Oxygen-Mediated Coupling of Alcohols over Nanoporous Gold Catalysts at Ambient Pressures

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Introduction

✓ Heterogeneous catalysis is very important to address the ever-increasing demand for the cost effective and environmentally friendly production of fine chemicals.

✓ A major challenge is the development of catalytic processes that operate at low temperatures with high conversion and high selectivity for the desired product.

✓ The steady-state concentrations of surface species remain low as binding of molecules (including H_2O) with metallic gold surface is weak.

✓ The selective oxidative coupling of methanol to give methyl formate, which was studied on metallic Au(111) containing atomic O and over nanoporous Au (npAu) catalysts using O_2 as an oxidant were correlated.

✓ Whether the transferability of UHV-based insight is more universal and can be extended to the oxidation of other alcohols as well???

✓ This gold material for low-temperature oxidation of CO using molecular oxygen was first reported independently by two research groups in 2006 and 2007.

✓ Several reports have dealt with npAu as a catalyst in the liquid as well as in the gas phase, underlining the potential and versatility of this material for catalytic applications.

✓ Why gold?? It activates selectively heteroatom-carbon bonds. e.g., Oxidation and coupling of primary alcohols, etc.

In this paper,

➢ Gas phase studies of aerobic oxidation and coupling of primary alcohols- methanol, ethanol and n-butanol using npAu as an unsupported catalyst at ambient pressures and low temperatures.

➢ To understand the mechanistic key factors by comparing these reactions with model studies as in gas phase moisture can be avoided which will not lead to formation of hydrolysis products.

Synthesis of material

Disks of npAu with a diameter of 5 mm and a thickness of 200–300 μm were prepared by etching Ag/Au alloys (70:30 atom%) in conc. nitric acid (65 wt%, Fluka Chemicals) for 48 h. This treatment is known to result in npAu material with a continuous porosity of 70 vol% consisting of more than 99 atom% gold.

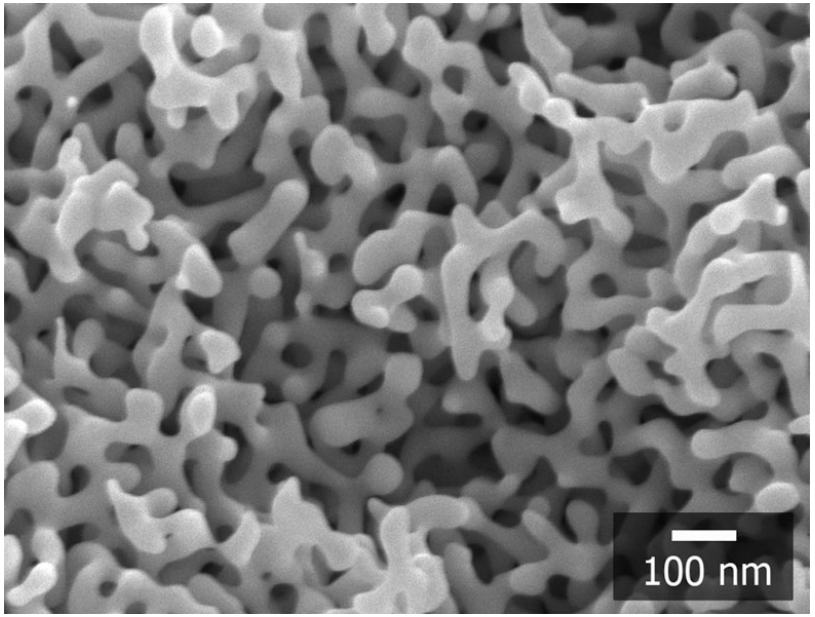


Figure. Scanning-electron micrograph of a cross-section of a npAu disk.

