Integrating exsolution into the aqueous phase reforming for renewable hydrogen production from ethanol-rich wastewaters

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Significance and Relevance

This study explores the dual benefit of aqueous phase reforming (APR) in simultaneously reducing the organic fraction (COD) of ethanol-rich wastewater and producing renewable H2. By developing an innovative synthesis method, a 2 wt.% Ru-CeO_2 catalyst was successfully exsolved, minimizing noble metal usage. By integrating this catalyst into the APR process, the approach leverages the known advantages of exsolution, such as increased resistance to deactivation and improved stability and activity. This combination offers a promising pathway to address renewable energy demands, mitigating environmental impacts, and enhancing the economic feasibility of scaling up sustainable technologies.

Preferred and 2nd choice for the topic: Green chemistry and biomass transformation, renewable resources conversion (preferred), H_2 storage and transportation, green H_2 production, hydrogen vectors
Preferred presentation: (Oral only / Oral preferred or Short Oral)

Introduction and Motivations

The Aqueous Phase Reforming (APR) is a thermo-catalytic process explored in late 1995 by Dumesic et al.[1,2] to convert oxygenated hydrocarbons into H_2 and CO_2 under mild conditions, between 200-270 °C and pressures between 15 to 57 bar, using a heterogenous catalyst. Several studies have shown that among the most promising model compounds for the APR, ethanol and glycerol are particularly noteworthy due to their availability in industrial streams and high H_2 yields[3,4]. These compounds are selected for their efficiency in reforming processes and availability as biomass-derived or industrial waste feedstocks. Considering the APR potential to reform biomass-derived feedstocks, ethanol specifically is a key candidate, given its prevalence in fermentation-based industrial wastewaters, such as those from alcoholic beverages and bioethanol production[5], as these streams often contain residual ethanol. Catalysis plays a pivotal role in the APR performance. Platinum-based catalysts have historically shown high activity but remain costly. Ruthenium, a less expensive noble metal, offers excellent catalytic performance in C-C bond breaking and water-gas shift reactions, making it a preferred choice for APR applications[6]. Traditional supports, such as alumina, are effective but prone to deactivation through coking. Ceria (CeO_2), with its superior oxygen storage capacity and redox behavior, emerges as a promising alternative support material[3]. A key innovation in this study is the use of exsolution—a synthesis method where nanoparticles nucleate from the bulk of the support under reducing conditions, growing anchored to its surface. This method offers enhanced dispersion, increased stability, and reduced noble metal usage, addressing the challenges of catalyst deactivation and cost. Since the chosen Ru-exsolved CeO_2 catalyst demonstrated the ability to undergo exsolution, it is a promising candidate for its testing in the APR reactions to assess the possible improved performance under reaction conditions.

Materials and Methods

APR experiments were conducted in a 300 mL batch reactor with 1% ethanol solution at 230°C, 250°C, and 270°C, under stirring conditions and loading 0.1 g of catalyst. Reaction times ranged from 1 to 6 hours, with gas-phase composition measured by a SRA micro-GC and liquid phase a by Shimadzu TOC-VCSH analyzer and a Shimadzu HPLC. The tests were performed using a 5 wt. % Ru/Al_2O_3 commercial catalyst (Sigma Aldrich-Merck) and a 2 wt.% Ru-CeO_2 catalyst, synthesized using a co-precipitation method by mixing Cerium(III) nitrate hexahydrate and ruthenium nitrosyl nitrate precursors in an oxalic acid-ethanol. After 2 h of aging at room temperature, the catalyst was dried overnight and underwent sequential calcination steps of 4 h, first at 450°C and then at 550°C, followed by an exsolution step of 4 h at 750°C, under a 5% H_2/N_2 atmosphere. The catalyst was then characterized by XRD, ICP, SEM, TEM, BET, and H_2 and CO_2-TPR. The APR performance was evaluated using three key reaction parameters: ethanol conversion, hydrogen yield, and selectivity[5].

