



Exploiting basic principles to control the selectivity of the vapor phase catalytic oxidative cross-coupling of primary alcohols over nanoporous gold catalysts



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ABSTRACT

Achieving high selectivity for high volume chemical synthesis is important for lowering energy consumption through reduction in waste. We report the selective synthesis of methyl esters—methyl acetate and methyl butyrate—through catalytic O₂-assisted cross-coupling of methanol with ethanol or 1-butanol using activated, support-free nanoporous gold (npAu). Both well-controlled studies on ingots in UHV and experiments under ambient pressure catalytic conditions on both ingots and microspherical hollow shell catalysts reveal guiding principles for controlling selectivity. Under UHV conditions, the ester products of the cross-coupling of methanol with both ethanol and 1-butanol evolve near room temperature in temperature-programmed reaction studies, indicating that the reactions occur facilely. Under steady-state catalytic operation, high stable activity was observed for cross-coupling in flowing gaseous reactant mixtures at atmospheric pressure and 423 K with negligible combustion. Optimum selectivity for cross-coupling is obtained in methanol-rich mixtures due to a combination of two factors: (1) the relative coverage of the respective alkoxys and (2) the relative facility of their β-H elimination. The relative coverage of the alkoxys is governed by van der Waal's interactions between the alkyl groups and the surface; here, we demonstrate the importance of these weak interactions in a steady-state catalytic process.

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1. Introduction

Achieving high selectivity for catalytic processes increases energy efficiency and reduces waste in chemical synthesis, which is especially important for high volume chemicals [1–5]. Low molecular weight methyl esters serve as platform chemicals for further synthesis as well as basic elements of various consumer products, and there is potential for substantial improvement in their production. Ideally, methyl esters would be selectively produced above all other products and combustion, in particular, would be suppressed.

Herein, we establish a foundation for understanding and predicting selectivity for Au-catalyzed methyl ester synthesis that spans a wide range of reaction conditions. Specifically, we demonstrate that the competitive adsorption between methanol and

longer-chain alcohols to form their respective alkoxides is key for determining reaction selectivity. The selectivity is directly controlled by the surface coverages of respective alkoxides, which is determined by the composition of alcohols in the gas phase and the surface binding energies of their alkoxides. The binding energies of alcohols to the surface are not factors in this relationship. The dependence of this competition on chain length is attributed to the contribution of weak van der Waal's interactions between the alkyl chain and the catalyst surface [6].

Gold-based catalysts have been shown to be effective for selective oxidation of alcohols [3,4,7–14], including the production of methyl esters [3,4,8,10–12,14,15], providing a promising route to sustainable synthesis. Nanoporous Au (npAu) has been demonstrated to promote selective oxidative coupling of methanol to methyl formate [10], and more recently, coupling of ethanol and 1-butanol to ethyl acetate and butyl butyrate, respectively [11,15]. These processes use O₂ as an oxidant and require relatively mild conditions (1 atm. total pressure, 1–10% alcohol, 1–20% O₂, 303–473 K). Hence, npAu was selected as a catalyst for this

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detailed investigation of the more complex coupling of methanol with longer-chain alcohols (ethanol or 1-butanol) in order to understand how to enhance and control selectivity for methyl ester production. A new activation procedure [15] that improves the reproducibility of the npAu catalyst performance was key to the studies described herein, because it allows for the systematic investigation of reactivity over vast pressure ranges.

The fundamental underpinnings for controlling selectivity for the partial oxidation and oxygen-assisted coupling of mixtures of methanol and other alcohols have been established by mechanistic investigations of Au(111) [16–18]. All primary alcohols investigated are oxidized through the same general mechanism, which requires atomic oxygen for activation of the alcohols, as illustrated for ethanol oxidation in Scheme 1. Key to this reaction is the activation of the O–H bond in the alcohol by adsorbed atomic oxygen to form the adsorbed alkoxy intermediate and the subsequent β -C–H bond activation in the alkoxy to yield the aldehyde, which reacts further with the adsorbed alkoxy. The selectivity for oxidation of a pure alcohol, such as ethanol, thus depends on the initial coverage of atomic oxygen and on the chain length of the alcohol. Specifically, selective oxidation is favored over combustion at low oxygen coverage [17–19]; at constant oxygen coverage, the amount of aldehyde formed increases with the length of the alkyl chain due to greater ease of β -C–H bond activation [16,20]. This general mechanism for oxidative coupling of alcohols has been demonstrated to be operative under operating catalytic conditions for npAu catalysts [10,11], as well as on single-crystal Au surfaces.

