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PROMOTER EFFECT OF POTASSIUM ON AN IRON CATALYST IN THE CARBON DIOXIDE HYDROGENATION REACTION

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Abstract

The effect of the K content on a Fe catalyst for the CO_2 hydrogenation was studied. Very pronounced changes in the selectivities to C2+ hydrocarbons, as well as in the olefin ratios were observed. The addition of K favored the reoxidation of Fe during the reaction.

Keywords: Hydrogenation of CO_2, Fe catalysts, K promotion

INTRODUCTION

The CO_2 hydrogenation to fuels and chemicals has attracted attention as an alternative to the recycle of CO_2 into the atmosphere. Fe offers possibilities to produce C2+ hydrocarbons by this reaction, which are formed by the hydrogenation of CO produced in a primary stage of reverse water gas shift reaction [1-5]. The promoter effect performed by K over Fe catalysts in the CO hydrogenation is well known. The changes are consistent with an increase in the C/H surface ratio. In the CO_2 hydrogenation reaction the promoter effect of K has been also reported [2,5-6].

In order to shed some light in the degree of modification that can be achieved by K promotion in the CO_2 hydrogenation reaction, the effect of K content of a catalyst prepared by thermal decomposition of Fe citrate and physical mixture with alumina was investigated.

EXPERIMENTAL

The catalyst was prepared from an equimolar solution of Fe nitrate $(Fe(NO)_3.6H_2O)$ and citric acid $(C_6H_8O_7.H_2O)$. The solvent was evaporated at 60°C, then the citrate was dried at 150°C for 2 h and decomposed at 400°C for 1.5 h in air flow [7]. The final catalyst was obtained by physical mixing of this precursor with γ-Al_2O_3 (Ketjen CK-300 particle size <0.15 mm) in a ratio to produce 20 wt. % of Fe. The addition of K (0-10 wt.%) was carried out by incipient wetness impregnation of K_2CO_3 over the Fe/Al_2O_3 catalyst.

Before reaction the catalysts were pretreated with H_2 at 350°C during 16 h followed by syngas (H_2/CO=2) at 160 (2 h)-300°C (19 h). The catalytic tests were performed in a fixed bed reactor at 290°C, 1.2 MPa, H_2/CO_2=2, 1.2 $l/(g_{cat}.h)$ during two days. The effluent gases were analyzed by gas chromatography; details have been given elsewhere [8]. Conversion was determined using N_2 as internal standard. Selectivities were based on carbon converted.

The chemical analysis of the catalysts was performed using atomic absorption and emission spectroscopy. The pretreated and spent catalysts were analyzed by Mössbauer spectroscopy at room temperature, using a γ ray source of ^{57}Co in a Pd matrix. Near 0.2 g of the samples were placed in an aluminium holder and sealed with epoxy. Spectra were adjusted by means of a least squares program.

RESULTS AND DISCUSSION

The actual preparation procedure of the catalysts was preferred to impregnation or precipitation of Fe in the presence of alumina because of the slightly better results on selectivities obtained (less methane, more C2-C4 olefins) [8]. Fe and K contents, as determined by chemical analysis were close to the nominal values.

Mössbauer spectra of the catalysts after pretreatment and reaction showed the presence mainly of Hägg carbide and magnetite. Figure 1 shows the Fe carbide proportion of the catalysts. Previous studies have shown that Fe carbide formed by a pretreatment of reduction-carburisation, tend to be oxidized to magnetite under the reaction conditions used [8]. Reoxidation is attributed to the water coproduced in the transformation of CO_2 to CO and hydrocarbons. However, the unpromoted catalyst prepared by thermal decomposition of citrate and physical mixture with alumina did not show a significant variation in the Fe phase composition when exposed to the environment of the CO_2 hydrogenation reaction. Residual carbon produced by an incomplete decomposition of the citrate [7] could give an hydrophobic character to the surface. The disappearance of the greyish tone of the solid (purple color) observed after calcination at 800°C tends to corroborate the presence of residual carbon in the

