Contents lists available at ScienceDirect



# Applied Catalysis B: Environmental



journal homepage: www.elsevier.com/locate/apcatb

# Revealing property-performance relationships for efficient CO<sub>2</sub> hydrogenation to higher hydrocarbons over Fe-based catalysts: Statistical analysis of literature data and its experimental validation



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## ARTICLE INFO

Keywords: CO<sub>2</sub> hydrogenation Fischer-Tropsch Data science Statistical analysis Fe-based catalyst Light olefins

# ABSTRACT

 $CO_2$  hydrogenation into  $C_{2+}$ -hydrocarbons is an attractive way to mitigate the green-house effect and provides new opportunities to produce valuable chemicals from the longer available raw material. The present manuscript introduces and experimentally validates a mathematical approach for identifying fundamentals affecting catalyst performance to provide guidelines for tailored catalyst design or for reactor operation. Literature data were analyzed by regression trees, ANOVA, and comparison of mean values.

The Pauling electronegativity of dopant for Fe<sub>2</sub>O<sub>3</sub> can be used as a descriptor for CO<sub>2</sub> conversion and CH<sub>4</sub> selectivity. In addition, combining alkali and transition metals as promoters for Fe<sub>2</sub>O<sub>3</sub> is a promising route to enhance C<sub>2+</sub>-hydrocarbons selectivity and the ratio of olefins to paraffins. So-developed Mn-K/Fe<sub>2</sub>O<sub>3</sub> catalyst (K/Fe of 0.005 and Mn/K of 0.4) hydrogenated CO<sub>2</sub> to C<sub>2</sub>-C<sub>4</sub> olefins at 300 °C with the selectivity of 30.4 % at CO<sub>2</sub> conversion of 42.3 %. The selectivity to C<sub>2+</sub>-hydrocarbons (C<sub>2</sub>-C<sub>4</sub> olefins are included) was 83.1 %.

# 1. Introduction

For the last two centuries, oil, natural gas and coal have become essential raw materials to produce energy and various commodity products necessary for our everyday life. Their production is, however, accompanied by emissions of carbon dioxide, which is the number one greenhouse gas. Since the industrial revolution, its concentration in the atmosphere has strongly increased. Such changes have raised serious concerns about the possible negative impact of increased CO<sub>2</sub> emissions on our environment because of their effect on global warming and other harmful climate change phenomena [1]. Besides reducing CO2 emissions, usage of this chemical as a feedstock for production of valueadded products offers a complementary strategy to close the anthropogenic-carbon cycle and to reduce our dependence on limited fossil fuels. Against this background, CO<sub>2</sub> capture/storage approaches [2,3] or CO2 conversion into various products (carbon monoxide, methane, methanol or higher hydrocarbons) [4,5] has attracted attention in both academic and industrial research. Among the latter options, direct production of higher hydrocarbons from  $CO_2$  [6–8], called as  $CO_2$  Fischer-Tropsch (CO2-FT) synthesis, is of substantial research and

economic interest. So-generated lower olefins or long-chain hydrocarbons find their application to produce plastics, dyes and coatings or transportation fuels. As  $CO_2$  is an awfully stable molecule, there is need for high-energy input or chemical reductants to enable  $CO_2$  conversion into the desired products. In view of environmental compatibility,  $H_2$ required for the  $CO_2$ -FT reaction should be produced from environmentally friendly processes [9,10], e.g. water splitting powered by solar and/or wind energy.

Typically, CO<sub>2</sub>-FT synthesis can be divided into two steps: (i) reverse water gas shift (RWGS) reaction to generate CO and (ii) subsequent classical FT synthesis with CO. Iron- or cobalt-based catalysts have been applied for almost one century in the latter process [11,12] using syngas (a mixture of CO and H<sub>2</sub>) as feed. When the feed is changed to CO<sub>2</sub> and H<sub>2</sub> as required for the CO<sub>2</sub>-FT synthesis, CH<sub>4</sub> is the main product over Co-based catalysts, which were not concluded to be suitable for this reaction [13]. Contrarily, Fe-based materials show significantly higher selectivity to the desired higher hydrocarbons (C<sub>2+</sub>-hydrocarbons) owing to their ability to catalyze both the RWGS and CO-FT reactions [14,15]. CO<sub>2</sub> methanation also known as the Sabatier reaction is the main undesired reaction during CO<sub>2</sub>-FT.

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https://doi.org/10.1016/j.apcatb.2020.119554

Received 12 June 2020; Received in revised form 1 September 2020; Accepted 11 September 2020 Available online 14 September 2020

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Thus, the main challenge of on-going research is to reduce methane formation in favor of higher hydrocarbons and to improve CO2 conversion. In general, selectivity improvements are achieved through promoting of Fe-based catalysts with oxides of K, Zn, Co, Cu and/or Ce [16-21]. The kind of support (e.g. Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, ZrO<sub>2</sub>, carbon materials or other materials) is also an important activity- and selectivity-governing factor [22-26]. From a fundamental view point, alkali metal promoters are suggested to donate electron density to Fe and thus enhance the surface basicity of Fe catalysts [27,28]. Such changes result in an increase in CO<sub>2</sub> adsorption and a decrease in H<sub>2</sub> adsorption. The lower the H/C surface ratio, the more favorable the formation of olefins and C2+- products is. The addition of K was also concluded to accelerate the formation of iron carbides, which are selective species [29,30]. A few years ago, our group proved that the desired selectivity can be strongly improved without usage of any promoters [31]. Fe<sub>2</sub>O<sub>3</sub> synthesized through a cellulose-templated method outperformed the state-of-the-art promoted Fe-based catalysts in terms of the selectivity to C2+- hydrocarbons. The preparation method affects redox properties of Fe<sub>2</sub>O<sub>3</sub>, which were assumed to play an important role for the reaction-induced conversion of this metal oxide to iron carbides. In addition to various physicochemical properties of catalysts, reaction conditions such as temperature, (total and partial) pressure, space velocity and pre-treatment procedure have a strong effect on CO<sub>2</sub> conversion and product distribution [15,30].

It is worth mentioning that catalytic materials for the CO<sub>2</sub>-FT reaction are typically developed on the basis of empirical approaches under consideration of the fundamental knowledge accumulated in the preceding studies. However, due to the large number of such studies dealing with specific aspects of catalyst preparation and characterization, it is difficult to establish general relationships required for purposeful catalyst design and preparation and to identify the most suitable experimental conditions. Under this view, various statistical and optimization tools can provide the desired information when analyzing available experimental data [32-37]. For example, Zavyalova et al. [32] analyzed (analysis of variance, decision tree and correlation analysis) about 1870 data sets on catalyst composition and performance in the oxidative coupling of methane and suggested a strategy for designing multicomponent catalysts. This strategy was experimental validated in a separate study [38]. Very recently, the above approach was applied by our group for analyzing literature data about methane oxidation to methanol or formaldehyde [39]. The Allen electronegativity of the active metal was concluded to be an important descriptor for the selectivity to formaldehyde. Recently, Smith et al. [35] demonstrated how a machine learning framework can contribute to discovery of catalysts for water-gas shift reaction. In that work, artificial neural network was used to analyze the effects of catalyst composition and reaction conditions on catalytic performance.

On this basis, the main aim of the present study was to establish statistically significant correlations between catalyst composition, reaction parameters and performance in CO<sub>2</sub>-FT through mathematical analyses of available literature data. Another objective was to experimentally check the predictive power of such analysis. To this end, using previously reported studies we created a database and applied various statistical methods for deriving the desired fundamentals. To validate the derived relationships,  $Fe_2O_3$ -based catalysts promoted with K, Mn or K and Mn were prepared, characterized, and tested for their activity and selectivity under industrially relevant conditions for about 135 h on stream.

