Development of catalytic materials for methane valorization on the basis of statistical analysis of literature data

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Abstract: Artificial neural networks and Gaussian processes have been applied to analyze available literature data for the oxidative coupling of methane and the selective oxidation of methane to formaldehyde. The idea behind this approach was (i) to identify parameters, i.e. catalyst composition, preparation method, and reaction conditions, which have the most decisive effect on the activity and, particularly, selectivity and (ii) to check the potential of the established relationships for tailored catalyst design. To this end, selected materials were prepared applying the obtained knowledge and experimentally tested for their performance in the target reactions.

Keywords: Methane, oxidative coupling, formaldehyde, statistical analysis.

1. Introduction

Methane being the major component of natural gas, methane clathrates and biogas is the most promising “green”, cheap and sustainable carbon feedstock for the chemical industry. Currently, it is, however, mainly combusted for mobility and energy generation. To meet future requirements with respect to limited petroleum reserves and environmental issues, efficient direct routes of methane conversion into value-added products are highly required. Among different possibilities for methane valorization, the most intensively investigated routes are the oxidative coupling of methane (OCM) to C_2H_6 and C_2H_4 (C_2 hydrocarbons) and the selective oxidation to methanol and/or formaldehyde.[1,2] They are, however, still not commercialized. The reason is that the known catalysts suffer from low selectivity to the desired products as a consequence of their higher reactivity towards further oxidation to carbon oxides in comparison with methane. Hence, the ongoing research is focused on establishing fundamental relationships required for tailored catalyst design. One option in this direction is the application of mathematical tools for analyzing of ready-available experimental data as has been demonstrated in our recent OCM studies.[3,4] The purpose of the present study was (i) to further validate our approach for the OCM reaction and (ii) to check its potential for the partial oxidation of methane to formaldehyde.

2. Experimental and Theoretical

A regression tree analysis was applied for testing the effect of various input variables (e.g. the kind of active component and support, catalyst preparation method, reaction temperature, CH_4/O_2 ratio) on methane conversion, product selectivity, and yield. Sophisticated statistical models, in particular, artificial neural networks and Gaussian processes were applied for suggesting potential catalyst compositions. Catalytic materials were prepared according to the incipient wetness impregnation method. Steady-state tests were carried out at ambient pressure and different temperatures (550-800°C) in a multi-channel reactor system using feeds with methane (20 or 40 vol%) and air in CH_4/O_2 ratios between 2 and 8. Selected catalysts were characterized by XRD, H_2 TPR, EPR spectroscopy and high-resolution STEM.

3. Results and discussion

Our strategy for designing of multicomponent catalysts is schematically shown in Figure 1 (a). As a first step, we analyzed available literature data on methane conversion into C_2 hydrocarbons or formaldehyde with the aim to identify the most relevant parameters affecting catalyst activity and selectivity. The parameters were catalyst composition, preparation method and reaction conditions. On the basis of such analysis for the OCM reaction, catalysts consisting of one host oxide (La_2O_3 or MgO) and two dopants from oxides of Li, Na, Cs, Sr, Ba, La, or Mn should show promising performance. To validate this statement, we prepared catalysts for each host oxide, which were divided into 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%. Li and Sr were established to have the most decisive influence on the yield of C_2 hydrocarbons. Figure 1(b) exemplarily illustrates the yield experimentally determined over the catalysts from the La-Sr-Li group as a function of La_2O_3 content. As expected, promoting of La_2O_3 resulted in an increase in the yield. However, the most positive effect was achieved when the ratio of Sr/Li was larger than 1 and overall dopant content was around 10 wt%.

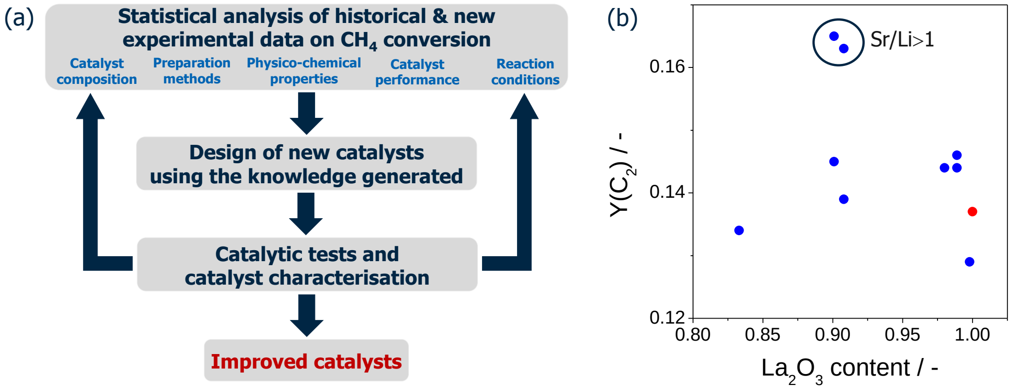

Figure 1. (a) Combined statistical and experimental approach for tailored design of catalysts for methane valorization. (b) The yield of C_2 hydrocarbons obtained over $La_kSr_lLi_mO_x$ at 1073 K using a feed with CH_4/O_2 ratio of 2. The red circle represents bare La_2O_3. The ratio of Sr/Li was ≤1 for all other catalysts with exception for those noted especially.

For partial oxidation of methane to formaldehyde, our statistical analysis predicted that the kind of support and surface site density (SSD) of active metal oxide play an important role for catalyst activity and selectivity. Therefore, we initially screened various bare supports with β-SiC being identified as the most inert support. To investigate the effect(s) of the kind of active metal and its SSD, we used this support for preparation of catalysts with low SSD values (≤ 0.34 nm^{-2}) of supported VO_x, FeO_x, CuO_x, or MoO_x. Fe-based catalysts revealed the highest activity, which also increased with SSD as for VO_x/β-SiC and MoO_x/β-SiC. In contrast, a positive effect of copper loading in CuO_x/β-SiC on methane conversion was observed only for the catalysts with 0.02 or 0.15 nm^{-2}. A further increase in the loading did not affect the conversion. The selectivity to formaldehyde at 600 °C decreased with an increase in SSD from 0.02 to 0.34 nm^{-2} in FeO_x/β-SiC and CuO_x/β-SiC. No obvious dependence of product selectivity on V loading was established for VO_x/β-SiC, while the selectivity increased over MoO_x/β-SiC. For all materials, the selectivity to formaldehyde increased with an increase in the apparent activation energy of methane oxidation.

4. Conclusions

Statistical analysis of available literature data aimed at identification of parameters affecting catalyst performance relevant for design of novel materials was experimentally validated for the OCM reaction and the methane oxidation to formaldehyde. To generate active and selective OCM catalysts, it is important to combine oxides of alkali and alkali-earth (especially Sr) metals as dopants for La_2O_3 and MgO. For the selective oxidation of methane to formaldehyde, inertness of support for VO_x, FeO_x, CuO_x, or MoO_x and their surface density have the most decisive effect on catalyst performance. β-SiC was identified as the most inert support among the tested materials including SiO_2.

References

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