Catalysis Today 159 (2011) 29–36

Contents lists available at ScienceDirect

Catalysis Today

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

Catalyst design based on microkinetic models: Oxidative coupling of methane

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ARTICLE INFO

Article history:
Available online 6 October 2010

Keywords:
Methane oxidative coupling
Microkinetic model
Catalyst descriptor
Catalyst design
Simulation

ABSTRACT

An extended microkinetic model for methane oxidative coupling (OCM) including so-called catalyst descriptors has been used for the simulation of experimental data on various catalysts in different setups. The good agreement between experimental data and calculated results over a large range of operating conditions proves the capability of the model being incorporated in a high throughput workflow for OCM catalyst development. The model allows the selection of the optimal operating conditions for catalyst evaluation. The effects of operating conditions and catalyst texture properties such as feed flow rate, temperature, pressure and porosity, BET-surface area, and tortuosity, have been investigated using the model. By varying the value of catalyst descriptors, C_2 product yields have been calculated to show the effects of these descriptors on the catalytic chemistry. With this microkinetic model the yield of methane oxidative coupling products was optimized using a genetic algorithm followed by the Rosenbrock and the Levenberg–Marquardt method. The optimized parameters include catalyst descriptors, operating conditions and catalyst texture properties. Results show that even with optimal surface chemistry and operating conditions, limits exist on the attainable yield. Nevertheless, these limits were found to be beyond the yields obtained with state of the art OCM catalysts, which opens up perspectives for further catalyst improvement.

1. Introduction

The oxidative coupling of methane (OCM) to C_2 and higher hydrocarbons has been seen as a promising way to upgrade natural gas since the work of Keller and Bhasin [1] and continues to attract both industrial as well as academic interest. OCM proceeds efficiently at temperatures above 900 K with ethylene as desired product. The overall reaction, accounting for microscopic reversibility, $2CH_4 + O_2 \leftrightarrow C_2H_4 + 2H_2O$, has been found to occur through a reaction network involving homogeneous as well as heterogeneous reaction steps [2–5]. Methane interacts with oxygen species in the gas phase as well as on the catalyst surface. The latter are generated by dissociative chemisorption of oxygen and produce methyl radicals by hydrogen abstraction of methane. The radicals desorb from the catalyst surface and can couple in the gas phase to form ethane, that, in turn, can be dehydrogenated into ethylene [6–8]. The undesired deep oxidation of methyl radicals, ethane and ethylene leading to CO and CO_2 also occurs in gas phase as well as on the catalyst surface [2,7].

Various metal oxides have been proven to be effective OCM catalysts [2,9], but none has reached the stage of commercial application yet. A variety of promoters has already been tested to improve the performance of OCM catalysts. This unavoidably increases the size of the searching space for OCM catalysts. Fortunately, high throughput experimentation (HTE) combined with combinatorial chemistry is capable of evaluating a large number of candidate catalysts in a relatively short period of time [10]. The following aspects are included in the HTE methodology: the preparation of catalyst libraries, the screening of the catalyst properties in this library including the kinetic properties and the use of suitable software for experimental design and data treatment [11]. The catalyst optimization occurs through various catalyst generations. For each generation knowledge can be systematically extracted from the screening experiments and applied in the design of a next generation of the catalyst library [11]. Model based knowledge extraction is an important part of HTE to accelerate the development of catalyst and minimize the number of experiments required.

Boudart [12] suggested that a microkinetic analysis is the best guiding technique in the search for new or improved catalysts by combinatorial chemistry. Microkinetic analyses, as started by Dumesic et al. [13], enable incorporating the fundamental catalytic

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doi:10.1016/j.cattod.2010.09.002

surface chemistry into a kinetic model in the form of catalytic cycles and elementary steps. The model starts from some well-selected physical and chemical properties than can be measured independently or calculated by theoretical chemistry. The properties can be brought into relation with the unknown kinetic parameters of the elementary steps through correlations such as Polanyi's that exploit chemical similarity between various elementary steps. Understanding the subtle details of the surface chemistry and their effect on the conversion and selectivity, the catalyst composition and structure can be modified to tune the relevant rate coefficients and, hence, improve the catalyst behavior in an optimum way. Such a detailed understanding can only be obtained through microkinetic modelling which proves the benefits of such a methodology [11]. As an example, the microkinetic model of ammonia synthesis, assisted in revealing the effect of catalysts on elementary reactions at microscopic level and provided useful information for faster catalyst development [14]. Caruthers et al. [15] proposed a forward and inverse model to integrate microkinetic modelling into HTE through a so-called "knowledge extraction engine". The forward model involves two components: a catalyst chemistry model that relates the catalyst composition or descriptors of composition to the kinetic rate coefficients and a microkinetic model that is at least a qualitative, if not a quantitative representation of experiments of catalyst screening.

Another potential benefit of incorporating microkinetic models into an HTE workflow is the reliable verification of the effects of reaction conditions. As catalyst screening in HTE is generally done under unique identical conditions, there is a possibility of missing good catalysts that have better performance under different conditions [11,14]. Process parameters have been known to affect the activity and selectivity of the OCM reaction to a certain extent [9]. Featuring the consolidation of the fundamental chemical information and the reliable extrapolation of this information to other reaction conditions, a microkinetic model of OCM can help identifying the best operating conditions for the formation of the desired products, and, hence, for the use in HTE catalyst development for OCM.

