

Neural network modeling the effect of oxygenate additives on the performance of Pt–Sn/ γ -Al₂O₃ catalyst in propane dehydrogenation

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Received: 11 January 2013 / Accepted: 22 May 2013 / Published online: 23 June 2013
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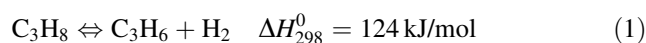
Abstract The effect of oxygenate additives, water and methanol, to the feed on the performance of industrial Pt–Sn/ γ -Al₂O₃ catalyst in dehydrogenation of propane was studied by neural network modeling. Because of the complex nature of the system and very low levels of oxygenate addition, neural networks were employed as an efficient and accurate tool to obtain the behavior of the system. Dehydrogenation reaction was carried out in a fixed-bed quartz reactor in the temperature range of 575–620 °C. Steady state modeling was performed in three different levels of oxygenate addition, and conversion and selectivity at different levels. The optimum amounts of water and methanol for reaction temperatures of 575, 600 and 620 °C were found to be 83.60, 125.40 and 139.34 ppm, respectively, for water and 9.98, 24.94 and 49.88 ppm for methanol by neural network method. The neural network-based optimum was compared with that obtained from experimental data. In this case, various architectures have been checked using 70 % of experimental data for training of artificial neural network (ANN). Among the various architectures multi layer perceptron network with trainlm training algorithm was found as the

best architecture. Temperature and water or methanol amount for the present constituents in the feed were network input data. Output data were conversion, selectivity to propylene and yield of propylene. Comparing the obtained ANN model results with 30 % of unseen data confirms ANN excellent estimation performance. The influence of different operating conditions on the accuracy of the results was also investigated and discussed. The propylene yields, however, passed a maximum at the optimum levels of oxygenates coincided with a substantial reduction of coke formation as well. The modeling results were accurate with <0.9 % error.

Keywords Propane dehydrogenation · Pt–Sn/ γ -Al₂O₃ · Oxygenates · Catalyst modifiers · Coke formation · Artificial neural network

Introduction

Dehydrogenation of light alkanes to the corresponding alkenes is growing because of growing demand for lower alkenes for the production of polymers, polygas chemicals and oligomers as gasoline blending stocks additives [1, 2]. Propane dehydrogenation (PDH) has been considered as an alternative route for production of propylene. The reaction is a highly endothermic and equilibrium limited requiring relatively high temperatures and low pressures to achieve high propylene yields [3]:



The reaction is generally operated at 525–625 °C near atmospheric pressures over supported platinum or chromia catalysts. Despite the simple chemistry, the reacting system is very complex due to occurrence of several side reactions

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and rapid catalyst deactivation. The commercial technologies differ in the catalyst formulation, reactor design, heat supply, and method of catalyst regeneration.

Pt–Sn/ γ -Al₂O₃ catalyst exhibits a high activity and selectivity to propylene in PDH [4, 5]. Promoting effects of Sn on Pt/ γ -Al₂O₃ have been described in terms of its role as a poison for acid sites on the alumina support as well as enhanced mobility of adsorbed hydrogen and increased dispersion of Pt on the support [6–9]. Side reactions including hydrogenolysis and cracking result in the formation of lower hydrocarbons which impact catalyst performance [10].

Deactivation of Pt–Sn/ γ -Al₂O₃ by coke depositions in the dehydrogenation is an important operation problem [11, 12]. The carbonaceous deposits on catalyst surface can be removed by treatment with oxygen or steam. Some technologies use hydrogen or steam as diluents to reduce coke formation and elongate catalyst lifetime.

Steam can serve as catalyst modifier when added in low levels to the feed stream [13–15]. Recently, Barghi et al. [13] performed the kinetic modeling of PDH in presence of oxygenated additive over industrial Pt–Sn/ γ -Al₂O₃ in which the effect of water addition in low level on coke formation was mathematically investigated. Pt-based catalysts are poisoned by high level of oxygenate by various mechanism. Oxygenates deplete chlorine, essential for re-dispersion of sintered platinum during catalyst regeneration in continuous catalyst regeneration (CCR) plant, from the catalyst and increase the selectivity to carbon oxides. When used in appropriate levels, however, they could exhibit beneficial effects on catalyst performance without perceptible adverse effects [16]. Nevertheless, very few investigations have reported the effect of oxygenates and its interaction mechanism in catalytic dehydrogenation of light alkanes [16, 17].

