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NO_2-promoted oxidation of methane to formaldehyde at very short residence time – Part II: Kinetic modeling

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HIGHLIGHTS

- ▶ A kinetic model is proposed to simulate the NO_2-promoted oxidation of methane.
- ▶ The effects of various operating parameters are well captured by the model.
- ▶ The model is also compared to several published experimental data.
- ▶ The model is in good agreement with the experiments in a wide range of conditions.

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ABSTRACT

Partial oxidation of methane in the presence of NO_2 at short residence time (20–80 ms) provides a promising route to yield formaldehyde. In this paper, an approach for modeling the kinetics of the complex reaction system $CH_4/O_2/NO_2$ is presented. A detailed kinetic model is proposed, which is based on the previous mechanism of Zalc et al. (2006) [34] in which some changes were made, including the correction of several rate constants, the addition of two reactions involving HONO and the updating of the thermodynamic data for CH_3NO_2 and HONO. The final kinetic model is compared with our experimental results in terms of CH_4 conversion as well as product concentrations. The simulation results are in good agreement with the experiments for various temperatures, residence times, X_{O2}/X_{CH4} ratios and initial NO_2 concentrations. The proposed kinetic model is also tested against the previously published experimental data for the oxidation of methane in the presence of NO_x ($x = 1$ or 2). The overall good agreement further confirms the reliability of the kinetic model.

1. Introduction

Producing formaldehyde through a single-pass process by direct partial oxidation of methane is considered as an attractive route to replace the conventional multi-step synthesis, in which the step of steam reforming is costly and energy-intensive. Although numerous studies were conducted on the direct oxidation of methane to formaldehyde by various methods (homogenous gas phase reactions [1–3], catalytic reactions [4–10], plasma technologies [11–14], etc.), the achieved formaldehyde yield was still not high enough to compete with the current multi-step process. This is mainly because of the high stability of methane and reactivity of formaldehyde.

It is well known that small amounts of NO_x ($x = 1$ or 2) enhance the oxidation of hydrocarbons (e.g. [15–20]), and the hydrocarbons promote in the meantime the inter-conversion among the nitrogen compounds (e.g. [21–23]). The enhanced effect of NO_x on the formaldehyde production in the oxidation of methane was reported by many authors [24–34]. However, it has to be pointed out that the reaction conditions of these studies differ from each other by a large number of operating parameters (pressure, temperature, reactant composition and residence time). The dependence of the formaldehyde yield on the various factors seems very difficult to establish. As a result, an intrinsic kinetic model is necessary to further clarify ways to improve the formaldehyde production.

In the literature, considerable attempts have been made for modeling the $CH_4/O_2/NO_x$ chemistry. For instance, the oxidation of methane in the presence of NO_x ($x = 1$ or 2) at atmospheric pressure was modeled by Bromly et al. [35] as well as Bendtsen et al. [28]. Faravelli et al. [17] developed a general and detailed kinetic model relevant to NO_x in order to investigate the interactions between NO and the hydrocarbons (C_1–C_4) at low temperatures. The influence of NO_x on the partial oxidation of methane was also studied by Konnov et al. [36,37] by using the latest release 0.5 of the Konnov's gas phase combustion mechanism [38]. In order to simulate the potential heterogeneous reactions on the surface of the reactor wall, these authors also used a simplified

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heterogeneous mechanism. It should be noted that the residence times applied in their experiments are relatively long. More recently, Rasmussen et al. [19] developed a kinetic model to simulate the NO_x-sensitized oxidation of methane at high pressure (>2 MPa). However, to the best of our knowledge, only two models have referred to optimize the formaldehyde production in the NO_x-sensitized oxidation of methane. Takemoto et al. [30] proposed a detailed kinetic mechanism for the gas phase selective oxidation of methane in $CH_4/O_2/NO$. Several modifications to the Gri-Mech 2.1.1 [39] were made in their work. The reactions related to N, NH, NH_2, NH_3, NNH, NCO, HCN, H_2CN, HCNN, HCNO, HOCN and HNCO, were excluded. In the meanwhile, the kinetic model was supplemented with the reactions that are related to NO_x, HONO, $HONO_2$, CH_3NO_2, CH_3ONO, CH_2NO_2, CH_3NO, CH_3OO and CH_3OOH. The rate constants of the added reactions were taken from Arutyunov et al. [40], Mackie [41], Bromly et al. [35] and Tricot et al. [42]. The simulation results were in general good agreement with the experiments at low conversion of methane (<10%). Zalc et al. [34] further developed the mechanism Gri-Mech 3.0 [43] by adding the reactions that were not already present in Gri-Mech 3.0 [43], to the kinetic network of Takemoto et al. [30]. The kinetic model was qualitatively validated by the comparison of the model with the experimental data of Takemoto et al. [30] and it was used to investigate the formaldehyde production by the NO_x-promoted oxidation of methane.