# 2. Statistical methods and experimental details

#### 2.1. Mathematical analysis

#### 2.1.1. Regression trees analysis

domains, where the components can be both intervals of real numbers and finite sets with or without ordering. Their value sets are intervals of real numbers, to which they map through repeatedly splitting the set of available input data into disjoint subsets. The splits are made in such a way that the sum of squared errors (SSE) with respect to the average values of the response in the above subsets is minimal. To this end, a set  $S = \{x_1, ..., x_n\}$  of input data with the dependent variables  $y_1, ..., y_n$ , e.g. the rate of CO<sub>2</sub> conversion, is considered. If the set *S* can be split into two disjoint subsets  $S_1$  and  $S_2$ , then the SSE for the split ( $S_1, S_2$ ) is:

$$SSE(S_1, S_2) = \sum_{x_i \in S_1} \left( y_i - \frac{1}{|S_1|} \sum_{x_i \in S_1} y_i \right)^2 + \sum_{x_i \in S_2} \left( y_i - \frac{1}{|S_2|} \sum_{x_i \in S_2} y_i \right)^2$$
(1)

where  $|S_i|$  denotes the number of elements for the set  $S_i$ .

Among all possible splits  $(S_1, S_2)$ , a split  $(S_1^*, S_2^*)$  leading to the minimal SSE is chosen.

$$SSE(S_1^*, S_2^*) = \min\{SSE(S_1, S_2): (S_1, S_2) \text{ is some split of } S\}$$
(2)

This method is firstly applied to the entire set *S* of available input data, then to the resulting sets  $S_1^*, S_2^*$ , etc. As long as necessary, this splitting would continue, thus forming a hierarchy of regions in the input space.

The most appropriate tree size is usually chosen using cross-validation:

- The available dataset of catalytic performance is randomly divided into *k* parts of approximately equal size.
- For each possible tree size, k trees from Tr(1) to Tr(k) are constructed, in such a way that the tree Tr(i) is constructed using all parts excluding the *i*-th, whereas the *i*-th part is reserved as test data to calculate the error of Tr(i) predictions.
- In order to evaluate the appropriateness of the considered tree size, the SSE values of the test data are averaged on all *k* trees with this size.

# 2.1.2. Analysis of Variance (ANOVA)

ANOVA is a method of testing whether a numerical response variable is influenced by some factor with two or a small number of possible values [40]. In catalysis, examples of such response variables are yield, selectivity or conversion, whereas examples of influencing factors are the presence of a certain element or the simultaneous presence of several elements. To this end, ANOVA considers the measured variance of the response for possible values of the factor, e.g., the measured variance of yield between an element being and not being present. It then calculates how likely it is to get a variance at least as large as the measured one if the factor has no influence on the response, i.e. if the probability distribution of the response is the same for all possible values of the factor. The calculated likelihood of the measured variance is called achieved significance of the factor for the response, also known as p value. Conventionally, the factor is called significant for the response if the achieved significance is < 5%, it is called weakly significant if the achieved significance is < 10 %, and it is called strongly or highly significant if the achieved significance is < 1%.

#### 2.2. Catalyst preparation

The Mn-K/Fe catalysts with different Mn/K atomic ratios were prepared in two steps. Firstly,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> was synthesized from an aqueous solution of Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O using a precipitation method. 20.2 g of iron nitrate nonahydrate were dissolved in 91.2 mL of deionized H<sub>2</sub>O followed by stirring for 30 min. Then, 6.7 M ammonium solution was added dropwise under continuous stirring until the value of pH of 9.5 was reached. The formed precipitate was aged at room temperature for 3 h, filtered and washed several times with deionized water. The solid was dried at 100 °C overnight and calcined (heating rate of 3 K/min) at 400 °C for 6 h and denoted as Fe<sub>2</sub>O<sub>3</sub>-P. In a second step, the obtained

 $\rm Fe_2O_3$  was impregnated with an aqueous solution of KNO\_3 and/or Mn (NO\_3)\_2·4H\_2O followed by drying at 100 °C for 10 h. The catalyst precursors were calcined in a muffle oven at 400 °C (heating rate of 5 K/min) for 5 h. The final catalysts are abbreviated as xMn-K/Fe, with x standing for the atomic ratio of Mn/K. The K loading was kept constant at the K/Fe atomic ratio of 0.005 in all samples. A Mn-promoted Fe\_2O\_3 catalyst was also prepared. The Mn/Fe atomic ratio was 0.005.

## 2.3. Catalyst characterization

X-ray diffraction (XRD) experiments were performed on a Stoe Stadi P transmission diffractometer equipped with a DECTRIS Mythen2 1 K detector applying Ge(111) monochromatized Mo K $\alpha$ 1 radiation (50 kV, 40 mA, 0.70930 Å) at the step of 0.01°/s. Positions and profiles of reflexes were fitted with a Pseudo-Voigt function using the HighScore Plus software package (Panalytical). The phase composition was identified using the PDF-2 database of the International Center of Diffraction Data (ICDD). Crystallite size of Fe<sub>2</sub>O<sub>3</sub> was calculated according to the Scherrer equation using the integral breadth under the assumption of spherically shaped crystallites. The reported size value is the mean value of the values calculated individually for the 012, 104, 110, 113 and 024 reflexes. The *K* factor is set to 1.0747.

The loading of Mn and K in the catalysts was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) on Varian 715-ES ICP-Emission-Spectrometer. 10 mg of each sample was mixed with 8 ml of aqua regia. The sample preparation system "Multiwave PRO" from Anton Paar was used at 220 °C and 50 bar for the sample digestion with a microwave-assisted method. The digested solution was filled up to 100 ml and measured with ICP-OES. The data analysis was performed on the Varian 715-ES software "ICP Expert".

The catalyst surface area was measured on a BELSORP-mini II instrument in liquid nitrogen and using the Brunauer-Emmett-Teller (BET) method. Before the measurements, the samples were heated at 250  $^{\circ}$ C in vacuum for 2 h.

H<sub>2</sub> temperature-programmed reduction (H<sub>2</sub>-TPR) experiments were conducted in an in-house developed setup containing eight continuous-flow quartz reactors. Each fresh catalyst sample (15 mg) was initially heated to 300 °C in Ar flow for 1 h to remove adsorbed water. After cooling down to 50 °C in the same flow, the catalysts were heated (heating rate of 10 °C/min) in a flow of 5 vol% H<sub>2</sub> in Ar (10 mL/min) to 900 °C. The consumption of H<sub>2</sub> was detected by an online mass spectrometer (Pfeiffer Vacuum OmniStar GSD 320). The signals at *m*/*z* of 2, 18, and 40 were recorded for monitoring H<sub>2</sub>, H<sub>2</sub>O, and Ar, respectively.

CO<sub>2</sub> temperature-programmed desorption (CO<sub>2</sub>-TPD) experiments were carried out in the same setup used for H2-TPR tests. 50 mg of samples (spent and fresh catalysts) were heated in Ar at 350 °C for 2 h and then cooled down to 50 °C.  $CO_2$  was adsorbed at the same temperature upon feeding a gas mixture containing 50 vol% CO<sub>2</sub> in Ar until the MS signal of CO<sub>2</sub> did not change. Hereafter, the samples were purged in Ar and kept at this temperature for 1 h to remove physically adsorbed CO<sub>2</sub>. Finally, the catalysts were heated in a flow of Ar to 800 °C with a heating rate of 10 °C/min. Argon and CO<sub>2</sub> were detected at m/z of 40 and 44, respectively, using an online mass spectrometer (Pfeiffer Vacuum OmniStar GSD 320). To ensure same reduction degree of the catalysts before CO<sub>2</sub> adsorption for CO<sub>2</sub> temperature-programmed desorption (CO2-TPD) tests and before CO2 hydrogenation tests, fresh catalysts were pre-reduced in the set-up used for the latter tests under the same treatment conditions. To minimize/avoid oxidation of the reduced catalysts, they were cooled down to room temperature in nitrogen before transferring them into reactors for CO2-TPD tests.

