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PAPER

Developing catalytic materials for the oxidative coupling of methane through statistical analysis of literature data†

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Based on available 1870 literature data for the oxidative coupling of methane (OCM), various statistical models were applied i) to design three-component catalysts consisting of one host metal oxide (La_2O_3 or MgO) and two oxide (Li, Na, Cs, Sr, Ba, La, or Mn) dopants and ii) to predict their OCM performance. To validate this approach for catalyst design, selected materials were prepared and experimentally tested for their activity and selectivity in the target reaction. The effects of kinds of host oxides, dopants and their interplay on the OCM performance of differently composed catalysts were statistically evaluated.

Introduction

Owing to the large fossil resources of natural gas (shale gas) and renewability of methane (biogas), a strong economic interest exists in developing processes for methane conversion into value-added products. Currently, methane is industrially converted through catalytic steam or autothermal reforming to synthesis gas, *i.e.* a mixture of CO and H_2.[1] This mixture finds its application in the large-scale production of methanol and higher hydrocarbons. There are commercial technologies for methanol conversion into ethylene and propylene,[2,3] which are the two most important building blocks of chemical industry. However, each step in the synthesis gas route of methane conversion into useful products has its own drawbacks negatively influencing the overall process economy. Therefore, direct (one step) conversion of methane to methanol, formaldehyde, or C_2 hydrocarbons (C_2H_4, and C_2H_6) is highly desired. For this purpose, a large amount of research has been carried out over the last 30 years. Most of such studies were devoted to the oxidative coupling of methane (OCM) to produce C_2 hydrocarbons. Since the pioneering works of Keller and Bhasin[4] as well as Hinsen and Baerns,[5] various catalytic materials have been investigated for this reaction.[6–13] Unfortunately, the performance of known OCM catalysts is significantly lower than in steam cracker of

ethane to ethylene: ethylene selectivity of 0.8 at around 0.7 ethane conversion. Under this consideration, the OCM reaction can become profitable when the ethylene selectivity would be close to the above value at a methane conversion higher than 0.30.[14–16] The low selectivity to C_2 hydrocarbons at industrially relevant degrees of methane conversion is related to higher reactivity of the target products tending to oxidation to CO and CO_2 (CO_x). To overcome such problems, methane can be converted into C_2 hydrocarbons including acetylene in the absence of oxygen at temperatures above 2000 °C as had been previously utilized by Hüls AG and BASF.[17] However, such process suffers from high energy demand. Hall reported about an alternative process concept for converting methane into ethylene and hydrogen or hydrocarbon liquids.[18] In this concept, methane (less than 10% of the fed methane) is combusted in an internal-combustion thermal cracker where non-reacted methane is converted to mainly acetylene and hydrogen. The acetylene can then be hydrogenated with very high selectivity to ethylene using the hydrogen from the cracker. Recently, a dual-reactor concept was introduced for improving selectivity to higher hydrocarbons in the OCM reaction with a simultaneous decrease in CO_x selectivity.[19,20] In this concept, the OCM reaction is performed in a first reactor, while a second reactor operating at a lower temperature and located downstream to the first one is used for hydrogenation of OCM-generated CO_x to hydrocarbons in presence of additional hydrogen. More than 50% of CO_x products formed in the OCM reactor were hydrogenated to desired C_3, C_4 and C_5 hydrocarbons, with propane selectivity being up to 0.10. An overall yield of C_{2+} hydrocarbons of 0.38 was achieved. Further progress of this concept can be expected when active and selective catalysts for CO_x hydrogenation will be developed. Alternatively, this concept

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or the OCM reaction itself would profit from new catalytic materials with improved OCM selectivity.

Some years ago, Thybaut et al.[21] have suggested a methodology for catalyst design based on the kinetics of the OCM reaction. The idea behind their approach is to correlate catalytic performance with specific catalyst descriptors influencing individual reaction pathways. The following descriptors were defined and applied: i) reaction enthalpy of hydrogen abstraction from CH_4, ii) chemisorption energy of O_2, CH_2O, HCO, CO, CO_2, H_2O, and C_2H_4, iii) initial sticking probabilities of O_2, $CH_3^·$, CO, CO_2, and H_2O, and iv) concentration of active sites. By optimizing these parameters and reaction conditions, a yield of C_2 hydrocarbons of 0.35 was predicted but not experimentally verified.

From a general viewpoint, the chemical composition of catalysts should influence such descriptors. Therefore, establishing relationships between the catalyst composition and OCM performance may open the possibility for designing effective catalytic materials. To this end, Zavyalova et al.[22] have statistically analysed about 1000 scientific papers and patents reporting quantitative data on the chemical composition of OCM catalysts and their performance under different reaction conditions. These authors suggested a strategy for designing multicomponent catalysts; promising OCM catalysts should consists of host basic metal oxide (MgO or La_2O_3) promoted with metal oxide dopant(s) influencing positively C_2-selectivity (Cs, Na, Sr, Ba) and activity (Mn, W).

Unfortunately, no theoretically based relationship between catalyst composition and performance is known for the oxidative coupling of methane. Thus, such a relationship can only be established empirically, i.e. through fitting some mathematical function(s) to the available experimental data. The simplest kind of such empirical models is linear regression, which is however not suitable for this purpose because catalytic data typically do not reveal any linear dependence on catalyst composition. Consequently, quadratic or some special cubic models known as response surface have been traditionally used.[23] Owing to the increasing power of modern computers, it became possible to use more sophisticated and complex nonlinear models, such as artificial neural networks,[24] kernel regression,[25] or Gaussian processes[26] for catalyst research[27–29] and for mathematical modelling in catalysis.[30–32] Such empirical models can be trained on the basis of available catalytic data and hereafter used to predict performance of other catalysts that had not been used in the training. There are two typical purposes of such prediction approaches:

i) To check the trained model for its predictability, catalytic materials with compositions predefined by researchers are experimentally prepared and tested. Since only the catalysts from this predefined set are taken into account, it doesn't matter whether some of the available catalysts used for training the model have better performance than the catalysts from this set. However, some good-performing materials can be discovered because the composition of virtual catalysts is varied in a more systematic way compared to classical trial and error approach.

ii) To find the best catalyst, the search, is performed in the whole considered set of catalyst compositions with the use of an optimization method, e.g. an evolutionary algorithm.[25] When the model from (i) fits the experimental data well enough, it can be used for suggesting catalyst formulations in such evolutionary approach.