The neural network, which arose from attempts to model the functioning of the human brain, appears to be useful in the study of dehydrogenation reaction. It seems to be a promising tool to solve modeling problems in cases where the governing mechanisms cannot be formulated due to insufficient knowledge. Models based on artificial neural network (ANN) exhibit the rule-following behavior without containing any explicit representation of those rules that is the main feature of the neural network approach, which results in its wide range of applications. In recent years, the concept of neural networks (NNs) has gained wide popularity in many areas of chemical engineering such as dynamic modeling of chemical processes [18, 19], catalyst design [20], estimation of catalyst deactivation, reaction modeling [21, 22], modeling of chemical reactors [23] and modeling of complex chemical processes [24].

Applying ANN for modeling can render pre-mentioned problems and facilitate the forecasting of catalyst activity.

Based on our literature survey, there was no attempt on ANN modeling of catalyst performance for dehydrogenation reactions. In this paper, we have demonstrated the use of ANN in prediction of the performance of commercial Pt–Sn/ γ -Al₂O₃ catalyst in the presence of oxygenate additives, namely water and methanol, in PDH. Furthermore, the results of the modeling have been compared with the experimental data.

Materials and methods

A laboratory scale tubular flow fixed-bed quartz reactor was used for the PDH experiments. The inside diameter of the reactor was 13 mm, the length of the reactor was 90 cm, and the commercial Pt–Sn/ γ -Al₂O₃ catalyst was loaded in the middle section of the reactor in between two layers of quartz particles. The catalyst loading was 1 g. All experiments were conducted at weight hourly space velocity (WHSV) of 2/h and hydrogen to propane ratio, H₂/HC, of 0.8 that are typical of industrial conditions. PDH was performed at 575, 600 and 620 °C near atmospheric pressure (0.8 bar) with different amounts of water in the feed. The product samples were analyzed 3 h after the start of the run when stable conditions were achieved. Product samples were then analyzed hourly up to 7 h after the start of the run. Details of the experimental procedures and analyses are reported elsewhere [25].

Water and methanol were introduced to the reactor feed stream using a syringe pump. The exit gasses were analyzed for light hydrocarbons and CO and CO₂ using an online Agilent 6890 gas chromatograph equipped with TCD and FID detectors. Propane conversions, product selectivities and propylene yield were defined as follows [26]:

$$\text{Propane Conversion (\%)} = \frac{\sum_i \left(\frac{n_i}{3}\right) [F_i]_{\text{out}} - [F_{\text{C}_3\text{H}_8}]_{\text{out}}}{\sum_i \left(\frac{n_i}{3}\right) [F_i]_{\text{out}}} \times 100 \quad (2)$$

$$\begin{aligned} \text{Selectivity for component } i \text{ (\%)} \\ = \frac{\left(\frac{n_i}{3}\right) [F_i]_{\text{out}}}{\sum_i \left(\frac{n_i}{3}\right) [F_i]_{\text{out}} - [F_{\text{C}_3\text{H}_8}]_{\text{out}}} \times 100 \end{aligned} \quad (3)$$

$$\begin{aligned} \text{Propylene Yield (\%)} \\ = \frac{\text{Propane Conversion} \times \text{Selectivity of Propylene}}{100} \end{aligned} \quad (4)$$

where i includes all the components with carbon atoms in the exit gas stream, and n_i and F_i are the number of carbon atoms and molar flow of component i , respectively.

Spent catalysts were characterized by thermal gravimetric analysis (TGA). TGA tests were performed using a PL-STA 1500 model by PL Thermal Science (England)

where weight measurements were registered at a rate of 50 measurements/min using a temperature ramp of 5 °C/min from the base temperature of 25 °C up to 950 °C.

Artificial neural networks modeling

NNs are inductive models inspired by the structure and the functions of biological neurons. A network is composed of units or nodes that represent the neuron bodies. The units are in the shape of conjunct loop structure which, in fact, functions like axons and dendrites [27].

Information passes among these units along interconnections. Any incoming connection has two associated values, an input value and a weight. The output of the unit is a function of the summed value. ANNs are not programmed to perform specific tasks; rather, they are trained with respect to data sets until they learn patterns used as inputs. Once they are trained, new patterns may be presented to them for prediction or classification. ANNs can automatically learn to recognize patterns in data from real systems or from physical models. An ANN can handle many inputs and produce answers that are in a form suitable for the designers.

