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Gasification of metal-containing coals and carbons *via* their reaction with carbon dioxide

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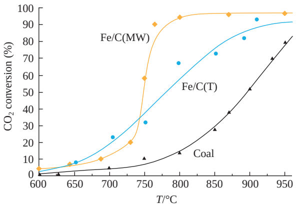
The effect of the nature of the metals (Cu, Ni, and Fe) deposited on carbon materials (coals) and the methods of preparation (conventional and microwave heating) of the most active Fe/C samples on their efficiency in the reaction of CO_2-assisted conversion of coal into carbon monoxide is estimated.



Due to the current world trend of a constantly growing energy consumption, there is an increasing trend to use alternative sources of organic raw materials, including low-quality coals. It is possible to produce liquid fuels and practically most of all important products of petrochemistry *via* advanced processing of coals and other carbon materials (soot, coal dust, brown coal, turf, *etc.*).[1–4] The above trend is also related to the utilization of a greenhouse gas (CO_2),[5] but the majority of works are aimed at the hydrogenation of CO_2 in order to produce the synthetic natural gas (methane) or carbon monoxide.[6]

Carbon dioxide assisted gasification of coal (CDGC) is well known in the mining industry for underground gasification of coal.[7] However, this process leads only to the formation of carbon monoxide.[8] In the gasification zone, the following endothermic reaction occurs:

$$CO_2 + C \rightarrow 2CO\ (\Delta H = -173\ \text{kJ mol}^{-1}).$$

One of the reports[9] proposed an application of additives containing catalytically active metals (iron, nickel, zinc or their oxides) for the intensification of CDGC process. The greatest activity was revealed[10] for the supported nickel, which provided a much higher degree of CO_2 conversion in the temperature range of 600–800 °C as compared to the non-catalytic process.

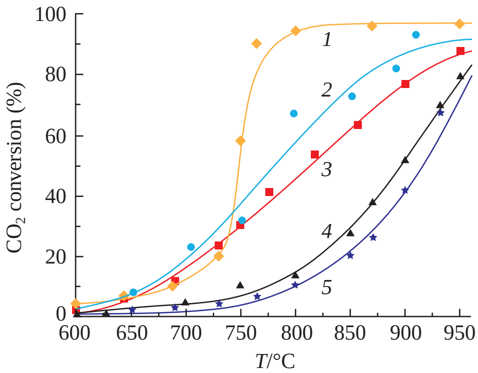


Figure 1 CO_2 conversion curves for the samples: (*1*) Fe/C(MW), (*2*) Fe/C(T), (*3*) Ni/C, (*4*) coal, (*5*) Cu/C recorded during CDGC into carbon monoxide.

Thus, very high temperatures (up to 1000 °C) are needed for efficient CO_2 conversion of coal into carbon monoxide, and in terms of the recovery of coals and other spent carbon materials, the temperature reduction in the CDGC process remains a very urgent task, which requires new approaches.

Figure 1 shows CO_2 conversion curves recorded during CDGC reaction for original and metal-containing coals,† wherein one may see that not all metals supported on coal can catalyze the CDGC reaction. For example, the conversion curve for the Cu/C sample is shifted to the range of higher temperatures. Such an inefficient behavior can be explained by easy reduction of copper into the metal phase Cu^0 in the CO environment and by a subsequent agglomeration at high temperatures.[11] It is also evident that supported nickel significantly intensifies the reaction. However, the most surprising results were obtained for the iron-containing samples. In case of the Fe/C(T) sample prepared under conventional heating conditions similar to the nickel-containing sample,

