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K and Sr promoted Co alumina supported catalysts for the CO_2 reforming of methane

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ABSTRACT

K and Sr promoted Co alumina supported catalysts for the CO_2 reforming of methane (973 K, CH_4:CO_2 (1:1)) have been prepared by the coimpregnation and successive impregnation methods. The catalysts (fresh and used (after reaction)) have been characterized using the following techniques: Atomic Absorption Spectroscopy (ICP-OES), Transmission Electron Microscopy (TEM), Energy Dispersive X-ray (EDX) and Temperature Programmed Oxidation (TPO). The obtained results indicate that K is a more effective promoter than Sr and that the preparation method does not affect the catalyst performance. Because of that, the coimpregnation method (the simplest one) has been selected to prepare a series of K promoted catalysts with variable amount of potassium. It has been found that the amount of potassium influences both, the methane conversion and the amount of deposited carbon. The optimum amount of potassium seems to be around 0.6 wt.%, as the catalyst with this K loading presents a relatively high methane conversion (60%) and a quite low amount of deposited carbon (0.08% molar of the converted carbon) after 6 h reaction.

1. Introduction

In the last years, the CO_2 reforming of methane (1) has attracted increasing interest as it is a reaction that produces synthesis gas with a H_2/CO ratio close to unity, and contributes to the removal of methane and carbon dioxide, the two most important greenhouse gases. In addition, this reaction allows to upgrade the biogas (a renewable resource composed by CH_4 and CO_2 [1–3]), and it is appropriate for energy storage and transport due to its high enthalpy [4–6].

$$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2 \quad (1)$$

Co is a very interesting catalyst for this reaction [7] because of its high activity, availability and relatively low price. It is usually used as a supported species, being Al_2O_3 one of the most common supports [7]. However, Co catalysts are prone to lose activity due to reasons such as: sintering, metal oxidation [8–10], formation of inactive chemical species (e.g. cobalt aluminate) [11,12] and fouling by carbon deposits [9,13].

In a previous study [14], it was concluded that an alumina supported Co catalyst with a nominal metal content of 9 wt.%, shows high conversion values in the CO_2 reforming of methane, but it produces, as well, a high amount of deposited carbon (0.53% molar of the converted carbon). Although the deposited carbon does not deactivate the catalyst during 6 h reaction time, it can, presumably, cause the blockage of the reactor at longer reaction time. Thus, in order to increase the potential interest of this catalyst, it is mandatory to reduce the carbon deposit.

In this context, it has to be mentioned that the side reactions that generate carbon during the CO_2 reforming of methane are the following two:

$$CH_4 \leftrightarrow 2H_2 + C \quad (2)$$

$$2CO \leftrightarrow CO_2 + C \quad (3)$$

To avoid the formation of carbon deposits, the catalysts can be modified by the addition of promoters, being alkaline and alkaline earth metals [15–18] among the most used. The role of these promoters can be described as follows [16,19–22]: (i) the promoter can migrate from the support to the metal particles surface, deactivating sites where methane decomposition takes place (reaction (2)) and (ii) the promoter can catalyze the CO_2 gasification of the carbon formed during reaction (reverse of reaction (3)).

The use of promoters in the case of Co supported catalysts has been scarcely studied. As mentioned above, a Co/Al_2O_3 (9 wt.%) catalyst has shown to give very good conversion but also a large carbon deposit [14]. Thus, the objective of this work is to investigate the effect of promoters in the catalytic properties and carbon deposit of the mentioned supported Co catalysts. In a previous work

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it was found that K and Sr are convenient promoters for alumina supported Ni (10 wt.%) catalyst [23], and thus, these are also the promoters used in the present work.