Experimental section

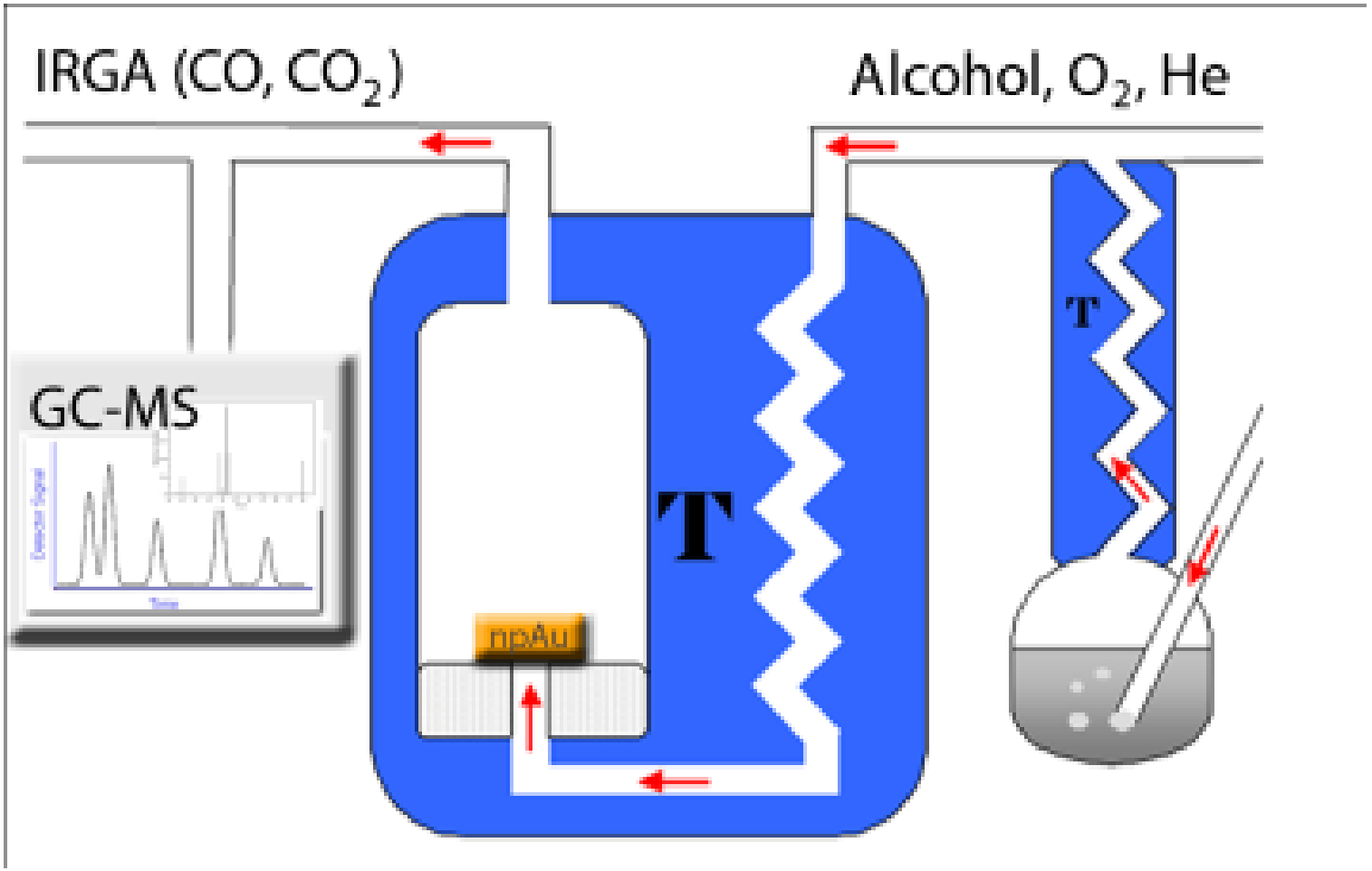
