CO_2 hydrogenation to olefins over alkali metal-doped FeZn catalysts

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Resumo/Abstract

RESUMO – FeZn, Na/FeZn e K/FeZn foram preparadas por coprecipitação seguida de impregnação ao ponto úmido para serem avaliados na hidrogenação de CO_2 a olefinas. A adição de Na e K influenciou significativamente as propriedades físico-químicas e catalíticas do FeZn. Os resultados mostram o papel essencial dos metais alcalinos na formação de carbeto de ferro e na produção de olefinas, com K/FeZn apresentando o melhor desempenho em termos de atividade catalítica e rendimento de olefinas.
Palavras-chave: hidrogenação do CO_2, olefinas, catalisadores de Fe, promotores.

ABSTRACT – FeZn, Na/FeZn, and K/FeZn were prepared by coprecipitation followed by incipient wetness impregnation to be investigated in CO_2 hydrogenation to olefins. The addition of Na and K significantly influences the physicochemical and catalytic properties of FeZn. The results show the essential role of the alkali metals in the iron carbide formation and in the olefins production, with K/FeZn showing the best overall performance in terms of catalytic activity and olefins yield.
Keywords: CO_2 hydrogenation, olefins, Fe-based catalysts; promoters.

Introduction

Among the various CO_2 upgrading strategies, catalytic hydrogenation of CO_2 to olefins is an attractive approach (1). The hydrogenation of CO_2 to olefins mainly occurs via the CO-mediated route, combining the reverse water-gas shift reaction (RWGS) to convert CO_2 into CO, followed by CO hydrogenation via Fischer-Tropsch Synthesis (RWGS-FTO) using Fe-based catalysts (2).

Iron-based catalysts are widely used because they efficiently catalyze both RWGS and FTS reactions. Alkali metals are usually added as promoters to increase the catalyst´s basicity, improving CO_2 adsorption, and more importantly, they inhibit H_2 activation, suppressing the excessive hydrogenation of olefins, minimizing the formation of methane and other paraffins (2,3).

Transitions metals are also investigated as promoters of iron-based catalysts. Yang *et al*. (4) studied the performance of Fe-Na, FeZn-Na, FeCu-Na, and FeMn-Na catalysts in CO_2 conversion into olefins. FeZn-Na showed the highest activity, stability, and olefin yield. Characterizations revealed that Zn improved CO_2 adsorption, facilitated iron reduction and iron carbide formation, and prevented sintering.

In this sense, the aim of this work is to investigate the catalytic performance of FeZn, Na/FeZn, and K/FeZn in the CO_2 hydrogenation to olefins, elucidating the influence of the alkali metals.

Experimental

Catalysts preparation

The FeZn catalyst was synthesized by coprecipitation. NaOH solution (1.5 mol L^{-1}) was added dropwise to a 150 mL aqueous solution containing 0.12 mol of $Fe(NO_3)_3{\cdot}9H_2O$ and 0.04 mol of $Zn(NO_3)_2{\cdot}6H_2O$ under vigorous stirring at 60 °C, until pH 10. The suspension was aged for 1 h, washed, dried at 100 °C overnight, and calcined at 400 °C for 4 h (5 °C/min). After that, 2 wt.% of Na or K was added by incipient wetness impregnation of an aqueous solution of $NaNO_3$ and KNO_3, respectively, dried and calcined following the same procedure. The catalysts were labeled FeZn, Na/FeZn, and K/FeZn.

Catalysts characterization

X-ray diffraction (XRD) patterns were obtained using a Bruker D8 Advance diffractometer equipped with a CuKα radiation source (1.5418 Å), recorded in an angular range of 10–90°, at a scanning rate of 1.2°/min and increments of 0.02°. The surface area of the samples was determined by N_2 physisorption at -196 °C in the ASAP 2020 Micromeritics instrument. Temperature programmed reduction (H_2-TPR) analyses were conducted using a multipurpose unit coupled to a Pfeiffer QME 200 mass spectrometer. 100 mg of the samples were pretreated under He flow at 200 °C for 1 h, cooled down, and then reduced under H_2 flow (50 mL.min^{-1}) up to 1000 °C. The reduction profile was monitored via the m/z = 18 (H_2O) signal.

Catalytic evaluation

Catalytic tests were performed in a fixed bed reactor at 320 °C, 3 MPa, H_2/CO_2 molar ratio equal to 3, and GHSV 4000 mL.g_{cat}^{-1}.h^{-1}. The catalysts were pretreated *in situ* at 350 °C for 8h under pure H_2 flow (50 mL.min^{-1}). The effluent gases were analyzed by a GC-2030 Shimadzu gas chromatograph, equipped with 1 Carboxen 1010 plot column, 1 CP-SIL 5 CB column, 1 TCD, and 1 FID detector.

