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Modeling of Pt-Sn/γ-Al_2O_3 deactivation in propane dehydrogenation with oxygenated additives

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Abstract−A reduction in catalyst activity with time-on-stream and formation of side products are the major problems associated with catalytic propane dehydrogenation. Coke formation on the catalyst surface is the most important cause for catalyst deactivation. Experiments have indicated that the presence of very small amounts of oxygenated additives such as water can reduce the amount of coke accumulated on the catalyst surface and enhance catalyst activity. Addition of water beyond an optimum level, however, would result in a loss of activity due to sintering of catalyst. Propane dehydrogenation over a Pt-Sn/γ-Al_2O_3 catalyst in the temperature range of 575 to 620 °C was investigated in the presence of small amounts of water added to the feed. A monolayer-multilayer mechanism was used to model the coke growth kinetics. Coke deposition and catalyst sintering were considered in a catalyst deactivation model to explain the observed optimum level in the amounts of water added to the feed. The model predictions for both propane conversion and coke formation with time-on-stream were in good agreement with experimental data.

Key words: Propane Dehydrogenation, Coke Formation, Deactivation, Oxygenated Additives, Side Reactions

INTRODUCTION

The increase in the demand for lower olefins during the last decade has initiated the development of new alternative processes in addition to traditional petrochemical or refinery processes, where lower olefins are obtained as by-products [1]. The dehydrogenation of light alkanes is an important reaction from an industrial point of view, since it is a selective process to produce the corresponding short-chain alkenes via direct catalytic dehydrogenation [2]. Dehydrogenation reactions of lower alkanes are highly endothermic and are carried out at high temperatures because of thermodynamic constraints. At these high temperatures carbonaceous deposits, collectively termed coke, are rapidly formed causing catalyst deactivation and necessitating catalyst regeneration [3]. Traditionally, the most important processes to obtain propylene have been steam cracking of hydrocarbon feedstocks and refinery conversion processes (e.g., fluid catalytic cracking, visbreaking and coking). The increasing demand for propylene derivatives, outstripped the availability from these established sources, and processes for the “on-purpose” production of propylene by the dehydrogenation of propane have been developed commercially. Moreover, there are other paths to obtain the alkenes from corresponding alkanes including oxidative dehydrogenation and metathesis [4-7]. Propane dehydrogenation (PDH) has been considered as an alternative route for production of propylene, which is an important raw material in the production of polypropylene, acrolein, acrylic acid, polygas chemicals and oligomers [8,9]. Dehydrogenation of propane is a highly endothermic and equilibrium limited reaction that requires relatively high temperatures and low pressures to achieve high yields of propylene [10,11]:

$$C_3H_8 \Leftrightarrow C_3H_6 + H_2 \qquad \Delta H^0_{298} = 124\ \text{kJ/mol} \tag{1}$$

The reaction is generally carried out at 525-625 °C near atmospheric pressures using supported platinum or chromia catalysts. Pt-Sn/γ-Al_2O_3 has been used extensively as a catalyst for propane dehydrogenation both at laboratory and industrial scales. This catalyst exhibits a high activity and a high selectivity to propylene in propane dehydrogenation [12-14]. The role of platinum modifiers is to selectively weaken the platinum-paraffin interaction. Arsenic, tin or germanium are among the metals reported as being platinum activity modifiers. The formation of short chain hydrocarbons (cracking and hydrogenolysis) and coke (coking) are the main undesired reactions associated with propane dehydrogenation. Furthermore, coke is rapidly formed at high temperatures, and as a consequence the catalyst is deactivated [15,16]. The main problem in catalytic PDH is the rapid catalyst deactivation due to coke formation [3,17].

Water and light oxygenates could serve as catalyst modifier when used in low levels in the feed stream. Pt-based catalysts are poisoned by high levels of oxygenates by various mechanisms. Oxygenates could also deplete chlorine, essential for re-dispersion of sintered platinum, from the catalyst. When used in appropriate levels, however, they could exhibit beneficial effects on catalyst performance without the adverse effects [18]. The addition of water as an oxygenated modifier to the feed in optimum amounts could result in a substantial reduction in coke formation as well as an increase in the catalyst activity. Some studies have indicated that addition of small amounts of oxygen can improve pretreatment in catalytic PDH [19]. In this work catalytic PHD was carried out in a fixed-bed quartz reactor in the temperature range of 575 to 620 °C using a Pt-Sn/γ-Al_2O_3 catalyst with feed containing small amounts of water. We present a kinetic model for the propane dehydrogenation and coke formation and investigate the effect of small amounts of water added to

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the feed and its influence over catalyst deactivation.