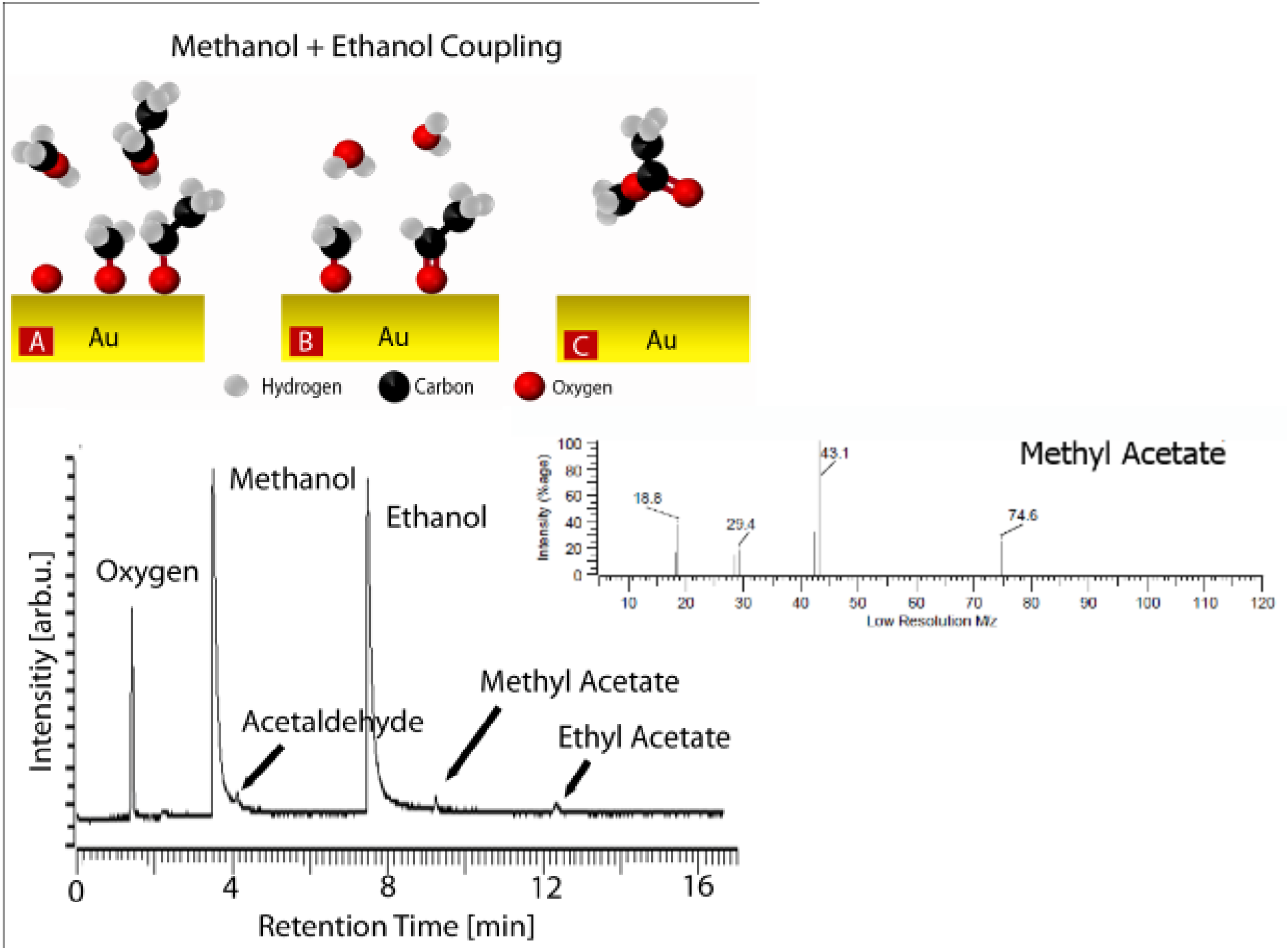
