary for integration of biomass into the downstream oil refining infrastructure.

In comparison with reforming and dehydrogenation, which involve C-C and C-H bond breaking, a significant

challenge exists for the design of a selective C-O scission catalyst. Activity and selectivity maps for small oxygenates on transition metals reveal the best deoxygenation metal catalysts to be orders of magnitude slower than good reforming catalysts at the same reaction conditions (Saliccioli & Vlachos, 2011). Similarly, if metal oxides are used as catalysts, high temperatures (>320 °C) are required to obtain appreciable C-O scission activity (Prasomsri, Shetty, Murugappan, & Román-Leshkov, 2014). It is clear that monofunctional catalysis is ineffective for C-O bond activation.

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Combination of transition metals and metal oxides results in a surprisingly high activity for selective C-O bond cleavage at moderate temperatures, <200°C. Selected examples include glycerol hydrogenolysis to either 1,2-propanediol on Ru/ReO_x (Ma & He, 2010), and deoxygenation and ring-opening reactions in diols, triols, furans, and pyrans on Rh-ReO_x and Rh-MoO_x (Chia et al., 2011). The mechanism explaining the synergy between metallic and metal oxide functionalities remains poorly understood and occasionally controversial.

In this contribution, we employ multiscale chemical kinetics approaches to reveal the mechanism and compare to experimental data.

Methods and Findings

Here, we elucidate the metal/oxide synergy for C-O bond activation using a model reaction system: catalytic transfer hydrogenolysis of furfural on a Ru/RuO₂ catalyst using 2-propanol as a hydrogen donor. Yields of 2-methyl furan (sustainable platform chemical) up to 76% have been reported (Panagiotopoulou, Martin, & Vlachos, 2014). By combining density functional theory (DFT), microkinetic modeling, and electronic structure analysis, we gain insights into why neither the Ru nor the RuO₂ phase alone is capable of catalyzing C-O bond hydrogenolysis.

DFT energy profiles on Ru(0001) and RuO₂(110) surfaces (Figure 1) reveal that metallic sites are active in breaking the C-O bond, but become poisoned by oxygen, due to high Ru oxophilicity. On the other hand, metal oxide Lewis acid sites are effective for oxygen removal as water, but cannot break the C-O bond. These findings are consistent with the experimental data.

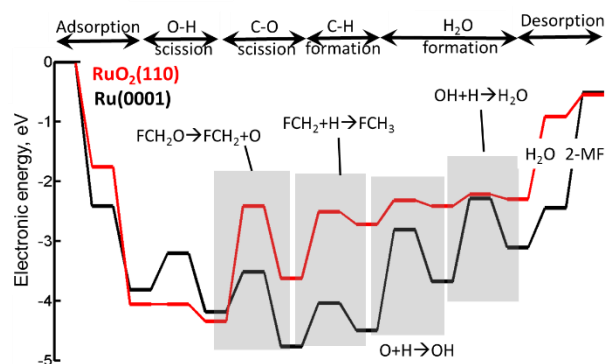


Figure 1. Minimum energy DFT reaction pathways for furfuryl alcohol conversion to 2-methyl furan on Ru(0001) and RuO₂(110) surfaces.

DFT and microkinetic modeling (not shown) indicate a trifunctional catalytic mechanism involving both Ru and RuO₂ to be responsible for low temperature catalyst activity. For example, hydrogenation of the carbonyl group of furfural proceeds via an interhydride transfer in a

concerted step between furfural and the hydrogen donor, 2-propanol. Electronic structure analysis indicates that the mechanism is mediated by radical intermediates and is in quantitative agreement with H/D tracing and recent kinetic isotope effect measurements (Gilkey et al., 2015).

Conclusions

Our results provide for the first time strong support for a trifunctional reaction mechanism operative at temperatures < 200 °C during furfural conversion to 2-methyl furan on the Ru/RuO₂ catalyst. This finding provides opportunities for reaction pathway and multifunctional catalyst design.

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