2. Experimental

K and Sr promoted Co catalysts (with nominal composition 1.0 wt.% K or Sr and 9.0 wt.% Co) have been prepared by excess solution impregnation, using a pelletized γ-alumina as support (S_{BET} = 90 m^2/g), and aqueous solutions of the corresponding metal nitrates. Two preparation procedures have been employed: (i) successive impregnation, where the promoter was first introduced, then the sample was heat treated (773 K in air, 12 h) to decompose the nitrate, and finally cobalt was added and (ii) coimpregnation, where the promoter and cobalt were introduced at the same time. In both cases, the excess solution impregnation was carried out using 10 mL of the corresponding aqueous nitrate solution per gram of support, and keeping the mixture in contact at 333 K in an oven until solvent evaporation, about 3 days. After that, the catalysts were dried overnight at 373 K, also in an oven. Previous to the catalytic tests, the catalysts were heated in situ in helium (60 mL/min) to 773 K; then, the He flow was replaced by H_2 flow (40 mL/min) for 90 min to reduce the catalysts, and finally, the H_2 flow was changed again to He flow and the temperature was raised to 973 K (the reaction temperature). It must be pointed out that a calcination step was skipped.

After the analysis of the results obtained with these four samples, a new series of K promoted Co catalysts with different nominal amount of K (0.2, 0.6, 1.5 and 5.0, wt.%) have been prepared by the coimpregnation method.

The catalysts, fresh and after reaction (i.e. used), were characterized using the following techniques: (i) Atomic Absorption Spectroscopy (ICP-OES) to determine the K, Sr and Co content; (ii) Transmission Electron Microscopy (TEM) and Energy Dispersive X-ray (EDX) to analyze the morphology of the deposited carbon, the average particle size and the composition of the metal particles; and (iii) Temperature Programmed Oxidation (TPO) to determine the amount of deposited carbon.

The catalytic tests were carried out at 973 K during 6 h using a mixture CH_4:CO_2 (1:1, 60 mL/min), and 0.18 grams of catalyst (space velocity of 20,000 h^{-1}). The experimental system was a U shaped quartz reactor coupled to a gas chromatograph (HP5890 series II) with a thermal conductivity detector that allows a continuous analysis (every 7.6 min) of the exhaust gases. A scheme of the used experimental set up is shown in Fig. 1.

Table 1
Metal content of catalysts.

Catalyst	wt.% K	wt.% Sr	wt.% Co
Co(9.0)	–	–	7.6
KCo(1.0–9.0)	0.6	–	8.0
SrCo(1.0–9.0)	–	1.0	8.3
K–Co(1.0–9.0)	0.5	–	8.5
Sr–Co(1.0–9.0)	–	1.1	8.5
KCo(0.2–9.0)	0.1	–	7.1
KCo(0.6–9.0)	0.3	–	7.1
KCo(1.5–9.0)	1.2	–	7.7
KCo(5.0–9.0)	4.3	–	7.4

3. Results and discussion

3.1. Effect of promoter and preparation method

Table 1 shows the K, Sr and Co content of the catalysts, named according to the symbol of the loaded metals (hyphenated when prepared by successive impregnation), and the corresponding nominal metal content. The data of Table 1 indicate that the impregnation method does not affect the cobalt, potassium or strontium content. Also, it can be observed that the metal content measured by ICP-OES is lower than the nominal metal content, which usually occurs when catalysts are prepared by excess solution impregnation.

Table 2 shows the CO_2 and CH_4 conversion at 6 h reaction time obtained with the series of K and Sr promoted catalysts (nominal content of promoter = 1 wt.%), the catalysts deactivation (calculated as the difference between the CH_4 conversion at 1/2 h and 6 h, divided by the conversion at 1/2 h and multiplied by 100), and the molar percentage of deposited carbon (in mol of carbon deposited per mol of carbon converted and multiplied by 100). The data corresponding to the unpromoted catalyst Co(9.0) (also presented in Table 1), tested in a previous work [14], have been included as a reference. It can be observed that the CH_4 conversion is lower than the CO_2 conversion for all catalysts. It means that the side reaction $CO_2 + H_2 \rightarrow CO + H_2O$ takes place, increasing the CO_2 conversion. In all cases, the presence of a promoter leads to a lower carbon deposit