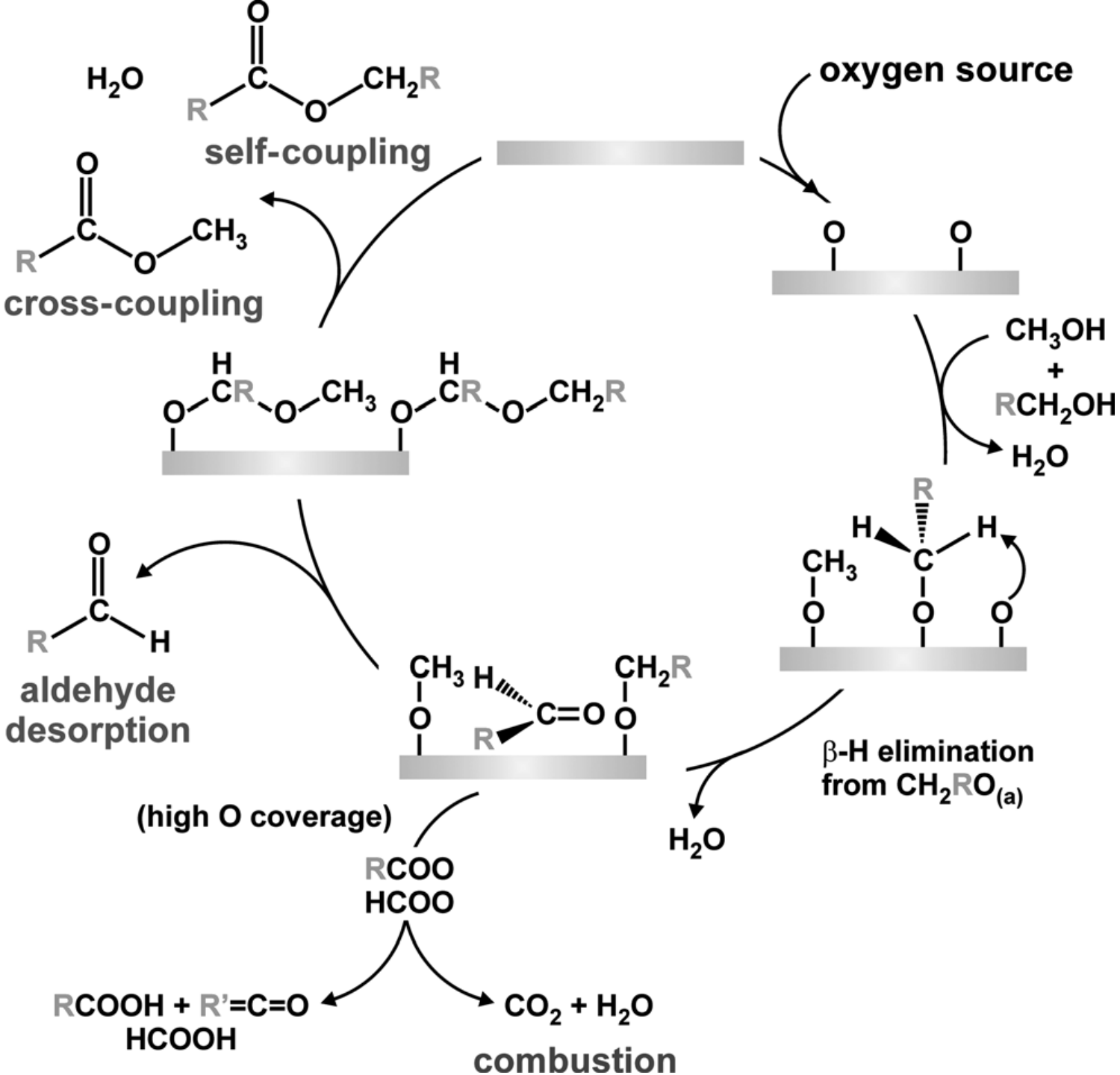


