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APPLICATION OF THERMAL ANALYSIS IN RADIOCARBON DATING

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Abstract

Thermal analysis combined with mass spectrometry was applied to radiocarbon dating procedures (age determination of carbon containing samples) to determine the optimal temperature range for the reduction of CO_2 over metallic cobalt of various particle sizes. Experiments were carried out to show the different catalytic activities of cobalt of particle sizes 1, 1–45 and 44 μm. The morphology of the cobalt samples and the deposited carbon were investigated. The quantification of CH_4 and CO formed during the reduction of CO_2 was done by means of pulse thermal analysis.

Keywords: pulse thermal analysis, thermal analysis in radiocarbon dating

Introduction

Radiocarbon dating is one of the main methods used for estimating the age of carbon containing materials [1]. It is based on the measurement of the concentration of the radioactive isotope ^{14}C that occurs in extremely small quantities. ^{14}C is continuously produced in the atmosphere by the interaction of cosmic ray neutrons with nitrogen molecules. The half-life of this isotope is 5 600 years. ^{14}C formed in the atmosphere oxidises to $^{14}CO_2$ and mixes with common $^{12}CO_2$. The ratio of ^{14}C to ^{12}C is, in nature, constant but when the continuous, dynamic cycle of carbon isotope exchange is stopped (e.g. death) then the amount of ^{14}C slowly reduces by radioactive decay (to ^{14}N) at a rate governed by its half-life. Thus, the age of carbon-containing matter can be determined by measuring its ^{14}C content. Elemental carbon isolated from the sample is the target used in ^{14}C-dating by accelerator mass spectrometry. Elemental carbon is produced by the catalytic reduction of CO_2 over magnesium [2], iron [3, 4], zinc [5] or metallic cobalt [6, 7]. In the presented paper thermal analysis was used to investigate and optimise the processes necessary for the formation of elemental carbon by the catalytic reduction of CO_2 over metallic cobalt.

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Experimental

A sample for radiocarbon dating is treated with hydrochloric acid to remove non-organic carbon in the form of carbonates, followed by a treatment with sodium hydroxide to remove humic acids formed during the rotting process. This procedure should leave only the carbon that was incorporated into the organism during its life-time. In order to obtain the carbon dioxide that is later used for the synthesis of elemental carbon a sample is heated in an evacuated sealed quartz tube with CuO as an oxygen source. The resulting carbon dioxide is mixed with hydrogen in the ratio 2.5:1 and catalytically reduced over cobalt powder to elemental carbon.

Cobalt powders of particle sizes 1, 1–45 and 44 μm (Johnson Matthey) were selected in order to study their catalytic activities in the laboratory-designed system used for catalytic conversion. In order to check the morphological properties of the different cobalt samples the BET surface area (krypton adsorption) and SEM analyses were undertaken. The determination of the amount of oxide in the cobalt samples was made under a 20 vol% H_2 atmosphere on a Netzsch STA 409 thermoanalyzer coupled to a QMG 420 (Balzers) quadrupole mass spectrometer. Investigation of the behaviour of the cobalt samples under a CO atmosphere was carried out under a 20 vol% CO, balance He, atmosphere. To study the reaction(s) that occur during the catalytic reduction of CO_2 the cobalt samples were heated in a CO_2:H_2 (1:2) atmosphere. The temperature was raised at a rate of 3 K min^{-1} over a range of 30 to 700°C. The formation of H_2O, CO and CH_4 over Co (1–45 μm) during the injection of 1 mL of CO_2 was quantified by pulse thermal analysis [8]. The same method was also applied for measuring the amount of H_2O, CO_2 and CH_4 formed during the injection of 1 mL of CO over Co (1–45 μm). The determination of the optimum temperature for the reduction of CO_2 by hydrogen over metallic cobalt (44 μm) was investigated in the range 480 to 580°C in the laboratory-designed system used for catalytic conversion.

Results and discussion

The dependence of pressure change, during the reduction of CO_2 in the laboratory-designed system, on the various particle sizes of the cobalt samples is presented in Fig. 1. The changes of pressure at the beginning of the reaction, as well as the pressure changes during the course of the reaction, indicate that the activity of the cobalt samples depends on their particle sizes. The particle size also influences the formation of undesirable gaseous products, manifested as a higher pressure in the system, which considerably delay the formation of carbon deposited as a result of CO disproportination (Boudouard reaction).