One of the well-known topologies of NN is the multi-layer perception (MLP) which is used for classification and estimation problems. One example of the layered networks is depicted in Fig. 1. In the figure, ANN input, hidden and output layers are shown. ANN training is an optimization process in which an error function is minimized by adjusting the ANN weights. When an input training pattern

is introduced to ANN, output is calculated. Output is compared with the real output provided by the user [28, 29].

Output signals from each of the nodes are triggered by the signals emanating from the input nodes which can be modeled as a sigmoid relation:

$$f(\theta) = \frac{1}{1 + e^{-\theta}} \quad (5)$$

where $f(\theta)$ is the output signal from each node and θ is the activity of each node. The activity of each node is obtained as the sum of the signals received from the preceding nodes and defined as:

$$\theta = \sum \omega_i x_i \quad (6)$$

where ω_i are the weights connecting input node i to hidden node j , x_i is the input value (normalized to unity) to input node i . Signals from the hidden nodes then propagate to the output layer and generate output signal similarly as the input did.

Training of the ANN is an improvement process by which error functions can be minimized according to the network weights. When an input training pattern is introduced to ANN, output is calculated. Output is compared with the real output provided by the user. These differences can be used by improvement technique to teach neural network. The error function used here was mean square error (MSE) which is given by the following formula:

$$\text{MSE} = \frac{1}{n} \sum_{i=1}^n (y_i - y_{i,\text{real}})^2 \quad (7)$$

Fig. 1 Structure of a neural network

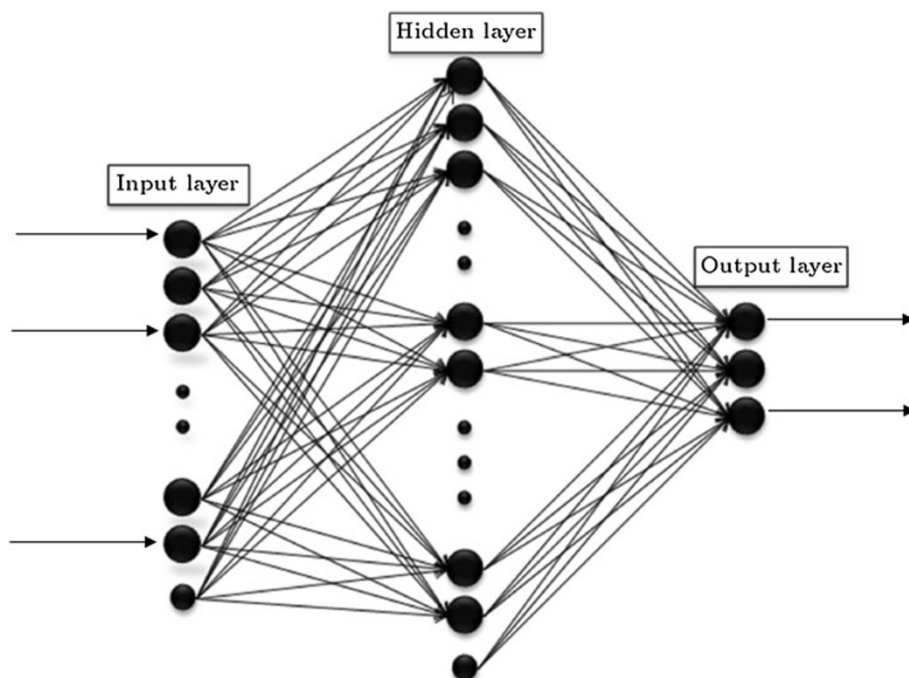
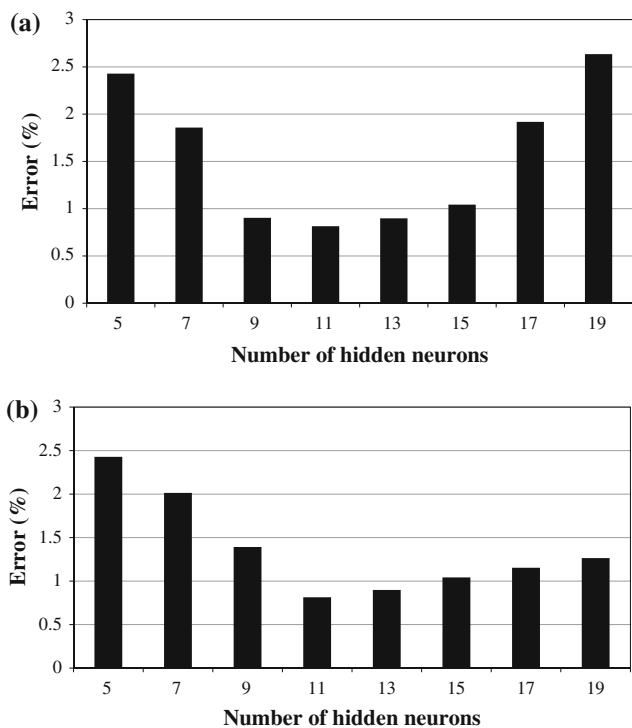