Fe precursor. The addition of K increased notoriously the reoxidation tendency of this catalyst (Fig. 1). K could increase the adsorption ability or affinity to water favoring this phenomenon. A maximum on reoxidation with the K content was observed. Probably, the higher K contents (≥ 5 wt.%) led to a coverage of the Fe particles retarding reoxidation. Concerning the pretreated catalysts, the proportion of Fe carbide decreased for the higher K contents. Also this result could be explained by the coverage of Fe by K, which would retard the transformation.
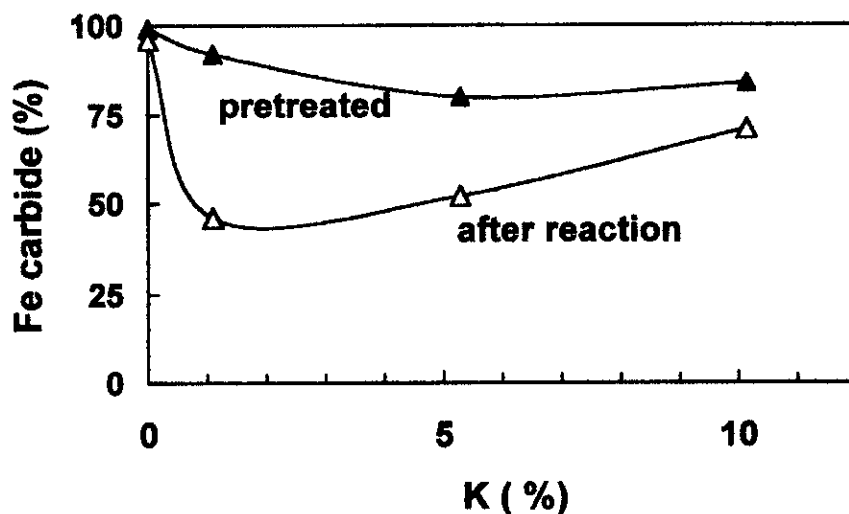

Fig. 1. Fe carbide proportion as a function of the K content

CO_2 conversion went through a maximum with the increase on K content (Fig. 2). This result agrees with the already reported tendencies for CO hydrogenation [9]. The increase could be related to an enhancement of CO_2 and CO adsorption and dissociation. The subsequent diminution of the activity at increasing K contents has been often explained by the coverage of Fe active sites. However, the variation in conversion was not pronounced, which seems to be a characteristic behaviour for this reaction. Thus, the sensitivity of CO_2 conversion to different preparation procedures [8] and promoter additives [5] is low, at least at relatively high CO_2 conversions (20-30 %). This could be related to an inhibition effect of the water produced. This effect, which has been probed for CO hydrogenation [10], could be more important for CO_2 hydrogenation because of the greater proportions of water formed in the last reaction.

It is also worth noting that those catalysts active in reoxidation did not show a lower activity (Figs 1 and 2). Similarly, it has been observed in CO hydrogenation that reoxidation during reaction of Fe carbide to magnetite did not seem to have a deleterious effect on activity [11]. The need of transformation of Fe to carbide in order to observe CO_x hydrogenation activity has been recognised [12]. However, the nature of the surface species during reaction and the unambiguous establishment of those really active is still controversial, even for the more studied CO hydrogenation reaction. In addition, it would also be possible for K to retard deactivation by carbon deposition in the presence of water because of its effect to promote carbon gasification.
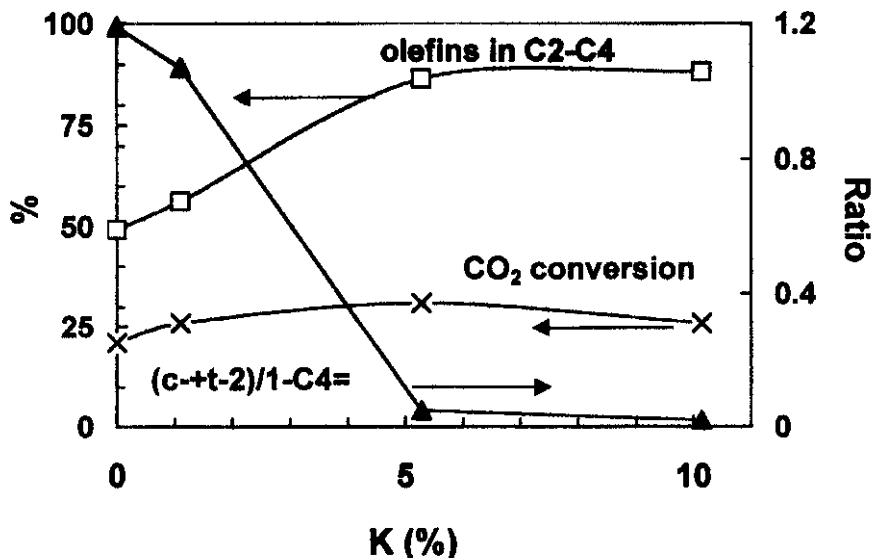