In order to check the morphological properties of the cobalt samples under study, the BET surface area (krypton adsorption) and SEM analyses were undertaken. The surface areas of the cobalt samples were determined to be:

44 μm:0.54 m^2 g^{-1} 1–45 μm:0.95 m^2 g^{-1} 1 μm:1.22 m^2 g^{-1}

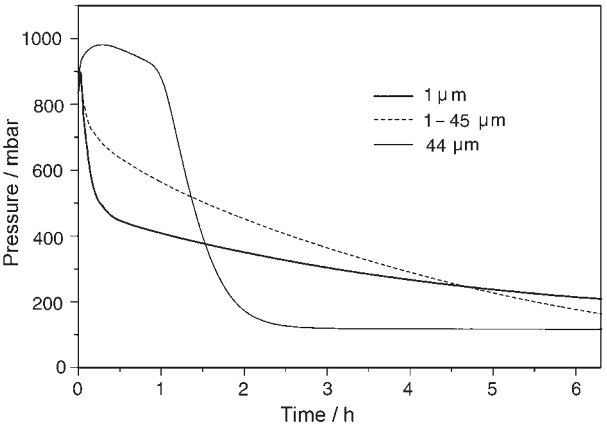

Fig. 1 Change of pressure due to reduction of CO_2 by hydrogen in the laboratory-designed system over metallic cobalt powder (1, 1–45, 44 μm) at 550°C

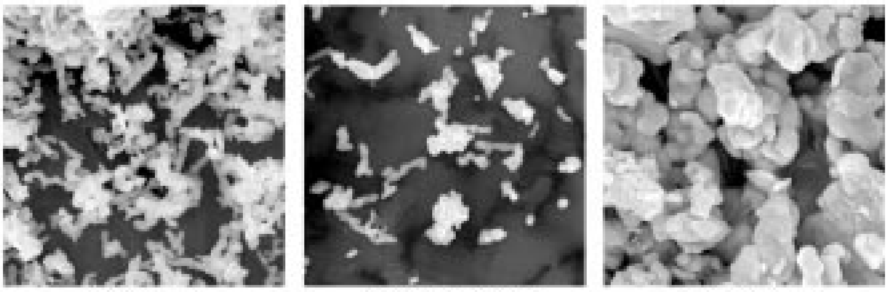
Cobalt 1 μm Cobalt 1–45 μm Cobalt 44 μm

Fig. 2 SEM microphotographs of the cobalt samples, the horizontal side has a length of 27.0 μm

The microphotographs presented in Fig. 2 show the morphology of the samples. The microphotographs of graphite (Fig. 3) deposited on these cobalt samples show the different morphologies in accordance to their particle sizes. The 1–45 μm cobalt particles catalyse the formation of filamentous carbon [9], common hexagonal graphite is formed on the 44 μm cobalt.

Thermal analysis combined with mass spectrometry was applied to optimise the formation of carbon by the catalytic reduction of CO_2 over metallic cobalt to CO and finally to carbon. Carbon formation should be: (i) fast, (ii) occur with maximum yield and (iii) lead to optimal morphological properties so that it can be used as a target in accelerator mass spectrometry. In the first step of the investigation, the amount of oxide phase present in the cobalt samples was investigated. The results of the TA-MS analysis (Fig. 4) of the reaction of CoO by hydrogen show that the amount of CoO present in the samples was: 3.7 mass% in the 1 μm, 3.2 mass% in the 1–45 μm and 1.6 mass% in the 44 μm sample. The reduction of the 1 μm cobalt sample occurs in

