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Kinetic modeling of heterogeneous–homogeneous radical processes of the partial oxidation of low paraffins

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Abstract

A new approach to kinetic modeling of heterogeneous–homogeneous radical processes of the partial oxidation of low paraffins over oxide catalysts is suggested. It is based on the elucidation of gas phase and heterogeneous reactions taking part in the overall process and on the correlation between their thermochemistry and kinetics. The model calculations explain: (1) the magnitudes of the reaction rates at different temperatures; (2) the mechanism of catalysts re-oxidation; (3) the influence of the addition of peroxides on the rate of oxidative coupling of methane.

1. Introduction

The possibility of the combined heterogeneous–homogeneous mechanism of catalytic reactions was formulated in ref. [1] and after that was discussed repeatedly. Traditionally the process is reputed to be heterogeneous–homogeneous if the substantial fraction of the reaction products forms outside the catalyst layer on the distance exceeding the mean free path in the gas, for example, as the result of homogeneous transformations of free radicals generated by the catalyst. However, their role in the overall process can be more complex: the radicals once formed in the interaction of the reactants with the surface of the catalyst can undergo several transformations in the gas phase and then can be captured again by the surface or produce the final product in the interactions with the surface of the catalyst. Thus, in this paper the process will be characterized as a heterogeneous–homogeneous one if some of its substantial steps proceed on the surface and the others — in the gas phase.

For example, since the work of Lunsford et al. [2], oxidative coupling of methane (OCM) to higher hydrocarbons is believed to be a heterogeneous–homogeneous process. Both higher hydrocarbons and oxygen containing by-products are believed to form in the homogeneous and heterogeneous reactions of CH_3 radicals generated by the surface of the oxide catalyst.

The significant role of both the heterogeneous processes and the gas phase reactions in a processes of this type demand their adequate kinetic description. Whereas the kinetics of homogeneous gas phase oxidation of methane can be successfully simulated with the use of multi-step reaction schemes [3–6] in a wide range of temperatures and pressures, attempts to extend this approach to catalytic oxidation is limited by poor knowledge of the stoichiometry and kinetics of the heterogeneous reactions of free radicals.

In ref. [7] we proposed a kinetic model which assumes the equilibrium between CH_3 and CH_3O_2 radicals and takes into account selected bimolec-

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ular reactions of radicals in the gas phase. This model was able to describe the trends in selectivity at temperature and oxygen concentration variations but it could not predict the total reaction rates and the rate of surface-assisted total oxidation.

In ref. [8] a gas phase methane oxidation scheme was added with a set of heterogeneous processes such as adsorption–desorption equilibria, radical trapping and some other types of reactions. Their rate and equilibrium parameters were estimated or evaluated from experimental kinetic and adsorption/desorption data. This way looks attractive, but the general principle for the choice of the set of heterogeneous reactions and for estimation of their parameters was not formulated. So, it is difficult to take into account the properties of a concrete catalyst and to provide the complete set of reactions with well grounded parameters.

Recently a new approach for kinetic modeling of heterogeneous–homogeneous reactions over oxide catalysts was suggested [9]. It is based on two main assumptions:

(1) the overall process can be described as the combination of heterogeneous and gas phase elementary steps (H- and O-atom transfer and radical capture were considered as the main types of heterogeneous reactions);

(2) the main features of heterogeneous processes over insulators and wide-gap semiconductors are similar to those existing in homogeneous reactions of the same types including correlation between thermochemistry and kinetics of elementary reactions.

In the present paper this approach was used to simulate:

- the 'apparent' kinetic features of catalytic methane oxidation;
- the features of oxidative dehydrogenation of methane and ethane in redox cycles;
- the effect of addition of gas promoters (peroxides).

2. Description of the model

Three states of the active sites of the catalyst were considered: (1) oxidized (denoted further as LO, where L is the fragment of the oxide lattice in the nearest environment of active site); (2) reduced (hydroxy-group LOH); (3) surface oxygen vacancy (L).

For the simulations of methane and ethane oxidation the gas phase reaction scheme similar to ref. [3] was added with a set of heterogeneous steps including reactions of C_1–C_2 hydrocarbons and radicals usually present in the reaction mixture with active sites in the LO, LOH and L states. The total number of reactions in the model is about 350.