#### 2.4. Catalyst testing

Catalytic tests were carried out in an in-house developed setup containing 50 continuous-flow fixed-bed stainless-steel tube reactors (outer and inner diameters are 6 and 4 mm, respectively) operating in parallel. The total flow of fed gases was equally distributed among the reactors. Typically, each catalyst sample (300 mg,  $250-450 \mu \text{m}$  fraction) was placed into each reactor within its isothermal zone. 700 mg of SiC (ESK-SiC, F30,  $500-710 \mu \text{m}$  fraction) was placed on top of the catalyst bed to ensure plug flow and preheat reaction feed. Before starting the CO<sub>2</sub>-FT reaction, the catalysts were reduced at 400 °C and 15 bar in a flow of  $\text{H}_2/\text{N}_2 = 1/1$  (12 mL/min per reactor) for 2 h followed by replacing this flow by a flow N<sub>2</sub>. The catalysts were cooled to  $250 \,^\circ\text{C}$  in N<sub>2</sub>. After reaching this temperature, the reaction mixture ( $\text{H}_2/\text{CO}_2/\text{N}_2 = 3/1/0.3$ ) was fed with a flow rate of 5.8 mL/min per reactor for 45 h. Hereafter, the temperature was increased initially to 300 °C and then to  $350 \,^\circ\text{C}$  in the reactive feed. At each of these three temperatures, the catalysts were exposed to this flow for 45 h on-stream.

The feed components and the reaction products were analyzed by an on-line Agilent 7890A gas chromatograph equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD). HP Plot/Q (for CO<sub>2</sub>) and MolSieve 5A (for H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, and CO) columns were connected to TCD, while AL/S (for C<sub>1</sub>-C<sub>8</sub> hydrocarbons) and FFAP (for C<sub>9</sub>-C<sub>18</sub> hydrocarbons) columns were connected to FID. To avoid condensation of higher hydrocarbons, stainless steel lines between the reactor outlet and the GC inlet were heated to around 180 °C.

The conversion of CO<sub>2</sub> (X(CO<sub>2</sub>)), selectivity to each gas-phase product (S<sub>i</sub>) and an integral apparent rate of formation of light olefins (r  $(C_2^{=}-C_4^{=}))$  were calculated according to Eqs. (3)–(5).

$$X(CO_2) = 1 - \frac{\dot{n}_{CO_2}^{out}}{\dot{n}_{CO_2}^{in}}$$
(3)

$$S(i) = \frac{a_i \dot{n}_i^{out}}{\sum_{i=1}^n a_i \dot{n}_i^{out}}$$

$$\tag{4}$$

$$r(C_2^{=} - C_4^{=}) = \frac{F_{feed} \cdot \frac{P(CO_2)}{P_{(total)}} \cdot X(CO_2) \cdot S(C_2^{=} - C_4^{=})}{V_m \cdot m_{cat}}$$
(5)

where  $\dot{n}_{CO_2}^{in}$  and  $\dot{n}_{CO_2}^{out}$  represent the molar fraction of CO<sub>2</sub> at the inlet and outlet, respectively. S(i) is the selectivity to product *i*,  $a_i$  is the carbon number in each product.  $\dot{n}_i$  with superscripts  $\dot{n}$  and  $\dot{o}$  out  $\dot{r}$ stands for molar flow of components at the reactor inlet and outlet respectively.  $F_{feed}$  is a volumetric feed flow rate (mL/min), P(total) is the total pressure,  $p(CO_2)$  is the partial pressure of CO<sub>2</sub>,  $V_m$  is molar volume (22.4L/mol) and  $m_{cat}$  is catalyst amount (g). Reaction-induced changes in the number of moles were taken into account by using N<sub>2</sub> as an internal standard.

# 3. Results and discussion

#### 3.1. Approach for statistical analysis of literature data

For establishing statistically relevant property-performance relationships in CO<sub>2</sub> hydrogenation to higher hydrocarbons and for identifying suitable process parameters, we initially searched open literature for papers dealing with this reaction over differently composed Fe-based catalysts. Only articles that include quantitative catalyst composition, fully described reaction conditions (e.g. pretreatment and total pressure during pretreatment and reaction processes, reactants partial pressures, as well as gas hourly space velocity) and complete catalytic performance (e.g. conversion of CO<sub>2</sub>, product selectivity and the ratio of olefins to paraffins) were selected. On this basis, a database containing 352 data sets was created. It includes catalyst elemental composition, the kind of promoter and support material, alkali metal to Fe ratio, iron precursor, catalyst preparation method, treatment and reaction conditions, feed composition and catalyst performance. As catalytic tests were carried out at different contact times, a direct comparison of the tested catalysts in terms of their activity and productivity on the basis of CO<sub>2</sub> conversion and C<sub>2+</sub>- hydrocarbons yield is

Statistical analysis of literature data Reaction Parameters Different group Catalyst kind of promoters	Fundamentals of catalyst functioning	Improved catalysts Optimized process
<ul> <li>A database with about 350 different Fe-based catalysts was created</li> <li>Regression tree and ANOVA analysis</li> <li>1<sup>st</sup> descriptor group:         <ul> <li>Catalyst type and reaction parameters</li> <li>Elemental composition</li> <li>Support material</li> <li>Alkali metal to Fe ratio</li> <li>Iron precursor</li> <li>Catalyst preparation method</li> <li>Pre-treatment and reaction conditions</li> </ul> </li> <li>2<sup>nd</sup> descriptor group: Kind of promoter</li> </ul>	<ul> <li>Performance in CO<sub>2</sub>-FT         <ul> <li>CO<sub>2</sub> reaction rate, R(CO<sub>2</sub>)</li> <li>Olefin to paraffin ratio, O(C<sub>2</sub>-C<sub>4</sub>)/P(C<sub>2</sub>-C<sub>4</sub>)</li> <li>The selectivity of C<sub>2</sub>, hydrocarbons, S(C<sub>2</sub>,)</li> <li>The formation rate of C<sub>2</sub>, hydrocarbons, r(C<sub>2</sub>,)</li> </ul> </li> <li>Identifying the most significant descriptors affecting the above performance</li> </ul>	<ul> <li>Synthesis of bare Fe<sub>2</sub>O<sub>3</sub> materials through different methods</li> <li>Promoting of Fe<sub>2</sub>O<sub>3</sub> with a single promoter, i.e. K or Mn or their combination</li> <li>CO<sub>2</sub>-FT tests <ul> <li>T: 250, 300, 350°C</li> <li>P: 15 bar</li> <li>CO<sub>2</sub>:H<sub>2</sub>:N<sub>2</sub> = 1:3:0.3</li> </ul> </li> </ul>

Fig. 1. A schematic representation of our approach for establishing property-performance relationships.

not straightforward. To enable the comparison, we used the reported relevant experimental data for calculating an overall integral rate of  $CO_2$  conversion and an integral rate of  $CO_2$  conversion into  $C_{2+}$ - hydrocarbons according to Eqs. (6) and (7), respectively. It builds the basis for our approach for analyzing the literature data. The approach is schematically shown in Fig. 1.

$$R(CO_2) = \frac{F_{feed} \cdot \frac{p(CO_2)}{P(total)} \cdot X(CO_2)}{V_m \cdot m_{cat}}$$
(6)

$$r(C_{2+}) = \frac{F_{feed} \cdot \frac{r(C_{2})}{P_{(total)}} \cdot X(CO_2) \cdot S(C_{2+})}{V_m \cdot m_{cat}}$$
(7)

Here,  $F_{feed}$  is a volumetric feed flow rate (mL/min), P(total) is the total pressure,  $p(CO_2)$  is the partial pressure of CO<sub>2</sub>,  $V_m$  is molar volume (22.4 L/mol) and  $m_{cat}$  is catalyst amount (g).

