Cu,Zn-ZSM-5 catalysts for CO_2 conversion via reverse water gas shift (RWGS)

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Resumo/Abstract

RESUMO - A hidrogenação via reação de deslocamento gás-água reversa (RWGS) tem sido usada para ativar o CO_2 a CO, que é empregado como intermediário na produção de metanol e éter dimetílico (DME). Catalisadores Cu/ZnO-Al_2O_3 são comumente estudados para RWGS e se mostram bastante ativos, mas desativam por sinterização da fase ativa e são sensíveis à água formada. Neste trabalho, catalisadores Cu,Zn-ZSM-5 foram preparados por troca iônica (simultânea ou sucessiva), introduzindo íons Cu^{2+} e/ou Zn^{2+} (1,5%) em zeólito ZSM-5, visando superar essas limitações. Os materiais foram caracterizados e avaliados na RWGS. Todos os catalisadores mostraram alta seletividade ao CO, com formação desprezível de CH_4. A fase ativa é o Cu metálico disperso no suporte zeolítico. A introdução de Zn^{2+} antes de Cu^{2+} aumentou significativamente a atividade catalítica. O catalisador mais ativo apresentou conversão de CO_2 de 82% e seletividade de 100% a CO a 800°C. Os parâmetros reacionais (Razões F/W e H_2/CO_2) foram investigados a 600 °C para otimizar o desempenho do catalisador. As possíveis rotas de desativação do catalisador foram investigadas.

Palavras-chave: RWGS, Conversão de CO_2, Catalisadores zeolíticos.

ABSTRACT - Hydrogenation via reverse gas-water shift (RWGS) reaction has been used to activate CO_2 to CO, which is used as an intermediate in the production of methanol and dimethyl ether (DME). Cu/ZnO-Al_2O_3 catalysts are commonly studied for RWGS and are quite active but deactivate by sintering of the active phase and are sensitive to the water formed. In this work, Cu,Zn-ZSM-5 catalysts were prepared by ion exchange (simultaneous or successive), introducing Cu^{2+} and/or Zn^{2+} ions (1.5%) into ZSM-5 zeolite, aiming to overcome these limitations. The materials were characterized and evaluated in RWGS. All catalysts showed high selectivity to CO, with negligible formation of CH_4. The active phase is the metallic Cu dispersed in the zeolite support. The introduction of Zn^{2+} before Cu^{2+} significantly increased the catalytic activity. The most active catalyst showed 82% of CO_2 conversion and 100% selectivity to CO at 800°C. The reaction parameters (F/W and H_2/CO_2 ratios) were investigated at 600°C to optimize the catalyst performance. The possible deactivation routes of the catalyst were investigated.

Keywords: RWGS, CO_2 conversion, Zeolite catalysts.

Introduction

Since the industrial revolution, the growing use of fossil fuels (coal, oil, and natural gas) for energy production has significantly contributed to climate change (1). To mitigate the environmental impacts of greenhouse gas emissions, particularly CO_2, it is essential to expand renewable sources in the energy matrix and develop efficient carbon capture and conversion (CCC) strategies (2). However, CO_2 activation remains a major challenge due to its high thermodynamic stability and kinetic inertness, which require significant energy input and highly efficient catalytic systems.

Among the various strategies for CO_2 utilization, the reverse water gas shift (RWGS) reaction stands out as a key process, as it converts CO_2 into CO – a valuable building block for the synthesis of fuels and chemicals. The CO produced via RWGS can be further transformed through downstream processes (3) such as methanol synthesis (4), dimethyl ether (5) production, or Fischer-Tropsch synthesis (6), broadening the applicability of CO_2 conversion technologies (7).

The most widely studied catalyst for the RWGS reaction is $Cu/ZnO-Al_2O_3$. However, alternative formulations have been investigated to improve catalytic activity, selectivity, and stability under diverse conditions. Various metals (Cu, Zn, Fe, Ni, Mo, Ce) supported on oxides such as Al_2O_3, ZrO_2, SiO_2, and mesoporous materials like MCM-41 have been explored, with promoters including ZnO, K, La, Mg, and Pd (3, 8). Notably, catalysts such as RuNi/CeZr, 4%Ru/γ-Al_2O_3, and Cu/CeO_2 have demonstrated promising CO selectivity and CO_2 conversion under suitable test conditions (9).