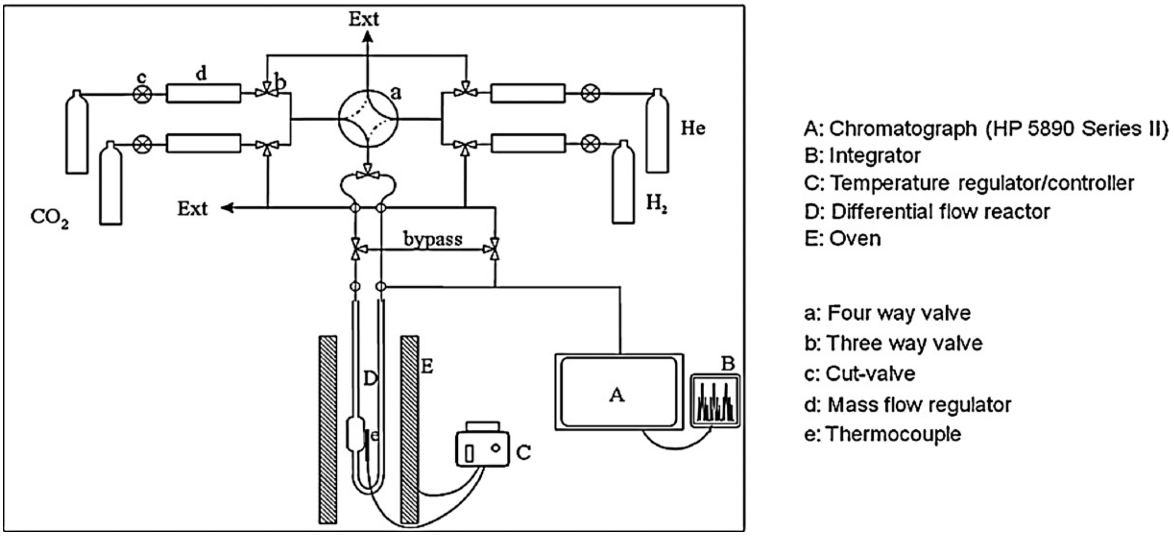

Fig. 1. Schematic diagram of the experimental set up.

Table 2
CO_2 and CH_4 conversion, deactivation and amount of deposited carbon for K and Sr cobalt promoted catalysts.

Catalyst	Impregnation method	% CO_2 conv.	% CH_4 conv.	Deac.[a] (%)	Deposited carbon[b]
Co(9.0)	–	82	73	1	0.53
KCo(1.0–9.0)	Coimpregnation	70	58	3	0.08
SrCo(1.0–9.0)	Coimpregnation	72	62	2	0.24
K–Co(1.0–9.0)	Successive	68	56	5	0.09
Sr–Co(1.0–9.0)	Successive	70	58	2	0.19

[a] Calculated as ((CH_4 conversion at 1/2 h – CH_4 conversion at 6 h)/CH_4 conversion at 1/2 h)) × 100.
[b] Calculated as (mol of deposited carbon/mol of converted carbon) × 100, after 6 h reaction time.

but a certain decrease of the CH_4 conversion is also detected. Data of Table 2 show a negligible effect of the preparation method (successive impregnation or coimpregnation) in all parameters evaluated, i.e. conversion values, stability and percentage of deposited carbon. Concerning the catalysts selectivity, it has to be underlined that the amount of deposited coke represents a very low percentage of the carbon involved in the reaction. In the case of the sample with the largest amount of deposited carbon (Co(9) reference catalyst [14]), the amount of coke is close to 0.5% molar of the carbonaceous products (C, CO).

Regarding the nature of the promoter, it can be clearly stated that K is more effective than Sr to hinder the carbon deposition and that both promoters produce a similar decrease in the CH_4 conversion. The performance of Sr and K as promoters in the present work agrees with that previously observed for Ni/Al_2O_3 catalysts [23]. Thus, it can be concluded that K is a better promoter than Sr to diminish the carbon deposition on the Co(9) catalyst (Co/Al_2O_3 (actual Co content = 7.6 wt.%)), and also that the promoter addition by coimpregnation can be used without any drawback respect to the successive impregnation method.