METHODS AND MATERIALS

A laboratory scale tubular flow reactor was used for the PDH experiments. The inside diameter of the reactor was 12 mm, the length of the reactor was 100 cm, and the catalyst was loaded in the middle section of the reactor in between two layers of quarts particles. The commercial Pt-Sn/γ-Al_2O_3 catalyst was supplied by a European company. Details of the chemical composition of the catalyst, catalyst particle size, and pretreatment conditions are provided elsewhere [20]. The catalyst loading was 1 gram. All experiments were conducted at WHSV=2 h^{-1} and hydrogen to propane ratio, H_2/HC, of 0.8 that are typical of industrial conditions. Propane dehydrogenation was performed at 575, 600, 620 °C near atmospheric pressure (0.8 bar) with different amounts of water in the feed. The product samples were analyzed 3 hours after the start of the run when stable conditions were achieved. Product samples were then analyzed hourly up to 7 hours after the start of the run. Experimental propane conversions for different amounts of water in the feed are presented in Tables 1, 2 and 3 for reaction temperatures of 575, 600, and 620 °C, respectively. Details of the experimental procedures and analyses are reported elsewhere [20,21]. The influence of external and internal mass transfer limitations were examined for propane dehydrogenation over the same industrial Pt-Sn/Al_2O_3 catalyst at typical operating conditions (i.e., P=1 bar and T=550-630 °C) in

Table 1. Experimental and predicted propane conversions for T= 575 °C

Temperature (°C)	Time from start of run (h)	Water added to feed (ml/h)	Model predicted conversion	Experimental conversion
575	3	0.2	29.41	28.56
575	4	0.2	28.51	27.95
575	5	0.2	27.71	27.87
575	6	0.2	27.01	27.34
575	7	0.2	26.41	26.48
575	3	0.25	29.92	29.74
575	4	0.25	29.06	29.13
575	5	0.25	28.28	28.65
575	6	0.25	27.57	28.23
575	7	0.25	26.95	27.88
575	3	0.3	30.45	30.89
575	4	0.3	29.65	29.76
575	5	0.3	28.89	29.54
575	6	0.3	28.19	28.51
575	7	0.3	27.56	28.17
575	3	0.35	26.72	24.96
575	4	0.35	25.71	24.15
575	5	0.35	24.71	23.68
575	6	0.35	23.76	23.18
575	7	0.35	22.87	22.87
575	3	0	27.65	26.79
575	4	0	26.71	26.28
575	5	0	25.97	25.64
575	6	0	25.39	24.38
575	7	0	24.94	24.18

Table 2. Experimental and predicted propane conversion for T= 600 °C

Temperature (°C)	Time from start of run (h)	Water added to feed (ml/h)	Model predicted conversion	Experimental conversion
600	3	0.4	39.28	38.76
600	4	0.4	38.53	38.42
600	5	0.4	37.81	37.75
600	6	0.4	37.13	37.05
600	7	0.4	36.50	36.54
600	3	0.45	39.73	39.95
600	4	0.45	39.07	39.07
600	5	0.45	38.38	38.57
600	6	0.45	37.73	37.64
600	7	0.45	37.11	37.13
600	3	0	36.12	36.12
600	4	0	35.18	35.84
600	5	0	34.45	35.73
600	6	0	33.87	34.16
600	7	0	33.42	33.43

Table 3. Experimental and predicted propane conversion for T= 620 °C

Temperature (°C)	Time from start of run (h)	Water added to feed (ml/h)	Model predicted conversion	Experimental conversion
620	3	0.3	47.12	46.18
620	4	0.3	46.32	46.09
620	5	0.3	45.60	45.53
620	6	0.3	44.96	44.94
620	7	0.3	44.41	43.22
620	3	0.4	47.82	47.57
620	4	0.4	47.08	46.19
620	5	0.4	46.39	46.03
620	6	0.4	45.76	45.76
620	7	0.4	45.18	45.02
620	3	0.5	48.55	48.67
620	4	0.5	47.91	48.29
620	5	0.5	47.28	47.66
620	6	0.5	46.67	46.62
620	7	0.5	46.11	46.29
620	3	0.6	42.04	45.17
620	4	0.6	42.11	43.29
620	5	0.6	41.57	43.01
620	6	0.6	40.77	41.49
620	7	0.6	39.91	39.85
620	3	0	45.33	45.34
620	4	0	44.48	45.09
620	5	0	43.81	44.76
620	6	0	43.28	43.19
620	7	0	42.87	42.98

a different investigation [14]. Both external and internal mass transfer limitations were negligible under the feed flow rates and catalyst particle sizes that were employed in the present study.