In the first part of the present research [44], we reported the experimental results obtained in the partial oxidation of methane in the presence of NO_2 (0.03–0.6%) at short residence time (20–80 ms). The other reaction conditions were as follows: 0.2 MPa, 873–1123 K, $X_{O2}/X_{CH4} = 0.5–9$, balanced in Ar ($X_{Ar} + X_{NO2} = 90\%$). The highest formaldehyde yield was 9% and the corresponding methane conversion was 24.3%. The main objective of this paper is to develop and validate a detailed chemical kinetic model for the NO_2-promoted oxidation of methane under the above-mentioned conditions. In the present work, the model of Zalc et al. [34] was further evaluated and developed. The proposed kinetic model was then compared with our experimental data and also with some data of the literature. The validated kinetic model will be used to help clarify the role of NO_2 in the reaction system and explore the optimal conditions for the formaldehyde synthesis, in a following paper.

2. Reaction modeling

2.1. Base mechanism

In the literature, the available mechanisms of $CH_4/O_2/NO_x$ chemistry are developed for various purposes and under different conditions. Zalc et al. [34] used the latest release of Gri-Mech 3.0 [43] as a base set and they extended it by adding some important reactions drawn from the kinetic mechanism of Takemoto et al. [30]. The validation conditions were in the range of a few seconds for the residence time, 748–823 K for the temperature and atmospheric pressure. To the best of our knowledge, this is the most recent kinetic model that was developed for investigating the influence of NO_x on formaldehyde production from direct oxidation of methane. Therefore, in this study, we used the model of Zalc et al. [34] as a starting point. This kinetic model consists of 419 reactions involving 65 species. Its Chemkin format is available from the web [45], including the reactions, the rate constants (A, n, E_a) and the thermodynamic properties of the species.

2.2. Mechanism modification

With the original model of Zalc et al. [34], the main products of the simulation fit well to those of our experiments. However, the agreement between the modeling and our experimental data could be improved. That could be explained by the validation conditions of the mechanism that are different in comparison to those of the present work. Thus, we made a few changes so as to improve the performance of the kinetic model for our reaction conditions (shorter residence time and higher temperature). All the modifications are based on the data available in the literature [21,28,35,38,46–50] and are summarized in Table 1. The details of some important reactions are discussed below.

Table 1
Kinetic modifications to the mechanism of Zalc et al. [34].

n°-R	Reaction	A	n	E_a	Ref.
Corrected reactions					
R326	$O^{\cdot} + O_2 + M \Longleftrightarrow O_3 + M$	1.88×10^{21}	−2.8	0	[35]
R359	$CH_2^{\cdot}(s) + M \Longleftrightarrow CH_2^{\cdot} + M$	1.0×10^{13}	0	0	[35]
R379	$HO_2^{\cdot} + NO + M \Longleftrightarrow HONO_2 + M$	2.23×10^{12}	−3.5	2200	[35]
R385	$NO_2 + H^{\cdot} + M \Longleftrightarrow HONO + M$	1.40×10^{18}	−1.5	900	[35]
R403	$NO_3 + M \Longleftrightarrow O_2 + NO + M$	2.05×10^{8}	1	12,122	[35]
	$NO_2/0.0/$				
R329	$O^{\cdot} + CH_2^{\cdot} \Longleftrightarrow CH^{\cdot} + OH^{\cdot}$	3.0×10^{14}	0	11,920	[35]
R360	$O_2 + CH_3^{\cdot}(+M) \Longleftrightarrow CH_3O_2^{\cdot}(+M)$	7.8×10^{8}	1.2	0	[46]
	Low-pressure limit	5.6×10^{25}	−3.3	0	
	Troe parameters	0.36	1.0	1×10^{8}	[47]
Modified reactions					
R371	$2CH_3O_2^{\cdot} \Longleftrightarrow CH_3OH + CH_2O + O_2$	4.0×10^{9}	0	−2210	[28]
R390	$CH_3NO_2(+M) \Longleftrightarrow CH_3^{\cdot} + NO_2(+M)$	1.78×10^{16}	0	58,500	[48]
	Low-pressure limit	1.26×10^{17}	0	4200	
	Troe parameters	0.183	1×10^{-30}	1×10^{30}	
R189	$NO_2 + H^{\cdot} \Longleftrightarrow NO + OH^{\cdot}$	2.02×10^{10}	0	675	[49]
Added reactions					
R420	$NO_2 + HO_2^{\cdot} \Longleftrightarrow HONO + O_2$	6.31×10^{8}	1.25	5000	[21]
R421	$NO + OH^{\cdot}(+M) \Longleftrightarrow HONO(+M)$	2.00×10^{12}	−0.05	−721	[45]
	Low-pressure limit	15×10^{23}	−2.51	−67.6	
	Troe parameters	0.62	10	1×10^{5}	
	$H_2O/10.0/O_2/2.0/Ar/0.75/H_2/2.0/CO_2/0.0/$				[37]
R422	$NO + OH^{\cdot}(+CO_2) \Longleftrightarrow HONO(+CO_2)$	2.00×10^{12}	−0.05	−721	[45]
	Low-pressure limit	1.70×10^{23}	−2.51	−67.6	
	Troe parameters	0.62	10	1×10^{5}	

Note: The rate constants are expressed as $k = AT^n\exp(-E_a/RT)$; A units: mol, cm, s, K; E_a unit: cal mol^{-1}; the n°-R corresponds to the order in the kinetic model.