Zeolite-based catalysts have also attracted attention due to their high surface area, tunable acidity, and ion-exchange capacity. Transition metals supported on zeolites (MFI structures like ZSM-5) (10, 11) can offer bifunctional catalytic properties combining redox and acidic functionalities. Transition metal oxides can also be introduced via impregnation, yielding redox species dispersed across the high surface area of the support (12). During synthesis, zeolites may incorporate transition metal ions with appropriate charge/radius ratios as charge compensation cations (13). Moreover, zeolites such as 13X (FAU topology) may serve as water adsorbents, shifting the RWGS equilibrium toward CO production (14).

Despite the advances in catalyst development for RWGS, challenges remain regarding the stability, dispersion, and interaction of active metal phases. The synergistic effect of promoters like ZnO is known to enhance Cu dispersion and performance (15). However, few studies systematically evaluate the influence of the sequence in which metal ions are introduced into the zeolite framework. Previous reports on Cu-ZSM-5 and Cu,Zn-ZSM-5 for the water gas shift reaction (WGS) suggest that Zn^{2+} can improve Cu^{2+} dispersion in zeolitic matrices (16).

In this context, the present work investigates the impact of ion-exchange procedure (sequential vs. simultaneous) of Cu^{2+} and Zn^{2+} in ZSM-5 zeolite in the catalytic performance in RWGS reaction, aiming to elucidate structure–activity relationships relevant to CO_2 valorization.

Experimental

Preparation and characterization of catalysts

The catalysts were prepared by simultaneous (SIM) or sequential (SEQ) ion exchange of Cu^{2+} and/or Zn^{2+} ions in a commercial zeolite Na-ZSM-5 (Degussa, Si/Al = 21) to achieve nominal Cu and/or Zn contents of 1.5%. To aid the insertion of copper in the exchange sites, the Iwamoto method of pH adjustment between 7 and 7.5 was applied (17). Afterwards, the catalysts were filtered, washed with deionized water, dried and calcined at 550°C under synthetic air flow. The calcination temperature was determined based on thermogravimetric analysis.

All samples (pristine and post-test) were characterized by X-ray diffractometry on a Shimadzu XRD6000 diffractometer, with graphite monochromator, operating with CuKα radiation generated at 40 kV, 30 mA, at 2°min-1 speed, with 2θ scanning angle of 5° to 80°. X'Pert HighScore Plus software was used to determine the semi-quantitative phase composition.

Elemental analysis was performed by energy dispersive X-ray spectrometry on a Shimadzu EDX-720 equipment, using a rhodium anode as radiation source, a 10 mm collimator slit and operating at 15 kV (Na to Sc) or 50 kV (Ti to U). The samples were analyzed as powders under vacuum on 5 mm diameter polypropylene supports and with a 5 µm thick polypropylene film.

Nitrogen physisorption isotherms were collected in Micromeritics ASAP 2020 equipment at -196°C. The samples were initially subjected to a pretreatment for 3h at 350°C under high vacuum (2 µmHg), with the objective of removing physisorbed species of the sample surface. The NLDFT method was used to obtain the area, volume and diameter of micropores and mesopores, adopting cylindrical pores. Specific areas were also calculated using the BET and Dubinin-Raduskevich (DR) methods for comparison.

Thermogravimetric analysis under oxidant atmosphere of post-test samples was used to quantify the carbonaceous deposits (coke) eventually formed on catalyst surface.

Catalytic evaluation

The materials were tested under fixed bed continuous flow conditions, with a quartz wool bed in a U-shaped quartz reactor, at atmospheric pressure, 0.2 g of catalyst and a total flow rate of 50 mL min^{-1}, consisting of 30 mL min^{-1} of H_2, 15 mL min^{-1} of Ar, and 5 mL min^{-1} of CO_2, resulting in a 6:3:1 molar ratio. All materials were pre-reduced in situ at 600°C under a hydrogen flow for 1 h. Temperature was varied from 300°C to 800°C to assess its effect on the catalytic reaction. The effects of F/W ratio between 15000 to 45000 mL g^{-1} h^{-1}, H_2/CO_2 molar ratio of 1:1 to 6:1, and long-term stability from 600°C to 700°C were also evaluated. All the products were analyzed with a GC 2014 Shimadzu operating with FID and TCD detectors, a packed Carboxen 1010 and a capillary Innowax columns. The following equations were used to calculate conversion of CO_2 and selectivity to CO.

$$X(\%) = \frac{n_{CO2,i} - n_{CO2,f}}{n_{CO2,i}} x100 \quad (1)$$

$$S(\%) = \frac{n_{CO(formed)}}{n_{CO2(converted)}} x100 \quad (2)$$

Results and Discussion

Catalysts characterization

The elemental analysis performed by EDX generated the results described in Table 1, which were expected due to the preparation method used and quantities previously chosen.