To further investigate the role of K as promoter, the next section is devoted to the study of the effect of the potassium amount in the promoted Co catalysts.

3.2. Effect of the K content

As indicated in the experimental section, four K catalysts with different nominal potassium content – KCo(0.2–9.0), KCo(0.6–9.0), KCo(1.5–9.0), KCo(5.0–9.0) – have been prepared, characterized and tested for the dry reforming of methane. The actual K and Co content of these catalysts is shown in Table 1.

Fig. 2 shows the methane conversion profiles and the molar percentage of deposited carbon of the K promoted catalysts. Data corresponding to the unpromoted catalyst Co(9) [14] have been also included as a reference. CO_2 conversion profiles are similar to those of CH_4 and are not shown for simplicity.

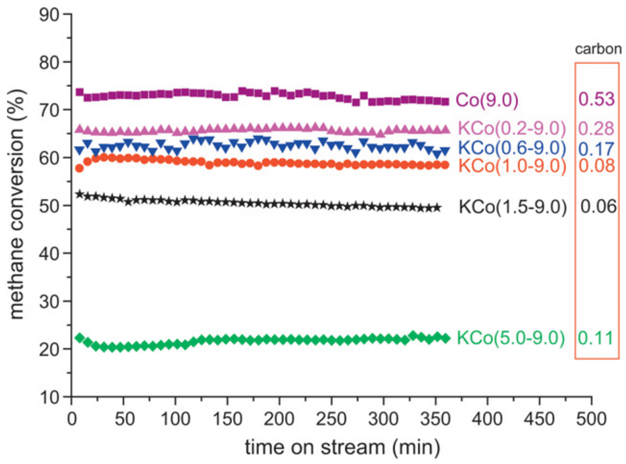

Fig. 2. CH_4 conversion profiles and amount of deposited carbon (in mol of carbon deposited per mol of carbon converted and multiplied by 100) of the KCo/Al_2O_3 catalysts. Effect of potassium content (6 h, 973 K, SV = 20,000 h^{-1}, $CH_4:CO_2$ 1:1).

It is observed that, in general terms, as the K content increases, both, the methane conversion and the molar percentage of deposited carbon decrease. Note that CH_4 conversion values for catalysts KCo(0.2–9.0), KCo(0.6–9.0) and KCo(1.0–9.0) are quite similar and high enough, however, marked differences are observed in the percentage of deposited carbon. It has to be pointed out that, compared to the unpromoted catalyst, the CH_4 conversion of catalyst KCo(1.0–9.0) is acceptably high but carbon deposition is drastically reduced (from a molar percentage of 0.53% to 0.08%). It is also remarkable that when the K content increases from 0.6 wt.% (catalyst KCo(1.0–9.0)) to 1.0 wt.% (catalyst KCo(1.5–9.0)), the CH_4 conversion decreases from 58% to 49% but the effect in the percentage of deposited carbon is very low, as it is reduced from 0.08% to 0.06% molar of converted carbon. Finally, for the sample with the highest K loading (KCo(5.0–9.0)) the percentage of deposited carbon is low (0.11%) but the CH_4 conversion is seriously diminished (to about 20%). Catalyst KCo(1.0–9.0) must be pointed out among the samples investigated, as it presents a relatively high CH_4 conversion and the percentage of deposited carbon is quite low. From these data it can be concluded that the optimum K content seems to be around 0.6 wt.%.

In order to explain the role of potassium, which reduces the carbon deposit but also produces some decrease of the methane conversion, the used catalysts have been characterized by TEM and EDX. TEM images show some differences in the average size of the Co particles in the KCo catalysts (Fig. 3 shows, as an example, pictures corresponding to catalysts KCo(1.0–9.0) and KCo(5.0–9.0)). The catalysts with low K content (i.e. KCo(0.2–9.0), KCo(0.6–9.0), KCo(1.0–9.0) and KCo(1.5–9.0)) present an average metal particle size around 10 nm, while the average metal particle size in catalyst KCo(5.0–9.0) is 40 nm. These results suggest that the notable decrease of CH_4 conversion given by catalyst KCo(5.0–9.0) can be due to the loss of dispersion, i.e. to the decrease in the amount of active sites for methane decomposition that, obviously, will also contribute to decrease the amount of deposited carbon.

