

## Mixtures of Steel-Making Slag and Carbons as Catalyst for Microwave-Assisted Dry Reforming of CH<sub>4</sub>

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**Abstract:** The use of steel-making slag as catalysts for microwave-assisted dry reforming of CH<sub>4</sub> was studied. Two carbon materials (an activated carbon and a metallurgical coke), mixtures of the carbon materials and Fe-rich slag, and mixtures of the carbon materials and Ni/Al<sub>2</sub>O<sub>3</sub> were tested as catalysts. The mixtures of slag with carbons gave rise to higher and steadier conversions than those achieved over the carbon materials alone. In addition, the use of the metallurgical coke mixed with metal-rich catalysts gave rise to remarkable results. Thus, no CH<sub>4</sub> and CO<sub>2</sub> conversions were achieved when coke was used alone, whereas high conversions were obtained when it was mixed with the metal-rich catalysts.

**Key words:** steel-making slag; carbon catalyst; dry reforming; microwave heating

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In recent years, the process of dry reforming (CH<sub>4</sub> + CO<sub>2</sub> ↔ 2H<sub>2</sub> + 2CO) has been proposed as a promising technology, not only because syngas is produced with an adequate H<sub>2</sub>/CO ratio for the production of liquid hydrocarbons but also because methane and carbon dioxide, both greenhouse gases, are converted into valuable feedstock [1]. One of the major obstacles for the industrial application of this technology is that there are no effective catalysts which operate without undergoing deactivation due to carbon deposition. Numerous attempts have been carried out in order to develop catalysts for this process. Noble metals have been addressed as the most efficient catalysts for the CO<sub>2</sub> reforming of CH<sub>4</sub> reaction. Nevertheless, Ni-based catalysts are preferred since they are cheaper and exhibit high activity for dry reforming with moderate resistance to carbon deposits [2]. Other conventional metal-based catalysts have also been evaluated, such as Fe catalysts. In general, Fe catalysts have shown poorer activity and selectivity than Ni-based catalysts [3]. However, the substitution of Ni by low contents of Fe (i.e. Ni-Fe catalysts) has promoted more stable catalysts [4].

The use of carbon materials as catalysts for the dry reforming reaction has also been proposed [5,6], including chars from biomass residues [7]. Carbon-based catalysts offer some advantages over metal catalysts, such as availability, durability, and low cost. In addition, carbon materials usually have the ability to absorb microwaves, which makes them adequate catalysts for microwave-assisted CO<sub>2</sub>

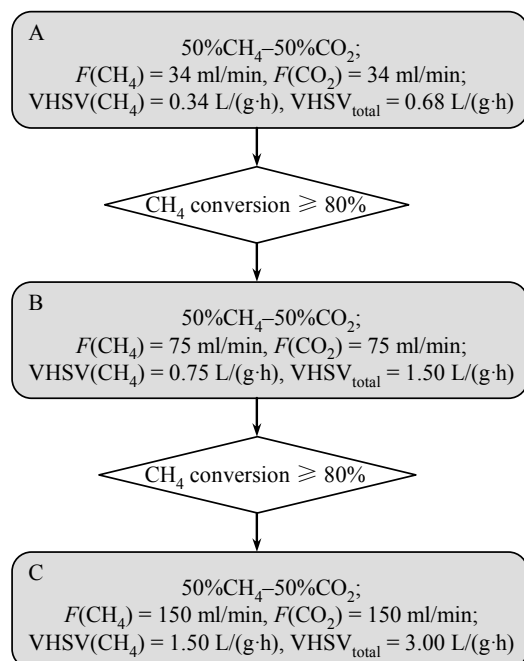
reforming of methane. Microwave heating, which is an alternative to conventional heating methods, is known to enhance heterogeneous and homogeneous catalytic reactions [6,7].

The aim of this work is to investigate the catalytic activity of steel slag, a Fe-rich waste material produced during the process of steel making, in the microwave-assisted dry reforming of CH<sub>4</sub>. In order to compare the performance of this residue as catalysts, alternative carbon catalysts and conventional Ni-based catalyst are also studied.

### 1 Experimental

Microwave-assisted CO<sub>2</sub> reforming of CH<sub>4</sub> was carried out using as catalyst Fe-rich steel-making slag (labeled as eFe, with 15.2 wt% of Fe content) mixed with a carbonaceous material (an activated carbon, FY5, or a metallurgical coke, CQ) in a proportion 1:1 (wt%). In order to evaluate the performance of the Fe-rich residue as catalyst, mixtures of the carbon materials with an in-lab prepared catalyst of Ni/Al<sub>2</sub>O<sub>3</sub> (5 wt% of Ni content) were also tested.