The comparison between samples Cu,Zn-ZSM-5 (SEQ), where Zn^{2+} ions were exchanged in the ZSM-5 before Cu^{2+}

ions, and Zn,Cu-ZSM-5 (SEQ), where this order is reverted, leads to conclude that the incorporation of Cu^{2+} species hinders the Zn^{2+} ion exchange, probably because Iwamoto's method favors the formation of oligomeric species that cannot be easily displaced from the ion exchange sites (17).

Table 1. Elemental analysis of Cu,Zn-ZSM-5 catalysts.

Samples	Cu (%)	Zn (%)	Cu/Zn
Zn-ZSM-5	-	1.00	-
Cu-ZSM-5	1.40	-	-
Cu,Zn-ZSM-5 (SEQ)	1.48	1.41	1.05
Zn,Cu-ZSM-5 (SEQ)	1.48	0.80	1.85
Cu,Zn-ZSM-5 (SIM)	1.77	1.11	1.59

Figure 1 presents the powder X-ray diffraction patterns of the samples. The XRD patterns exhibited only the characteristic peaks of the MFI topology of the ZSM-5 zeolite, with no peaks corresponding to CuO and ZnO. This indicates that the exchanged cations are well dispersed or, if present as oxide phases, they do not exceed 4 nm in size, as aggregates smaller than 4 nanometers are undetectable by X-rays in the analysis conditions (18).

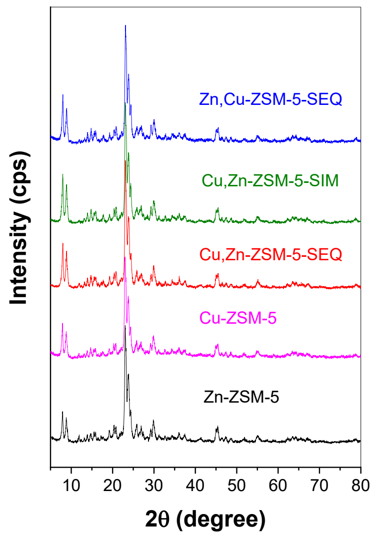
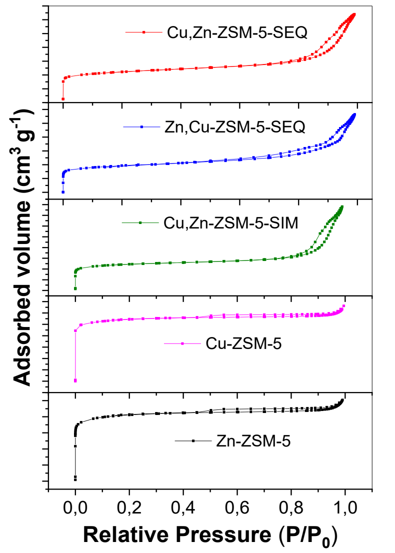


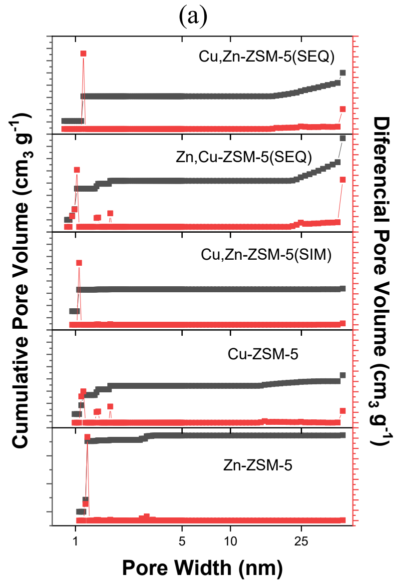
Figure 1. X-ray diffraction of Cu,Zn-ZSM-5 catalysts.

The N_2 physisorption isotherms and NLDFT plots of Cu,Zn-ZSM-5 catalysts are shown in Figure 2. The catalysts exhibited type I isotherms (Figure 2.a), which are characteristic of microporous materials. Hysteresis loops at high relative pressures suggest the presence of secondary mesopores ($P/P_0 > 0.8$).