Table 1 Neural network variables and domain

Variables	Domain
Oxygenate (water or methanol) (ml/h)	0–0.6
Temperature (°C)	575–620
Conversion (mol.%)	10–50
Selectivity (mol.%)	20–100
Yield (mol.%)	10–50

**Fig. 2** Error versus number of hidden layer for **a** water and **b** methanol through the best obtained MLP network

where $y_{i,\text{real}}$ is the i th real target and y_i is the network output corresponding to input. Thus, training process is a path from input layer to output layer to calculate an output, obtaining the error and a backward path to update the weights [30].

In this work, the neural network was trained to learn the ‘function’ using training set of the input and output data, in which both input and output data were experimental. Then, conversion and selectivity to propylene over the catalyst was calculated by introducing the input data of the left-out catalyst into thus trained network. This procedure was repeated for all the experimental data and conditions, and the calculated values were compared with the experimental values.

The simulation of processes with NN requires a large number of experimental data. The data were shuffled and split in two subsets: training set and test set. The splitting of samples plays an important role in evaluation of an ANN

Table 2 Experimental and ANN modeling conversion results for catalytic PDH in presence of water

T (°C)	Water amount (ml/h)	Conversion (mol.%)			
		Experimental		ANN Modeling	
		Start ^a	End ^b	Start	End
575	0.20	28.56	26.48	27.59	26.39
	0.25	29.74	27.88	28.65	27.54
	0.30	30.89	28.17	29.04	27.88
	0.35	24.96	22.87	–	–
	Without	26.79	24.18	26.53	24.86
600	0.40	38.76	36.54	36.73	35.41
	0.45	39.95	37.13	38.34	36.08
	Without	36.12	33.43	33.88	31.88
620	0.30	46.18	43.22	46.15	42.75
	0.40	47.57	45.02	47.91	44.61
	0.50	48.67	46.29	48.49	45.60
	0.60	45.17	39.85	44.14	40.63
	Without	45.34	42.98	44.51	41.84

^a Start, reaction time after 3 h

^b End, after 7 h

performance. The training set is used to estimate model parameter, and the test set is used to check the generalization ability of the model. The training set must be representative of the whole population of input samples. In this investigation data were obtained under various experimental conditions including different reaction temperatures and different amounts of water or methanol as additives. The use of more than 60 % of data for training and the remaining for testing is the most common approach for ANN [31]. The network was taught by 70 % of data and the remaining data were used to test the generalization capacity of the network. ANN variables and their domains are illustrated in Table 1.

Using MLP network according to Fig. 2, in which MSE is plotted in conformity with the number of neurons in hidden layers for water and methanol, the optimal number for hidden layers is seven corresponding to the least square error.

Results and discussion

The developed ANN model was employed for studying variables affecting the catalyst performance. Experimental and neural network modeling results of propane conversions and selectivity and yield to propylene in the presence of small amounts of water are summarized in Tables 2, 3 and 4 and those for methanol in Tables 5, 6 and 7. Figure 3 presents the ANN modeling and experimental data on propane conversions, product selectivity and yield of

Table 3 Experimental and ANN modeling selectivity to propylene results for catalytic PDH in presence of water

T (°C)	Water amount (ml/h)	Selectivity to C ₃ H ₆ (mol.%)			
		Experimental		ANN modeling	
		Start ^a	End ^b	Start	End
575	0.20	75.64	78.30	78.47	78.29
	0.25	77.87	79.18	79.91	79.84
	0.30	77.92	81.65	79.57	81.06
	0.35	67.53	70.25	–	–
	Without	79.26	82.64	77.76	80.38
600	0.40	84.18	87.15	87.71	89.13
	0.45	85.74	90.03	87.82	90.61
	Without	90.59	94.84	94.78	97.81
620	0.30	77.26	79.76	77.13	80.37
	0.40	75.44	79.65	74.47	79.64
	0.50	77.93	82.76	76.97	83.44
	0.60	75.73	78.32	78.98	78.22
	Without	82.78	87.98	84.03	88.93

^a Start, reaction time after 3 h^b End, after 7 h**Table 4** Experimental and ANN modeling yield of propylene results for catalytic PDH in presence of water