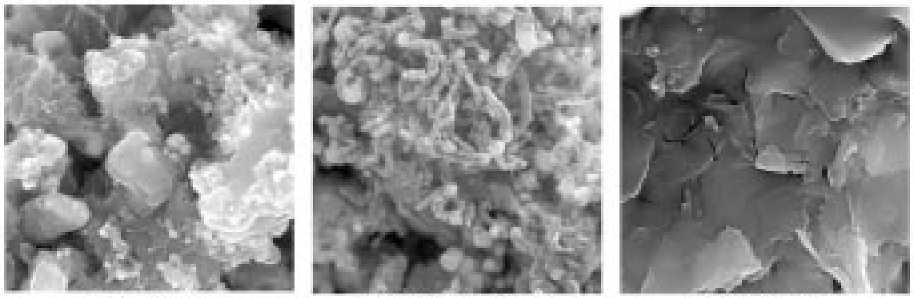
Cobalt 1 μm Cobalt 1–45 μm Cobalt 44 μm

Fig. 3 SEM microphotographs of graphite formed on the cobalt samples, the horizontal sides have lengths of 4.3, 2.1 and 27.0 μm respectively

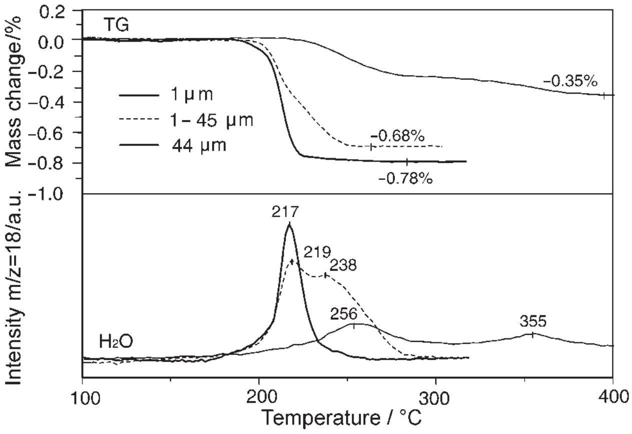

Fig. 4 TA-MS investigation of the reduction of the cobalt samples by 20 vol% H_2

the range 180–250°C with a maximum at 217°C. In the case of the 1–45 μm and 44 μm samples the reductions occur in two steps within the ranges 180–290 and 200–400°C, respectively.

To study the disproportionation of CO over the cobalt samples experiments were carried out under a 20 vol% CO atmosphere. Disproportionation of carbon monoxide takes place according to the Boudouard equilibrium, which can be presented by the equation:

$$2CO \leftrightarrow C+CO_2 \quad \Delta H=-173.4 \text{ kJ mol}^{-1} \tag{1}$$

The formation of carbon is exothermic and is favored at low temperatures. The reduction of CoO, present in the investigated cobalt samples, followed by carbon formation due to CO disproportionation, is shown in Fig. 5. The disproportionation of CO over the 1 and 1–45 μm samples starts at ca 330°C and at ca 300°C for the 44 μm sample and is reflected by the mass gain due to carbon formation. The interpretation of the TG and MS curves is difficult due to the simultaneous occurrence of both processes i.e. reduction of CoO and CO disproportionation.

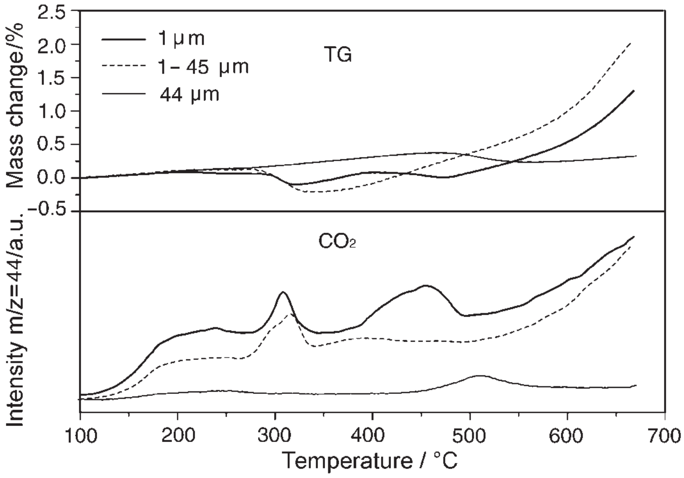

Fig. 5 TA-MS investigation of the reduction of the cobalt samples by 20 vol% CO and of carbon formation due to CO disproportionation

