SELECTIVE ACETIC ACID ELECTROCHEMICAL SYNTHESIS ON ACID SUPPORTING SINGLE ATOMS CATALYST

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Introduction

Methane vs. a valuable product

Methane is present in large amounts on the earth:

- it is the main constituent of natural gas;
- more and more fields have been discovered in remote areas in which the construction of gas pipelines is not very convenient;
- it is availabe as shale gas, a reserve of 206,000 billion m^3 is estimated in the world (equal to 32% of natural gas reserves);
- It is availability as biogas.

CH_4 is a greenhouse gas

Like carbon dioxide, methane isn't a toxic gas itself **but humanity is contributing to a progressive accumulation in the atmosphere.**
Understanding and developing ways to mitigate it, will play an important role in maintaining the Earth's climate for the future.

More and more attention for a fruitful **methane oxidation and conversion**, versus an effective utilization and emission reduction, is required.

Combustion
smaller amount of CO_2-to-energy content compared to emissions from the coal and potentially from other fossil fuels

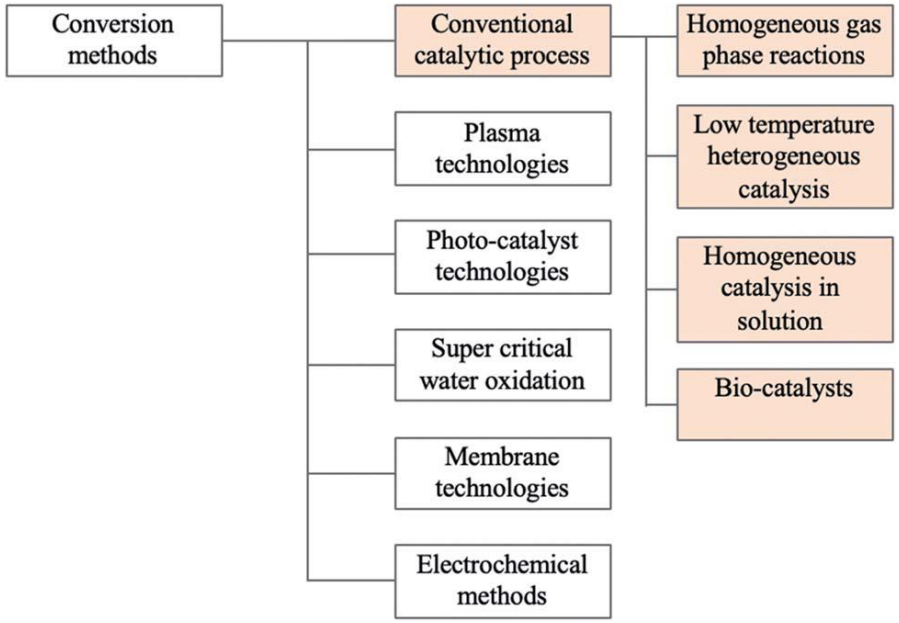
Upgrading methane into value-added products

Introduction

Methane vs. a valuable product

Upgrading methane into value-added products

- **It is extremely difficult to partially oxidize methane to oxygenated products due to the following two reasons:**
  - non-polar structure of methane requires high activation energy for C–H bond dissociation (439.3 kJ/mol).
  - the target oxygenates, which are intermediate products, are easily activated and form thermodynamically more favorable COx products



Possible approaches studied in the literature for partial oxidation of methane to oxygenates

Introduction

Acetic acid as a possible valuable product

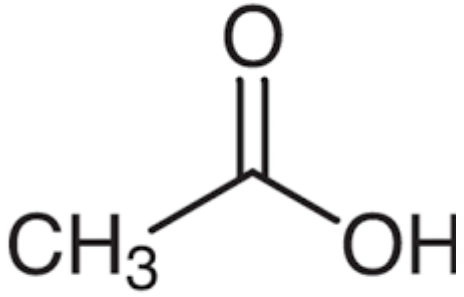
Acetic acid

An important petrochemical

It is currently synthesized from methane (or coal) in a three-step capital- and energy- intensive process

based on:

1. **high-temperature conversion of methane (or coal) to syngas,**
2. **conversion of syngas to methanol**
3. **carbonylation of the methanol to acetic acid**



Introduction

Electrochemical methods and a suitable catalyst for methane conversion

With the continuous drop in renewable electricity price, electrochemical methods have emerged as a promising alternative for partial oxidation of methane to oxygenates:

- **fast formation of highly reactive compound**
- **partially oxidized stable products at relatively low temperatures formation**

The catalyst

A suitable catalyst able to fulfill different functions for product selection and activity maintenance, i.e., avoid deposition of carbonaceous materials, must be designed:

- **methane adsorption and activation;**
- **carbonylation;**
- **hydrolysation;**
- **formation of acetic acid;**
- **further oxidation avoided.**

In this scenario, the key to selective methane oxidation is the ability to generate reactive species at metal active sites capable of attacking the strong C–H bonds of methane while avoiding over-oxidation into carbon dioxide.

We show that Rh and Pd mononuclear species, anchored on NH_4BF_4 modified Al_2O_3 support, catalyze the direct conversion of methane to acetic acid, using carbon monoxide under mild conditions:

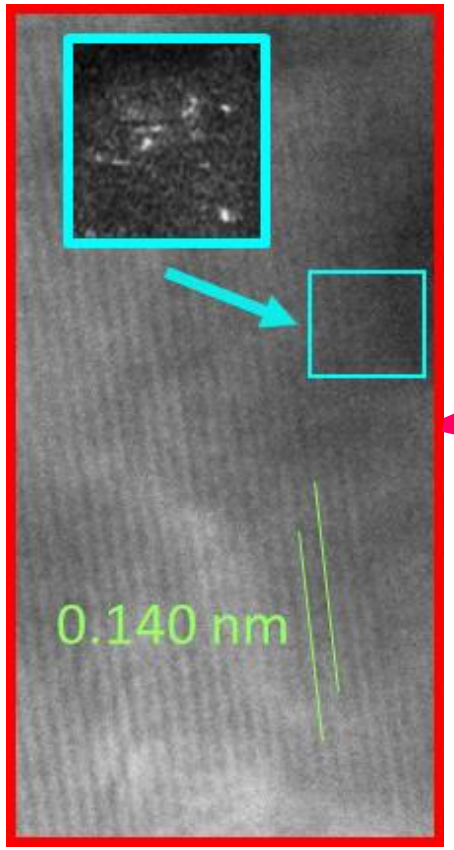
Methane is activated in the presence of O_2 on isolated atoms (M) under mild conditions to produce M–CH_3.

CO may insert directly into M–CH_3 bonds through carbonylation insertion to form M–$COCH_3$ species, which can be further hydrolysed to acetic acid in water.

Brønsted acid sites, important for carbonylation reaction and acetic acid yield, were generated by NH_4BF_4 modification.

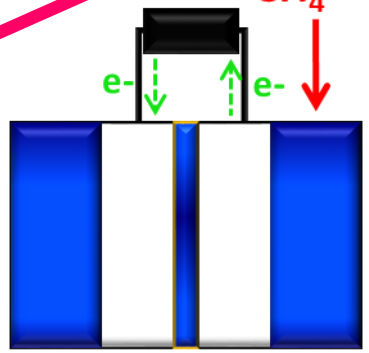
After the reaction steps, isolated active species are available for the next catalytic cycle.