KINETIC MODEL

1. Propane Dehydrogenation

A widely accepted mechanism for PDH over supported platinum on γ-Al_2O_3 has been suggested by Biloen et al. [22] where β H-elimination is considered as the rate-determining step in dehydrogenation of propane. The addition of small amounts of water can result in the formation of hydroxyl groups that could enhance the β H-elimination step. The proposed kinetic scheme for the propane reactions over Pt-Sn/γ-Al_2O_3 catalyst in the presence of water is a parallel network of reactions including:

Dehydrogenation reaction: $C_3H_8 \leftrightarrow C_3H_6+H_2$ (2)

Cracking reaction: $C_3H_8 \rightarrow C_2H_4+CH_4$ (3)

Ethylene hydrogenation: $C_2H_4+H_2 \rightarrow C_2H_6$ (4)

Coke formation: $C_3H_6 \rightarrow 3CH_{0.5}+2.25H_2$ (5)

The following reactions can also occur in propane dehydrogenation in the presence of water [23]:

$$C_3H_6+3H_2O \rightarrow 3CO+6H_2 \tag{6}$$

$$C_3H_6+6H_2O \rightarrow 3CO_2+9H_2 \tag{7}$$

When water is present in only small amounts, the rates of reactions (6) and (7) are negligible compared with dehydrogenation, cracking and coking reaction rates. The main influence of water is on coke formation and catalyst sintering. According to Lobera et al. [15], the kinetic expression for the main dehydrogenation reaction (2) is:

$$-r_{C_3H_8} = a\frac{k_1(P_{C_3H_8} - (P_{C_3H_6}P_{H_2}/K_{eq}))}{1+(P_{C_3H_6}/K_{C_3H_6})} \tag{8}$$

where a is the catalyst activity and $K_{C_3H_6}$ is propylene adsorption constant given by:

$$K_{C_3H_6} = K_{C_3H_6,0}\exp\left[\frac{-\Delta H_{C_3H_6}}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right] \tag{9}$$

where $K_{C_3H_6,0}$ is propylene adsorption constant at reference temperature, T_0, and $\Delta H_{C_3H_6}$ is propylene adsorption enthalpy. This model is based on a Langmuir-Hinshelwood model and assumes that propane adsorption is negligible. The reaction rate constants are described by the Arrhenius equation as follows:

$$k_i = k_{0i}\exp\left[\frac{-E_{ai}}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right] \tag{10}$$

where E_{ai} is the activation energy, T_0 the reference temperature (taken as 870.65 K), R is the gas constant (8.31451 $J\cdot mol^{-1}\cdot K^{-1}$) and k_{0i} the kinetic rate constant at T_0. K_{eq} is the equilibrium constant given by:

$$\frac{-\Delta G}{RT} = \ln(K_{eq}) \tag{11}$$

The Gibbs free energy was calculated from data provided by Perry and Green [24] and the calculated values for the equilibrium constant at 575, 600, and 620°C were 0.2924, 0.3776, and 0.4673, respectively. The rate of side reactions for propane cracking and ethylene hydrogenation (as taken from ref. [15]) was expressed by:

$$-r_{cracking} = k_2 \cdot P_{C_3H_6} \tag{12}$$

$$-r_{Ethylene\ hydrogenation} = k_3 \cdot P_{C_2H_4} \cdot P_{H_2} \tag{13}$$

where k_i are the reaction rate constants described by the Arrhenius equation.