Figure. Schematic of the experimental setup for catalytic experiments.


Methanol + Ethanol Coupling
A
Au
B
Au
C
Au
Hydrogen
Carbon
Oxygen
Intensitiy [arb.u.]
Oxygen
Methanol
Ethanol
Acetaldehyde
Methyl Acetate
Ethyl Acetate
0
4
8
12
16
Retention Time [min]
Methyl Acetate
Intensity (%age)
18.6
29.4
43.1
74.6
Low Resolution M/z


oxygen source
self-coupling
cross-coupling
CH3OH
+
RCH2OH
H2O
aldehyde
desorption
β-H elimination
from CH2RO(a)
H2O
(high O coverage)
RCOO
HCOO
RCOOH + R'=C=O
HCOOH
CO2 + H2O
combustion

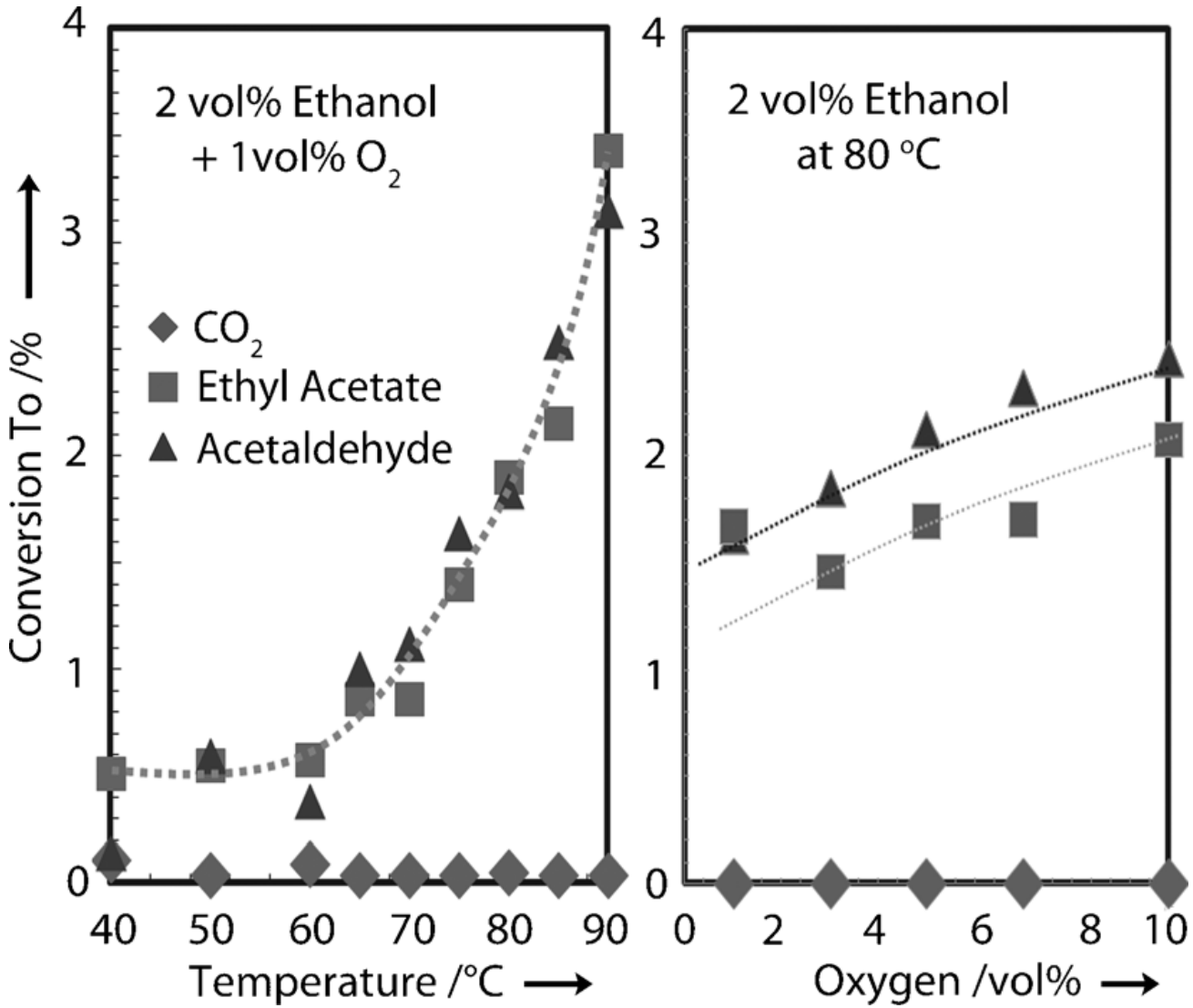


Figure. Oxidation of ethanol to ethyl acetate and acetaldehyde for temperatures between 40 ^{0}C and 80 ^{0}C (left) and for various oxygen partial pressures at a reaction temperature of 80 ^{0}C (right).

