

Effective conversion of CO₂ at lower temperatures in an electric field

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Significance and Relevance

We investigated the reverse water–gas shift (RWGS) reaction using an electric field at temperatures below 473 K. Highly dispersed Ru/ZrTiO₄ catalysts with 2 nm particles exhibited high RWGS activity, while larger Ru particles favored CO₂ methanation. The electric field enhanced hydrogen migration, maintaining high CO selectivity and preventing CO hydrogenation into CH₄. Reaction mechanisms were explored through various techniques, including *in-situ* DRIFTS, providing insights into the lowtemperature RWGS process.

Preferred and 2^{nd} choice for the topic: CO_2 utilization and recycling and Catalysis to electrify the chemical promotion Preferred presentation: Oral only

Introduction and Motivations

Many countries are aiming to reduce CO_2 emissions to near zero, and catalytic CO_2 conversion with green hydrogen is a key focus. The reverse water–gas shift (RWGS) reaction, which produces carbon monoxide (CO), plays a central role in converting CO_2 into value-added chemicals. However, RWGS is endothermic and requires high temperatures for significant conversion. Recent studies have explored unconventional methods like electrocatalysis to enable CO_2 conversion at milder conditions. Applying an electric field to semiconductor-catalysts can enhance reactions by promoting proton migration, and opening new reaction pathways. This work investigates the use of electric fields for efficient, lowtemperature RWGS on highly dispersed Ru catalysts.

Materials and Methods

The catalysts were prepared using a complex polymerization method with citric acid, ethylene glycol, and metal precursors, followed by calcination. Ruthenium (Ru) nanoparticles were synthesized *via* colloidal reduction with ethylene glycol and then mixed with supports. Activity tests were conducted in a fixed-bed reactor with an electric field applied across the catalyst bed, monitoring gas compositions by GC. Catalysts were characterized using ICP-OES, FE-TEM, XAFS, H₂-TPR, and *in-situ* DRIFTS to analyze Ru loading, particle size, electronic states, and catalytic behavior. The electric field enhanced selectivity and activity for CO formation, with reaction conditions evaluated through various testing parameters such as temperature, H_2/CO_2 ratio, and contact time.

Results and Discussion

We investigated the use of Ru-supported catalysts for the reverse water-gas shift (RWGS) reaction in an electric field, comparing two preparation methods for 1.5wt% Ru-supported catalysts: a Rucolloid supporting method and an impregnation method. The colloidal Ru catalyst exhibited superior performance, achieving 95.9% selectivity for RWGS, compared to only 24.7% for the impregnated catalyst, alongside better Ru dispersion and smaller particle size (2.37 nm vs. 7.97 nm). The colloidal Ru catalyst was selected for further tests, as it showed better performance in the RWGS reaction, particularly in an electric field.

The application of an electric field enhanced the RWGS reaction at lower temperatures (as low as 423 K), where conventional RWGS showed no activity. The electric field reduced the apparent activation energy to 6.74 kJ/mol, significantly lower than the 64.5 kJ/mol observed without the field. Additionally, CO_2 conversion increased proportionally to the applied current, while CO selectivity remained high (>90%), suggesting that the electric field promotes the reaction through a different mechanism.



Stability tests revealed that the catalytic activity without the electric field decreased with time course, while the activity in the electric field remained stable at any temperature. The electric field also helped in regenerating activity by purging with hydrogen, which removed CO₂-derived adsorbates. Further tests showed that in the electric field, high selectivity for RWGS was maintained even in H₂-rich conditions, where conventional systems tend to favour methane (CH₄) formation. The electric field suppressed side reactions like CO₂ methanation and maintained high CO selectivity even at longer contact times.



Figure 1 Activities (left) and Arrhenius plots (right) for the RWGS reaction over the Ru/ZrTiO₄ catalyst in and without the electric field; CO₂: H₂: Ar = 1: 1: 2; total 100 SCCM; 100 mg catalyst; 0 or 5.0 mA input current. (A) Without the electric field (593 K)
(B) With the electric field (423 K)



Figure 2 CO and CH₄ formation rate over the Ru/ZrTiO₄ catalyst under various H_2/CO_2 ratios (A)without the electric field at 593 K and (B)in the electric field at 423 K; 100 SCCM total flow rate; 100 mg catalyst weight.

The proposed mechanism suggests that the electric field promotes hydrogen migration from the Ru surface to the support, enhancing the formation of oxygen vacancies on the metal oxide support. These vacancies help activate CO₂, leading to more efficient CO formation and reduced byproduct formation (e.g., CH₄). *In-situ* DRIFTS measurements revealed that the electric field altered surface species, decreasing the intensity of formate species and increasing the formation of CO and more reactive intermediates, such as carboxylate and carbonate species.

This study shows that highly dispersed ruthenium (Ru) catalysts have high reverse water-gas shift (RWGS) activity in an electric field, even at low temperatures where conventional methods are inactive. These catalysts achieve high CO selectivity, especially under high H₂ concentrations or short contact times, thanks to fast hydrogen migration. The electric field shifts the reaction from a formate-mediated path to a redox mechanism, enhancing both hydrogen spillover and CO₂ activation, resulting in improved low-temperature RWGS activity and selectivity.

References

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