2. Coke Formation

Formation of coke deposits during propane dehydrogenation originates almost solely from propylene [25]. The model used in this work to describe coke formation is a simple mechanistic model called the monolayer-multilayer coke growth model (MMCGM). This model was first proposed by Nam and Kittrell [26], generalized and used successfully by several authors [27]. In this model, the rate of coke deposition with time is given by the sum of coke formation on the surface of the catalyst (monolayer coke) and the rate of the simultaneous multilayer coke deposition:

$$\frac{dC_C}{dt} = \frac{dC_m}{dt} + \frac{dC_M}{dt} \tag{14}$$

where C_m is the coke concentration in monolayer and C_M is the coke concentration in multilayer. The formation of monolayer coke is proportional to the fraction of sites uncovered on the first layer. The kinetic order for monolayer coke formation is equal to 2, which would support the fact that the coke formation step involves two sites and also satisfactorily describes the significant initial increase in the coke formation rates versus time [15]. This type of coke quickly covers the catalyst surface and decreases the catalyst activity. The maximum coke concentration in the monolayer is fixed and is shown by C_{max}. The concentration of monolayer coke with reaction time, t, is given by:

$$C_m = C_{max}^2\left[\frac{k_{1C}t}{1+C_{max}k_{1C}t}\right] \tag{15}$$

where k_{1C} is a kinetic coefficient. The formation of multilayer coke can start as soon as there is monolayer coke available and is proportional to the fraction of sites covered on the monolayer. The kinetic order for multilayer coke formation is zero and its concentration is given by:

$$C_M = k_{2C}t \tag{16}$$

where k_{2C} is a kinetic coefficient. Arrhenius-type parameters are used for both monolayer (i=1) and multilayer (i=2) coke formation:

$$k_{iC} = k_{0iC}\exp\left(-\frac{E_{aiC}}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right) \tag{17}$$

The above equations can predict a sharp increase with time-on-stream during the initial stage of the reaction followed by a moderate linear increase during the later stage of the reaction stage.

The presence of steam in the reaction mixture leads to a continuous gasification of the deposited coke so that the experimentally measured rate of coke formation is a net rate resulting from both deposition and gasification [28]. Addition of water in optimum amounts would significantly reduce the coke deposition on the catalyst. The experimental results indicate that the spent catalyst coke content continuously decreases with an increase in the feed water content [29]. To properly describe the kinetics of coke deposition on the catalyst leading to a decrease in the catalyst activity, it is important to include a kinetic expression for coke gasification which occurs in parallel with monolayer-multilayer coke formation. The following expression was used for the amount of gasified coke [29]:

$$\mathrm{C}_g = \frac{\mathrm{k}_{2G} \times (\mathrm{C}_m + \mathrm{C}_M)^{n_G} \times \mathrm{time}^{0.5}}{1 + \left(\frac{\mathrm{K}_{WG}\mathrm{p}_{H_2}}{\mathrm{p}_{H_2O}}\right)} \tag{18}$$

where k_{2G} is the gasification rate constant and is described by the Arrhenius equation, K_{WG} is the equilibrium constant for the first stage of gasification and n_G is the dependency of the number of active sites for gasification on the catalyst coke content; its value was found to be close to 1/3. The interaction between coke formation and gasification leads to a dynamic equilibrium coke content on the catalyst. Total coke content, C_c, in presence of water is given by:

$$\mathrm{C}_c = \mathrm{C}_m + \mathrm{C}_M - \mathrm{C}_g \tag{19}$$

3. Catalyst Deactivation Model

Two important mechanisms are responsible for catalyst deactivation: coke formation and sintering. The catalyst activity declined with time-on-stream as coke was accumulated on the catalyst surface covering part of the active sites. According to the kinetic scheme, only monolayer coke would promote deactivation. This would imply that after all the monolayer coke was formed, the catalyst would have some remaining activity. The activity reduction due to monolayer-multilayer coke formation [15] is given by:

$$\mathrm{a}_{coke} = -\gamma_1 \mathrm{C}_m + \gamma_2 \mathrm{C}_m \mathrm{e}^{-\gamma_3\left(\frac{C_M}{C_m}\right)} \tag{20}$$

where γ_i are parameters of the deactivation model. γ_1 is given by an Arrhenius equation, and γ_2 and γ_3 are constants. Eq. (20) is modified when some coke is gasified in the presence of water. To account for this reduction in the coke content, we assumed that gasification would first involve the multilayer coke. The multilayer coke C_M would be reduced by C_g, and if C_g is greater than C_M, the balance would be deducted from C_m.

