22º Congresso Brasileiro de Catálise
25 a 29 Setembro de 2023
Bento Gonçalves / RS

SBCAT
SOCIEDADE BRASILEIRA DE CATÁLISE

Correlating metal speciation and product selectivity during CO_2 hydrogenation over Pd/CeO_2 catalyst

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Abstract

ABSTRACT - This study investigates palladium speciation on Pd/CeO_2 catalysts and its impact on CO_2 hydrogenation at high pressure. DRIFT spectroscopy was employed to monitor Pd speciation changes using CO as a probe molecule. Calcination temperature influences the distribution of single $Pd^{\delta+}$ species and Pd^0-containing nanoparticles. Isolated $Pd^{\delta+}$ atoms enhance the rWGS reaction by weakening CO adsorption and suppressing H_2 dissociation. The control of $Pd^{\delta+}$ and Pd^0 fractions improved methanol productivity at low temperatures. Enhanced CO_2 conversion rates occur with atomic dispersion. This work offers a protocol for Pd dispersion control and highlights its correlation with product distribution during the reaction.

Keywords: palladium, carbon dioxide, hydrogenation, methanol, reverse water-gas shift

Introduction

CO_2 hydrogenation to methanol and the reverse water gas-shift (rWGS) reaction are critical chemical processes that play a significant role in sustainable energy, environmental mitigation, and producing valuable chemicals. As competing reactions, controlling reaction routes to obtain the desired product with high selectivity is challenging. The Pd/metal oxide systems recently emerged as candidate catalysts for CO_2 hydrogenation reactions [l]. Although the effects of different supports [1,2] and support exposed facets [3] were already evaluated, the influence of Pd speciation on the catalyst surface remains unclear. In this contribution, we systematically correlate the palladium speciation on the surface of Pd/CeO_2 catalysts with product distribution during CO_2 hydrogenation at high pressure.

Experimental

CeO_2 support was prepared by precipitation from $Ce(NO_3)_3$ aqueous solution by adding NaOH solution until pH 9.5. The precipitate was washed, dried, and calcined. The Pd was deposited over precipitated CeO_2 support by simple wet impregnation employing H_2PdCl_4 aqueous solution, followed by washing, drying, and calcination in air flow at different temperatures. The calcination in air at high temperatures induces the formation of vapor-phase PdO species, which detach from nanoparticles and are trapped by defects in the support surface. Herein, we investigated catalysts containing 3 wt% of Pd treated at 350, 500, and 700 °C in an air stream for 4h, named 3PdCe350, 3PdCe500, and 3PdCe700, respectively. Additionally, we evaluated the influence of Pd loading and calcination time on dispersion by preparing catalysts containing 1 and 0.3 wt% of Pd thermally treated at 700 °C in an air stream for 10h, named 1PdCe700 and 0.3PdCe700, respectively.

CO-DRIFTS spectra were collected in a Shimadzu IRPrestige-21 spectrometer equipped with an MCT detector and a Harrick cell with ZnSe windows. Catalysts were reduced in H_2 at 250 °C, followed by purging with N_2. After cooling to room temperature, CO was introduced in the cell for 10 min, followed by purging with N_2 for the same time before spectra collection.

Catalytic tests were conducted in a Microactivity Effi system from PID Eng&Tech / Micromeritics. The compounds on the reaction stream were quantified by gas chromatography in an Agilent 6890 GC system.

Results and discussion

The speciation was elucidated by monitoring CO adsorption bands on Pd sites by DRIFT spectroscopy, as shown in Figure 1a-c [3]. The 3PdCe350 catalyst presented mainly bands related to bridge and 3-fold CO, characteristic of the adsorption on Pd^0 sites in the metallic surface, emphasizing the formation of larger nanoparticles [4]. By increasing the temperature of calcination, these bands significantly decreased, with the predominance of bands in 2060 and 2093 cm^{-1} related to linear CO adsorbed on Pd^0 (green) and $Pd^{\delta+}$ (red) sites, respectively, as noted by the fraction of integrated IR bands in Figure 2b. The band at 2060 cm^{-1} is related to small Pd^0 clusters, indicating a decrease in particle size, while the band at 2093 cm^{-1} is related to linear CO adsorbed on a highly dispersed electron-deficient site ($Pd^{\delta+}$) strongly interacting with CeO_2 [5]. Spezatti et al. [6] recently attributed this band to isolated palladium atoms stabilized in the form of Ce-[ ]-Pd-O-Ce. In our work, the formation of these species suggests that fully oxidized isolated palladium (Ce-O-