The main purpose of the present study was to experimentally validate the strategy for generating OCM catalysts based on host and dopant metal oxides as theoretically suggested in ref. 22. The specific objectives of the study were: (i) to elucidate the potential of statistical models for predicting OCM performance of multicomponent materials, (ii) to prove if there is a systematic difference in catalytic performance between materials possessing different main components, and (iii) to check if there is a synergy effect between two dopants. To this end, we applied various statistical models for suggesting potential catalyst compositions and tested their OCM performance experimentally. Finally, the models are critically evaluated in terms of their predictive accuracy.

Theoretical approach and experimental details

Mathematical modelling

From a mathematical viewpoint, eqn (1) represents an empirical model of a scalar performance feature, such as yield, selectivity or conversion as a function of catalyst composition or/and reaction conditions. Such function for a quadratic model is given by eqn (2). Other models considered in this paper are several variants of a particular kind of artificial neural networks, called radial basis function (RBF) networks.[33] They are thoroughly explained in the electronic ESI† together with the corresponding functions in eqn (1). Model parameters in artificial neural networks are called weights.

$$f : \mathcal{R}^{d+p} \to \mathcal{R}, \ i.e., f(x, w) \in \mathcal{R}, \tag{1}$$

$$f(x, w) = w_0 + \sum_{j=1}^{d} \left(w_j x_j + w_{j,j} x_j^2 \right) + \sum_{j=2}^{d} \sum_{k=1}^{j-1} w_{j,k} x_j x_k. \tag{2}$$

where $\mathcal{R}^{d+p}$ denotes the space of $(d + p)$-dimensional real vectors, d is the dimension of input data x (catalyst composition, reaction parameters), and p is the number of model parameters, i.e. the dimension of the vector of model parameters w. For a quadratic function $p = \dfrac{d(d+3)}{2} + 1$ and $w = (w_0, w_{1,\dots d}, w_{1,1}, \dots w_{1,d}, w_{2,1}, \dots w_{d,d})$.

The choice of a particular model kind, i.e. a particular definition of f in eqn (1), is the most important modelling decision. However, it does not enable to make model predictions for a particular input x. To this end, a particular value $\hat{w}$ of the vector w of parameters must also be chosen. The process of choosing $\hat{w}$ is called model learning or model training. For model learning, we need a set $\mathcal{M}$ of input data (in our case, a set of catalyst compositions) such that for each $x \in \mathcal{M}$, one or more measured values of the

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considered catalyst performance are available. The overall number of measurements available for x is denoted $n(x)$, whereas the notation $m(x) = (y_1,\ldots,y_{n(x)})$ is used for the whole sequence of the corresponding measured values. Most frequently, $n(x)$ is equal to 1, but a model must be able to also deal with a situation that several different performance values have been measured for the same input x, *e.g.* in different experiments or by different laboratories. Each pair (x, y), in which $x \in \mathscr{M}$ and y is one of the corresponding values y_i from the sequence $m(x)$, is called a training pair for the model. Mathematically, model learning is the minimization of some error E with respect to its parameters using the available training pairs, thus the resulting $\hat{w}$ fulfils eqn (3),

$$E\left(f, \hat{w}, \mathscr{M}\right) = \min_{w \in W} E\left(f, w, \mathscr{M}\right). \tag{3}$$

To solve the minimization task in eqn (3), two further decisions must be made:

• Within which set W should the vector w be sought? Frequently, W is simply the space of all p-dimensional real vectors. Sometimes, however, some restrictions are imposed to some components of w, *e.g.*, they have to be positive.

• How to compute the error $E(f, w, \mathscr{M})$? The kinds of errors most frequently used are the mean absolute error (MAE) and the mean squared error (MSE) defined in eqn (4) and (5), respectively.

$$\mathrm{MAE}\left(f, w, \mathscr{M}\right) = \frac{1}{\sum_{x \in \mathscr{M}} n(x)} \sum_{x \in \mathscr{M}} \sum_{\substack{i=1, \\ m(x)=\left(y_1,\ldots,y_{n(x)}\right)}}^{n(x)} \left| f\left(x, w\right) - y_i \right|, \tag{4}$$

$$\mathrm{MSE}\left(f, w, \mathscr{M}, \mathscr{M}\right) = \frac{1}{\sum_{x \in \mathscr{M}} n(x)} \sum_{x \in \mathscr{M}} \sum_{\substack{i=1, \\ m(x)=\left(y_1,\ldots,y_{n(x)}\right)}}^{n(x)} \left(f\left(x, w\right) - y_i \right)^2. \tag{5}$$

Since the physical units of MAE and MSE are different, the root mean squared error (RMSE) is frequently used instead of MSE, which has the same units as MAE,

$$\mathrm{RMSE}\left(f\left(x, w\right), \mathscr{M}\right) = \sqrt{\mathrm{MSE}\left(f, w, \mathscr{M}\right)} \tag{6}$$

Model learning (eqn (3)) based on RMSE gives, of course, the same result as model learning based on MSE. In our research, we employed model learning based on RMSE, and for comparison, we also recorded MAE.

It is important to note that MAE, MSE and RMSE measure the error of the model but are not suitable to estimate the error of a particular prediction by the model because they do not include the information about the particular input for which the prediction is computed. Therefore, to estimate the error of a particular prediction in our experiments, we used a

heuristics based on nearest neighbours,[34,35] which proceeds in two steps:

1. Given the input x_{new}, in which the prediction $f(x_{\mathrm{new}}, \hat{w})$ has been computed, and a number k chosen in advance, the elements of $\mathscr{M}$ are ordered increasingly according to their distance from x_{new}, and the average of the measured values $y^{(1)},\ldots,y^{(k)}$ corresponding to the k elements $x^{(1)},\ldots,x^{(k)}$ of $\mathscr{M}$ closest to x_{new} is computed, *i.e.* $\bar{y}^{(k)} = \frac{1}{k} \sum_{i=1}^{k} y^{(i)}$. For ordering the elements of $\mathscr{M}$, any distance can be used. When estimating the errors of predictions in our experiments, we used the Euclidean distance standardized with respect to different variance of proportions of different elements, which form the dimensions of the points in $\mathscr{M}$.