Presence of small amounts of water in the feed reduces coke deposition on the catalyst, thus reducing catalyst deactivation. Sintering, on the other hand, is enhanced by the presence of water. Sintering is the loss of a catalyst's active surface due to crystal growth of either the bulk material or the active phase. Sintering on supported metal catalysts involves complex physical and chemical phenomena. Experimental observations have shown that sintering is strongly temperature-dependent, but is also affected by the surrounding gas atmosphere. The sintering of precious metals becomes significant around 600 °C. The underlying mechanism of sintering of small metal particles is the surface diffusion, or at higher temperatures, the mobility of larger agglomerates. Supported metal catalysts sinter relatively rapidly under an oxidizing atmosphere. Sintering is also generally accelerated in the presence of water vapor. In this study, the following equation based on an empirical model [19] is proposed to account for loss of activity due to sintering:

$$\mathrm{a}_{sin} = \mathrm{k}_{sin} \cdot \mathrm{f}_{H_2O} \cdot \mathrm{e}^{\left(\frac{\kappa_0 \cdot f_{H_2O}^2}{\tau}\right)} \tag{21}$$

where k_{sin} is given by $\mathrm{k}_{sin} = \mathrm{k}_{0,\,sin} \cdot \exp[(-\mathrm{E}_{a,\,sin}/\mathrm{R})(1/\mathrm{T} - 1/\mathrm{T}_0)]$, K_0 is a sintering constant and f_{H_2O} is molar flow of water. The overall catalyst activity is given by:

$$\mathrm{a} = 1 - \mathrm{a}_{coke} - \mathrm{a}_{sin} \tag{22}$$

The initial catalyst activity is taken as unity. The activity loss due to coking is decreased with increasing water content in the feed and the activity loss due to sintering is increased with increasing water content. These opposing effects of water would explain the observed optimum in the amount of water added to the feed to obtain maximum activity.

4. Estimation of Kinetic Parameters

Molar flow rates of the major species, including propane, propylene, ethane, ethylene, and hydrogen, were obtained according to the reaction scheme given by reactions (2) to (5) and their corresponding kinetic expressions. The isothermal plug flow assumption for the fixed bed reactor leads to the following set of differential equations for the above species:

$$\frac{\mathrm{dF}_i}{\mathrm{dw}} = -\mathrm{r}_i \tag{23}$$

where F_i is the molar flow rate of species i, w is the catalyst mass, and r_i is the net rate of formation of species i. The above equations with appropriate initial conditions corresponding to the feed inlet to the reactor were solved simultaneously using the ODE45 function in MATLAB programming software to obtain the exit propane conversion. The optimum parameter estimates in the kinetic model for propane dehydrogenation, coke formation and catalyst deactivation were obtained by minimizing the root mean square (RMS) of error as the objective function defined by:

$$\mathrm{RMS} = \sqrt{\frac{1}{l}\sum_{i=1}^{l}\left(\frac{\mathrm{X}_{predicted} - \mathrm{X}_{exp}}{\mathrm{X}_{exp}}\right)^2} \tag{24}$$

where l is the number of experimental points, and $\mathrm{X}_{predicted}$ and X_{exp} are model predicted and experimental propane conversions, respectively. The fminsearch toolbox in MATLAB programming software was used for optimization.

RESULTS AND DISCUSSION

Experimental propane conversions presented in Tables 1 to 3 for the three different reaction temperatures employed in this study indicated that addition of water up to a certain optimum level enhanced the propane conversion. For all three temperatures, when more than the optimum amount of water was added, propane conversions fell even below the conversion levels in the absence of water. The optimum amount of water was found to increase with increasing temperature. The optimum amounts of water for reaction temperatures of 575, 600, and 620 °C, were 0.3, 0.45, and 0.5 ml/h, respectively. In all cases any further increase in the feed water content beyond the optimum value would result in an abrupt loss in catalyst activity and propane conversion. These observations are consistent with opposing effects of water on catalyst activity. An increase in the water content of the feed would reduce coke formation through the gasification mechanism, thus enhancing catalyst activity leading to slightly higher propane conversions compared with experiments with no