The more complex process of cross-coupling methanol with other primary alcohols also has been demonstrated to occur readily on O/Au(111) [16,20]. In such a case, the reactant alcohols both react with adsorbed O in a competitive fashion. Cross-coupling then occurs via reaction of one alkoxy with the aldehyde produced by the other. Optimum selectivity for cross-coupling requires that the relative concentrations of the dissimilar adsorbed alkoxy species be controlled. Thus, the competition between the reactant

alcohols for reactive sites on the gold is a critical factor; the number of active sites is determined by adsorbed O.

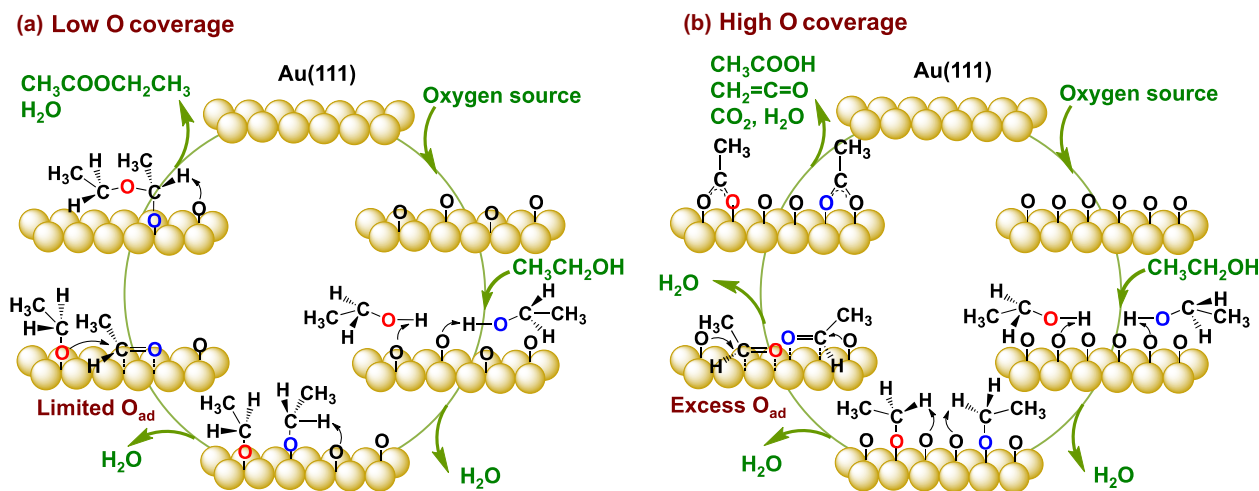
Using Au single crystals, it was demonstrated that the relative population of the different alkoxy species on the surface is determined by their alkyl chain lengths—longer-chain alkoxy species compete more effectively for active sites. The underlying reason for this is a pre-equilibrium that determines the relative concentration of the alkoxy species, illustrated for methanol and ethanol in Scheme 2. The preference for binding of longer-chain alkoxy species on gold is attributed to stronger interactions of the alkyl group with the surface via van der Waal's forces based on theoretical studies [6].

In this paper, we test these principles for a functional catalytic material, npAu, under a wide range of reaction conditions, spanning ultrahigh vacuum to atmospheric pressure. We establish that the same reaction mechanism applies on npAu and Au single crystals; thus, the selectivity for production of the methyl esters is controlled by the same factors under working catalytic conditions as in the model studies, including the competition for sites between the reactant species on the more complex catalytic material. This further establishes the predictive value of fundamental investigations for catalytic processes and specifically demonstrates the importance of van der Waal's interactions in determining selectivity.

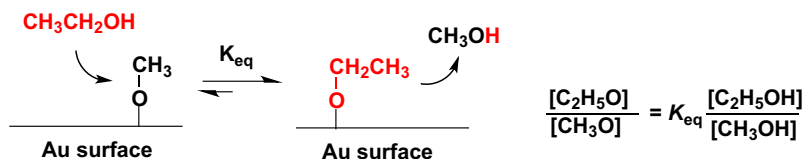
2. Experimental

2.1. Catalyst materials

Two different forms of npAu were investigated in this work—ingots (~ 5 mm diameter; 200–300 μm thick, BET surface area 4.6 $\text{m}^2 \text{g}^{-1}$) and spherical hollow shells (~ 8 μm diameter; ~ 400 nm thick shell, BET surface area 7.2 $\text{m}^2 \text{g}^{-1}$). The synthesis of these materials is described in detail elsewhere [10,11,15]. The bulk Ag content of these materials is $\sim 3\%$ and $\sim 1.5\%$ for the ingots and shells, respectively, determined using EDS. The surface silver



Scheme 1. Reaction pathways for ethanol oxidation at (a) low and (b) high oxygen coverage as established from ultrahigh vacuum studies on oxygen-covered single-crystal Au(111) surface [16].



Scheme 2. The adsorption pre-equilibrium between methanol and ethanol determined from UHV studies on single-crystal Au(111) surface [16].

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