2. As an estimate of the prediction $f(x_{\mathrm{new}}, \hat{w})$, its distance from $\bar{y}^{(k)}$ is then taken, *i.e.* the value $\left| f\left(x_{\mathrm{new}}, \hat{w}\right) - \bar{y}^{(k)} \right|$. According to step 1, this distance depends on the choice of k. Therefore, we have always computed it for k = 2, 3, 4, 5 and used the maximum of those 4 values.

For modelling the dependence of yield of C_2 hydrocarbons on composition of OCM catalysts, we used 2 different model types mentioned below. Their mathematical description is provided in the ESI.†

I. The traditional quadratic response surface model described in eqn (2).

II. Clustered RBF network with diagonal Gaussian radial basis functions centred in data, optionally in addition combined with linear regression.

Catalyst preparation

La_2O_3 and MgO were used as host oxides for preparation of catalytic materials. Each host oxide was impregnated with an aqueous solution of two dopants at room temperature according to the incipient wetness impregnation method. The dopants were nitrates of lithium, sodium, caesium, barium, strontium and manganese. The impregnated materials were dried at 393 K for 4 hours followed by their calcination in a muffle furnace in static air at 1073 K for 5 hours.

Catalytic testing

Catalytic tests were carried out in a multi-channel reactor system at ambient pressure using a feed with methane and air in a stoichiometric $CH_4 : O_2$ ratio of 2. This setup consists of 48 plug-flow fixed-bed quartz tube reactors (i.d. = 4 mm) operating in parallel. 78 mg of the fresh catalyst (sieve fraction of 250–450 μm) diluted with SiC in the ratio of 1/3 were filled into each reactor. An in-house developed flow restrictor equally distributed the total gas flow to 48 reactors to ensure the modified contact time of 0.0039 g min ml^{-1} per reactor. Before testing, the catalysts were heated up to 1073 K in a flow of air. Hereafter, the methane–air mixture was fed to the reactors.

The feed components and the reaction products were analysed by an on-line gas chromatograph (Agilent 7890) equipped with PLOT/Q (for CO_2) AL/S (for hydrocarbons) and Molsieve 5 (for H_2, O_2, N_2, and CO) columns as well as flame ionization and thermal conductivity detectors. The GC analysis started after the system reached reaction temperature and was carried out sequentially for each individual reactor. The CH_4 conversion was calculated from the inlet and outlet molar flows of CH_4. The product selectivity was calculated on feed basis.

Results and discussion

Selection of catalyst compositions based on literature data

For modelling, we defined 378 three-component catalyst formulations consisting of one host oxide (La_2O_3 or MgO) and two dopants from oxides of Li, Na, Cs, Sr, Ba, La, or Mn. For each host oxide, there were 21 individual groups differing in dopant combinations. In addition, each group consisted of 9 catalyst formulations based on individual dopant concentrations varying from 0.1 to 10 wt.%. In order to estimate the yield of C_2 hydrocarbons for these materials, we used various models of type (II) as defined in section "Mathematical modelling". In total, there were 13 models. All the models were trained using available literature data on catalysts and their OCM performance from ref. 22. The individual models differ from each other in:

i. The definition of the model described by eqn (1), in particular, in the number of clusters and of basic functions (*cf.* ESI†) used for modelling in each cluster,

ii. The details of the minimization procedure used to solve the optimization problem described by eqn (3),

iii. The data used for their training. Three subsets of the available literature data were considered:

A. 4 models for yield of C_2 hydrocarbons were trained using catalysts based on host oxides of La or Mg (495 catalysts, 50 elements);

B. 4 models for yield of C_2 hydrocarbons were trained using catalysts based on host oxides of La or Mg prepared *via* impregnation (181 catalysts, 31 elements);

C. 5 models for yield of C_2 hydrocarbons were trained using catalysts containing only elements from the pool of oxides of Mg, La, Sr, Ba, Na, Cs, Li, Mn, and W (386 catalysts, 9 elements).

To compare the trained models with respect to their predictive accuracy, a 10-fold cross-validation on the considered subset of literature data was performed. Such subset was randomly divided into ten parts of approximately equal size. Hereafter, for each part, the RMSE of a model trained on the remaining 9 parts was computed and finally, the RMSE was averaged over all 10 parts. The two lowest average RMSE values were obtained for models trained on the subset C of literature data. Therefore, only predictions made by models trained on the subset C were finally taken into account for the decision which catalysts will be experimentally prepared and tested for the OCM reaction. To this end,

a weighted average prediction of the yield of C_2 hydrocarbons was calculated for each catalyst composition using the predictions by the five models trained on the subset C.

The weights of the 5 predictions were inversely proportional to the RMSE of each model. Within each catalyst group consisting of nine materials, the catalyst composition with the highest weighted average yield was synthesized. Table 1 reports these compositions and their predicted OCM performance. For clarity purposes, we classified the catalysts into 8 systems differing in host metals and promoters: La–Sr, La–Ba, La–Mg, La–alkali, Mg–Sr, Mg–Ba, Mg–La, and Mg–alkali. On average, catalysts based on La_2O_3 as host oxide should perform superior to their MgO-based counterparts. The highest average C_2 yield of around 0.156 is predicted for