Experiments were conducted in a quartz reactor charged with 6 g of catalyst, previously dried overnight at 100 °C, and heated up to 800 °C in a single mode microwave oven (MW). Details of this equipment setup have been described elsewhere [6]. As shown in Scheme 1, experiments were carried out in three steps of 180 min each, according to the operating conditions and conversion requirements.



**Scheme 1.** Protocol followed in the evaluation of the mixtures of metal-rich fraction with a carbonaceous material used as catalysts in the dry reforming reaction.  $F(\text{CH}_4)$ , flow rate of methane;  $F(\text{CO}_2)$ , flow rate of carbon dioxide;  $\text{VHSV}(\text{CH}_4)$ , methane volumetric hourly space velocity, defined as  $\text{CH}_4$  flow rate (L/h)/mass of catalyst (g);  $\text{VHSV}_{\text{total}}$ , total volumetric hourly space velocity, defined as total flow rate (L/h)/mass of catalyst (g).

Produced gases were analyzed in a Varian CP-3800 gas-chromatograph equipped with a TCD detector. Concentrations in the effluent gas were used for calculating the conversions of  $\text{CH}_4$  and  $\text{CO}_2$  as follows.

$$\text{CH}_4 \text{ conversion} = [\text{H}_{2,\text{out}}/2]/[\text{CH}_{4,\text{out}} + \text{H}_{2,\text{out}}/2]$$

$$\text{CO}_2 \text{ conversion} = [\text{CO}_{\text{out}}/2]/[\text{CO}_{2,\text{out}} + \text{CO}_{\text{out}}/2]$$

## 2 Results and discussion

Preliminary heating tests of steel-making slag (eFe) showed that this residue does not absorb microwave energy, i.e. steel slag is not a microwave receptor. Therefore, it must be mixed with an absorber material (in the present work, a carbonaceous material) in order to be heated and used as catalyst for the microwave-assisted dry reforming reaction.

Proximate and elemental analyses of the carbon materials are summarized in Table 1. Chemical composition of the steel-making slag is reported in Table 2. Additionally, tex-

**Table 2** Chemical composition of the steel-making slag eFe

Composition	Content (wt%)
CaO	41.7
$\text{Fe}_2\text{O}_3$	21.7
$\text{SiO}_2$	15.0
MgO	3.7
MnO	3.5
$\text{Al}_2\text{O}_3$	2.3

tural data of FY5 and  $\text{Ni}/\text{Al}_2\text{O}_3$  are shown in Table 3. Data for the metallurgical coke and Fe-rich slag are not included since they showed no textural development (negligible BET surface area and pores volume).

**Table 3** Textural properties of the materials used as catalysts

Sample	$A_{\text{BET}}/$ ( $\text{m}^2/\text{g}$ )	$V_t/$ ( $\text{cm}^3/\text{g}$ )	$V_{\text{mes}}/$ ( $\text{cm}^3/\text{g}$ )	$V_{\text{mic}}/$ ( $\text{cm}^3/\text{g}$ )	$V_{\text{umic}}/$ ( $\text{cm}^3/\text{g}$ )
FY5	826	0.34	0.03	0.32	0.25
$\text{Ni}/\text{Al}_2\text{O}_3$	166	0.51	0.50	0.07	—