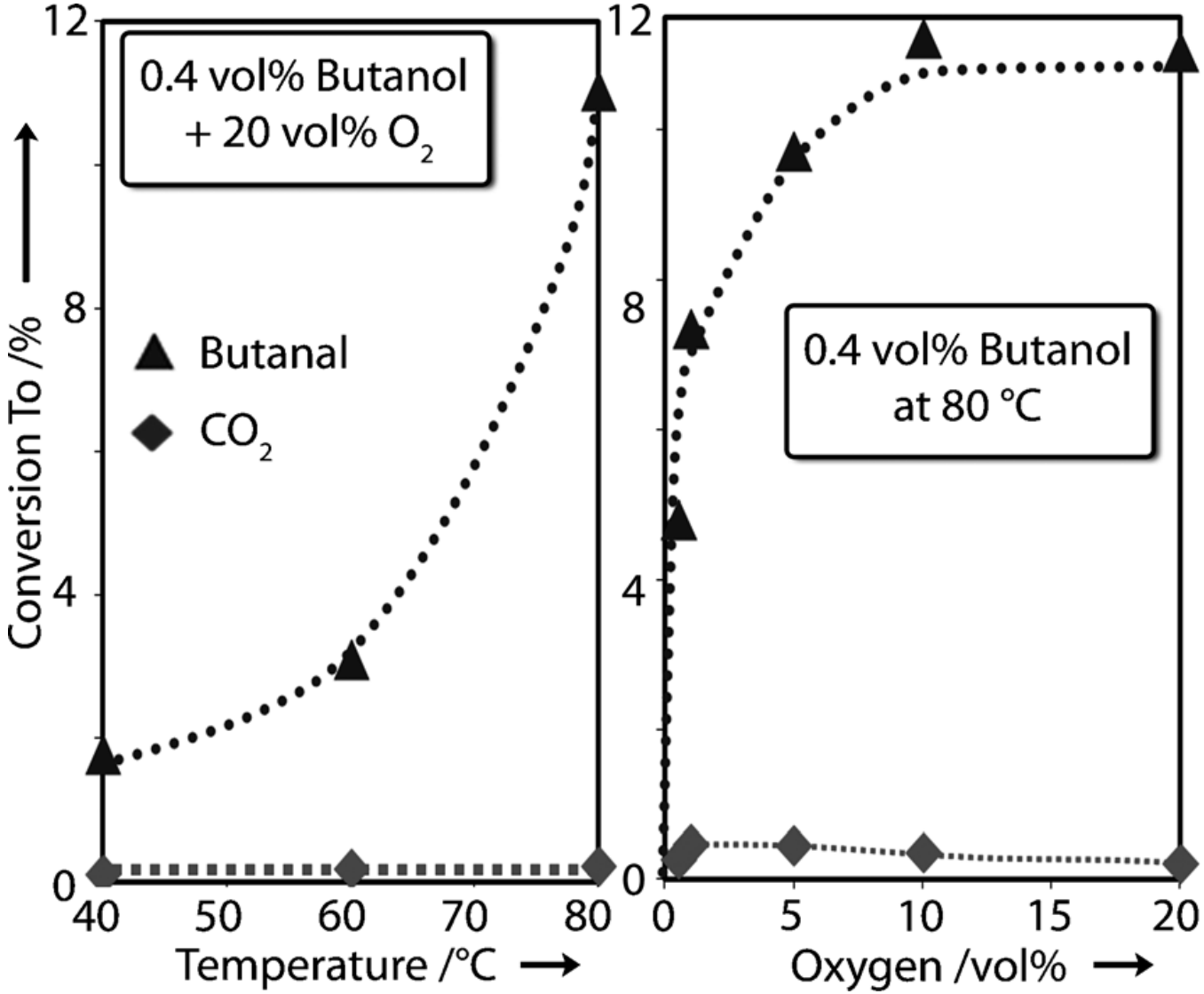
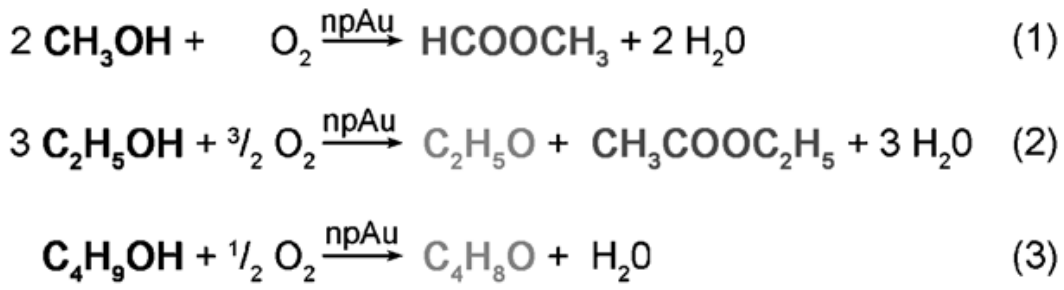