Our target catalyst properties were the overall rate of CO<sub>2</sub> conversion (R(CO<sub>2</sub>)), the rate of CO<sub>2</sub> conversion into  $C_{2+}$  - hydrocarbons (r  $(C_{2+})$ ), the selectivity to  $C_{2+}$ - hydrocarbons  $(S(C_{2+}))$  and the ratio of olefins to paraffins calculated for C2-C4 hydrocarbons (O(C2-C4)/P(C2-C<sub>4</sub>)). Possible descriptors relevant for the above-defined performance were divided into two groups: (i) catalyst type and reaction parameters and (ii) promoters (Fig. 1). Ammonium ferric citrate, iron (III) chloride, iron nitrate, iron (III) chloride / iron (II) chloride, and iron (III) acetvlacetonate are iron resource precursors. The catalysts used in literature were classified into four different groups: (i) bulk & non-promoted, (ii) bulk & promoted, (iii) supported & non-promoted and (iv) supported & promoted. For assessing the effect of various input descriptors on R (CO<sub>2</sub>),  $r(C_{2+})$ ,  $O(C_2-C_4)/P(C_2-C_4)$  and  $S(C_{2+})$ , regression tree analysis, multiway ANOVA and the comparison of mean values of catalytic performance were applied. The obtained results are presented and discussed in the next sections.

#### 3.2. Regression trees analysis

Based on the two groups of descriptors defined in Fig. 1, two independent regression-tree analyses were carried out with their specific purposes. We shall start with the discussion of the descriptors from the first group (catalyst type and reaction parameters), to identify the most decisive catalyst properties and reaction parameters for the CO<sub>2</sub>-FT reaction. The first four nodes in the regression trees for R(CO<sub>2</sub>),  $r(C_{2+})$ ,  $O(C_2-C_4)/P(C_2-C_4)$  and  $S(C_{2+})$  are shown in Fig. 2. The numbers in the circles stand for the average value of each catalytic performance. The square root of SSE for each split is also shown below each circle in brackets. The corresponding complete trees are given in Fig. S1-S4 (see the Supporting Information). The numbers stand for the average value of each catalyst performance. The root node in the hierarchy means the average value among all data in the database. The path from root to leaf states the influence of a certain descriptor on catalytic performance. Its relevance for the  $CO_2$ -FT reaction decreases from top to bottom. The most decisive descriptors and promoters extracted from the regression trees are listed in Table 1.

For the total  $CO_2$  conversion rate, the most decisive reaction parameters are total pressure, catalyst reductive pre-treatment time and the kind of iron precursor. Their significance decreases in the order they are mentioned above. The temperatures of catalyst pre-treatment and reaction, the molar ratio of promoter to iron and the kind of support material are less important and appear at lower levels of the tree (Fig. S1). On average, increasing reaction pressure has positive effect on the reaction rate of  $CO_2$ . The time of catalyst pre-treatment should be below 6.5 h. Iron nitrate should be used for catalyst preparation to achieve high rate of  $CO_2$  conversion.

Total pressure has also the most decisive effect on the rate of  $CO_2$  conversion into  $C_{2+}$ -hydrocarbons. Catalyst pre-treatment time, the second most decisive descriptor, should be lower 6.5 h. In contrast to the overall rate of  $CO_2$  conversion, iron precursor is not so important for the rate of  $CO_2$  conversion into  $C_{2+}$ - hydrocarbons. Reaction temperature should be above 335 °C. All other descriptors from Fig. 1 do not seem to be relevant for this catalyst performance.

Now we turn our discussion to the factors affecting the  $O(C_2-C_4)/P(C_2-C_4)$  ratio. Compared with catalyst activity (Fig. 2 (a,b)), the kind of catalyst is the most decisive factor for this ratio (Fig. 2(c)). Promoted bulk catalysts should be applied for improving this catalyst characteristic. The second most important descriptor for the  $O(C_2-C_4)/P(C_2-C_4)$  ratio is iron precursor. Commercial Fe<sub>2</sub>O<sub>3</sub>, iron nitrate and iron (II or III) chlorides should be applied. For optimizing the ratio, CO<sub>2</sub>-FT should be carried out above 268 °C. The ratio of promoter to Fe should be larger than 0.005.

Concerning the selectivity to  $C_{2+}$ - hydrocarbons, promoted bulk catalysts outperform their supported counterparts and unpromoted materials (Fig. 2 (d)). This performance can be further improved when operating at pressure above 20 bar and using catalysts with the ratio of dopant to Fe larger than 0.02 (Fig. S4). The catalysts should also be reductively treated above 400 °C.

For identifying the key promoter(s) affecting the desired catalyst



**Fig. 2.** Regression trees made on the basis of first-group descriptors from Fig. 1 for (a)  $CO_2$  conversion rate, (b) formation rate of  $C_{2+}$  hydrocarbons, (c) the ratio of olefins to paraffins and (d) selectivity to  $C_{2+}$  hydrocarbons. Each node is labeled with the mean value of performance and the square root of SSE for each split (italic, in brackets). Decoding of the kind of catalyst: (1) bulk & non-promoted, (2) bulk & promoted, (3) supported & non-promoted and (4) supported & promoted. Iron precursors: (I) ammonium ferric citrate, (II) iron(III) chloride, (III) commercial oxide, (IV) iron nitrate, (V) iron(III) chloride/iron(II) chloride and (VI) iron(III) acetylacetonate. Support materials: (1)  $Al_2O_3$ , (2) Carbon materials, (3)  $SiO_2$ , (4)  $TiO_2$  and (5)  $ZrO_2$ .

Table 1

The most decisive descriptors and promoters for  $CO_2$  conversion rate, (b) formation rate of  $C_{2+}$ - hydrocarbons, (c) olefins to paraffins ratio and (d) selectivity to  $C_{2+}$ - hydrocarbons as derived from the regression trees analysis.

	The most decisive descriptor	The most decisive promoter
CO <sub>2</sub> reaction rate	Reaction pressure	Na
Formation rate of C <sub>2+</sub> -	Reaction pressure	K
Olefins to paraffins ratio	Catalyst kind	Na
Selectivity of C <sub>2+</sub> - hydrocarbons	Catalyst kind	Na

performance, i.e.  $R(CO_2)$ ,  $r(C_{2+})$ ,  $O(C_2-C_4)/P(C_2-C_4)$  and  $S(C_{2+})$ , we performed additional regression tree analysis using the descriptors from the second group in Fig. 1. The obtained trees as a function of different promoters are shown in Fig. 3, while the corresponding complete trees are shown in Fig. S5-S8. The most decisive parameter for the overall rate of  $CO_2$  conversion is sodium promoter. This promoter affects, however, this catalyst property negatively. In general, the highest rate can be achieved over unpromoted catalysts. When comparing various promoters in terms of their inhibiting effect on  $R(CO_2)$ , potassium seems to be less negatively influencing promoter. This promoter has the strongest effect on the rate of  $CO_2$  conversion into  $C_{2+}$  hydrocarbons. Combining Na and Zn promoters is also helpful for improving this rate (Fig. 3(b)).

