

# Steam reforming of methanol over Na-doped Ru/m-ZrO<sub>2</sub>

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## Abstract

A sodium (Na)-doped catalyst was developed to investigate methanol steam reforming, based on a Na-Pt/m-ZrO<sub>2</sub> formulation. The catalyst obtained was Na-Ru/m-ZrO<sub>2</sub>, which was evaluated in a transient microreactor. The results indicated that the increase in Na facilitated the release of hydrogen in greater quantities, due to changes in the selectivity of formate decomposition, going from decarbonylation to decarboxylation, because of the increased basicity of the system. It is proposed to make future comparisons with a plug flow microreactor between Na-Pt/m-ZrO<sub>2</sub> and Na-Ru/m-ZrO<sub>2</sub> catalysts to evaluate the differences in performance and economic viability of both.

## Introduction

There has been diverse research on catalysts for the optimization of hydrogen production. One of the catalysts that offered good results was a Na-PtZrO<sub>2</sub> catalyst, with a higher than 90% selectivity when 2.5 wt.% of sodium was added [1]. The challenge with that catalyst is the cost of platinum, being three times more than the price of ruthenium [2]. It is why research on a similar catalyst, ruthenium in this case has been made, to be able to assess the performance and be able to compare it in the future.

## Methods

- **Catalyst preparation.** 1% Ru/m-ZrO<sub>2</sub> was prepared by loading monoclinic ZrO<sub>2</sub> pellets with ruthenium nitrosyl nitrate, followed by drying and calcinating at 350 °C for 4 hours. Then that was divided into batches of 0.5 to 5 wt.% addition of sodium by incipient wetness impregnation and finally dried and calcined.
- **Catalyst activation H<sub>2</sub> by TPR.** Profiles for the programmed reduction of the temperature of the catalyst were made by an Altamira AMI-300R with a thermal conductivity detector. A flux of 10% hydrogen in argon at 30 cm<sup>3</sup>/min was introduced while the temperature was incremented from 30 to 1000 °C by 10 °C/min, using approx. 150 mg sample of the catalyst. Scaped gases were then analyzed with a mass quadrupole spectrometer.
- **Assessment of the capacity of the catalyst to adsorb and desorb CO<sub>2</sub>.** A programmed desorption by temperature of CO<sub>2</sub> was made (CO<sub>2</sub>-TPD) using an Altamira AMI-300R and a Hiden mass spectrometer (MS). The catalyst was reduced at 400 °C, purged with argon, cooled to 25 °C and saturated with CO<sub>2</sub>. The temperature was incremented until 1000 °C while monitoring the CO<sub>2</sub> MS signal. This evaluated the capacity of the catalyst to adsorb and desorb CO<sub>2</sub>, an acidic molecule, providing information about the basicity of the active sites.
- **Study of interactions between water and adsorbed species of methanol and subsequent reactions.** Methanol vapor reforming experiments were performed using a Nicolet iS-10 Fourier transform infrared (FTIR) spectrometer with a Harrick Scientific accessory. The catalyst was characterized at different temperatures and reduced to 400 °C before absorbing methanol and exposing the catalyst to flowing water vapor. Sodium contents were varied from 0% to 5.0% and temperature steps from 50 °C to 400 °C were performed. The objective was to study the interactions between water and adsorbed methanol species, and their subsequent reactions, identifying intermediates such as methoxy, formates, and carbonate species.
- **Temperature-Programmed Surface Reaction in Methanol Vapor Reforming.** The catalyst was activated at 400 °C with a flow of 30 cm<sup>3</sup>/min of 33% H<sub>2</sub> in argon, followed by cooling to 50 °C. The surface of the catalyst was saturated with 100 μL of methanol, purging out weakly adsorbed species with flowing argon. Water was then introduced into the system, purging again with argon. Finally, the catalyst was heated to 1000 °C while monitoring the H<sub>2</sub> signal to evaluate the effect of sodium promoter loading on the dehydrogenation activity.