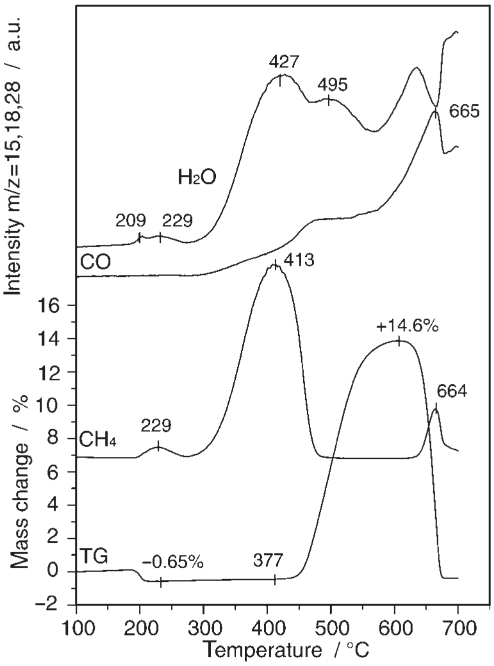

Fig. 6 TA-MS analysis of the 1 μm cobalt sample heated at a rate of 3 K min^{-1} under a CO_2:H_2 (1:2) atmosphere

To study the catalytic reduction of CO_2 over metallic cobalt the samples were heated in a CO_2:H_2 (1:2) atmosphere. The results are depicted in Figs 6–8. The 1 μm sample catalyses the formation of CH_4 with a maximum at 413°C. The results of TA-MS analysis show that the formation of carbon, due to CO disproportionation, occurs in the temperature interval ca 380–600°C (Fig. 6).

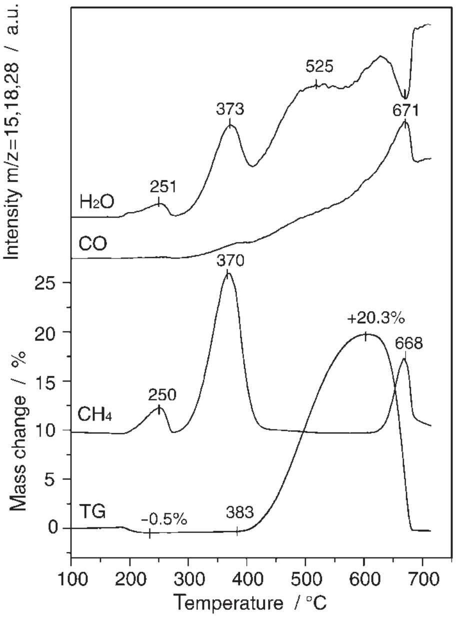

Fig. 7 TA-MS analysis of the 1–45 μm cobalt sample heated at a rate of 3 K min^{-1} under a CO_2:H_2 (1:2) atmosphere

The 1–45 μm sample also produces significant quantities of CH_4 with maximum production at 370°C. The carbon forms in the temperature interval 383 to 600°C (Fig. 7). The 44 μm cobalt sample does not catalyse CH_4 formation, CO begins to form at temperatures above 510°C (Fig. 8). The comparison of the change of mass and the formation of methane and carbon monoxide during the heating of each of the cobalt samples in a CO_2 : H_2 atmosphere shows the different catalytic activities of the cobalt samples, depending on their morphologies. The most active samples, 1 and 1–45 μm, catalyse the formation of CH_4 which leads to a decrease of carbon yield, moreover, above 600°C, carbon that has been already formed in the range 380–600°C reacts with gaseous products. This process distinctly decreases the yield of carbon formation by the reduction of CO_2 by hydrogen.

The quantification of the CO, CH_4 and CO_2 formed over the 1–45 μm cobalt sample during the injection of either 1 mL of CO_2 or 1 mL of CO into a 20 vol% H_2 atmosphere was carried out by pulse thermal analysis. The results shown in Figs 9 (CO_2 pulses) and 10 (CO pulses) allow the determination of the range of methane formation and the temperature of the beginning of CO disproportionation. In both cases, the