TEM image of $Pd-Al_2O_3$ nanocomposite

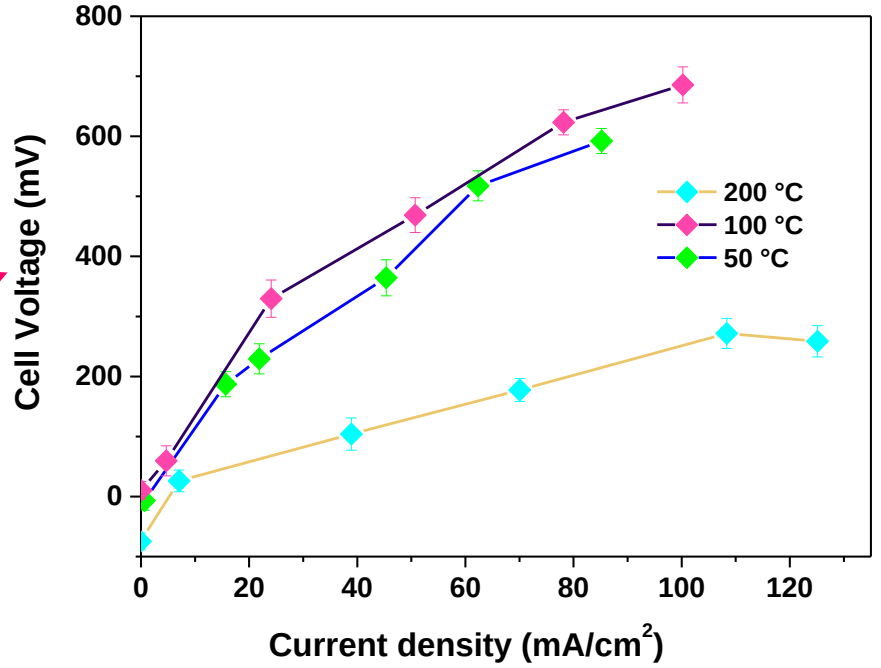


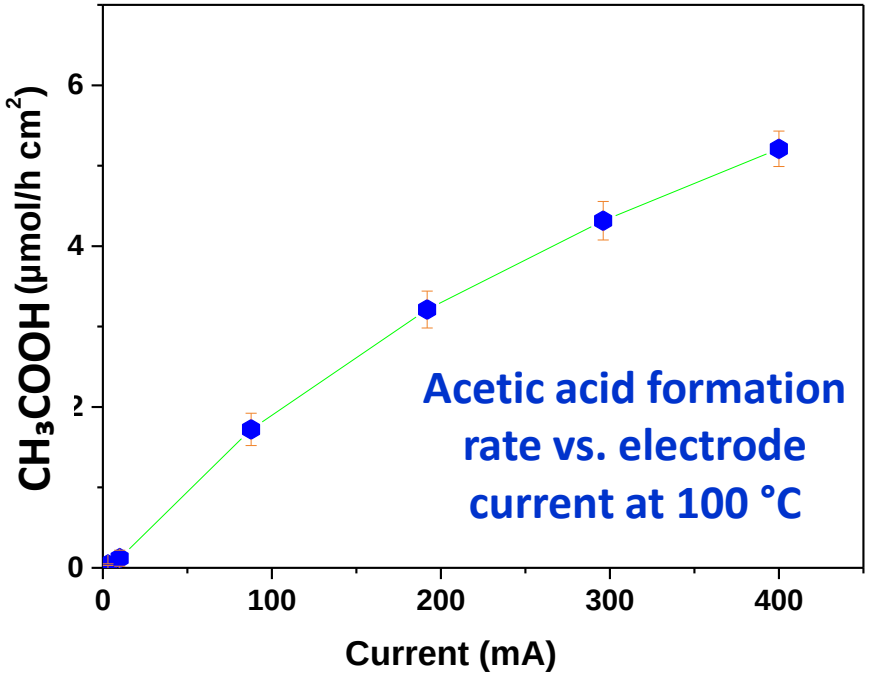
contrast points which are coherent with single atoms