Table 1 Nominal composition of catalysts prepared on La_2O_3 and MgO basis. Y_{Pr} and Y_{Ex} stand for their predicted and experimental yields of C_2 hydrocarbons respectively

| Nr. | Catalysts | Metals and their weight concentrations/wt.% | | | | | | | | Y_{Pr} | Y_{Ex} |
		La	Mg	Sr	Ba	Li	Na	Cs	Mn		
1	LaSrMn	90.8		9.1					0.1	0.148	0.141
2	LaSrBa	90.8		9.1	0.1					0.148	0.164
3	LaSrLi	90.8		9.1		0.1				0.139	0.173
4	LaSrNa	90.8		9.1			0.1			0.138	0.160
5	LaSrCs	90.8		9.1				0.1		0.148	0.147
6	LaBaMn	98.9			1.0				0.1	0.147	0.115
7	LaBaLi	99.8			0.1	0.1				0.135	0.154
8	LaBaNa	90.8			0.1		9.1			0.153	0.140
9	LaBaCs	99.8			0.1			0.1		0.146	0.149
10	LaMgMn	90.8	9.1						0.1	0.147	0.103
11	LaMgSr	83.3	8.3	8.3						0.151	0.148
12	LaMgBa	90.1	9.0		0.9					0.147	0.159
13	LaMgLi	90.8	9.1			0.1				0.134	0.141
14	LaMgNa	90.8	9.1				0.1			0.146	0.139
15	LaMgCs	90.1	9.0					0.9		0.146	0.127
16	LaLiMn	83.3				8.3			8.3	0.165	0.110
17	LaNaMn	90.1					9.0		0.9	0.155	0.137
18	LaCsMn	83.3						8.3	8.3	0.158	0.090
19	LaNaLi	83.3				8.3	8.3			0.156	0.130
20	LaNaCs	90.8					9.1	0.1		0.153	0.145
21	LaCsLi	90.8				9.1		0.1		0.147	0.147
22	MgSrMn		83.3	8.3						0.141	0.009
23	MgSrBa		83.3	8.3	8.3					0.13	0.167
24	MgSrLi		83.3	8.3		8.3				0.138	0.102
25	MgSrNa		83.3	8.3			8.3			0.146	0.157
26	MgSrCs		83.3	8.3				8.3		0.13	0.168
27	MgBaMn		90.8		9.1					0.135	0.119
28	MgBaLi		90.8		0.1	9.1				0.145	0.062
29	MgBaNa		90.1		0.9		9.0			0.153	0.018
30	MgBaCs		83.3		8.3			8.3		0.128	0.153
31	MgLaMn	9.1	90.8							0.146	0.088
32	MgLaSr	8.3	83.3	8.3						0.136	0.139
33	MgLaBa	9.0	90.1		0.9					0.145	0.127
34	MgLaLi	8.3	83.3			8.3				0.151	0.104
35	MgLaNa	8.3	83.3				8.3			0.156	0.158
36	MgLaCs	8.3	83.3					8.3		0.138	0.120
37	MgLiMn		90.8			9.1				0.145	0.097
38	MgNaMn		90.8				9.1			0.154	0.010
39	MgCsMn		90.8					9.1		0.135	0.093
40	MgNaLi		90.8			9.1	0.1			0.145	0.064
41	MgNaCs		90.8				0.1	9.1		0.135	0.112
42	MgCsLi		90.8			9.1		0.1		0.145	0.072

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La–Alkali system. The worst catalytic performance is predicted for catalysts from the Mg–Sr group.

Experimental catalytic data and their comparison with literature

To check the contribution of non-catalytic methane oxidation to products distribution determined in presence of catalytic materials, we initially performed tests with an empty reactor and reactors filled with SiC, Al_2O_3 or fused SiO_2. In all cases, carbon oxides and C_2 hydrocarbons were detected but methane conversion stayed below 0.025 and oxygen conversion below 0.04. When catalytic materials were tested, conversion of methane and oxygen was significantly higher. Thus, the below results can be safely ascribed to the effect of catalyst on the OCM reaction.

Fig. 1 exemplarily illustrates the yield of C_2 hydrocarbons experimentally determined over catalysts from the La–Sr and Mg–Sr groups as a function of time on stream. The corresponding conversion of methane is given in Fig. S1 in the ESI.† The results obtained over catalysts from the La–Ba, La–Mg, La–alkali, Mg–Ba, Mg–La, and Mg–alkali groups are summarized in Fig. S2–S7.† For comparative purposes, the OCM performance of non-doped La_2O_3 and MgO is also presented in these figures. It should also be noted that not all catalytic materials showed stable OCM performance over 40 h at 1073 K. Therefore, Table 1 reports initial yields of C_2 hydrocarbons. One can clearly see that the yield is influenced both by host oxide and dopants. With the exception
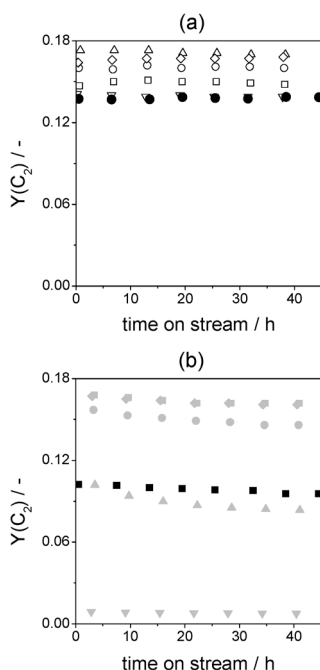
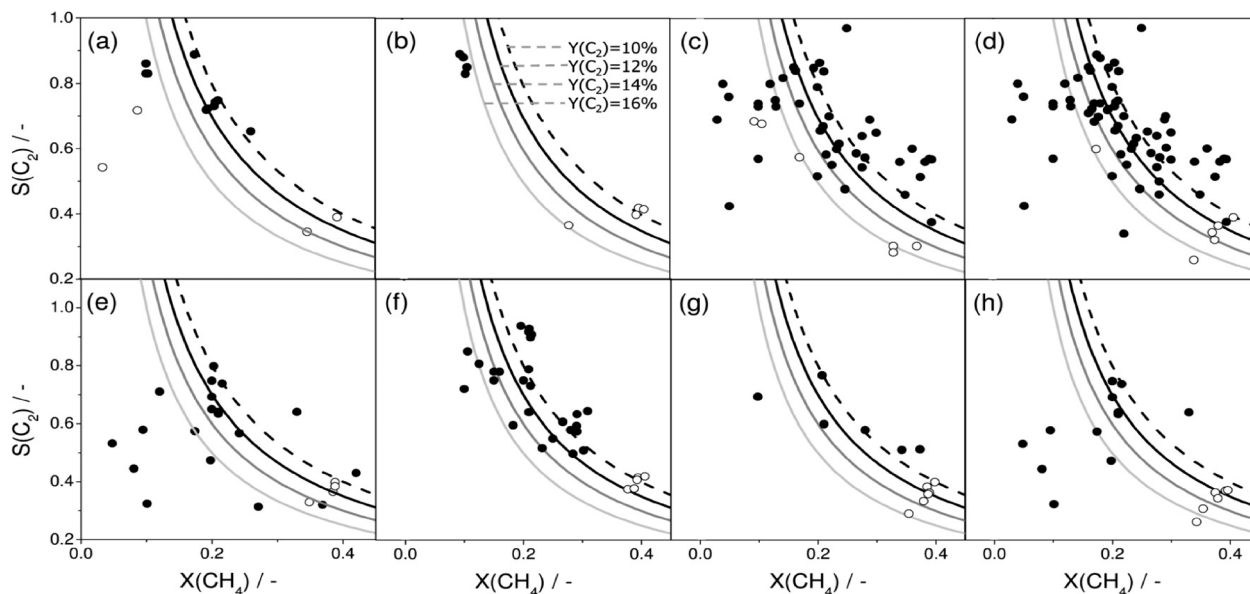of MgBaLi, MgBaNa, MgNaLi, MgCsLi, oxygen conversion was complete over all catalysts tested.