On the other hand, the EDX analysis of the metal particles reveals that cobalt is the main component but a small amount of potassium is also detected (one of the analyzed areas is marked in Fig. 3b). As described in the Introduction section, potassium can reduce the carbon deposits by inhibition of reaction (2) or by favoring the reverse of reaction (3). Taking into account the EDX analysis, it is presumed that K has a double role: (i) it covers a fraction of active sites, thus inhibiting the methane decomposition and, as consequence, decreasing both CH_4 reforming and decomposition and (ii) catalyzes the gasification of the generated carbon by the reverse of reaction (3). The partial coverage of the cobalt active sites by potassium allows explaining the relative low decrease of the CH_4 conversion for the low K content catalysts (KCo(0.2–9.0), KCo(0.6–9.0), KCo(1.0–9.0) and KCo(1.5–9.0)). In the case of the promoted catalyst with the highest K content (KCo(5.0–9.0)), the loss of cobalt active sites is also due to a larger average particle size and thus a significant decrease of the CH_4 conversion is observed.

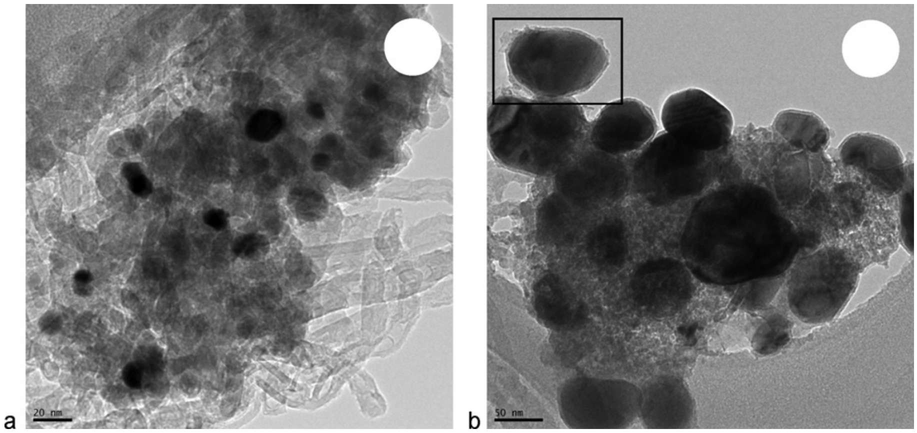

Fig. 3. TEM images of used catalysts: (a) KCo(1.0–9.0) and (b) KCo(5.0–9.0).

4. Conclusions

The study of the alumina-supported K and Sr promoted cobalt catalysts carried out in this work allows concluding that:

- Catalysts prepared by coimpregnation and by successive impregnation give similar results and thus, the first one, can be the method of choice because it is simpler.
- KCo and SrCo catalysts (nominal 1 wt.% K or Sr) show a similar catalytic activity, but the KCo catalysts give a lower carbon deposit, indicating that K is a more effective promoter than Sr.
- An increase of the K content produces a decrease of the percentage of deposited carbon but, also, of the methane conversion. The optimum K content for alumina supported Co catalysts (nominal 9 wt.%) seems to be around 0.6 wt.%. With this composition the catalyst presents an acceptably high methane conversion (60%) and a quite low percentage of deposited carbon (0.08% molar of the converted carbon).
- The effect of K, which reduces the carbon deposits but also the catalytic activity, can be explained by its ability to catalyze the carbon gasification and by a partial coverage of cobalt active sites for methane decomposition. In the case of catalyst KCo(5.0–9.0), potassium seems also to have lead to a larger average size of the Co particles and consequently to a reduction of the number of active sites.

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