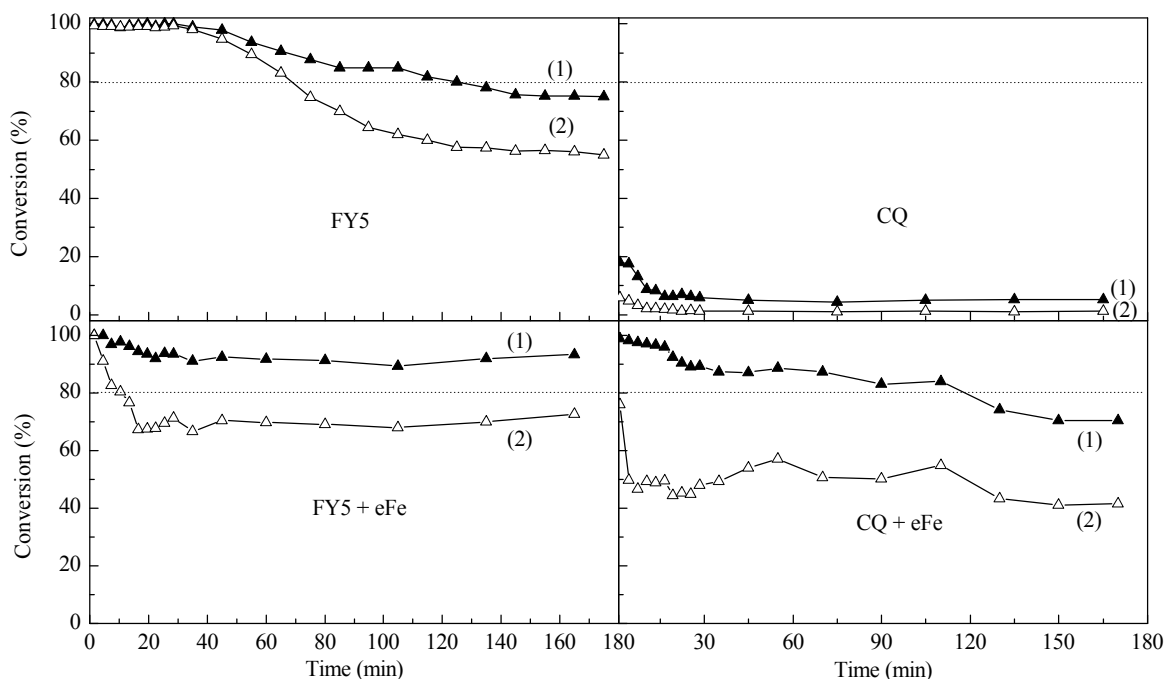
$A_{\text{BET}}$ : BET surface area;  $V_t$ : total pores volume;  $V_{\text{mes}}$ : mesopores volume;  $V_{\text{mic}}$ : micropores volume;  $V_{\text{umic}}$ : ultramicropores volume.

Conversions over FY5 and the mixture of FY5 + eFe and CQ and the mixture CQ + eFe are shown in Fig. 1.  $\text{CO}_2$  and  $\text{CH}_4$  conversions can be very different depending on the carbon material use as catalyst [5]. In general, active sites on carbon surface for dry reforming are high-energy surface defects. Initial catalytic activity of carbon materials seems to be related to the BET surface area or to the oxygen surface groups, specifically those are desorbed as CO in TPD experiments. The long-term stability of a carbon catalyst correlates with the BET surface area and the micropores volume, since the loss of catalytic activity of a carbon depends on the quantity of carbonaceous deposits that can accumulate before it becomes deactivated. Activated carbons present a high initial activity but they become rapidly deactivated as carbonaceous deposits block the pore mouths [8]. Thus, FY5, which has a large micropores volume, gave rise to high initial conversions followed by a rapid drop of conversion, especially in the case of  $\text{CH}_4$  [6], whereas metallurgical coke CQ, with no textural development, was found to be a poor catalyst for dry reforming reaction. As can be seen, the mixtures of carbon + eFe gave rise to higher and steadier conversions than those obtained with the carbon materials alone. Interestingly, the mixture of slag

**Table 1** Main chemical characteristics of the carbonaceous materials used as catalysts

Sample	Moist (wt%)	Ash content <sup>a</sup> (wt%)	Volatile matter content <sup>a</sup> (wt%)	Elemental content <sup>a</sup> (wt%)				
				C	H	N	S	O <sup>b</sup>
FY5	8.5	2.1	2.8	94.1	0.7	0.3	0.0	2.8
CQ	0.1	11.7	0.6	86.6	0.1	1.1	0.5	0.0

<sup>a</sup>Dry basis. <sup>b</sup>Calculated by difference.