Fig. 2 shows methane conversion and selectivity to C_2 hydrocarbons experimentally obtained over catalysts synthesized in the present study together with the literature data available through ref. 22. From a viewpoint of yield of C_2 hydrocarbons (used as criterion in our study for selecting catalytic materials), a visual inspection of all these figures suggests that the worst agreement between the previous literature and our present data was obtained for the Mg–Alkali and La–Mg systems, while the performance of other systems was reasonably predicted. To validate this interpretation statistically, we tested the equality of yield distributions between the literature data and our measurements using the 2-sample Kolmogorov–Smirnov test.[36] Table 2 summarizes the achieved significance level for rejecting the hypothesis that the distributions of literature and experimental yields of C_2 hydrocarbons are equal.

The achieved significance level is the probability that the obtained data can occur if the hypothesis is true, *i.e.* if both groups of data really follow the same distribution. If that probability is low, it is interpreted as the hypothesis being rejected by the test, and the lower the probability is, the higher is the significance of its rejection. For the La–Ba, La–alkali, La–Sr, Mg–Ba and Mg–Sr systems, the tested hypothesis cannot be rejected. It can be rejected at the low significance level of 10% for the Mg–La system, but not at the usual significance level of 5%. For the Mg–alkali and La–Mg systems, it can be rejected even at the high significance level of 1%. Based on this statistical analysis, it can be concluded that our models realistically predict the OCM performance of differently composed catalysts with the exception of those from the Mg–alkali and La–Mg systems. It is beyond the current study to elucidate possible reasons for the latter deviation.

Comparison between prediction and experiment

To illustrate the predictive accuracy of our modelling approach, we calculated the difference between predicted and experimental yields of C_2 hydrocarbons. The smaller the difference, the better the prediction is. If this difference has a negative value the modelling underestimates the experimentally determined OCM performance, while the situation is reverse when such value is positive. Fig. 3 compares the difference values for all catalysts. On average, the OCM performance of catalysts based on La_2O_3 is better predicted than that of their MgO-containing counterparts. The large difference for MgBaLi, MgBaNa, MgNaLi, MgCsLi is due to their low activity.

It is worth repeating that the predicted yields were obtained by using a model that is a weighted combination of five RBF network models trained with the subset C of the available literature data. To check the predictive accuracy of individual models, we selected six particular models. Their selection was made according to the model predictive

Fig. 1 Time on-stream yield of C_2 hydrocarbons over (a) La–Sr-based (●-La_2O_3, □-LaSrCs, ○-LaSrNa, △-LaSrLi, ▽-LaSrMn, ◇-LaSrBa) and (b) Mg–Sr-based (■-MgO, ▪-MgSrCs, ●-MgSrNa, ▲-MgSrLi, ▼-MgSrMn, ◆-MgSrBa) catalysts at 1073 K and τ of 0.0039 g min ml^{-1} using a feed consisting of 29% CH_4 in air.

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Fig. 2 Comparison between literature data (solid symbols) available through ref. 22 and data measured in the present study (open symbols) for the systems: (a) Mg–Ba, (b) Mg–Sr, (c) Mg–La, (d) Mg–Alkali, (e) La–Ba, (f) La–Sr, (g) La–Mg and (h) La–Akali. The experimental conditions are as in the caption of Fig. 1.

ability estimated by 10-fold cross-validation. They include three models of type I (quadratic response surface models), which were trained with the subsets A, B and C of the literature data, respectively, and three models of type II (RBF network models) again trained with the subsets A, B and C, respectively.

The MAE and RMSE values for each of the tested models are given in Table 3. It is important to note that, according to eqn (4) and (6), the lower these prediction errors, the better the predictive model accuracy is. Irrespective of the model applied, the lowest MAE and RMSE values were determined for the La–Ba system followed by the La–alkali, Mg–La and Mg–alkali systems. The values, however, depend on the model and literature data subset used. When using the subset C, the lowest error was obtained nearly always with a model of type I. For all other subsets, models of type II appear to have better predictive accuracy. This model type also provided the lowest MAE and RMSE values when it was trained on the subset A.