Figure. Oxidation of n-butanol to n-butanal for temperatures between 40 ^{0}C and 80 ^{0}C (left) and for various oxygen partial pressures at a reaction temperature of 80 ^{0}C (right).

a)



b)

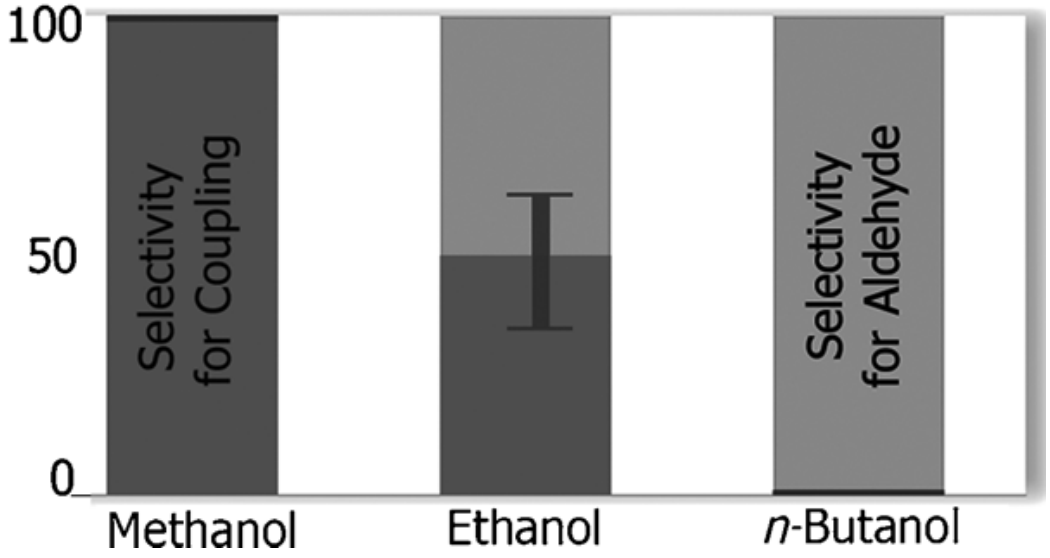


Figure. a) Oxidation and self-coupling of alcohols over nanoporous Au. b) Selectivity towards the aldehyde or self-coupling product (ester) depends on the chain length of the alcohol. The greater facility for β-hydride elimination from longer-chain alkoxy groups favors aldehyde production.

Summary

1. For the oxidative coupling of alcohols on unsupported npAu the mechanistic insights gained from UHV experiments can be transferred to reactions at ambient pressure.
2. The lack of a support material simplifies our understanding of npAu catalysis and enables the prediction of surface reactivity based on fundamental insights gained from UHV experiments.
3. Importantly, complex surface reactions involving several chemical entities, such as the cross coupling of alcohols, can still be fully anticipated on the molecular level.

Last slide

1. Loading clusters on mesoporous substrates may enhance the catalytic activity.