The method for rate constants evaluation was described in ref. [9]. It is based on the analogy of collision-type heterogeneous reactions to elementary reactions in the gas and on the correlations between enthalpy (ΔH) and activation energy (E_a) known as the Polanyi–Semenov equation:

$$E_a = a + b^* |\Delta H| \quad (1)$$

The values of coefficients in Eq. (1) were estimated based on data for gas phase reactions of the same types [10,11]. The principal thermochemical characteristics of the catalysts for this purpose are oxygen binding energy $E_{[O]}$ and hydrogen atom affinity E_{O-H} of active surface oxygen. Most of the activation energies involved in the model can be evaluated on the basis of these parameters. In this paper the parameters of 7% Li/MgO [12–14] were used: $E_{[O]} = 128$, $E_{O-H} = 76.5$ kcal/mol and [LO] ca. 2.5×10^{-6} mol/ml. The uniform thermochemical properties and reactivity of surface active sites were taken as the approximation for model calculations.

The surface methoxy groups formed in methane oxidation via the reactions of radicals capture ($LO + CH_3 \rightarrow LOCH_3$ and $L + CH_3O \rightarrow LOCH_3$) were assumed to be oxidized rapidly to CO_2 via surface formate formation. The activation energy of 'methoxide-to-formate' transformation (5–8 kcal/mol) was estimated from spectro-kinetic data [15].

Uniform (quasi-homogeneous) distribution of active sites and fast mixing were assumed, i.e. the transport restrictions which are very likely in case of real catalysts were ignored. Thus, the results presented here reflect only the reactivity of the active sites.

Most of the calculations were carried out for typical OCM conditions: T = 850–1100 K, $[CH_4]_o = 2\,[O_2]_o = 1 \times 10^{-6}$ mol/ml in nitrogen ($[N_2] = 1 \times 10^{-5}$ mol/ml).

3. Results and discussion

3.1. *'Apparent' kinetic features of methane oxidation*

The initial rate of methane oxidation increases and the time of 1% and 10% methane conversion decreases upon the increase of active sites concentration (see Fig. 1). At $[LO]_o = 10^{-8}$–10^{-7} mol/ml the sharp acceleration caused by chain propagation disappears. The rise of C_2 selectivity with increase of [LO] reflects the predominance of second-order CH_3 radicals recombination at higher rates of heterogeneous initiation (see Fig. 2). The C_2 selectivity reaches the maximum value at [LO] ca. 10^{-6} mol/ml and then decreases due to increase of contribution of heterogeneous total oxidation.

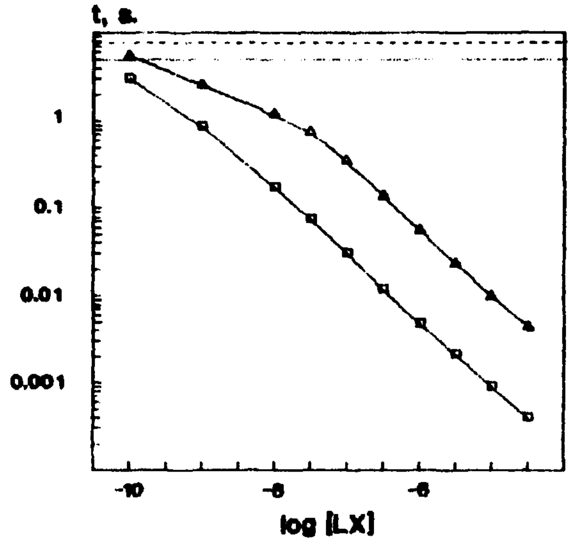

Fig. 1. t(0.01) and t(0.1) as the function of log[LX]. [LX] = [LO] + [LOH] + [L]; stationary state. (□) t(0.01). (—) t(0.01); [LX] = 0. (Δ) t(0.1). (- - -) t(0.1); [LX] = 0.

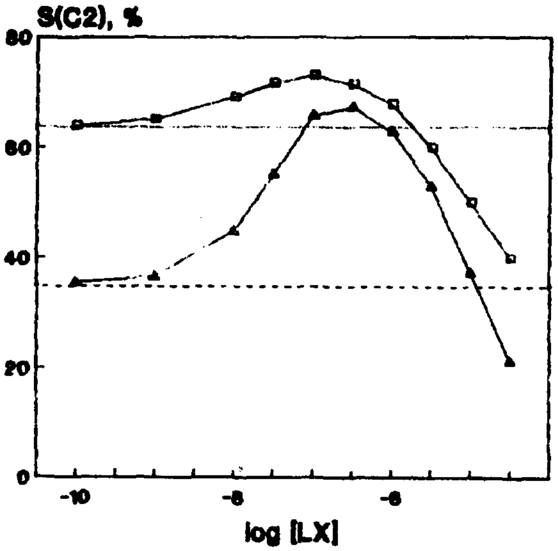

Fig. 2. S(0.01) and S(0.1) as the function of log[LX]. [LX] = [LO] + [LOH] + [L]; stationary state. (□) S(0.01). (—) S(0.01); [LX] = 0. (Δ) S(0.1). (- - -) S(0.1); [LX] = 0.