Pore size distributions obtained by NLDFT (Figure 2.b) indicate that the materials are predominantly microporous (48–97%), with a mesoporous contribution ranging from 3 to 52% as show in Table 2. Despite the variation in mesopore percentage, these are secondary mesopores, formed due to the spacing between crystalline structures, whereas the crystalline structure itself is predominantly microporous (19).



(a)



(b)

Figure 2. (a) N_2 adsorption isotherms; and (b) Pore size distribution by NLDFT method of Cu,Zn-ZSM-5 catalysts

Table 2. Textural properties of Cu,Zn-ZSM-5 catalysts

Samples	S_{BET} (m^2/g)	S_{DR} (m^2/g)	V_{micro} (cm^3g^{-1})	V_{meso} (cm^3g^{-1})
Zn-ZSM-5	301	371	0,1156 (97%)	0,0031 (3%)
Cu-ZSM-5	318	392	0,1283 (94%)	0,0084 (6%)
Cu,Zn-ZSM-5 (SEQ)	391	471	0,1042 (52%)	0,0551 (48%)
Zn,Cu-ZSM-5 (SEQ)	431	522	0,1588 (48%)	0,1743 (52%)
Cu,Zn-ZSM-5 (SIM)	340	405	0,1213 (74%)	0,0435 (26%)

The BET surface area results for these materials indicate surface areas ranging from 301 to 431 m² g^{-1}. The parent Na-ZSM-5 exhibited a BET surface area of 316 m² g^{-1}, suggesting that in some cases there was a partial blockage of the pores, and in others that BET surface areas increased. Despite this behavior, it is necessary to consider that BET model is not adequate to describe microporous materials, as zeolites (19).

For this reason, two different models were also evaluated. The Dubinin-Radushkevich model assumes for homogeneous microporous materials the adsorption occurs by filling the micropore and the adsorption energy depends on the distance of the probe of the microporous wall (Polanyi potential) (20). The S_{DR} areas show a similar behavior, despite higher values when compared to BET.

The NLDFT is the recommended model to analyze micro and nanoporous materials, because the NLDFT considers non-local interactions, resulting in a better resolution to pores diameters less than 2 nm (19). NLDFT shows that the behavior observed for both BET and DR areas is not correlated only to the micropore volume, but depends on the secondary mesopore increase, for Cu,Zn-ZSM-5(SEQ) and Zn,Cu-ZSM-5(SEQ) especially for the last one, for which a higher increase of secondary mesopores was observed.

Catalytic Activity

The results of catalytic activity in the reverse shift reaction are presented in Figure 3.

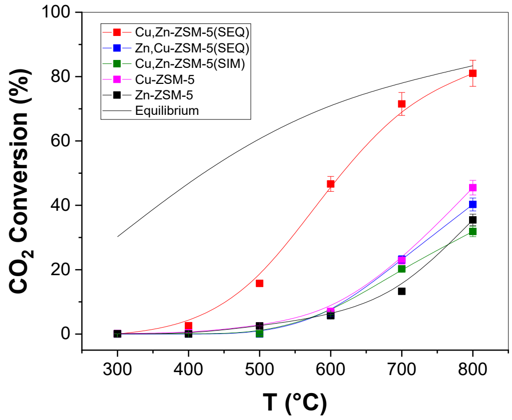
Evaluating the conversion and selectivity results of the tested materials, most materials exhibit similar conversion values, ranging between 30% and 40% between 500 and 800°C, independently of the ion exchange procedure employed, i.e., sequential or simultaneous. For these samples, the presence of Zn^{2+} exchanged in the zeolite ZSM-5 seems not to have a significant effect in the catalytic performance in RWGS.

However, for the Cu,Zn-ZSM-5 (SEQ) material, in which Zn was added prior to Cu, the catalytic behavior is superior. This catalyst presented a light-off temperature at least 100ºC lesser than the other catalysts. Its CO_2 conversion increases up to 82% at 800ºC. The CO selectivity of all catalysts increased sharply from 0 to 99%, depending only on the light-off temperature.

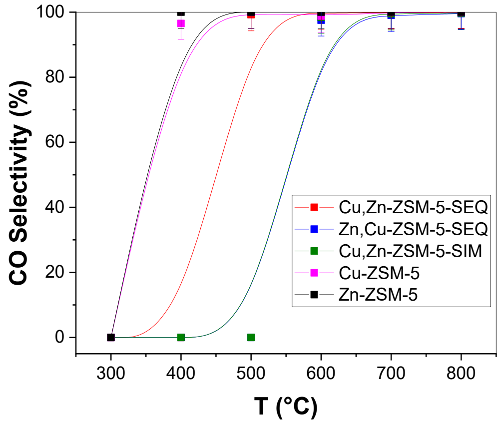
At lower temperatures, some methane was detected, but with selectivity lesser than 1.0% (not shown in Figure 3). In these cases, the molar ratio between converted H_2 and converted CO_2 is near 3.0, while for higher temperatures this molar ratio H_2/CO_2 tends to be 1.0.