(440) lattice plane of the γ- phase of alumina

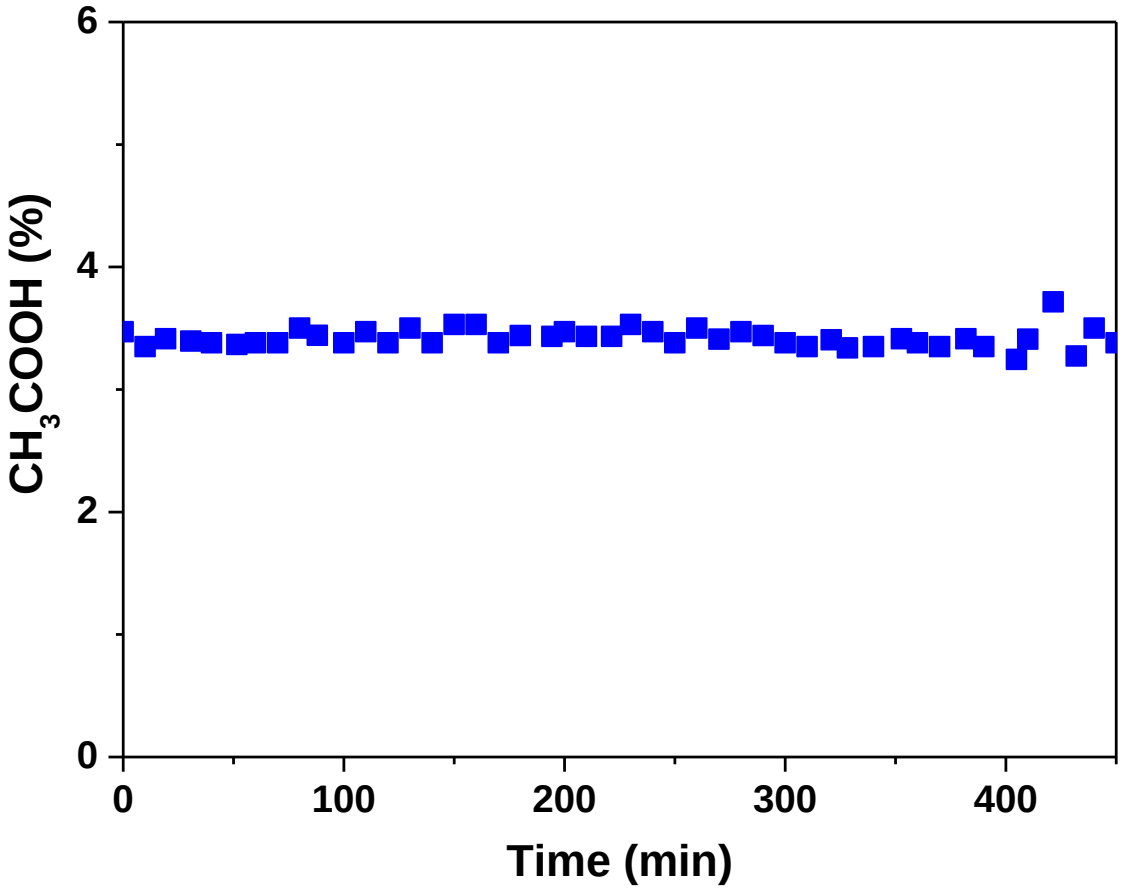


Cell voltage vs. current density at different temperatures

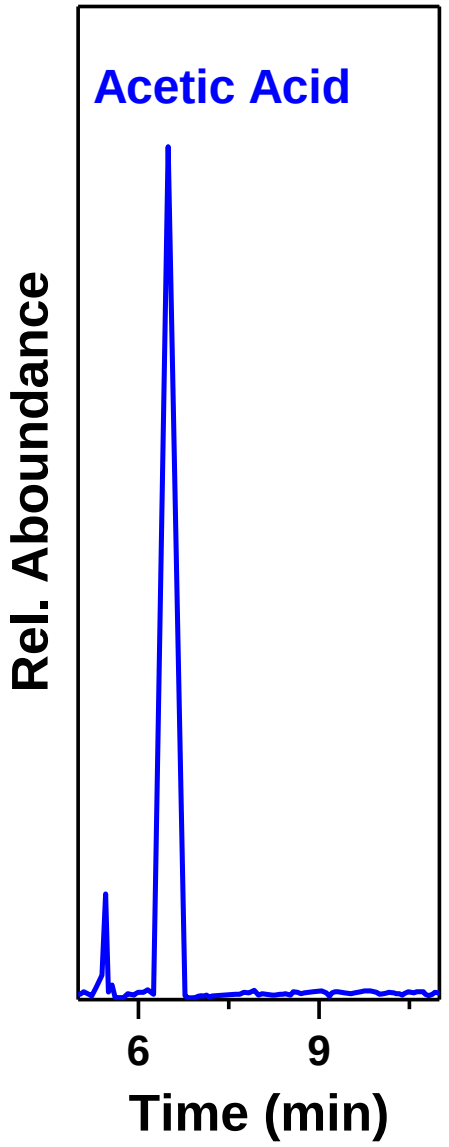




Stability test of acetic acid production at 100 mA and 100 °C



GC profile obtained at 100 °C



CONCLUSIONS

- Enhanced catalysts, for direct and selective oxidation of methane at low temperature, based-on Pd and Rh single atoms supported on modified Al_2O_3 support, were prepared.

- The analysis of the literature results highlights the high efficiency of our catalysts in selectively promoting acetic acid production with high yields.

- The excellent behavior of our nanocatalysts can be attributed to a combination of aspects, including the high surface area for electrode wettability; methane adsorption on single atoms inclusions dispersed in the catalyst matrix; formation of $M–OCH_3$ species by the insertion of an oxygen atom in the presence of CO ligands that bind with single atoms and hydrolysation by Brønsted acid sites of the modified alumina support.