T (°C)	Water amount (ml/h)	Yield of C ₃ H ₆ (mol.%)			
		Experimental		ANN modeling	
		Start ^a	End ^b	Start	End
575	0.20	21.60	20.73	21.65	20.66
	0.25	24.05	22.30	22.89	21.99
	0.30	23.17	22.76	23.15	22.61
	0.35	16.85	16.07	–	–
	Without	21.23	19.98	20.64	19.97
600	0.40	32.63	31.84	32.23	31.56
	0.45	34.25	33.83	33.67	32.73
	Without	32.72	31.70	32.12	31.17
620	0.30	35.68	34.47	35.59	34.36
	0.40	35.89	35.86	35.69	35.52
	0.50	37.93	38.31	37.38	38.05
	0.60	34.21	31.21	34.83	31.79
	Without	37.53	37.81	37.41	37.22

^a Start, reaction time after 3 h^b End, after 7 h

propylene versus time-on-stream at 575 °C with the optimum level 0.3 ml/h water added to the feed [25]. The agreement between the model predictions and the experimental data is good. In all runs the catalyst activity declined with time-on-stream as coke was accumulated on the catalyst surface while the selectivity to propylene

increased and it can be seen that the ANN model correctly predicts the trend. This model, approximately, can be generalized to the entire range of data for water since the differences between predicted and experimental value are small indicating the capability of ANN to predict unobserved data correctly.

The indicated graphs demonstrate the good performance of the created network. The ANN simulation is a useful tool for many situations including when information for the catalytic system, such as catalyst structure and material, are unavailable. The ANN simulation is solely based on the experimental results and as such here is no need for detailed information of catalyst structure, oxygenated additive and mechanism of reaction. This is an important advantage for simulation of catalytic processes by ANNs.

Similar observations can be made with respect to the effects of water on PDH at other reaction temperatures. The optimum amount of water was found to increase with increasing temperature. As indicated by Tables 2, 3 and 4, the optimum amounts of water at reaction temperatures of 575, 600, and 620 °C were 0.3, 0.45, and 0.5 ml/h, respectively, corresponding to a feed water composition of 83.6, 125.4, and 139.34 ppm. In all cases any further increase in the feed water content beyond the optimum value would result in a substantial loss in catalyst that could also be predicted by ANN.

Figure 4 presents the propane conversions and product selectivities for PDH at 620 °C with various amounts of methanol added to the feed. The trends were qualitatively similar to those obtained when water was added to the feed. The optimum amounts of methanol at reaction temperatures of 575, 600, and 620 °C were 0.02, 0.05, and 0.1 ml/h, respectively, corresponding to a feed methanol composition

Table 5 Experimental and ANN modeling conversion results for catalytic PDH in presence of methanol

T (°C)	Methanol amount (ml/h)	Conversion (mol.%)			
		Experimental		ANN modeling	
		Start ^a	End ^b	Start	End
575	0.02	29.13	26.97	28.95	26.29
	0.05	27.13	25.14	28.64	25.51
	Without	26.79	24.18	28.21	25.62
600	0.05	38.07	35.79	38.57	36.37
	0.10	34.18	34.72	37.02	34.47
	Without	36.12	33.43	36.95	33.59
620	0.10	47.96	45.78	46.40	45.37
	0.20	41.72	36.84	40.99	36.84
	Without	45.34	42.98	45.76	43.63

^a Start, reaction time after 3 h^b End, after 7 h

Table 6 Experimental and ANN modeling selectivity to propylene results for catalytic PDH in presence of methanol