Table 4. Optimized kinetic parameters of the proposed model

Parameter	Predicted value	Value from [15]	Unit
k_{01}	1.82×10^{-4}	5.242×10^{-4}	$mol\cdot g^{-1}\cdot min^{-1}\cdot bar^{-1}$
E_{a1}	2.06×10^{4}	3.4570×10^{4}	$J\cdot mol^{-1}$
$K_{C_3H_6,0}$	7.63	3.46	-
$\Delta H_{C_3H_6}$	-9.92×10^{4}	-8.5817×10^{4}	$J\cdot mol^{-1}$
k_{01c}	5.14×10^{2}	2.34×10^{2}	$(mg\ cat)\cdot(mg\ coke)^{-1}\cdot min^{-1}$
E_{a1c}	7.74×10^{4}	3.843×10^{4}	$J\cdot mol^{-1}$
k_{02c}	9.92×10^{-6}	1.45×10^{-6}	$(mg\ coke)\cdot(mg\ cat)^{-1}\cdot min^{-1}$
E_{a2c}	2.71×10^{5}	1.2551×10^{5}	$J.mol^{-1}$
k_{02G}	3.56×10^{7}	-	$(mg\ coke)^{2/3}\cdot(mg\ cat)^{-2/3}\cdot min^{-1/2}$
E_{a2G}	7.28×10^{4}	-	$J\cdot mol^{-1}$
K_{0WG}	1.17×10^{7}	-	-
E_{aWG}	1.13×10^{5}	-	$J\cdot mol^{-1}$
C_{max}	2.45×10^{-3}	1.04×10^{-3}	$(mg\ coke)\cdot(mg\ cat)^{-1}$
$\gamma_{0,1}$	1.33×10^{2}	9.4892×10^{2}	$(mg\ cat)\cdot(mg\ coke)^{-1}$
$E_{a\gamma 1}$	4.21×10^{2}	9.61×10^{3}	$J\cdot mol^{-1}$
$k_{0,sin}$	3.88×10^{6}	-	$min\cdot mol^{-1}$
$E_{a,sin}$	2.59×10^{-5}	-	$J\cdot mol^{-1}$
K_0	2.14×10^{13}	-	$min^2\cdot K\cdot mol^{-2}$
γ_2	3.00×10^{2}	3.99×10^{2}	$(mg\ cat)\cdot(mg\ coke)^{-1}$
γ_3	1.20	40.07	-
k_{02}	1.38×10^{-5}	0.465×10^{-5}	$mol\cdot g^{-1}\cdot min^{-1}\cdot bar^{-1}$
E_{a2}	1.61×10^{5}	1.3731×10^{5}	$J\cdot mol^{-1}$
k_{03}	2.24×10^{-7}	2.36×10^{-7}	$mol\cdot g^{-1}\cdot min^{-1}\cdot bar^{-2}$
E_{a3}	3.56×10^{5}	1.5454×10^{5}	$J\cdot mol^{-1}$

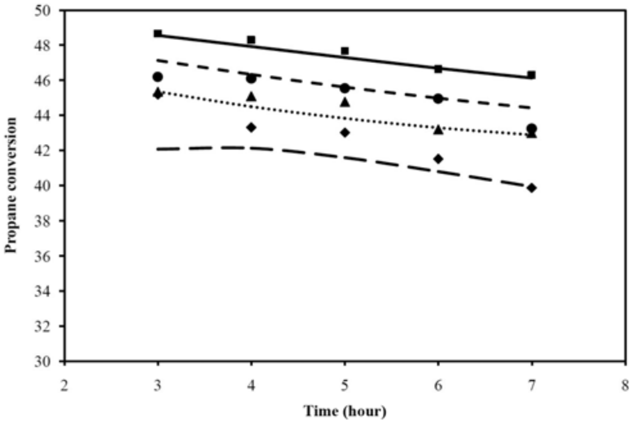

Fig. 1. Predicted and experimental propane conversions at T=620 °C for different amounts of water added to feed (Solid line: 0.5, Short dashed: 0.3, Long dashed: 0.6, Dotted line: 0.0).

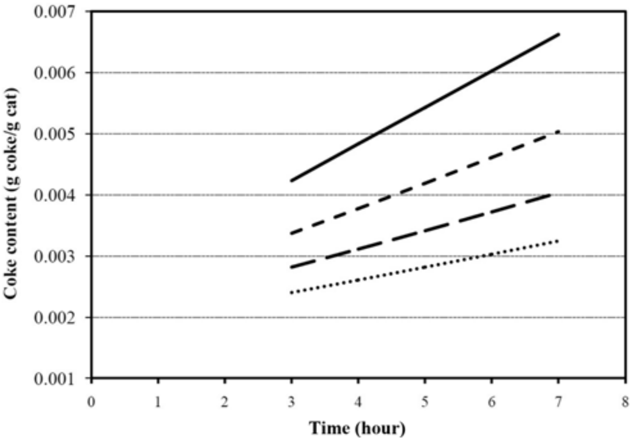

Fig. 2. Predicted coke contents at T=620 °C for different amounts of water added to feed (Solid line: 0.0, Short dashed: 0.3, Long dashed: 0.5, Dotted line: 0.6).

water added. Addition of too much water, however, would result in extensive sintering, leading to a decrease in propane conversions.