To get insights into the errors in prediction of yield of C_2 hydrocarbons, we checked the distribution of that error for

Table 2 Results of testing the equality of distributions between literature and experimental yields of C_2 hydrocarbons using the 2-sample Kolmogorov–Smirnov test

System	Significance level/%
La–Ba	30.0
La–Alkali	67.0
La–Mg	6.1
La–Sr	39.0
Mg–La	25.0
Mg–Alkali	0.2
Mg–Ba	68.0
Mg–Sr	63.0

the catalysts tested in our experiments, as well as for their most important subgroups. Those subgroups were obtained using a regression tree[37] for regression of the prediction error depending on the main component of the catalyst and on the presence of individual dopants. This tree is shown in Fig. 4 together with the distributions of prediction errors in the obtained subgroups. Analysing this tree, the following important influences on the prediction error on yield of C_2 hydrocarbons were identified:

i. Most important feature from the point of view whether the prediction error is high or low is presence of Mn among dopants.

ii. Among catalysts not having Mn as a dopant, the next most important feature is the usage of Sr as a dopant.

iii. In all 3 subgroups resulting from the above two subdivisions, the next most important feature is always the main component, *i.e.* La$_2$O$_3$ or MgO.

As seen from Fig. 4, the distributions of prediction errors for all tested catalysts is slightly shifted towards positive values (its mean value is 2.2) and is skewed to the right-hand side. Similar characteristics hold also for the specific subsets of catalysts containing neither Mn nor Sr as dopants or for catalysts containing Mn as a dopant, especially if MgO is the host oxide, though in those cases, they are based only on a rather low number of tested catalysts. On the other hand, the distribution of catalysts without Mn but containing Sr is slightly shifted towards negative values, though also this observation is based only on few catalysts.

The deviations between the predicted and the experimental values can originate from the facts that i) the models applied were inappropriate or ii) the literature data used to train the models strongly deviate from each other. To check the latter possibility, we analysed C_2 hydrocarbons yields
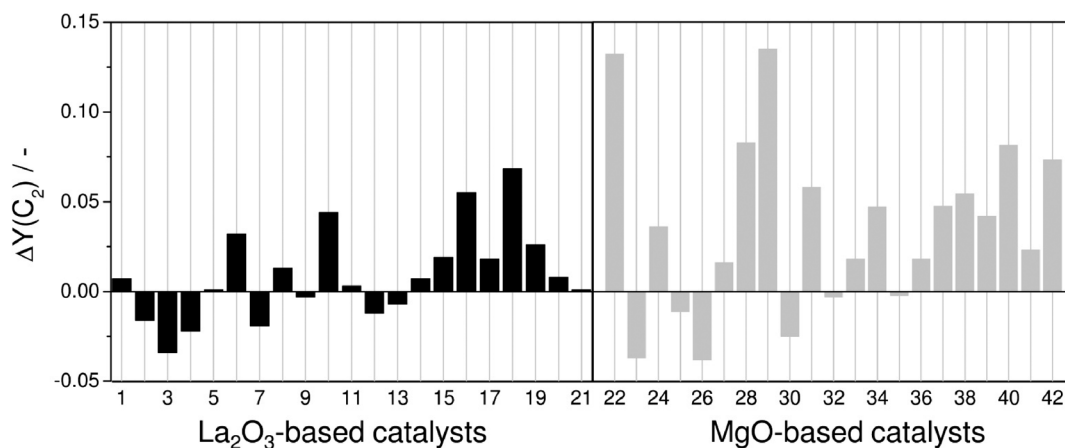
Fig. 3 Prediction error, *i.e.* the difference between predicted and experimental yield values of C_2 hydrocarbons (ΔYC_2). The numbers of catalysts are explained in Table 1.

Table 3 Comparison of the MAE and RMSE errors with which different models predicted the yield of C_2 hydrocarbons on various catalysts

		Best model of type I					
		Subset *A*		Subset *B*		Subset *C*	
		Kind of model error					
Systems	$EV(\mathcal{M})^a$	MAE	RMSE	MAE	RMSE	MAE	RMSE
La–Ba	5.6	2.6	3.2	3.5	3.9	1.4	1.6
La–alkali	5.9	401.9	401.9	28.9	28.9	1.9	2.0
Mg–La	3.6	2.6	2.8	2.1	2.5	2.6	3.2
Mg–Alkali	3.9	6.9	7.3	6.5	6.9	6.9	7.0

		Models of type II					
		Best				Combined	
		Subset *A*		Subset *B*		Subset *C*	
		Kind of model error					
Systems	$EV(\mathcal{M})^a$	MAE	RMSE	MAE	RMSE	MAE	RMSE
La–Ba	5.6	0.6	0.7	1.4	1.8	1.6	2.6	1.7	2.0
La–Alkali	5.9	1.6	2.0	2.5	3.2	1.9	2.6	1.9	2.7
Mg–La	3.6	2.4	2.7	2.5	2.3	2.8	3.4	2.4	3.2
Mg–Alkali	3.9	4.9	5.2	5.0	6.0	8.5	8.8	8.1	8.5

^{a} See eqn (7).

previously reported in literature for catalyst compositions, based on which the catalysts in the present study were prepared. The criteria for selecting literature data are summarized below:

i. La_2O_3 or MgO are host oxides with their weight percentages being between 83.3 and 99.8%.

ii. Depending on the kind of catalytic system various dopants were considered as follows:

- For the La–Ba system: Ba, Na, Cs, Li, Mn;
- Ffor the La–Alkali system: Na, Cs, Li, Mn;
- For the Mg–La system: La, Sr, Ba, Na, Cs, Li, Mn;
- For the Mg–Alkali system: Na, Cs, Li, Mn.