It is noticeable that at 800ºC, the CO_2 conversion tends to reach equilibrium conversion calculated for the same experimental conditions.

All the following optimizations were done only for the best catalyst, Cu,Zn-ZSM-5 (SEQ).



(a)



(b)

Figure 3. Performance of Cu,Zn-ZSM-5 catalysts in the reverse gas shift reaction (RWGS): (a) CO_2 conversion; and (b) CO selectivity. Conditions: catalyst mass = 0.2 g; gas flow rate = 50 mL min^{-1}; H_2:CO_2:Ar ratio = 6:1:3.

Effects of F/W ratio

A study about the variation of F/W ratio was performed by changing the total flow and maintaining the inlet composition and the catalyst mass. The results are presented in Figure 4.

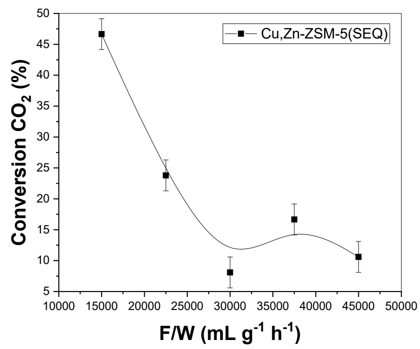


Figure 4. CO_2 conversion of catalyst Cu,Zn-ZSM-5 (SEQ) at 600ºC using different F/W ratio. Conditions: w_{cat} = 0.2 g; $H_2/CO_2/Ar$ = 6:1:3.

The catalytic test showed a reduction of CO_2 conversion with the increase of F/W until the 30000 mL g^{-1} h^{-1} when the conversions reach a similar value in comparison to the 37500 and 45000 mL g^{-1} h^{-1}. The reduction of conversion can be explained by diffusional limitations, because a high flow hinders reactants diffusion into the zeolite micropores. This fact also justifies stabilization from 30000 mL g^{-1} h^{-1}, since under high flow rates, the reagents have hindered their internal diffusion.

Long term stability

The long-term stability test was conducted at three temperatures, 600, 650 e 700°C for 30 h and the results are shown in Figure 5. The catalyst was reduced in the same manner as in the previous catalytic tests. The catalyst maintained stable conversion for 10 h at 600°C and, after 10 h of continuous test, the catalyst presents slightly deactivation, and after 20 h of test, the catalyst presents a more accentuated loss of conversion.

At 650°C a high deactivation occurs at the beginning of test, but tends to stabilize around 10 h on stream, but with a slight loss of conversion until 27 h, when conversion starts to decrease more significantly again. The behavior of Cu,Zn-ZSM-5 at 700°C is very similar to that observed at 650°C.

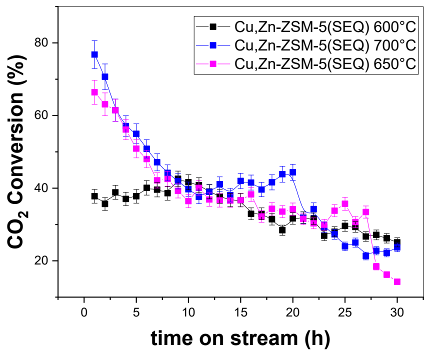


Figure 5. Conversion of catalyst Cu,Zn-ZSM-5 (SEQ) in long-term test of 30 h at 600°C. Conditions: w_{cat} = 0.2 g; total flow, F = 50 mL min^{-1}; $H_2/CO_2/Ar$ = 6:1:3.

The selectivity does not present a significant variation during all the 30 h of stability test, maintaining 100% selective to CO for all temperatures.

The activity loss during long-term runs can be due to coke formation, sintering of metallic copper or partial collapse of zeolite structure. To investigate the possible deactivation mechanism, post-test characterization was performed.

Effects of H_2/CO_2 ratio

The influence of H_2/CO_2 molar ratio was evaluated for the Cu,Zn-ZSM-5(SEQ) at constant temperature of 600°C and total flow of 50 mL min^{-1} (F/W = 15000 mL g^{-1} h^{-1}). Results are shown in Figure 6.