The optimum kinetic parameters were obtained with RMS=6% and are reported in Table 4. The overall quality of optimization can be judged from an acceptable agreement between experimental and predicted propane conversions as reported in Tables 1 to 3. An example is illustrated in Fig. 1 where predicted and experimental propane conversions are plotted against time-on-stream for different amounts of water in the feed on for reaction temperature of 620 °C, indicating the ability of the proposed model to predict the optimum amount of water for maximum propane conversion.

The predicted coke contents of the catalyst for different amounts of water added to the feed are presented in Fig. 2 for reaction temperature of 620 °C, indicating that the coke content would decrease with increasing amount of water added to the feed due to coke gasification and would increase with time-on-stream. Experimental data were only available for the end of run (7 hours time-on-stream) for five experimental conditions as reported in Table 5, indicating that

Table 5. Experimental and predicted coke content of catalyst

Temperature (°C)	Amount of water added to feed (ml/h)	(g coke/ g cat)$_{exp}$	(g coke/ g cat)$_{model}$
575	None	0.0056	0.0066
575	0.3	0.0048	0.0045
600	None	0.0059	0.0067
620	None	0.0080	0.0068
620	0.5	0.0038	0.0040

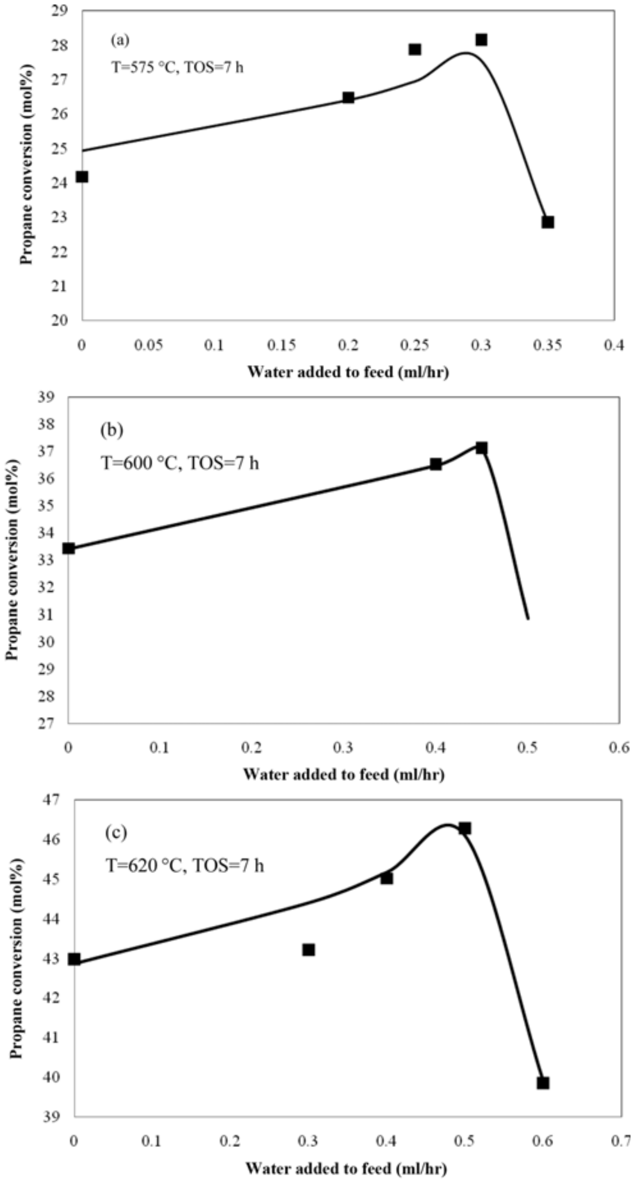

Fig. 3. Predicted and experimental propane conversions at different temperatures for different amounts of water added to feed (Solid line: predicted propane conversion).

the agreement between experimental and predicted coke contents was satisfactory. To summarize, experimental and predicted propane conversions at time-on-stream of 7 hours versus the amounts of water added to the feed are presented in Fig. 3 for different reaction temperatures.