In addition to the activity-affecting factors, our decision tree analysis revealed selectivity-determining descriptors. It indicates that sodium in combination with manganese used as promoters has a positive effect on the  $O(C_2-C_4)/P(C_2-C_4)$  ratio (Fig. 3(c)). From a quantitative viewpoint, it can be learned that the mean  $O(C_2-C_4)/P(C_2-C_4)$  value is higher than the mean value of 2.83 for the whole database when the following promoters or their combinations are used. They are sorted according to the strength of their impact on this catalyst characteristic.

- (1) Mean value of 6.77 is found for all catalysts containing Na and Mn;
- (2) Mean value of 5.49 is found for all catalysts containing Na and Zn;
- (3) Mean value of 5.31 is found for all catalysts containing Na;
- (4) Mean value of 3.78 is found for all catalysts containing Rb;
- (5) Mean value of 3.08 is found for all catalysts containing K;

A synergistic effect between Na and Mn was demonstrated by Liu et al. [41]. Those authors suggested that Mn nanoparticles dispersed on  $Fe_5C_2$  surface can hinder consecutive transformations of  $CH_2^*$  species with alkyl-metal chains to form higher hydrocarbons, so-called spatial hindrance effect. Therefore, the selectivity to light olefins increases. Liang et al. [42] also studied the role of Mn promoter in the Na/Fe catalysts and concluded that the increase in the selectivity to light olefins is due to the high content of  $Fe_5C_2$  species and due to a decrease in the amount of CO and its adsorption strength.

In summary, for achieving the selectivity to  $C_{2+}$ - hydrocarbons as high as possible, it is advantageous to promote catalysts with Na (Fig. 3(d)). Further improvements can be expected when combining Na with Mn. In addition to Na, K is also an important selectivity-affecting promoter when it is particularly combined with Zr.

#### 3.3. Component analysis

Although the above decision-tree analysis proved the importance of the usage of various promoters for improving performance of Fe-based



**Fig. 3.** Regression trees made on the basis of second-group descriptors (Fig. 1) for (a)  $CO_2$  reaction rate, (b) formation rate of  $C_{2+}$ - hydrocarbons, (c) olefins to paraffins ratio and (d) selectivity to  $C_{2+}$ - hydrocarbons. Each node is labeled with the mean value of performance and the square root of SSE for each split (see the values in the brackets).

catalysts, such approach cannot provide information about the significance of each individual promoter in the terms of its effect on a certain catalyst performance. Thus, our further analysis was focused on catalysts containing either one certain promoter or their binary combinations. To this end, we calculated the corresponding mean values of  $R(CO_2)$ ,  $r(C_{2+})$ ,  $O(C_2-C_4)/P(C_2-C_4)$  and  $S(C_{2+})$ .

Mean values of the above-mentioned catalyst performance were calculated when a certain element was included within Fe-based catalysts as promoter. It should be noticed that the catalysts may have other promoters in addition to this certain element. As seen in Fig. 4, an average R(CO<sub>2</sub>) higher or equal to 60 mmol  $g_{cat}^{-1}h^{-1}$  is achieved when Pt, Rh or Ca are used as promoters. They are also beneficial for achieving high values of  $r(C_{2+})$ . Pt and Rh are precious metals that can catalyze reverse water gas-shift reaction and facilitate the dissociation of H<sub>2</sub>. While Ca or Mg could enhance surface basicity of Fe-based catalysts, that has a positive effect on CO<sub>2</sub> adsorption rate. It should be noted that the significance of the statistical analysis of Pt- or Rh-containing catalysts is not very representative because there are only a few data sets on such catalysts or other precious metal-containing catalysts in the whole database. With respect to C2+ selectivity and O(C2-C4)/P (C2-C4), the most effective dopants are alkali (Na, K, Rb and Cs) and transition metals (Mn, Zr, Zn and Ru) (Fig. 4(c)).

To identify possible synergy effects between different dopants, Febased catalysts containing either one single dopant or a certain combination of this dopant with another dopant were also considered. The calculated mean values of the above-mentioned catalytic performance are shown in Fig. S9. Fe-based catalysts, in which Pt, Rh, Ca or Mg were used as a single promoter, show high CO<sub>2</sub> reaction rate. It means that Pt, Rh, Ca or Mg can enhance catalyst activity whether they present as a single promoter or in combination with other promoters. In addition to Pt, Rh or Ca, binary combinations of K with Zn or Na with Zn were identified to be significant for enhancing the rate of formation of C<sub>2+</sub>hydrocarbons. For the O(C<sub>2</sub>-C<sub>4</sub>)/P(C<sub>2</sub>-C<sub>4</sub>) ratio, when combining Na with Mn or Zn as promoters, a stronger positive effect is achieved in comparison with the catalysts containing sodium as a single promoter. The highest  $C_{2+}$  selectivity was achieved when combining K with Ru. Thus, catalysts with multi promoters seems to be more attractive in terms of achieving high  $O(C_2-C_4)/P(C_2-C_4)$  ratio and  $S(C_{2+})$  but less suitable with respect to  $R(CO_2)$ .

To identify the most significant promoter for Fe-based catalysts in the CO<sub>2</sub>-FT reaction, multiway ANOVA (analysis of variance) was performed. Table 2 lists the identified elements and the significance of their presence as an individual promoter or in combination with other elements. In the column of 'Significance level', the lower value, the more significant the element is. The elements can be classified into the following groups according to their position in the periodic table.

- (a) Precious metals: Pt, Rh, and Ru;
- (b) Alkali metals: K, Na, Rb and Cs;
- (c) Alkali-earth metals: Ca and Mg;
- (d) Transition metals: Mo, Zr, Cr and Cu;
- (e) Lanthanide metal: La.

For catalyst design, precious metals are typical catalysts in RWSG reaction which is the first step for the CO<sub>2</sub> hydrogenation to C<sub>2+</sub>- hydrocarbons [5]. Alkali metals, as well as alkali-earth metals, are regarded as essential promotors because of their positive role in CO<sub>2</sub> adsorption and modulation of electronic property of the catalyst, while transition metals are beneficial for H<sub>2</sub> dissociation [21,28]. Combining alkali metals with transition metals was also established to be an important requirement for preparation of catalysts resulting in high O(C<sub>2</sub>-C<sub>4</sub>)/P(C<sub>2</sub>-C<sub>4</sub>). This conclusion agrees with the results obtained from regression tree analysis. The identified significant binary combinations are alkali&transition metal, i.e. K&Mn, K&Cu, Na&Mn, K&Co, K&Mo and Na&Zn.

Further, Na, K, Zn and Mn were selected as representative promoters to illustrate how the presence or absence of other promoters affects catalyst performance in terms of olefin production (Fig. 5). For Na, Zn and Mn, combining with other elements can increase the  $O(C_2-C_4)/P(C_2-C_4)$  ratio. In contrast, the kind of co-promoter is decisive for



Fig. 4. Mean values of (a)  $CO_2$  reaction rate, (b) formation rate of  $C_{2+}$ - hydrocarbons, (c) ratio of olefins to paraffins and (d) selectivity to  $C_{2+}$ - hydrocarbons obtained over Fe-based catalysts with a certain element as promoter.

catalysts containing K. For example, an average value of O(C<sub>2</sub>-C<sub>4</sub>)/P(C<sub>2</sub>-C<sub>4</sub>) is 3.52 in the presence of K without Cu, however this value is 1.47 when Cu was present (Fig. S7). In a previous study, Su et al. [43] reported that O(C<sub>2</sub>-C<sub>4</sub>)/P(C<sub>2</sub>-C<sub>4</sub>) reached a value of 7.55 over Fe-K catalysts, while this value decreased to 5.09 when 3Fe-1Zr-K was used. The O(C<sub>2</sub>-C<sub>4</sub>)/P(C<sub>2</sub>-C<sub>4</sub>) ratio of 4.92 and 5.71 was achieved over FeZn/nanocarbon and FeZnK/nanocarbon respectively [24].