Figure 6 shows the conversion progress as the H_2/CO_2 increase, demonstrating that excess hydrogen is necessary to shift the thermodynamic equilibrium towards the formation of products. A curve showing the equilibrium conversion was calculated based on reaction parameters.

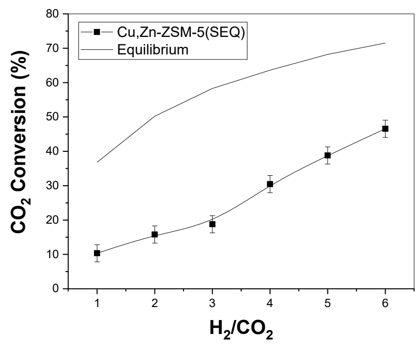


Figure 6. CO_2 conversion with different H_2/CO_2 ratio on Cu,Zn-ZSM-5 (SEQ) catalyst. Condition: w_{cat} = 0.2 g; total flow F = 50 mL min^{-1}; T = 600°C.

The selectivity does not show significant variation as a function of H_2/CO_2 molar ratio, with Cu,Zn-ZSM-5 (SEQ) maintaining 100% selective to CO.

Post-test characterization

Powder X-ray diffraction patterns of post-test experiments can be observed in Figure 7.

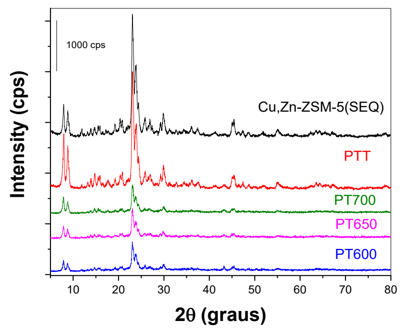


Figure 7. The XRD analysis of the catalyst Cu,Zn-ZSM-5(SEQ) before and after test.

As can be observed in Figure 7, no significant changes were observed in the Cu,Zn-ZSM-5 (SEQ) catalyst diffraction pattern when subjected to each investigated temperature (PTT), with negligible loss of crystallinity. But the catalyst structure has a significant loss of crystallinity in long term 30 h test at high temperatures. However, despite the low intensity of the peaks, no amorphous halo can be observed for the samples obtained after long-term runs at 600, 650 and 700ºC, indicating that zeolite structure did not suffer a collapse.

It is also important to mention that no peaks of metallic copper were identified in any case, indicating that no significant sintering has occurred.

The thermogravimetric analyses of post-test catalysts (not shown) present a pronounced mass loss event at low temperatures that can be associated with water loss. For higher temperatures, a mass gain event was observed, being attributed to the oxidation of copper to CuO. No carbonaceous deposits were detected.

The results of post-test characterization suggested that Cu,Zn-ZSM-5 catalysts do not deactivate in RWGS by coke deposition or copper sintering. The probable route of partial deactivation must be through the loss of crystallinity of the structure, which affects the diffusional properties of zeolite.

Comparison with literature

There are few studies in the literature that evaluate RWGS using Cu,Zn-ZSM-5 catalysts. Therefore, comparisons were preferably made with catalysts containing Cu as a similar active phase.

In the literature, catalysts present active phase content which varied from 5 and 20% (21). Cu,Zn-ZSM-5(SEQ) has only 1.5% of active phase. The most common preparation method is impregnation, while the catalyst in this work was prepared by ion exchange in the ZSM-5 catalyst. The conversions obtained by the different catalysts tested here are commonly equivalent or higher at the same temperatures, although operating at higher space velocities than those related in literature. The main disadvantage is that Cu,Zn-ZSM-5 required a high H_2/CO_2 ratio of 6:1, while in literature the H_2/CO_2 ratios are commonly 1:1 to 4:1 (8).

Conclusion

By evaluating the conversion and selectivity on reverse water gas shift reaction, it is possible to conclude that the preparation method, as well as the test conditions, influenced the catalytic results. The catalyst in which Zn^{2+} was exchanged before Cu^{2+}, showed a significant improvement in the activity, acting as a textural promoter, preventing the coalescence of the active Cu phase, preventing the sintering of the active sites and maintaining the active surface area. Unfortunately, the use of molar ratio $H_2/CO_2 = 6:1$ is not economically viable at this moment, but with increasing production and use of sustainable H_2 this picture could change. New improvements in the catalyst performance can be obtained by changing its composition by incorporating textural or electronic promoters.

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