Results and Discussion

Three temperatures (230 °C, 250 °C, and 270 °C) were tested to evaluate the best operating conditions in terms of ethanol conversion and hydrogen selectivity. At 270 °C, complete ethanol conversion occurred within 1 h, yielding 18 % H_2. In contrast, lower temperatures required extended reaction times (3 h at 250 °C and over 6 h at 230 °C). Interestingly, the hydrogen selectivity was highest at 230 °C, with gas compositions of 50±3 % H_2, 25±4 % CH_4, and 25±1 % CO_2. However, increasing the temperature led to a rise in CH_4 production, reducing the H_2 yield due to competing reaction pathways. The test performed at 250 °C offered the best compromise among the three key APR performance parameters, achieving a 14 % hydrogen yield and retaining over 50% selectivity over time. These findings establish 250 °C as the optimal operating temperature, balancing ethanol conversion, H_2 selectivity, and CH_4 suppression. Since the goal is to advance the industrial application of the APR, the choice of catalyst is crucial for balancing performance and economic feasibility. This involves minimizing the use of costly noble metals while ensuring long-term stability, thereby reducing overall costs without compromising H_2 yields. In this context, a Ru-doped pure-phase CeO_2 material was obtained, as shown by the XRD results reported in Fig. 1a, which confirmed the substitution of the Ce atoms by the dopant Ru without altering the CeO_2 structure. After this, Ru exsolution was successfully achieved, as evidenced by the TEM results in Fig. 1b, which highlight the formation of well-dispersed Ru nanoparticles on the CeO_2 surface. The exsolved catalysts were then employed in the APR reaction to determine whether the observed structural improvements translate into enhanced reaction performance. Overall, this study demonstrates the viability of ethanol-rich wastewater as a feedstock for hydrogen production via APR, achieving promising yields compared to literature values and effective COD abatement. Ru/CeO_2 catalysts underwent exsolution, and future work will focus on testing them to confirm their potential for improved stability and activity.

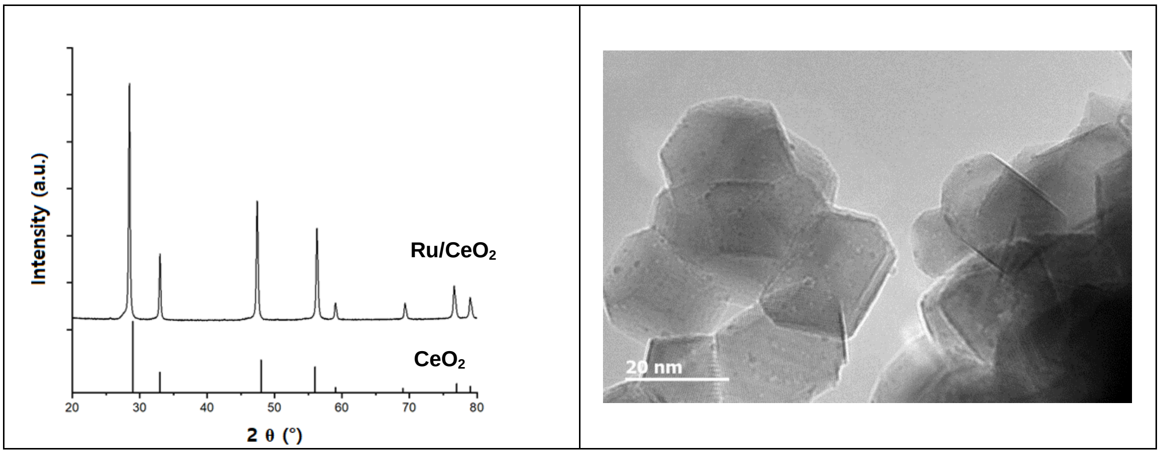

Figure 1: (a) XRD spectrum of CeO_2 and of Ru-CeO_2 (b) TEM image showing the Ru nanoparticles(dark spherical features) exsolved on the CeO_2 surface grains.

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