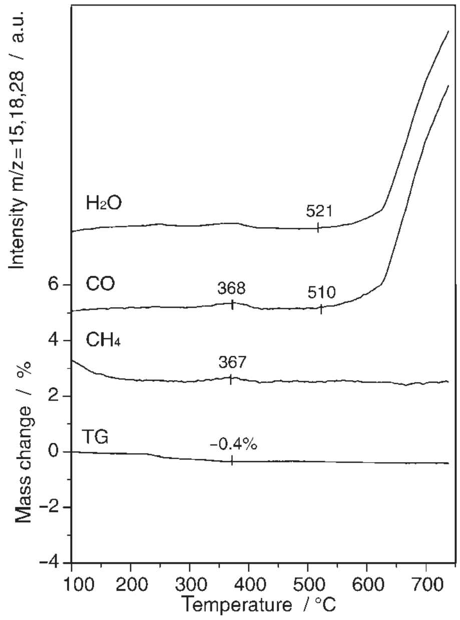

Fig. 8 TA-MS analysis of the 44 μm cobalt sample heated at a rate of 3 K min^{-1} under a CO_2:H_2 (1:2) atmosphere

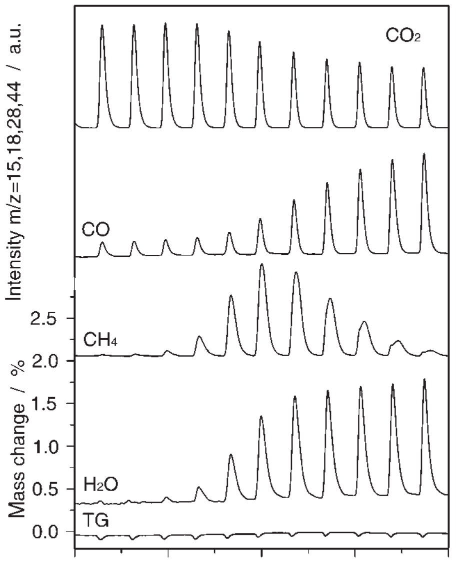

Fig. 9 Formation of H_2O, CO and CH_4 during the injection of 1 mL of CO_2 into a 20 vol% H_2, balance He, carrier gas stream flowing over the 1–45 μm cobalt sample heated at a rate of 3 K min^{-1}

amount of methane produced is negligible above 550°C but at temperatures below 400°C it is the main gaseous product. The reduction of CO_2 to carbon occurs in two steps; in the first, CO is formed in a reversed water-gas shift reaction:

$$H_2+CO_2 \rightarrow H_2O+CO \tag{2}$$

and in the second, CO disproportionation to carbon occurs according to reaction (1). In order to check the process of CO disproportionation in a hydrogen atmosphere, as carried out in the laboratory procedure, pulses of 1 mL CO were injected over the Co 1–45 μm sample into a 20 vol% H_2 atmosphere. The mass spectrometric signals m/z=15, 18 and 44, presented in Fig. 10, show the temperature range of possible processes such as methane formation, water-gas shift or Boudouard reactions. The formation of CH_4 occurs in the range 250–450°C, the visible mass gain due to carbon deposition begins at ca 350°C. Note the mass loss at temperatures above 500°C due to secondary reactions of the formed carbon with gaseous reactants and products. Similar phenomenon were observed in the experiments presented in Figs 6 and 7, however, direct comparison of all results can only be made qualitatively due to the varied experimental conditions. The yields of formation of CO and CH_4 during the injection of CO_2 into 20 vol% H_2 are presented in Fig. 11 A, the yields of formation of CH_4 and CO_2 during the injection of CO into 20 vol% H_2 are presented in Fig. 11 B.

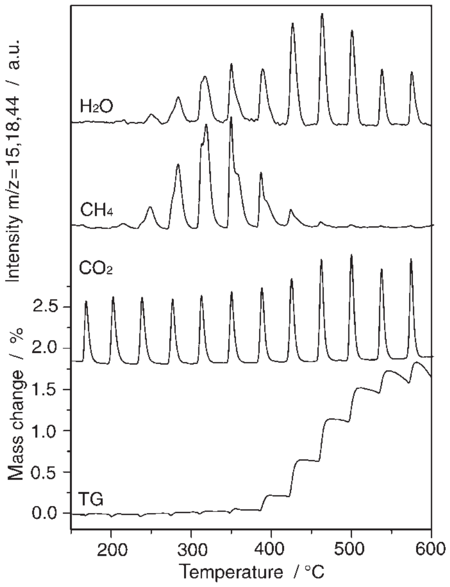

Fig. 10 Formation of H_2O, CO_2 and CH_4 during the injection of 1 mL of CO into a 20 vol% H_2, balance He, carrier gas stream flowing over the 1–45 μm cobalt sample heated at a rate of 3 K min^{-1}

The optimal temperature for the reduction of CO_2 over the 44 μm cobalt sample was investigated in the system used for the preparation of elemental carbon for radiocarbon dating. Changes of pressure, due to the reduction of CO_2 by hydrogen at various temperatures, are presented in Fig. 12.

