Reactive CO_2 capture using dual-function catalysts based on zeolitic structures and transition metals

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Resumo/Abstract

RESUMO – Com o crescente aumento da queima de combustíveis fósseis que resultam na liberação de gases relacionados ao efeito estufa e diversas mudanças climáticas, como o aquecimento global e acidificação dos oceanos, vem aumentando cada vez mais a importância do desenvolvimento de tecnologias capazes de mitigar os efeitos, através da utilização e reação desses gases nocivos. A utilização de catalisadores de dupla-função possui destaque nesse segmento, uma vez que são capazes de capturar e fornecer sítios ativos para as reações. A impregnação de metais de transição que apresentem boa seletividade em suportes, como as zeólitas, que possuam essas características permitem a otimização desses materiais. O estudo da reação de hidrogenação de CO_2 utilizando Rh suportados em NaZSM-5 e NaZSM-5 modificada com Na extra-rede, em temperaturas intermediárias de 300 a 450 °C, demonstra a capacidade de conversão desses catalisadores para produtos de interesse, acompanhado de bons rendimentos. Também foi observado o aumento desses valores, relacionados à modificação dos suportes catalíticos com Na, indicando que a mudança estrutural está associada ao aumento da conversão e à seletividade desses materiais.
Palavras-chave: conversão de CO_2, zeólita, deslocamento reverso de gás-água, espectroscopia in-situ.

ABSTRACT - With the increasing combustion of fossil fuels leading to the release of greenhouse gases and triggering various climate changes, such as global warming and ocean acidification, the development of technologies capable of mitigating these effects through the utilization and conversion of these harmful gases has become increasingly important. The application of dual-function catalysts has gained prominence in this field, as they can capture and provide active sites for these reactions. The impregnation of transition metals with high selectivity onto supports, such as zeolites, enables the optimization of these catalytic materials. The study of the CO_2 hydrogenation reaction using Rh supported on NaZSM-5 and NaZSM-5 modified with extra-framework Na, at intermediate temperatures ranging from 300 to 450 °C, demonstrates the conversion capability of these catalysts toward value-added products, accompanied by noteworthy yields. An increase in these performance indicators was also observed with the modification of the catalytic supports with Na, suggesting that the structural alteration is associated with enhanced conversion efficiency and selectivity of the materials.
Keywords: CO_2 conversion, zeolite, reverse water-gas shift, spectroscopy in-situ.

Introduction

The scientific community faces a challenge related to climate change due to the increase in carbon dioxide (CO_2) in the atmosphere, as global warming and ocean acidification. So, the development of technologies for the capture and reaction of CO_2 is increasing. Through the hydrogenation of CO_2, it is possible to produce methane (CH_4) and carbon monoxide (CO), value-added gases. The transition metals show high selectivity for this reaction when combined with zeolite materials, enabling application in heterogeneous catalysis. In this study, we evaluated the controlled application of rhodium encapsulated in modified ZSM-5 for the formation of C_1 compounds, presenting a novel approach in the field of CO_2 conversion technologies.

Experimental

Synthesis and reaction.

The sodium-exchanged zeolitic support (Na-ZSM-5) was obtained by ion exchange of commercial H-ZSM-5. Rh was deposited into micropores by incipient wetness impregnation in two different weight percentages (0.06 and 0.6 %). Catalysts containing extra-framework sodium were also prepared, first by impregnating sodium carbonate, followed by the addition of Rh. All catalysts were calcined in a static atmosphere at 400 °C for 2 hours. The catalytic tests were carried out at a WHSV of 44 $L.g^{-1}.h^{-1}$ and temperatures between 300 and 450 °C, using a simultaneous gas feed of CO_2, H_2, and N_2 as internal standard (ratio 1:4:0.5), after the reduction of catalysts in a hydrogen atmosphere at 400 °C. The output stream was analyzed by GC with TCD detectors.

Results and Discussion

The catalysts produced were tested, and the results presented in Figure 1 show the conversion and CO yield at different temperatures. The catalysts with 0.06% Rh present small conversions compared to 0.6%; however, a significant increase in conversion is observed after the addition of extra-framework Na to the catalyst, reaching 17% CO_2 conversion at 450 °C. The yield for this catalyst was equal to the conversion, as only CO was obtained, due to the high dispersion of Rh in the catalyst, which favors the selectivity for the rWGS route.

For the catalyst containing 0.6% Rh, the conversions were considerably higher, particularly at higher temperatures, where they achieved an average conversion of 50%. The addition of extra-framework Na sites in this catalyst, along with the increase in conversion rates, also resulted in a significant improvement in yield, indicating greater selectivity for producing CO over CH_4. This highlights the importance of extra-framework Na in tuning the coordination environments of metal, enhancing the catalyst's performance for this reaction.

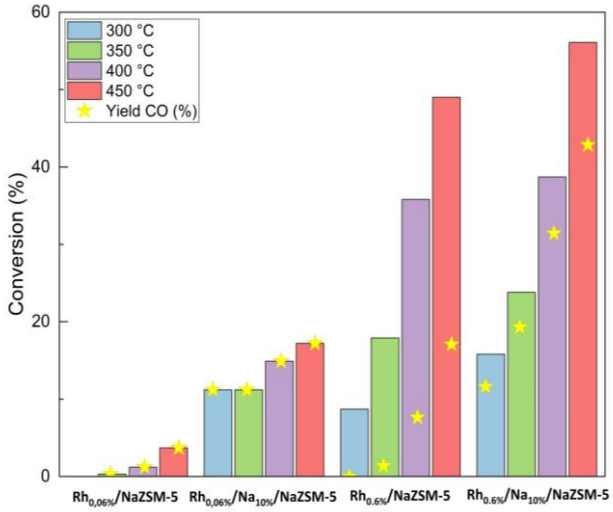

Figure 1. Conversion and CO yield of the catalysts.

Conclusions

This study on CO_2 hydrogenation using Rh catalysts supported on NaZSM-5, including those modified with extra-framework sodium, demonstrated the potential of these materials to mitigate atmospheric CO_2. The approach involving the encapsulation of Rh within modified ZSM-5 has been shown to be effective in promoting high activity and selectivity. Extra-framework sodium played a crucial role in enhancing performance, especially by increasing conversion and CO selectivity. Overall, the study confirms the effectiveness of bifunctional zeolite-based transition metal catalysts for reactive CO_2 capture and conversion, offering a promising strategy for producing value-added gases and mitigating climate change.

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