## Results

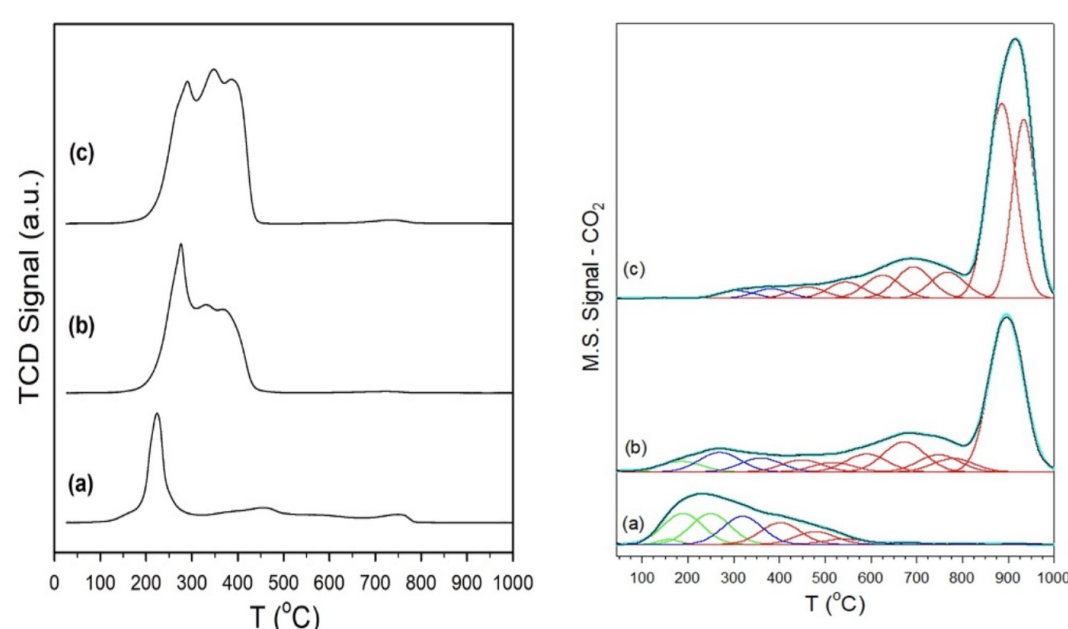


Figure 1. H<sub>2</sub>-TPR profiles (TCD signal) on the left. CO<sub>2</sub>-TPD profiles (CO<sub>2</sub> MS signal) on the right, including (solid black lines) data and (cyan) result of the fitting with Gaussian peaks having maxima (green) below 250 °C, (dark blue) between 250 °C and 400 °C, and (red) greater than 400 °C. For left and right: (a) unpromoted 1.0% Ru/m-ZrO<sub>2</sub> and the same catalyst doped with (b) 1.8% Na and (c) 2.5% Na.

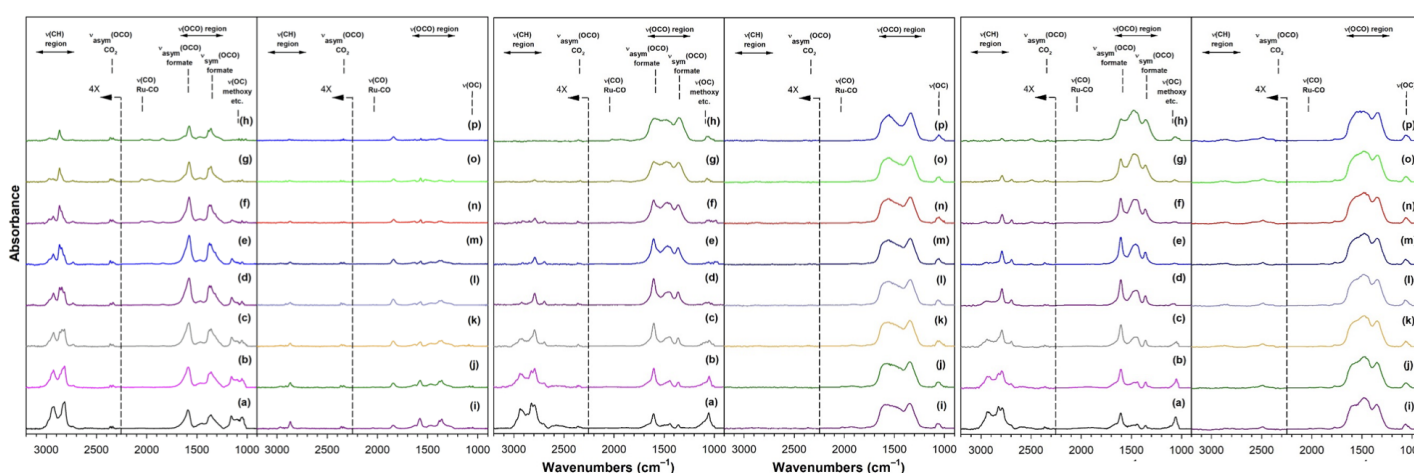


Figure 2. DRIFTS spectra during temperature-stepped MSR flowing steam over pre-adsorbed methanol in 30 cm<sup>3</sup>/min of 4.4% H<sub>2</sub>O (balance He) over unpromoted 1.0% Ru/m-ZrO<sub>2</sub> on the left, 1.8% Na-1.0% Ru/m-ZrO<sub>2</sub> in the middle and 2.5% Na-1.0% Ru/m-ZrO<sub>2</sub> on the right. Left, middle and right at (a) 50 °C, (b) 75 °C, (c) 100 °C, (d) 125 °C, (e) 150 °C, (f) 175 °C, (g) 200 °C, (h) 225 °C, (i) 250 °C, (j) 275 °C, (k) 300 °C, (l) 325 °C, (m) 350 °C, (n) 375 °C, and (o) 400 °C. (p) Helium purge at 400 °C to show residual surface carbonates adsorbed on m-ZrO<sub>2</sub>.