To derive a fundamental insight into the role of promoters for Febased catalysts in the  $CO_2$ -FT reaction, we established a correlation between the Pauling electronegativity of individual promoters and the rate of  $CO_2$  conversion and  $CH_4$  selectivity. As a major part of previous tests were carried out at 320 °C, we have selected such data obtained over catalysts possessing only one promoter. Importantly, we used average values from various papers dealing with same catalyst composition. In addition, to minimize the effect of  $CO_2$  and  $H_2$  partial pressures, the rate of  $CO_2$  conversion was related to these parameters. Both the rate and the selectivity seem to increase with an increase in the value of promoter electronegativity (Fig. 6), especially for these promoters with the electronegativity above 1.4. The Pauling electronegativity is defined as the ability of one atom to attract electron density when it interacts with another atom. The correlations in Fig. 6 imply that electronic properties of promoters are relevant for  $CO_2$  conversion and  $CH_4$  selectivity. In general, higher H/C ratios on catalyst surface lead to higher  $CH_4$  selectivity [44]. The presence of adsorbed hydrogen species is also relevant for  $CO_2$  conversion. Based on this general knowledge and the same dependence of the  $CO_2$  conversion rate and the  $CH_4$  selectivity on promoter electronegativity, we suggest that this catalyst property is beneficial for adsorption and dissociation of gas-phase hydrogen.

# 4. Validation and potential of statistical analysis for catalyst development

From the above-discussed statistical analysis, we identified that the selectivity to  $C_{2+}$ -hydrocarbons and the  $O(C_2-C_4)/P(C_2-C_4)$  ratio obtained over differently prepared Fe-based catalysts can be improved when the catalysts are promoted. Particularly, combining alkali metal with transition metal promoters seems to be a promising route to enhance the desired catalyst performance. To validate this conclusion experimentally, we prepared a series of catalysts on the bases of bulk

Table 2		
Significant promoters derived f	from the ANOVA	analysis.

R(CO <sub>2</sub> )		r(C <sub>2+</sub> )		O(C <sub>2</sub> -C <sub>4</sub> )/P(C <sub>2</sub>	-C <sub>4</sub> )	S(C <sub>2+</sub> )	
Promoter	Significance level	Promoter	Significance level	Promoter	Significance level	Promoter	Significance level
Pt	0.004	В	0.071	Na	1.30E-06	Na	1.27E-06
Rh	0.017	Pt	0.089	Rb	0.041	Мо	0.112
Ca	0.027	Zr	0.174	Cr	0.133	Cr	0.114
K	0.043	La	0.236	Cs	0.168	Mg	0.132
Mg	0.055	Rh	0.332	Cu	0.201	Ru	0.176
Na	0.094	K	0.360	K	0.223	Zr	0.184
Мо	0.197	Ru	0.461	Mo	0.266	Ca	0.199
K&Mn	0.105	K&Co	0.183	K&Cu	9.51E-05	Na&Mn	0.131
K&Cu	0.207	K&Cu	0.370	Na&Mn	0.145	Na&Zn	0.163
Na&Mn	0.518	K&Mo	0.448	K&Mn	0.249	K&Co	0.245



**Fig. 5.** The  $O(C_2-C_4)/P(C_2-C_4)$  ratio for Fe-based catalysts containing either a single (Na, K, Zn or Mn) promoter (open bars) or in combination with other possible promoters (solid bars).



Fig. 6. Dependence of methane selectivity and  $CO_2$  conversion rate normalized by partial pressure of  $CO_2$  and  $H_2$  on the electronegativity of promoters.

 $Fe_2O_3$  promoted with K, Mn or K and Mn. The ratio of K/Mn was varied, while the loading of K was constant (Table 3). These materials were characterized and tested for their activity and selectivity in the CO<sub>2</sub>-FT reaction. We shall start the discussion with characterization data

followed by catalytic results.

# 4.1. xMn-K/Fe catalysts and their physicochemical properties

The XRD patterns (Fig. S10) of all fresh xMn-K/Fe catalysts exclusively contain reflexes characteristic for the hematite phase (ICDD 01-072-0469). The absence of reflexes typical for K- or Mn-containing phases even in the 5Mn-K/Fe catalyst is probably due to low concentration of these elements and accordingly high dispersion on the surface of Fe<sub>2</sub>O<sub>3</sub>. An average size of Fe<sub>2</sub>O<sub>3</sub> crystallite in the bare Fe<sub>2</sub>O<sub>3</sub> and xMn-K/Fe catalysts is 16-19 nm as estimated from the Scherrer equation (Table 3). Thus, the promoters do not affect the phase composition and crystallite size of Fe<sub>2</sub>O<sub>3</sub>. The surface area of catalysts decreased after addition of the promoters to Fe<sub>2</sub>O<sub>3</sub>-P. The XRD patterns of the spent catalysts after 135 h on-stream show predominantly contribution of Fe<sub>3</sub>O<sub>4</sub> with a small fraction of Hägg iron carbide species  $(Fe_5C_2)$  which is regarded as the active phase for the FT reaction (Fig. S11). Reflexes characteristic of this carbide were found in the XRD patters of spent 0.005 K/Fe and xMn-K/Fe. It is obvious that promoting of Fe<sub>2</sub>O<sub>3</sub> with Mn does not affect the reaction-induced formation of carbide species, while K is a critical promoter for the carburization of iron. Combining Mn and K (0.4Mn-K/Fe) facilitates the formation of Fe<sub>5</sub>C<sub>2</sub>.

H<sub>2</sub>-TPR experiments were performed to investigate the effect of Mn or K promoters as well as their molar ratio on the reduction behavior of Fe<sub>2</sub>O<sub>3</sub>. Fig. 7(a) shows the obtained H<sub>2</sub>-TPR profiles. They are characterized by two H<sub>2</sub> consumption peaks. The first peak located at 350 – 450 °C reflects the reduction of hematite to magnetite (Fe<sub>2</sub>O<sub>3</sub> → Fe<sub>3</sub>O<sub>4</sub>), while the second broader peak is assigned to the reduction of Fe<sub>3</sub>O<sub>4</sub> to FeO or/and Fe. Thus, regardless of the kind of promoter and its concentration, the overall reduction steps of Fe<sub>2</sub>O<sub>3</sub> follow the mechanism: Fe<sub>2</sub>O<sub>3</sub> → Fe<sub>3</sub>O<sub>4</sub> → FeO → Fe, which agrees with a previous study [45]. The temperature of the first maximum of H<sub>2</sub> consumption rate (T<sub>max,TPR</sub>) is listed in Table 3. The T<sub>max</sub> values determined for 0.005 Mn/Fe and 0.005 K/Fe were slightly higher than that for bare Fe<sub>2</sub>O<sub>3</sub>, i.e. 388, and 383 and 377 °C respectively. Similar results were observed for other K or Na promoted Fe-based catalysts [30,46].