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† Activated coal CKT-6A (Table S1 in Online Supplementary Materials) was used as a carbon material. The samples of metal-containing coals, Cu/C and Ni/C, were prepared *via* impregnation of the coal with water solutions of $Cu(NO_3)_2$ and $Ni(NO_3)_2$, respectively. The preparation of iron-containing samples, Fe/C(T) and Fe/C(MW), was also carried out *via* impregnation, but with a mixture of $Fe(NO_3)_3$ and $CO(NH_2)_2$ (at molar ratio of 2 : 1). The introduction of urea allows one to control the composition of oxide phases due to the reducing environment during the synthesis process,[12] and to obtain more dispersed samples.[13,14] After the impregnation, the wet sample Fe/C(T) was dried in air at 90 °C for 1 h and then calcined in air at 350 °C for 1 h. The wet sample Fe/C(MW) was placed in a Landgraf MW 4000 (800 W) laboratory microwave oven and dried in air for 5 min. The average temperature of sample Fe/C(MW) during the microwave treatment process was about 600 °C. The temperature was measured by a MEGEON 16900 IR-temperature meter. The metal content in all samples was 3 wt%.

The catalytic reaction of coal conversion with CO_2 was carried out under atmospheric pressure in a flow-type quartz reactor (diameter of 7 mm) with the gradual increase of temperature from 500 °C to 1000 °C at the steps of 50 °C (space velocity was 500 h^{-1}). Due to the coal oxidation into CO, the coal was taken in excess for the reaction. In each catalytic experiment, the amount of metal-containing coal was 1 g. The analysis of gas composition after the reaction was performed by GC.

the conversion curves exhibit a shift towards lower temperatures, which also proves the intensification of the catalytic reaction. However, the use of Fe/C(MW) sample prepared *via* the microwave heating in air as a catalyst caused a dramatic rise of the conversion curve at about 730 °C. To understand the reasons of this phenomenon, it is necessary to know the phase composition of the sample and its changes during the catalytic reaction.

Taking into account the XRD patterns (Figure S1 in Online Supplementary Materials), one can see that the initial Fe/C(T) sample before the CDGC reaction contained a mixture of iron oxides, Fe_2O_3 and Fe_3O_4. In contrast to Fe/C(T), the initial Fe/C(MW) sample contained only a magnetite phase, Fe_3O_4. The average crystallite sizes of iron oxide nanoparticles contained in both samples were calculated by the Debye–Scherrer equation as equal to 7–8 nm and 10–12 nm, respectively. The XRD results revealed that the iron oxides in the Fe/C(T) sample were reduced to FeO by CO formed during the CDGC reaction. It is also clear that in the case of Fe/C(MW) sample, the deeper reduction occurs with the formation of metallic iron (Fe^0) and iron carbide (Fe_3C). This fact allows one to conclude that the metallic iron (and, perhaps, iron carbide) formed at the initial step of CDGC reaction with the Fe/C(MW) sample (obtained *via* the non-traditional microwave heating in air at 600 °C) can catalyze this reaction, which is the reason of the sharp increase in the CO_2 conversion at 730 °C (see Figure 1).

To better understand the nature of the enhanced activity of Fe/C(MW) sample, the thermodynamic calculations of formation possibility for the different catalytically active iron phases were performed taking into account the CO_2 atmosphere and the interactions with all starting components.[‡]

Figures 2 and 3 show the thermodynamic calculation results for the Fe/C(MW) sample, which contains Fe_3O_4 only. Thus, Fe_3O_4 is capable of being reduced into FeO and Fe^0 even in the absence of carbon monoxide. The supported Fe_3O_4 phase on the coal can be also converted into iron carbide (Fe_3C), then the process starts at about 780 °C, and the complete stoichiometric transformation of Fe_3O_4 into Fe_3C is possible at 850 °C (see Figure 3). These calculations additionally confirmed the obtained XRD data for the Fe/C(MW) sample, which testified to the formation of catalytically active phases (Fe^0 and Fe_3C) after beginning of the catalytic reaction.