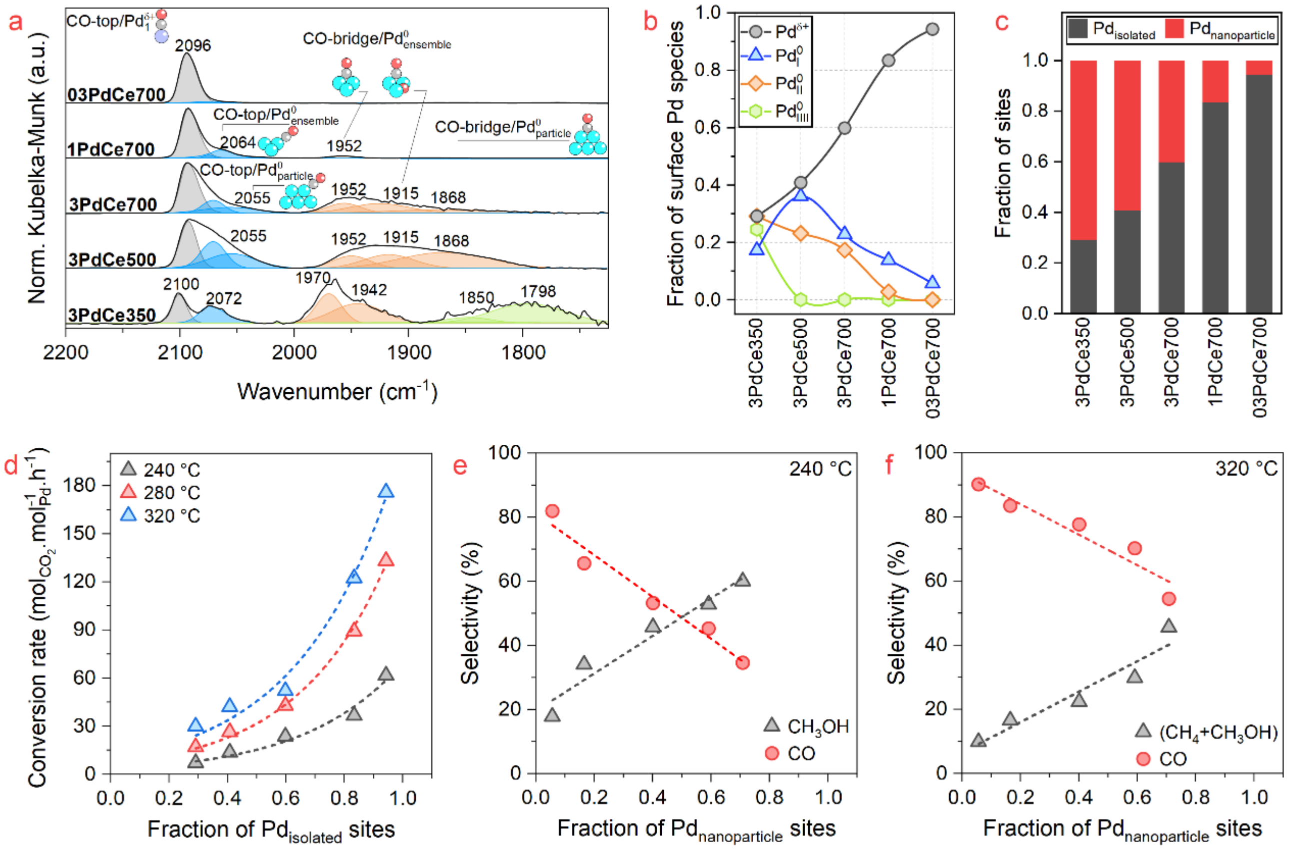

Figure 1. (a) CO-DRIFTS analysis and (b-c) fraction of Pd in nanoparticle and isolated sites. (d) Conversion rates and product selectivities (e-f) related to Pd speciation during CO_2 hydrogenation (T = 240-320 ºC, P = 4.5 MPa, WHSV = 6000 mL.g^{-1}.h^{-1}, CO_2:H_2 = 1:3 v/v).

Pd-O-Ce) was partially reduced by the formation of an oxygen vacancy in the presence of H_2. In the 0.3PdCe700 catalyst, the spectrum was completely dominated by the 2093 cm^{-1} band, indicating the predominance of fully isolated Pd$^{\delta+}$ atoms (~95%). The catalytic results in Figure 1d-f, indicate that activity and selectivity are strongly affected by Pd speciation. The predominance of Pd^0 nanoparticles favors hydrogenated products with a predominance of methanol at lower temperatures (240 ºC) and CH_4 at higher temperatures (320 ºC). The presence of isolated sites favors the rWGS reaction by partially suppressing H_2 dissociation, even at high pressures (4.5 MPa). Additionally, the atomic dispersion extends the metal-metal oxide interfaces leading to higher CO_2 conversion rates.

Conclusions

This work shows a simple protocol to control Pd dispersion over CeO_2 to select products from CO_2 hydrogenation at high pressures. By adjusting variables like metal loading, calcination temperature, and time, the fraction of isolated Pd$^{\delta+}$ and clusters/nanoparticles Pd^0 can be controlled, leading to a cooperative effect (CO_2 activation + H_2 dissociation) which increased methanol productivity at low temperatures. Additionally, the complete dispersion of Pd leads to high CO selectivity at high pressures, which is interesting in developing integrated rWGS-FT processes.

Acknowledgments

This research was supported by Sao Paulo Research Foundation, FAPESP (grant #2022/06419-2, #2023/05285-5 and 2022/10615-1).

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