In comparison with 0.005 Mn/Fe and 0.005 K/Fe, the reducibility of xMn-K/Fe can be either improved or hindered when these promoters co-exist. The T<sub>max.TPR</sub> values for 0.4Mn-K/Fe with the lowest Mn loading shifts to lower temperatures (Table 3). However, these values shift to higher temperature with an increase in the Mn/K ratio to 1.2. When the Mn loading increases further, the temperatures for maximal reduction rate of Fe2O3 and Fe3O4 decline from 396 °C for 1.2Mn-K/Fe to 370 °C for 5Mn-K/Fe, respectively. Thus, we cannot support previously reported positive effects of Mn promoter on the reducibility of  $FeO_x$  [47]. In addition, the effect of Mn on the reduction behavior of iron oxide is controversial in previous studies [27,48]. Instead, we prove that this effect depends on the ratio of Mn/K. However, the addition of Mn or K, especially Mn, increases the amount of the iron oxide which can be reduced (Table 3). The interaction of Mn and K enhances this amount to a large extent. Fe<sub>2</sub>O<sub>3</sub>-P shows the lowest H<sub>2</sub> consumption of 8.3 mmol  $H_2 g^{-1}$ , while it increases to 12.8 mmol  $H_2 g^{-1}$  for 5Mn-K/Fe. Therefore, the molar ratio of H<sub>2</sub> consumed to reduced iron oxide for 5Mn-K/Fe is 1.5 times to that for Fe<sub>2</sub>O<sub>3</sub>-P.

Basic properties of reduced and spent xMn-K/Fe catalysts were investigated by  $CO_2$  temperature-programmed desorption ( $CO_2$ -TPD) tests. For the fresh catalysts, there are several desorption peaks of  $CO_2$  (Fig. 7(b)). The first peak at 80 - 200 °C belongs to the desorption of weakly adsorbed  $CO_2$ . With the introduction of Mn, the intensity of the signal at around 150 °C becomes much lower. No  $CO_2$  desorption above 600 °C was determined for bare Fe<sub>2</sub>O<sub>3</sub> and 0.005 Mn/Fe. Potassium, however, enhances catalyst basicity strongly, which results in two high-temperature  $CO_2$  desorption peaks at around 470 and 650 °C and is expected to affect catalytic performance. With the addition of Mn and/ or K, the concentration of strong basic sites (desorption above 400 °C)

Table 3

Catalyst	Crystallite size <sup>a</sup> (nm)	BET surface $(m^2 g^{-1})$	Mn/Fe <sup>b</sup> molar ratio	K/Fe <sup>b</sup> molar ratio	n(H <sub>2</sub> ) (mmol H <sub>2</sub> g <sup>-1</sup> )	n(H <sub>2</sub> )/n(Fe <sub>2</sub> O <sub>3</sub> )	T <sub>max,TPR</sub> (°C)
Fe <sub>2</sub> O <sub>3</sub> -P	16	41	-	-	8.3	1.3	377
0.005 Mn/Fe	19	37	0.0053	-	11.2	1.8	388
0.005 K/Fe	19	25	-	0.0046	9.4	1.5	383
0.4Mn-K/Fe	19	38	0.0022	0.0051	11.8	1.9	375
0.7Mn-K/Fe	18	38	0.0044	0.0059	11.9	1.9	388
1.2Mn-K/Fe	18	27	0.0069	0.0055	11.4	1.8	396
2Mn-K/Fe	19	36	0.010	0.0051	10.6	1.7	392
5Mn-K/Fe	18	28	0.028	0.0051	12.8	2.0	370

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<sup>a</sup> Calculated by XRD.

<sup>b</sup> Determined from ICP.

increases (Table S1). The desorption peak at higher temperatures for 0.4Mn-K/Fe shifts to lower temperatures in comparison with 0.005 K/ Fe. When the ratio of Mn to K increases, the highest-temperature desorption peak shifts to higher temperature. This result indicates that the strength of basic sites becomes stronger with increasing the ratio of Mn to K for xMn-K/Fe catalysts.

The CO<sub>2</sub>-TPD profiles of spent catalysts are shown in Fig. S12. For spent catalysts, CO<sub>2</sub> desorption starts at about 400 °C and ends above 600 °C. Two distinct CO<sub>2</sub> desorption peaks can be identified for K- or Mn-doped catalysts and xMn-K/Fe except for 5Mn-K/Fe. The main desorption peak locates in the temperature range of 485 – 630 °C, which corresponds to the interaction of CO<sub>2</sub> with strong surface basic sites. However, the CO<sub>2</sub> desorption at the strongest basic sites over reduced catalysts occurs at around 650 °C (Fig. 7(b). It indicates that the strongest basic sites on the surface of spent catalysts become weaker in comparison with their fresh counterparts. In addition, no CO<sub>2</sub> desorption peak was observed below 400 °C for the spent catalysts, which means there is no relatively weak basic sites present on the surface of the freshly reduced catalysts (Fig. 7(b)). On the other hand, the amount of CO<sub>2</sub> desorbed above 400 °C was enhanced significantly after CO<sub>2</sub> hydrogenation reaction regardless of the presence of promoter (Table S1). Although the strength of basic sites on the surface of spent catalysts decreased, the number of these basic sites increased.

With the addition of K or Mn, the amount of  $CO_2$  desorbed greatly increased (Table S1). The desorption peak in the  $CO_2$  profile of 0.005 K/ Fe, particularly, shifts to higher temperature in comparison with the promoter-free Fe<sub>2</sub>O<sub>3</sub>. The main desorption peak shifts to lower temperature with increasing the ratio of Mn/K. Moreover, the amount of desorbed  $CO_2$  decreases for 2Mn-K/Fe and 5Mn-K/Fe significantly (Table S1). It can be concluded that too high Mn loading in K doped Febased catalyst has a negative effect on  $CO_2$  adsorption. Thus, the above results indicate that potassium or manganese enhances  $CO_2$  adsorption on the surface of Fe-based catalyst, which can explain the improvement in  $CO_2$  hydrogenation activity over Mn and/or K promoted catalysts (Fig. 8(a)).

# 4.2. Effect of the Mn/K ratio and reaction temperature on catalytic performance

To check if there is a synergy effect between K and Mn promoters for  $Fe_2O_3$  in terms of activity and product distribution, we performed a  $CO_2$ -FT test at 15 bar over 135 h on-stream between 250 °C and 350 °C. The test was started at 250 °C followed by an increase to 300 °C and then to 350 °C. As it was mentioned above, pretreatment of all samples took place at 400 °C in the flow of  $H_2/N_2$  for 2 h. The catalysts were exposed to the reaction feed at each temperature for about 45 h. The full time-on-stream profiles of  $CO_2$  conversion, product selectivity and the ratio of  $O(C_2-C_4)/P(C_2-C_4)$  are shown in Fig. S13-S18, while selected values of  $CO_2$  conversion and the selectivity to  $C_2-C_4$  olefins after 45 h on-stream at each temperature are reported in Fig. 8.

For all catalysts, the conversion of CO<sub>2</sub> increases with reaction temperature. The most significant effect was achieved upon increasing the temperature from 250 to 300 °C. A further increase to 350 °C results in a less pronounced effect particularly for the xMn-K/Fe catalysts. In terms of product selectivity, performing CO<sub>2</sub> hydrogenation at 300 °C results in the highest selectivity to C<sub>2+</sub>- products (Fig. S14). CH<sub>4</sub> production increases with an increase in reaction temperature to 350 °C. Thus, the below discussion is focused on the results obtained at 300 °C.

Regardless of reaction temperature, bare  $Fe_2O_3$  shows the lowest  $CO_2$  conversion and selectivity to  $C_2$ - $C_4$  olefins (Fig. 8) and, in general, to  $C_{2+}$ - hydrocarbons (Fig. S14). CH<sub>4</sub> is the dominant product as expected (Fig. S15). Promoting of  $Fe_2O_3$  with Mn has a positive effect not



Fig. 7. H<sub>2</sub>-TPR profiles (a) and CO<sub>2</sub>-TPD profiles (b) of fresh Fe<sub>2</sub>O<sub>3</sub>-P, 0.005 K/Fe, 0.005 Mn/Fe and xMn-K/Fe catalysts.