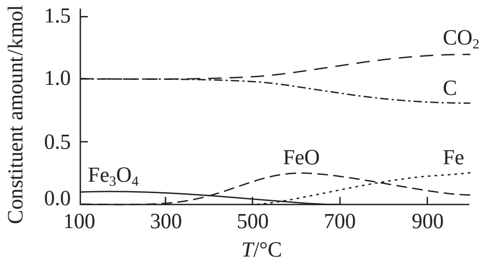

Figure 2 Concentrations of reagents and products at the thermodynamic equilibrium *vs.* temperature at atmosphere pressure for the reaction $Fe_3O_4 + CO_2 + C \rightarrow Fe + FeO$.

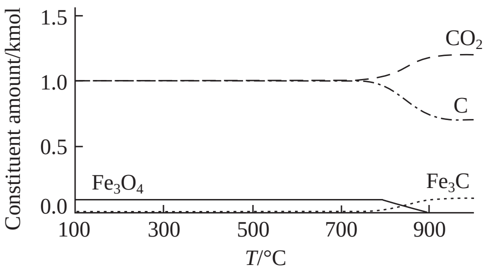

Figure 3 Concentrations of reagents and products at the thermodynamic equilibrium *vs.* temperature at atmosphere pressure for the reaction $Fe_3O_4 + CO_2 + C \rightarrow Fe_3C$.

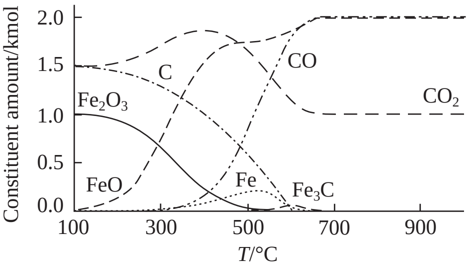

Figure 4 Concentrations of reagents and products at the thermodynamic equilibrium *vs.* temperature at atmosphere pressure for the reaction $Fe_2O_3 + CO + CO_2 + C \rightarrow Fe_3C + Fe^0 + FeO$.

The thermodynamic calculation for the Fe_2O_3 phase in the Fe/C(T) sample in the presence of CO_2 shows the intensive formation of FeO (similar to the microwave sample), but in contrast with the Fe/C(MW) sample, the formation of Fe^0 and Fe_3C phases is not observed (these results are not shown). The calculations (Figure 4) also indicate that the formation of Fe^0 and Fe_3C is possible only in the carbon monoxide atmosphere (which is a strong reducing agent). The largest amounts of Fe^0 and Fe_3C are formed at 540 and 600 °C, respectively, herewith the formation of carbon monoxide is not observed at these temperatures (the CO conversion does not exceed 5%, see Figure 1). It is necessary to note that even in the CO environment the stoichiometric amounts of Fe^0 and Fe_3C with respect to the initial Fe_2O_3 phase are much smaller than in the case of their formation from Fe_3O_4 in the Fe/C(MW) sample.

The performed thermodynamic calculations are in agreement with the results of both XRD and catalytic tests. The phase composition of the initial iron-containing component of coal was revealed as playing the key role in the coal conversion reaction with CO_2. It can be deduced that the reaction proceeds at the lower temperature range due to the presence of metallic iron nanoparticles (and, perhaps, iron carbide nanoparticles) formed in the Fe/C(MW) sample during the reduction of the Fe_3O_4 phase. The application of Fe_2O_3 as the metal-containing component led to negligible intensification of the catalytic process.

In summary, the new preparation method of Fe/C samples by the non-traditional high-temperature microwave activation in air atmosphere has been developed, which allows one to selectively obtain the certain iron oxide species supported on a carbon material. This microwave-assisted method can be promising for the preparation of different supported catalysts containing other metals and supports.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2018.09.027.

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[‡] The thermodynamic calculations for the equilibrium concentrations of reagents and products, including the metal oxides reduction, were carried out using a HSC-4 software (Haldor Topsoe AS). The Fe_3O_4/C and Fe_2O_3/C molar ratios of 0.1 and 0.66, respectively, were selected for the quantitative representation of the calculations.

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