Fig. 2. Effect of the K content on the CO_2 conversion and olefins selectivity (olefins in the C2-C4 fraction, internal/terminal olefins ratio in the C4 fraction)

Different to that observed for the activity of CO_2 transformation, the changes on selectivity performed by K promotion were well pronounced. The addition of K strongly increased the selectivity to olefin formation and also diminished the internal/terminal olefins ratio (Fig. 2). Terminal or 1-olefins are primary products in CO hydrogenation, which can undergo secondary reactions such as hydrogenation and double-bond isomerization. Both reactions are favored by an increase in H_2 partial pressure, and the parallelism between them has been

associated with the participation of a common intermediate [13]. The trends on selectivity obtained in this case are consistent with a lower C/H ratio at the catalytic surface in the presence of higher K contents.
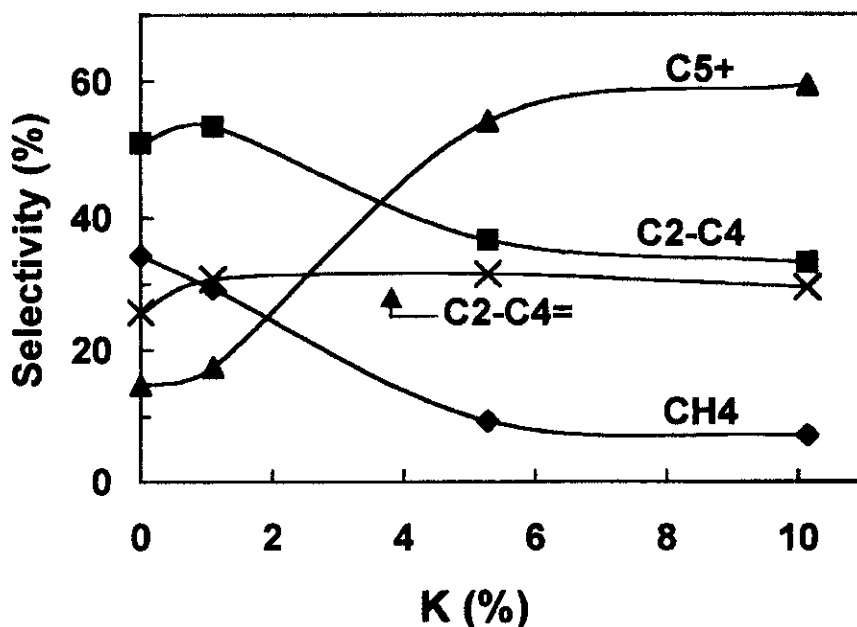

Fig. 3. CO free selectivities (carbon converted) as a function of the K content

Under the present conditions CO selectivities (as carbon converted) varied between 7 and 12%. The CO free methane selectivities showed a very notorious decrease with the increase in the K content approaching an asymptotic value (Fig. 3). For low K contents this decrease occurred at the expense of an increase in the proportion of the C2-C4 and C5+ fractions, while for the higher K contents the C5+ fraction increased and both methane and lighter hydrocarbons (C2-C4) decreased. This points to an increase in the chain growth probability by the addition of K, which at the same time would be a consequence of the increase in the C/H surface ratio caused by this promoter. The small changes observed for K content between 5 and 10 wt.% suggest that in this case the maximum interaction and/or interface area between Fe-K must occur for K contents close to 5 wt.%.

The variation on the C2-C4 olefins (C2-C4=) selectivities by increasing the K content was not very pronounced (Fig. 3). This parameter can be considered

to depend on two others, the tendency to olefin formation and the chain growth probability, both increasing with the K content. The increase in the olefin formation favors the attainment of high selectivities to the C2-C4= fraction, but as the chain growth probability increases the proportion of the C2-C4 fraction goes through a maximum, as predicted by the Anderson-Schulz-Flory kinetics. The results obtained seem to indicate that the increase in olefin selectivity that occurs upon K addition tends to be compensated by a diminution in the proportion of C2-C4 fraction.

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