**Fig. 8.** Effect of Mn, K and Mn/K molar ratio in xMn-K/Fe catalysts on (a) CO<sub>2</sub> conversion (X (CO<sub>2</sub>)) and (b) the selectivity to C<sub>2</sub>-C<sub>4</sub> olefins (S  $(C_2^--C_4^-))$  at different reaction temperatures. Reaction conditions: 15 bar; 1160 mL h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>; H<sub>2</sub>:CO<sub>2</sub>:N<sub>2</sub> = 3:1:0.3; 45 h on-stream at each temperature (for details see Fig. S13-S19). The values are after 45 h on-stream at each temperature.

only on CO<sub>2</sub> conversion, but also on product distribution. Moreover, Mn/Fe and xMn-K/Fe catalysts show stable performance in terms of formation of C<sub>2+</sub>-hydrocarbons (Fig. S14 and S18). In comparison with Fe<sub>2</sub>O<sub>3</sub>, CO<sub>2</sub> conversion and the selectivity to C<sub>2</sub>-C<sub>4</sub> olefins obtained over 0.005 Mn/Fe<sub>2</sub>O<sub>3</sub> at 300 °C increased from 20.0% to 30.0% and from 3.6% to 8.6% respectively. In contrast, the selectivity to CH<sub>4</sub> decreased from 37.2% to 29.9%. Both the activity and the selectivity to the desired hydrocarbons were improved when Fe<sub>2</sub>O<sub>3</sub> was promoted by K as expected from previous studies [18,30,49]. The conversion of CO<sub>2</sub>, the selectivity to C<sub>2</sub>-C<sub>4</sub> olefins and CH<sub>4</sub> obtained over 0.005 K/Fe at 300 °C are 43.2, 26.8 and 10.3 % respectively (Fig. 8, Fig. S13 and S17). The changes in catalyst performance are in line with the reaction-induced transformation of Fe<sub>2</sub>O<sub>3</sub> to Fe<sub>5</sub>C<sub>2</sub> (Fig. S11).

When increasing the Mn/K ratio from 0 to 5, there is no significant effect on CO<sub>2</sub> conversion as seen in Fig. 8(a) and Fig. S13. A small negative effect was determined for the catalyst with the highest Mn loading. The selectivity of C<sub>2</sub>-C<sub>4</sub> olefins and the ratio of  $O(C_2-C_4)/P(C_2-C_4)$  are enhanced when K and Mn co-exist (Fig. 8(b)). The highest values were achieved over 0.4Mn-K/Fe at 300 °C. In comparison with 0.005 K/Fe, the  $O(C_2-C_4)/P(C_2-C_4)$  ratio increases from 3.96 to 6.14 at 300 °C, while selectivity to CH<sub>4</sub> slightly decreases from 10.3% to 9.3%. This result implies that Mn further enhances the effect of K on suppressing CO<sub>2</sub> methanation. When increasing Mn content up to Mn/K of 2, the selectivity to C<sub>2</sub>-C<sub>4</sub> olefins decreases with a simultaneous increase in the selectivity to the corresponding alkanes. The selectivity to CH<sub>4</sub> drops to 8.8 % further when increasing Mn/K ratio to 0.7 (Fig. S19), but increases to 10.1 % when Mn/K ratio reaches to 2.

The positive effect of co-existence of K and Mn on the selectivity to olefins can be explained as follows. It has been reported that olefin adsorption/desorption properties are decisive for their secondary hydrogenation reactions to paraffins [44,50]. The presence of K hinders the adsorption of olefins due to electron-donating properties of K and olefins [26,28]. In the view of our results, the synergy effect between K and Mn may strength the essential role of K for Fe-based catalysts.

Compared with Fe<sub>2</sub>O<sub>3</sub>-P, the selectivity to C<sub>2+</sub>- and C<sub>5+</sub>-hydrocarbons over 0.005 K/Fe and Mn doped K/Fe catalysts does not change significantly with time on stream. The corresponding values at 300 °C are 46 %–50 % and 80 %–84 % respectively (Fig. S17 and S18). In contrast to previously tested Mn-Na/Fe catalysts, where the selectivity to C<sub>5+</sub>-hydrocarbons significantly decreases after adding Mn to Na/Fe [42], this property over 0.4Mn-K/Fe is practically not affected after addition of Mn to 0.005 K/Fe.

To benchmark our (0.005 K/Fe and 0.4Mn-K/Fe) catalysts, we compared their performance with literature data. To this end, the stateof-the art catalysts from the created database were selected. As a comparison criterium, we use the conversion of CO<sub>2</sub>, the selectivity to CO, CH<sub>4</sub>, C<sub>2</sub>-C<sub>4</sub> olefins and C<sub>2+</sub>- products as well as the rate of olefin formation and the O/P ratio. Table S2 shows that our catalysts give comparable or even superior performance in terms of the selected criteria. In average, the 0.4Mn-K/Fe catalyst was among top 5% materials in terms of the selectivity to C<sub>2+</sub>-hydrocarbons. The selectivity to C<sub>2+</sub>-hydrocarbons is 83.1 % with the fraction of C<sub>2</sub>-C<sub>4</sub> olefins is about 30.4 %, at CO<sub>2</sub> conversion of 42.3 % at 300 °C. Meanwhile, this catalyst resulted in the selectivity to CO and CH<sub>4</sub> of only 8% and 8.9 %, respectively. Hereby, it was shown that statistical analysis approach can be useful for elucidating key parameters affecting catalytic performance and on the basis of such data new materials with enhanced catalytic properties can be designed.

# 5. Conclusions

Using the large number of published studies on  $CO_2$  hydrogenation to higher hydrocarbons, we created a database. It includes catalyst performance as well as various descriptors such as catalyst composition, the kind of promoter, support material, alkali metal to Fe ratio, iron precursor, catalyst preparation method, treatment, reaction conditions and feed composition. Their effects on catalyst performance were elucidated by Multiway ANOVA, correlation coefficients and regression tree analysis. Such approach enabled us to identify property-performance correlations typically hidden in the vast body of existing experimental data.

With respect to reaction conditions, total pressure, catalyst treatment and reaction temperature have the most decisive parameters affecting the rates of overall CO2 conversion and formation of C2+- hydrocarbons. Moreover, the Pauling electronegativity of metal dopant for Fe<sub>2</sub>O<sub>3</sub> has been established as an appropriate descriptor for catalyst activity and selectivity. The kind of catalyst, total pressure, catalyst treatment time and the kind of iron precursors determine the selectivity to  $C_{2+}$ - hydrocarbons and the ratio of olefins/paraffins. These two characteristics are improved when combining alkali metal with transition metal promoters. Prepared Mn/K promoted Fe-based catalysts possess enhanced catalytic properties in terms of CO<sub>2</sub> conversion, the selectivity to C2+- hydrocarbons and C2-C4 olefins as well as the O(C2- $C_4)/P(C_2-C_4)$  ratio. Hereby, our statistical approach was proven to be suitable for designing catalysts with improved desired performance and may provide new concepts for efficient catalyst design and process optimization.

## CRediT authorship contribution statement

Qingxin Yang: Investigation, Writing - original draft, Writing - review & editing. Andrey Skrypnik: Investigation, Writing - review & editing. Alexander Matvienko: Funding acquisition, Writing - review & editing. Henrik Lund: Investigation, Writing - review & editing. Martin Holena: Formal analysis, Writing - review & editing. Evgenii V. Kondratenko: Conceptualization, Supervision, Funding acquisition, Writing - review & editing.

#### **Declaration of Competing Interest**

The authors report no declarations of interest.

#### Acknowledgement

Financial support from Deutsche Forschungsgemeinschaft (KO 2261/10-1) and Leibniz-Gemeinschaft e.V. (SAW-2017-LIKAT-1) is gratefully acknowledged. The authors thank Anja Simmula for ICP measurements.

# Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.apcatb.2020.119554.

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