The extent of variation ($EV(\mathcal{M})$) of yield of C_2 hydrocarbons in various literature studies was calculated according to eqn (7). In this equation, the set $\mathcal{M}$ for a certain catalytic system was selected according to the above criteria, x and y

stand for catalyst composition and the corresponding yield respectively. For an ideal case, if the set of training pairs contains (x_i, y_i) and (x_j, y_j) and $x_i = x_j$ then y_i should equal y_j. Inequality between y_i and y_j shows deviation between different published literature data.

$$EV(\mathcal{M}) = \frac{\sum_{\substack{x \in \mathcal{M}, n(x) > 1, \\ m(x) = (y_1, \ldots, y_{n(x)})}} \sum_{i=2}^{n(x)} \sum_{j=2}^{i-1} |y_i - y_j|}{\sum_{\substack{x \in \mathcal{M} \\ n(x) > 1}} \frac{n(x)(n(x)-1)}{2}} \quad (7)$$

The $EV(\mathcal{M})$ values for available literature data are compared in Table 3 with the MAE and RMSE values showing the extent of deviation between experimentally determined and predicted yields of C_2 hydrocarbons in the present study. From a general viewpoint, if the $EV(\mathcal{M})$ values are smaller

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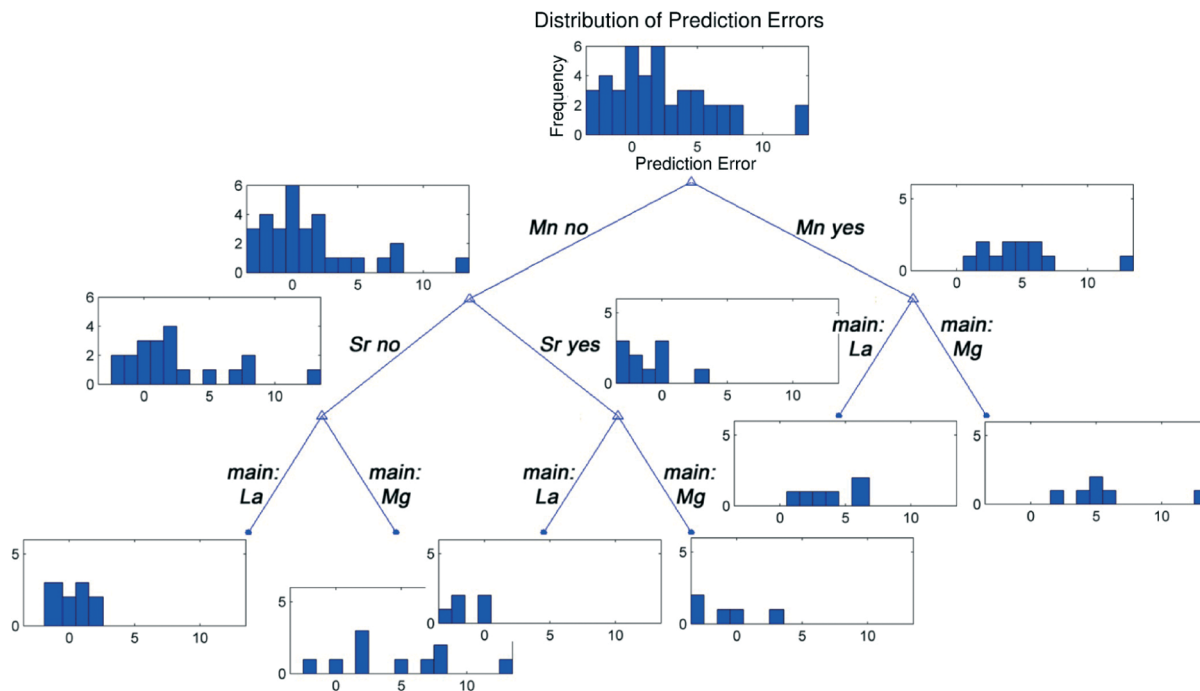This journal is © The Royal Society of Chemistry 2015

Fig. 4 Regression tree for the regression of the prediction error of yield of C_2 hydrocarbons (difference between the predicted and experimental yield) on the main component of the catalyst and on the presence of individual dopants. At each node and leaf of the tree, the distribution of the prediction error in the corresponding catalysts is shown.

than the errors (MAE or RMSE) between experimental and predicted values, then mainly the modelling approach is responsible for the problems with predictability. However, Table 3 shows that irrespective of the model applied, the MAE or RMSE values for the La–Ba and Mg–La systems are always smaller than $EV(\mathcal{M})$. In case of the La–Ba system, they are often substantially below (in particular, the error MAE of the RBF network trained with the subset B of data is only about 10% of $EV(\mathcal{M})$). For the La–Alkali system, the errors of all considered RBF networks are consistently below $EV(\mathcal{M})$, but among the traditional quadratic models, this is true only for the model trained with the C subset of data, whereas the other two quadratic models are completely unusable.

In summary, at least the models of type II can be expected to correctly predict catalytic performance of materials based on the La–Ba, La–Alkali and Mg–La systems. This is not valid for the Mg–Alkali system, because the errors of all considered models are consistently larger than $EV(\mathcal{M})$.

Relationships between catalyst composition and performance

The purpose of the discussion below is to analyse possible relationships between the composition of three-component catalysts and their OCM performance. Particularly, we focus on the role of host oxide (MgO $vs.$ La$_2$O$_3$) and dopants. In agreement with previous studies,[38] pure La$_2$O$_3$ performed superior to MgO with respect to the yield of C_2 hydrocarbons; 0.137 $vs.$ 0.102 at complete conversion of oxygen. For our multicomponent catalysts, promoting La$_2$O$_3$ or MgO with SrO has the most positive effect on the yield; the highest C_2 yields

of 0.173 and 0.165 were achieved over LaSrLi and MgSrCs respectively (Table 1). According to the database in ref. 22 these values are actually higher than those reported in literature for catalysts based La$_2$O$_3$ or MgO as host components with the exception of Li/MgO from ref. 39. This positive effect of SrO is valid for all tested catalysts irrespective of the second dopant used in our study, $i.e.$, Li, Na, Cs, Ba, Mg and Mn, with the last mentioned one showing a slightly negative effect. From a mechanistic viewpoint, promoting La$_2$O$_3$ with SrO results in the formation of anion vacancies in the lattice of the host oxide,[40] which help to transform non-selective bi-atomic oxygen species on the catalyst surface into selective mono-atomic ones.[41,42] When BaO was used as dopant, the yield of C_2 hydrocarbons was also improved compared to pure MgO and La$_2$O$_3$. However, this is not valid for all combinations of Ba with another dopant. Moreover, Ba-promoted catalysts showed lower on-stream stability compared to the Sr-doped counterparts. This can be explained by the fact that barium oxide is transformed to the corresponding carbonate, which is more stable than strontium carbonate. For both La$_2$O$_3$- and MgO-based catalysts, using alkali metal oxide as promoters also influenced this catalyst characteristics negatively.