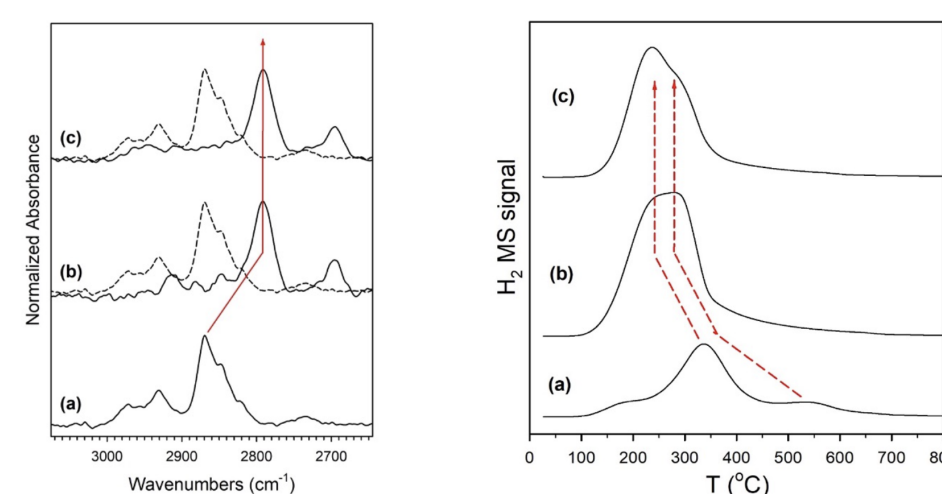


Figure 3. On the left: Main ν(C-H) band of (spectrum and dash-lined reference spectra) unpromoted 1.0% Ru/m-ZrO<sub>2</sub> and the same catalyst doped with (b) 1.8% Na and (c) 2.5% Na. On the right: H<sub>2</sub> evolution in temperature-programmed MSR using pre-adsorbed methanol and H<sub>2</sub>O for (a) unpromoted 1.0% Ru/m-ZrO<sub>2</sub> and the same catalyst doped with (b) 1.8% Na and 2.5% Na.

## Discussion

Regarding Figure 1, the TCD signal on the left shows that the reduction of Ru oxide particles to Ru metal during catalyst activation, and this process is completed by 400 °C in H<sub>2</sub>. This temperature is higher than with Pt catalysts, indicating a stronger interaction of Ru with the m-ZrO<sub>2</sub> support. The addition of Na increases the basicity of the catalyst, favoring the adsorption of CO<sub>2</sub> as carbonates, which requires a higher temperature for its removal in H<sub>2</sub> and greater hydrogen consumption. On the other side, on the right, the CO<sub>2</sub> TPD measured the basicity of the catalyst surface. By increasing the Na content, the basicity increased, which means that CO<sub>2</sub> is retained stronger and higher temperature is needed to desorb it. This is reflected in a shift towards higher temperatures in the CO<sub>2</sub>-TPD profile.

In Figure 2 it can be seen that at 50 °C, methoxy species are formed from methanol in m-ZrO<sub>2</sub>. With increasing temperature, these are converted to formate, whose bands shift to lower wavenumbers with the addition of Na, indicating greater basicity. Above 100 °C, formate converts to carbonate, a precursor to CO<sub>2</sub>. Catalysts with Na decompose formate more quickly due to the weakening of the C-H bond, also visible in Figure 3 on the left.

Catalysts with Na release more H<sub>2</sub> at lower temperatures by favoring the production of H<sub>2</sub> and CO<sub>2</sub> over CO. This is useful for obtaining H<sub>2</sub> from methanol for PEM fuel cells, which is exhibited in Figure 3 on the right.

A schematic of the effect of Na on Ru/m-ZrO<sub>2</sub> is shown in Figure 4:

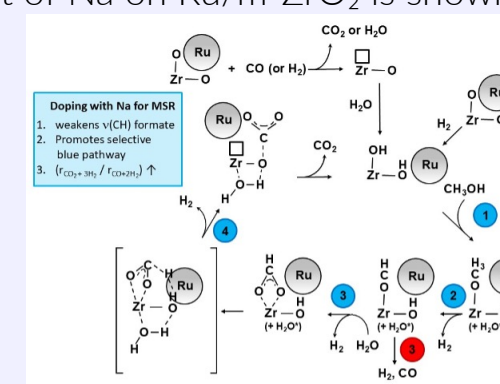


Figure 4. Proposed mechanistic effect of Na during MSR over Na-Ru/m-ZrO<sub>2</sub> catalyst.

## Conclusion

The addition of Na increases the basicity of the catalyst, favoring the adsorption of CO<sub>2</sub> as carbonates and displacing the reduction of Ru to higher temperatures. Na catalysts decompose formate faster and release more H<sub>2</sub> at lower temperatures, which is useful for obtaining H<sub>2</sub> from methanol in PEM fuel cells.

## References

- [1] — "Sodium Doping of Pt/m-ZrO<sub>2</sub> Promotes C-C Scission and Decarboxylation During Ethanol Steam Reforming." International Journal of Hydrogen Energy, vol. 45, no. 36, Sept. 2019, pp. 18490–501, doi:10.1016/j.ijhydene.2019.08.111.
- [2] — "A Single Site Ruthenium Catalyst for Robust Soot Oxidation Without Platinum or Palladium." Nature Communications, vol. 14, no. 1, Nov. 2023, doi:10.1038/s41467-023-42935-7.