An increase of temperature increases the reaction rates but formation of carbon, due to the Boudouard reaction, is favored at low temperatures. At higher tempera-

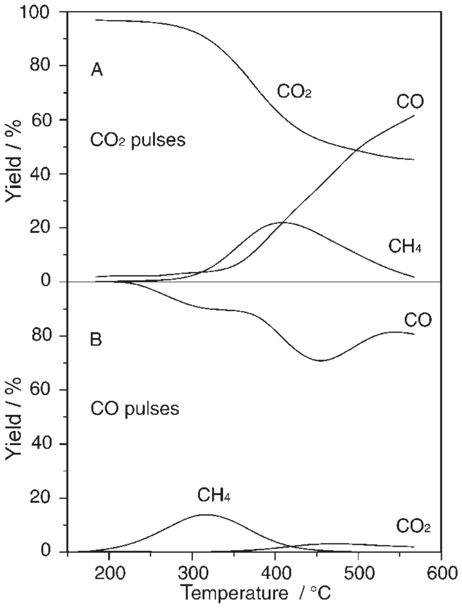

Fig. 11 (A) The yield of conversion of CO_2 into CO and CH_4 and (B) the yield of conversion of CO into CO_2 and CH_4 during the injection of 1 mL of CO_2, respectively CO, into a 20 vol% H_2, balance He, carrier gas stream flowing over the 1–45 μm cobalt sample heated at a rate of 3 K min^{-1}

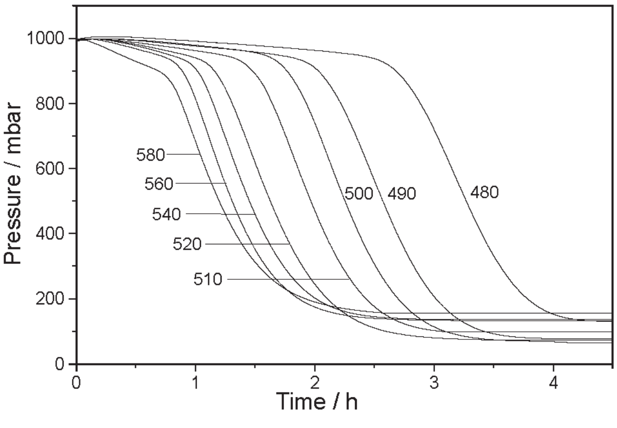

Fig. 12 Change of pressure due to the reduction of CO_2 by hydrogen in the laboratory-designed system over the 44 μm cobalt powder. The reduction temperatures (°C) are noted on the curves

tures the pressure drop in the system is smaller because, above 560°C, the carbon already formed reacts with the gaseous products. This process is undesirable because it decreases the amount of carbon produced.

Conclusions

The presented results indicate the necessity of choosing optimal temperature conditions and morphological properties of cobalt when it is used to catalytically reduce CO_2 to carbon. The cobalt samples exhibit different catalytic behaviors depending on their morphology.

The most active samples (1 μm) and (1–45 μm) catalyse the formation of CH_4 which decreases the carbon yield, moreover, above 600°C, carbon that has already been formed reacts with gaseous by-products and decreases the yield even further. In addition, the physical properties of these carbon–cobalt mixtures makes them unsuitable for accelerator mass spectrometry targets.

The 44 μm cobalt sample, as used in the laboratory system, does not catalyse CH_4 formation. The maximum reaction rate for this sample is reached at temperatures between 540 and 560°C but above 560°C, carbon that has already been deposited reacts with gaseous by-products, hence decreasing the yield. For optimal conditions the reaction temperature should not be set higher than 560°C. The 44 μm cobalt sample catalyses the formation of hexagonal graphite which, together with the cobalt, have physical properties that make it a very good target material.

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