With increase of temperature the C_2 selectivity also increases mainly due to the shift of equilibrium in the reaction

$$CH_3 + O_2 \Leftrightarrow CH_3O_2$$

to methyl radicals. At 1000 K the ratio $[CH_3]/[CH_3O_2]$ becomes very close to equilibrium after ca. 10^{-5} s from the start of the reaction. The 'apparent' activation energies of OCM and oxidation reactions are equal to 36 and 18.5 kcal/mol, respectively.

If the calculations are started from $\alpha = [LO]/([LO] + [LOH] + [L]) = 1$, the distribution of the states becomes stationary from ca. 10^{-3}–10^{-2} s ($\alpha = 0.03$–0.05 at $[LO]_o = 10^{-11}$–10^{-5} mol/ml and T = 850–1100 K) and the consumption of reactants proceeds mostly under these stationary conditions. The hydroxylated form of the active site is predominant and the fraction of vacant sites L is very low (ca. 10^{-4}).

3.2. *Methane and ethane oxidative dehydration in separated redox cycles*

If the catalyst contains strong oxidizing sites, the process of oxidation can be carried out in redox mode (alternating periods of reduction of the solid

Table. Regularities of methane and ethane oxidative dehydrogenation in redox mode.

Process / Parameter	Experiment	Model
Reduction /		
C2-selectivity	100 %	100 %
Ea, kcal/mole	21.5	25.1
r(CH4) / r(C2H6)	~ 0.1	~ 0.1
Re-oxidation with O2 /		
Ea, kcal/mol	18	24
Re-oxidation with N2O	no reaction	no reaction

with hydrocarbon and re-oxidation with oxidizing agent). The experimental data obtained for the processes of OCM and ethane oxidative dehydration in cyclic mode over Li/MgO catalyst [12–14] in the comparison with model simulations are given in the Table. The methane transformation to C_2 hydrocarbons over Li/MgO in cyclic mode proceeds with 100% selectivity [12,14]. The same result was obtained in modeling. The values of activation energy of OCM and the relative reactivities of methane and ethane obtained in modeling are also very similar to those obtained in the experiments.

3.3. Mechanism of catalyst re-oxidation

In refs. [13,14] we reported that in redox experiments the reduction of Li/MgO catalyst by H_2 and CH_4 can proceed without water formation and water forms at the re-oxidation stage of the cycle. Low reactivity of N_2O with respect to Li/MgO catalyst re-oxidation was observed. We assumed that in case of catalyst characterized by high $E_{[O]}$ the equilibrium in the reaction

$$2[LOH] \Leftrightarrow [LO] + [L] + H_2O$$

is shifted to the left side, and the de-hydroxylation of the surface is not a necessary step of re-oxidation.

According to the model calculations, in case of high values of $E_{[O]}$ water is formed predominantly via the following steps:

$$LOH + O_2 \rightarrow LO + HO_2 \qquad (1)$$

$$LOH + HO_2 \rightarrow LO + H_2O_2 \qquad (2)$$

$$H_2O_2 \rightarrow 2OH \qquad (3)$$

$$LOH + OH \rightarrow LO + H_2O \qquad (4)$$

The regularities of re-oxidation calculated using the measured values of $E_{[O]}$ and $E_{O\text{–}H}$ and the estimated values of reactions (1), (2) and (4) rate constants are in good agreement with experimental data [13,14] (see Table 1).

3.4. Effect of peroxides addition

Peroxides are known to promote gas phase oxidation due to their decomposition with the formation of radicals. But their effect on methane oxidation over oxides is complex: hydrogen peroxide promotes the reaction over oxides having poor catalytic activity, but inhibits methane oxidation over good catalysts; the inhibition effect increases at lower temperatures and at higher concentrations of H_2O_2 (see for example ref. [16]).

According to the model discussed here these effects can be explained by competition between the effects of homogeneous decomposition of H_2O_2 (leading to the acceleration of the reaction due to the formation of additional radicals) and its reaction with the [LO] site. Since the energy of the C–H bond in methane is higher than that of the O–H bond in H_2O_2, hydrogen peroxide can poison the active sites due to higher reactivity with respect to them as compared with methane. This negative effect increases at lower temperatures and at higher concentrations of H_2O_2. At higher temperatures the promotion effect increases due to higher activation energy of reaction (3).

4. Conclusion

The kinetic model proposed here is able to describe the kinetic features of the oxidation of low paraffins over oxide catalysts and to simulate several effects observed experimentally. The results were obtained within the unified approach and without any adjustment. The consideration of additional effects such as mass-transfer restrictions can give more precise conformity of simulated kinetics to experimental data.

5. Acknowledgement

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