Results and Discussion

Catalysts characterization

FeZn sample presented 86 $m^2.g^{-1}$ of surface area, while Na/FeZn 66 $m^2.g^{-1}$, and K/FeZn 79 $m^2.g^{-1}$. The decrease in surface area may be due to pores filling during Na and K impregnation. The diffractogram of FeZn (Fig.1-a) showed the predominant formation of $ZnFe_2O_4$ crystalline phase (PDF 33-0664). After the addition of Na and K, no diffraction peaks relative to these species were identified, possibly due to the formation of small crystallites undetectable by the XRD technique.

Fig.1-b presents the H_2-TPR profiles of the samples. FeZn exhibited sequential reduction peaks corresponding to the stepwise reduction of $ZnFe_2O_4$ to Fe_3O_4, Fe_3O_4 to FeO, and FeO to metallic Fe (4). The addition of K decreased the middle reduction peak (450 °C) and slightly shifted the final reduction peak to higher temperature (580 °C), while Na/FeZn exhibited two distinct high-temperature peaks (615 and 670 °C), indicating a stronger inhibition of iron reduction by Na. The XRD after reduction (Fig.2-a) confirmed that the addition of Na hindered iron oxide reduction, while K favored iron complete reduction to Fe^0.

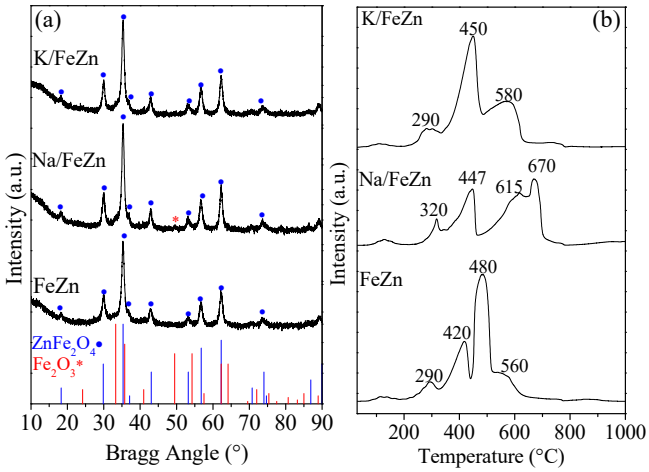

Figure 1. Characterization of the calcined catalysts**:** (a) XRD patterns and (b) H_2-TPR profiles.

Table 1 summarizes the results of the catalytic tests. FeZn catalyst exhibited a CO_2 conversion of 48.7%, which decreased to 39.8% upon Na addition but remained high (47.0%) after K addition. The incorporation of both Na and K led to a decrease in methane production and a notable increase in the olefin/paraffin ratio. Furthermore, as shown in Fig. 2-b, the presence of alkali metals promoted the formation of iron carbide (Fe_2C_5; PDF 36-1248), considered as the active phase for olefin production (2). K/FeZn achieved a slightly higher olefin yield, indicating improved catalytic performance.

Table 1. Catalytic performance of FeZn catalysts.

Sample	CO_2 Conv (%)	CO Sel (%)	Hydrocarbon distribution (molar%)					O/P	Olefins Yield (%)
			CH_4	C_{2-4}^0	$C_{2-4}^=$	C_{5+}^0	$C_{5+}^=$		
FeZn	48.7	4.1	31.9	32.3	15.7	12.7	7.4	0.5	11
Na/FeZn	39.8	6.8	16.1	5.6	41.4	10.1	26.7	4.3	25
K/FeZn	47.0	4.9	18.0	6.8	36.2	10.3	28.6	3.8	29

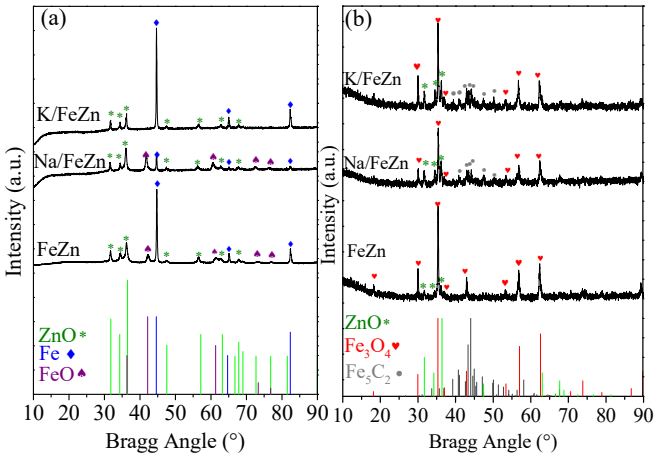

Figure 2. XRD patterns of the catalysts after (a) reduction, and (b) reaction for 24 h.

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Conclusions

The results showed the essential role of the alkali metals incorporation to increase olefins selectivity and to the formation of the active phase iron carbide. K/FeZn showed superior catalytic performance than Na/FeZn, which may be associated with the higher surface area and iron reducibility.

References

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