Several (micro)kinetic models of OCM have been reported [16–27]. One of the first studies combining catalytic reactions and gas-phase reactions was presented by Aparicio et al. [28], followed by various other kinetic models that appended heterogeneous steps to homogeneous reaction networks [29–31]. A kinetic model developed by Couwenberg et al. [16] included the irreducible mass transport phenomena of OCM reactions. Su et al. [17] developed a model based on thermodynamic constraints, with which the effect of radical diffusion was discussed and an upper bound of C_2 yield of OCM, 28%, was predicted. Based on these works, Sun et al. [18] constructed a microkinetic model including so-called catalyst descriptors that can be used to study the effects of operating conditions and the catalyst texture.

In this work, we present the progress of the application of a comprehensive microkinetic model for OCM [18] in HTE with the aforementioned strategy. The effect of operating conditions and the catalyst texture is investigated with the model. Yields and selectivities exhibited by virtual methane oxidative coupling catalysts are investigated by varying the catalyst descriptor values and operating conditions. The results illustrate the effect of the catalyst descriptor values on the energetics on the catalyst surface and allow predicting a maximum yield of the desired products as a function of the catalyst descriptors and the operating conditions. Hence, the model can assist in catalyst design and development and the establishment of relationships between catalyst composition and descriptors.

Table 1
Catalytic elementary reactions considered in methane oxidative coupling.

(1) $O_2 + 2^* \rightleftharpoons 2O^*$
(2) $CH_4 + O^* \rightleftharpoons CH_3\bullet + OH^*$
(3) $C_2H_4 + O^* \rightleftharpoons C_2H_3\bullet + OH^*$
(4) $C_2H_6 + O^* \rightleftharpoons C_2H_5\bullet + OH^*$
(5) $2OH^* \rightleftharpoons H_2O^* + O^*$
(6) $H_2O^* \rightleftharpoons H_2O + ^*$
(7) $CH_3\bullet + O^* \rightleftharpoons CH_3O^*$
(8) $CH_3O^* + O^* \rightleftharpoons CH_2O^* + OH^*$
(9) $CH_2O^* + O^* \rightleftharpoons HCO^* + OH^*$
(10) $CHO^* + O^* \rightleftharpoons CO^* + OH^*$
(11) $CO^* + O^* \rightleftharpoons CO_2{}^* + ^*$
(12) $CO + ^* \rightleftharpoons CO^*$
(13) $CO_2 + ^* \rightleftharpoons CO_2{}^*$
(14) $C_2H_4 + O\ast \rightleftharpoons C_2H_4O\ast$
(15) $C_2H_4O\ast + O\ast \rightleftharpoons C_2H_3O\ast + OH\ast$
(16) $C_2H_3O\ast + O\ast \rightleftharpoons CH_2O\ast + HCO\ast$
(17) $4HO_2\bullet \overset{\text{surf}}{\rightarrow} 3O_2 + 2H_2O$

2. Reaction mechanism

A more elaborate discussion of the catalytic reaction network, including a comparison with literature related mechanisms, has been given in a previous publication [18]. A summary of the most important features and reactions is given below. The microkinetic model for methane oxidative coupling is based on a reaction network that contains gas phase and catalytic reactions. This kinetic model is implemented in a one-dimensional heterogeneous reactor model, that is described in detail in the work of Couwenberg et al. [16]. Such a reactor model, making use of textural properties such as catalyst bed porosity, catalyst pellet porosity and tortuosity, allows accounting for pellet scale gradients of the reactive intermediates, even when no significant gradients for the reactants and products develop. Interactions between the catalytic elementary steps and the gas phase reactions are explicitly accounted for. The gas phase kinetics contain 39 elementary reactions among 13 molecules and 10 radicals [32]. The catalytic reaction network consists of 17 reactions, vide Table 1. It must be mentioned that while drafting the reaction network, a compromise has to be made between being as complete as possible on the one hand and having a reasonable number of adjustable parameters on the other hand, especially in the proposed methodology where microkinetics are coupled with mass transfer. In a recent publication from Sinev et al. [33] a more elaborate catalytic network was presented. The current network describes the activation of methane on the catalyst surface by the dissociation of oxygen (reaction (1)), hydrogen abstraction of methane (reaction (2)) and the regeneration of the active site (reactions (5) and (6)). It accounts for CO_2 generation through four reaction pathways: methyl radical scavenging followed by the sequential hydrogen abstraction from methoxy species on the catalyst (reactions (7)–(13)); hydrogen abstraction of C_2 surface species leading to radicals that are oxidized to CO_2 in the gas phase (reactions (3) and (4)); the oxidation of CO adsorbed from the gas phase (reactions (11)–(13)); and the heterogeneous oxidation of ethylene (reactions (14)–(16)). Ethylene has been recognized to be oxidized on the catalyst surface through an adsorption step followed by a single hydrogen abstraction and C–C bond cleavage. The adsorption of CO_2 and the hydroperoxy radical are also included to account for the inhibition effect of CO_2 and the quenching function of methane oxidative coupling catalyst. Especially on the nature of surface oxygen species there has been a lot of debate. Depending on the catalyst studied, surface-lattice oxygen or adsorbed oxygen species has been judged responsible for methyl radical formation [34]. On the other hand, a two-step adsorption of dioxygen followed by its dissociation [35] or a one-step dissociative adsorption of oxygen has been proposed [6], with the latter approach being followed in the present work.

2.1. Identification of catalyst descriptors

Catalyst descriptors correspond to a measured or calculated physical or chemical property of the catalyst in interaction with the reacting species. The catalyst descriptor can affect the reaction parameter values, such as the preexponential factor, the activation energy and the reaction enthalpy. A catalyst descriptor can be an