CONCLUSIONS

A kinetic model describing propane dehydrogenation, coke formation, and catalyst deactivation in presence of small amounts of water added as an oxygenated additive was presented for catalytic PDH over a Pt-Sn/γ-Al_2O_3 catalyst. Experimental propane conversions in the temperature range of 575 to 620 °C for various amounts of water added to the feed were used to obtain the optimized model parameters. The predicted propane conversions were in good agreement with experimental values. The model was also capable of predicting an optimum water content that would maximize propane conversion. The occurrence of the optimum water content was due to opposing effects of water. An increase in the water content of the feed would reduce deactivation due to enhanced coke gasification on the one hand, and on the other hand, it would enhance deactivation due to sintering. Limited experimental data was available for the coke content of the spent catalysts, and the agreement between experimental and predicted coke content was also satisfactory. The model predicts that adding water as an oxygenated additive up to the optimum levels would improve propane conversion and reduce coke formation. The optimum amount of water was found to increase with increasing reaction temperature.

SYMBOLS USED

a : activity [-]
a_{coke} : activity decrease by coke [-]
a_{sin} : activity decrease by sintering [-]
C_C : total coke concentration [(mg coke)·(mg catalyst)$^{-1}$]
C_m : monolayer coke [(mg coke)·(mg catalyst)$^{-1}$]
C_{max} : maximum coke concentration in monolayer [(mg coke)·(mg catalyst)$^{-1}$]
C_M : multilayer coke [(mg coke)·(mg catalyst)$^{-1}$]
E_{a1} : activation energy of propane dehydrogenation [J·mol^{-1}]
E_{a1C} : activation energy of monolayer coke [J·mol^{-1}]
E_{a2} : activation energy of cracking [J·mol^{-1}]
E_{a2C} : activation energy of multilayer coke [J·mol^{-1}]
E_{a2G} : activation energy of gasification [J·mol^{-1}]
E_{a3} : activation energy of ethylene hydrogenation [J·mol^{-1}]
$E_{a,\,sin}$: activation energy of sintering [J·mol^{-1}]
E_{aWG} : activation energy of first gasification by water [J·mol^{-1}]
$E_{a\gamma 1}$: activation energy of activity by coke monolayer [J·mol^{-1}]
f_{H_2O} : molar flow rate of water [mole·(min)$^{-1}$]
F_i : molar flow rate of species i [mole·(min)$^{-1}$]
i : species [-]
k_{01} : kinetic rate constant of propane dehydrogenation at T_0 [mol·g^{-1}·min^{-1}·bar^{-1}]
k_{01C} : kinetic rate constant of monolayer coke at T_0 [(mg catalyst)·(mg coke)$^{-1}$·min^{-1}]
$k_{0,\,sin}$: sintering rate constant at T_0 [min·(mole)$^{-1}$]
k_{02} : kinetic rate constant of cracking at T_0 [mol·(g)$^{-1}$·min^{-1}·bar^{-1}]
k_{02C} : kinetic rate constant of multilayer coke at T_0 [(mg coke)·(mg catalyst)$^{-1}$·min^{-1}]
k_{02G} : gasification rate constant at T_0 [(mg coke)$^{2/3}$·(mg catalyst)$^{-2/3}$·min$^{-1/2}$]
k_{03} : kinetic rate constant of ethylene hydrogenation at T_0 [mol·(g)$^{-1}$·min^{-1}·bar^{-2}]

K_0 : sintering constant [$K\cdot min^2\cdot mole^{-2}$]
K_{0WG} : equilibrium constant of first gasification by water [-]
$K_{C_3H_6,0}$: propylene adsorption constant at T_0 [-]
$K_{C_3H_6}$: propylene adsorption constant [-]
K_{eq} : propylene equilibrium constant [-]
l : number of experimental points [-]
n_G : number of active sites for gasification [-]
PDH : propane dehydrogenation [-]
r_i : net rate of formation of species i [$mol\cdot g^{-1}\cdot min^{-1}$]
R : gas constant [$J\cdot mol^{-1}K^{-1}$]
RMS : root mean square [-]
T : temperature [K]
T_0 : reference temperature [K]
w : mass of catalyst [g]
WHSV : weight hourly space velocity [-]
$X_{exp.}$: experimental conversion [-]
$X_{pred.}$: predicted conversion by model [-]
γ_{01} : parameter of activity by monolayer coke [(mg catalyst)·(mg coke)$^{-1}$]
γ_2 : parameter of activity by monolayer coke [(mg catalyst)·(mg coke)$^{-1}$]
γ_3 : parameter of activity by monolayer and multilayer coke [-]
$\Delta H_{C_3H_6}$: reaction enthalpy of propylene [$J\cdot mol^{-1}$]

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