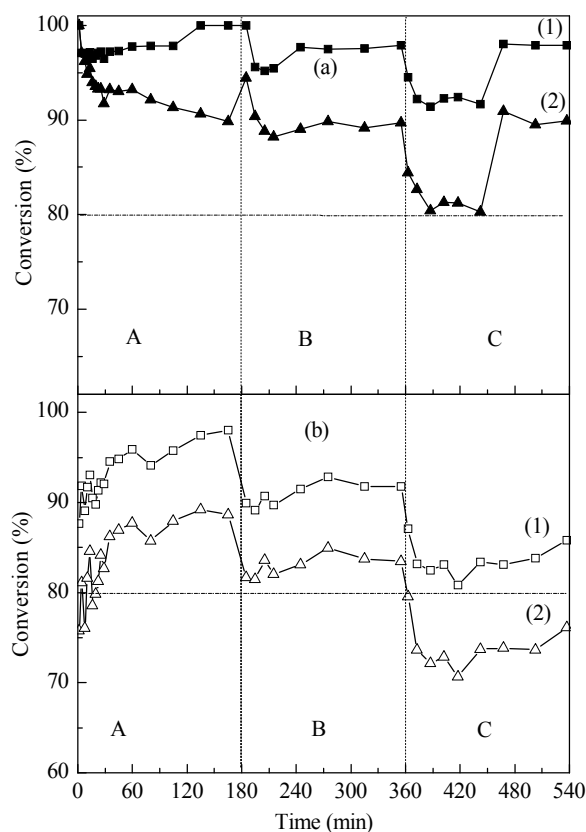


**Fig. 1.** CO<sub>2</sub> (1) and CH<sub>4</sub> (2) conversions for dry reforming carried out over FY5, FY5 + eFe, CQ, and CQ + eFe. All the experiments were carried out under the experimental conditions specified in step A of the protocol that is shown in Scheme 1.

and coke (CQ + eFe) gave rise to moderate but steady conversions (discarding first points). Thus, CH<sub>4</sub> and CO<sub>2</sub> conversions improved significantly regarding those achieved with CQ alone. In the case of FY5 + eFe, steady conversions were also obtained and the rapid deactivation observed over FY5 alone was avoided. Therefore, the addition of Fe-rich slag improved the activity of the catalytic mixtures. Nevertheless, the type of carbon material used had also a notably influence on the performance of the mixture. Thus, FY5 + eFe was better catalyst than CQ + eFe, which shows that the carbon fraction of the catalytic mixtures acted not only as microwave receptors but also as catalyst.

In order to assess the catalytic activity of steel-making slag, the mixtures of carbon + eFe were compared with mixtures of carbon + Ni/Al<sub>2</sub>O<sub>3</sub>. As it was expected, mixtures of carbon materials with Ni/Al<sub>2</sub>O<sub>3</sub> were better catalysts than mixtures those with eFe. As can be seen in Fig. 2, it is possible to maintain conversions near to 100% by using the catalytic mixtures of carbons with Ni/Al<sub>2</sub>O<sub>3</sub>, even though VHSV<sub>total</sub> was increased stage by stage (VHSV<sub>total</sub> was about six times higher than that used with FY5 and CQ alone, and the mixtures with eFe).

It can be observed that conversions over mixtures with FY5 were again higher than over mixtures with CQ. Nevertheless, improvement in catalytic activity was much more significant for CQ, changing from no CH<sub>4</sub> conversion to about 80%, even after increasing VHSV<sub>total</sub>. This result shows that residual fractions of metallurgical coke could be used as catalysts/microwave receptors for dry reforming.



**Fig. 2.** CO<sub>2</sub> (1) and CH<sub>4</sub> (2) conversions for dry reforming carried out over mixtures of two different carbon materials and an in-lab prepared Ni-based catalyst. (a) FY5 + Ni/Al<sub>2</sub>O<sub>3</sub>; (b) CQ + Ni/Al<sub>2</sub>O<sub>3</sub>. Reaction conditions of A, B, and C are shown in Scheme 1.

### 3 Conclusions

Steel-making slag can be used as catalyst for microwave-assisted dry reforming. However, they must be mixed with a microwave absorber, i.e. a carbon material, since slag is not an absorber and therefore it does not heat in the microwave oven. Conversions achieved using mixtures of carbon material + Fe-rich slag are found to be higher and steadier than those obtained over the carbon materials alone. Catalytic activity of the mixtures depends on the carbon material selected. Thus, higher conversions are achieved using an activated carbon in the mixture than using a metallurgical coke. In fact, the activated carbon alone is better catalyst than the metallurgical coke, which shows no activity for the dry reforming reaction. Nevertheless, the activity of metallurgical coke is dramatically improved when a metal-rich fraction is added, specially mixed with Ni-based catalyst. Actually, mixtures of carbon materials with Ni/Al<sub>2</sub>O<sub>3</sub> give rise to higher conversions than mixtures with slag, allowing

VHSV<sub>total</sub> to be increased while high conversions are kept.

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