The effect of individual dopants and dopant combinations on the yield of C_2 hydrocarbons was further analysed by regression trees. The trees for the yield regression as a function of the dopants were constructed for the catalysts based on La$_2$O$_3$ and those based on MgO, and they are shown in Fig. 5. The numbers in this figure stand for average C_2 yields, with the value in the root being an average
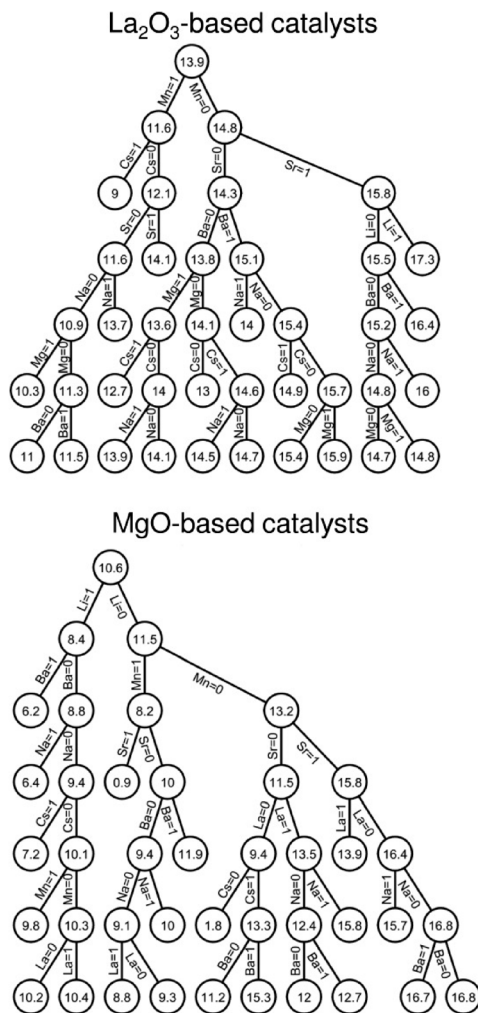
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La$_2$O$_3$-based catalysts

MgO-based catalysts

Fig. 5 Regression trees for the regression of yield (in percentage) of C$_2$ hydrocarbons over La$_2$O$_3$- and MgO-based catalysts on the presence of individual dopants. At each node and leaf of the tree, an average yield of the corresponding catalyst is given.

yield obtained over one of these two catalyst groups as a whole.

The paths from the root illustrate how the presence or absence of a certain dopant influences the yield. Among the catalysts from the La$_2$O$_3$ group, the presence of Mn has the most decisive influence on yield of C$_2$ hydrocarbons. On average, this dopant negatively affects the yield. This statement contradicts to the theoretical conclusion from ref. 22 where Mn was identified as an important element positively influencing this catalyst property. This contradiction is probably due to the fact that Mn has been reported to play an important role as promoter only for supported catalysts possessing Na$_2$WO$_4$. Its positive effect on OCM performance was ascribed to the formation of catalytically active Na–O–Mn species[43,44] and/or interconnected tetrahedral WO$_4$ and octahedral MnO$_6$ groups.[45] Such catalyst compositions were not investigated in the present study. In the subgroup containing Mn, the presence of Cs has the most decisive influence followed by the effect of Sr. The latter dopant also plays an

important role in the subgroup free of Mn. In the following leafs, the presence of Li and Ba is highly relevant for C$_2$ hydrocarbons yield over catalysts without and with Sr respectively. However, the latter condition appears to be more important for achieving high yields.

The presence of Li has the most decisive influence on the yield of C$_2$ hydrocarbons over catalysts based on MgO (Fig. 5). In the subgroup of Li-free materials, doping with Mn plays the second important role. The next important dopant influencing C$_2$ yield is SrO. On average, catalysts containing this dopant showed the highest yield not only among MgO- but also among La$_2$O$_3$-based catalysts.

Thus, taking the above statistically verified experimental results into account, we suppose that designing OCM catalysts based on one host metal oxide and two dopants may result in novel catalyst formulations with improved performance. Further progress can be expected when not only composition of catalysts but also their physico-chemical properties will be considered in statistical modelling. In addition, we strongly believe that supplementary information about the kinetics of individual reaction pathways should be taken into account in such approach to derive deeper fundamental relationships between catalyst composition and performance. We are currently performing such kinetic studies with the purpose to determine reaction constants of activation of O$_2$, CH$_4$, C$_2$H$_6$ and C$_2$H$_4$. Assuming that this statistical modeling turns out to be successful, evolutionary strategy in combination with high-through-put experimentation is to be applied for discovering optimal catalysts for maximal performance taking into account the multi-parameter space defined by the various variables (composition, solid-state properties, preparation methods, kinetic parameters and reaction conditions).

Conclusions

Statistical analysis of available literature data on OCM reaction was experimentally proven to have the potential for designing three-component catalysts based on one host metal oxide (La$_2$O$_3$ or MgO) and two dopants and for predicting their OCM performance. Catalysts prepared according to this approach performed superior to previously tested similarly composed materials. This analysis also enabled us to establish relationships between the catalyst composition and OCM performance. Compared with previous literature data, we cannot confirm that promoting with alkali metal oxides will always result in catalysts showing high yields of C$_2$ hydrocarbons. To generate active and selective catalysts, it is important to combine such dopants with oxides of alkali-earth metals. Irrespective of the kind of second dopant, our study claims that Sr is the most promising dopant for La$_2$O$_3$ and MgO.

From the point of view of modelling catalyst performance, our research has brought twofold experience:

1. Models based on RBF neural networks are more reliable than traditional quadratic response surface models.

2. The predictive accuracy of models based on literature data suffers from the high diversity of such data, which

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allows using only a part of the available information for model training, most naturally catalyst composition, whereas the remaining information, such as reaction conditions, is ignored and not incorporated into the model.

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