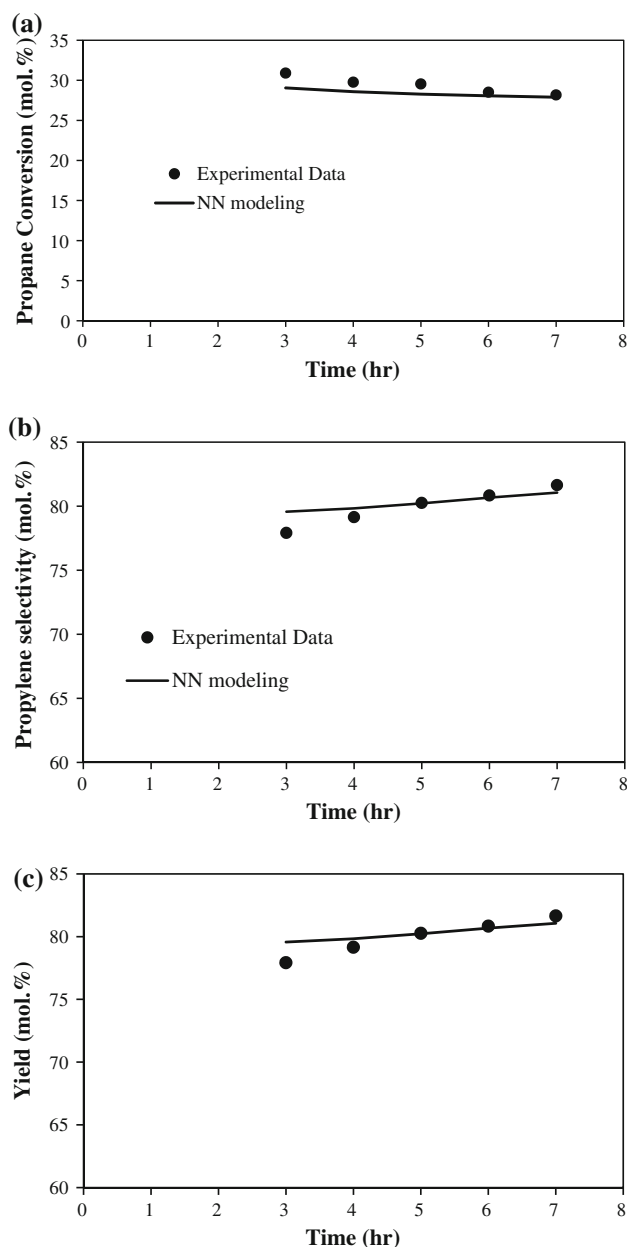
T (°C)	Methanol amount (ml/h)	Selectivity to C ₃ H ₆ (mol.%)			
		Experimental		ANN modeling	
		Start ^a	End ^b	Start	End
575	0.02	79.22	81.94	85.74	84.74
	0.05	75.87	77.41	82.98	81.14
	Without	79.26	82.64	87.37	86.70
600	0.05	86.79	90.16	91.43	91.82
	0.10	82.09	88.07	87.79	88.39
	Without	90.59	94.84	93.52	93.55
620	0.10	78.65	82.63	83.30	86.38
	0.20	64.95	69.46	68.68	74.50
	Without	82.78	87.98	87.51	88.51

^a Start, reaction time after 3 h^b End, after 7 h**Table 7** Experimental and ANN modeling yield of propylene results for catalytic PDH in presence of methanol

T (°C)	Methanol amount (ml/h)	Yield of C ₃ H ₆ (mol.%)			
		Experimental		ANN modeling	
		Start ^a	End ^b	Start	End
575	0.02	23.08	22.10	24.82	22.28
	0.05	20.58	19.46	23.77	20.69
	Without	21.23	19.98	24.65	22.21
600	0.05	33.04	32.27	35.27	33.39
	0.10	28.06	30.58	32.50	30.47
	Without	32.72	31.70	34.55	31.41
620	0.10	37.72	37.83	38.65	39.18
	0.20	27.10	25.59	28.15	27.44
	Without	37.53	37.81	40.04	38.62

^a Start, reaction time after 3 h^b End, after 7 h

of 9.98, 24.94, and 49.88 ppm. The agreements between the model predictions and the experimental data were slightly better for water compared with methanol as the additive. In all runs the catalyst conversion declined with time-on-stream that was correctly predicted by ANN modeling. The selectivity to propylene increased with increasing time-on-stream. This trend was also predicted by the ANN model although agreements between model predictions and experimental results are not satisfactory for the initial period. In case of the propylene yield, the predictions for methanol were not satisfactory in comparison with water. As indicated by the ANN results, the optimum amounts of methanol were lower compared with those for optimum water addition. The enhanced propane conversions and propylene yields were slightly higher when optimum

**Fig. 3** ANN modeling and experimental comparison effects of water for **a** propane conversion, **b** propylene selectivity and **c** propylene yield on PDH over industrial Pt-Sn/ γ -Al₂O₃ catalyst in optimum amount of water addition at 575 °C

amounts of water were used compared with those for optimum methanol addition. This implies that for equivalent amount of oxygen, methanol is a more efficient modifier than water.

At high temperatures carbonaceous deposits, collectively termed coke, are rapidly formed and as a consequence, catalyst deactivation and regeneration are important considerations for commercial processes. With increasing temperature, the activity of catalyst and the reaction rate increased which also resulted in an increase in

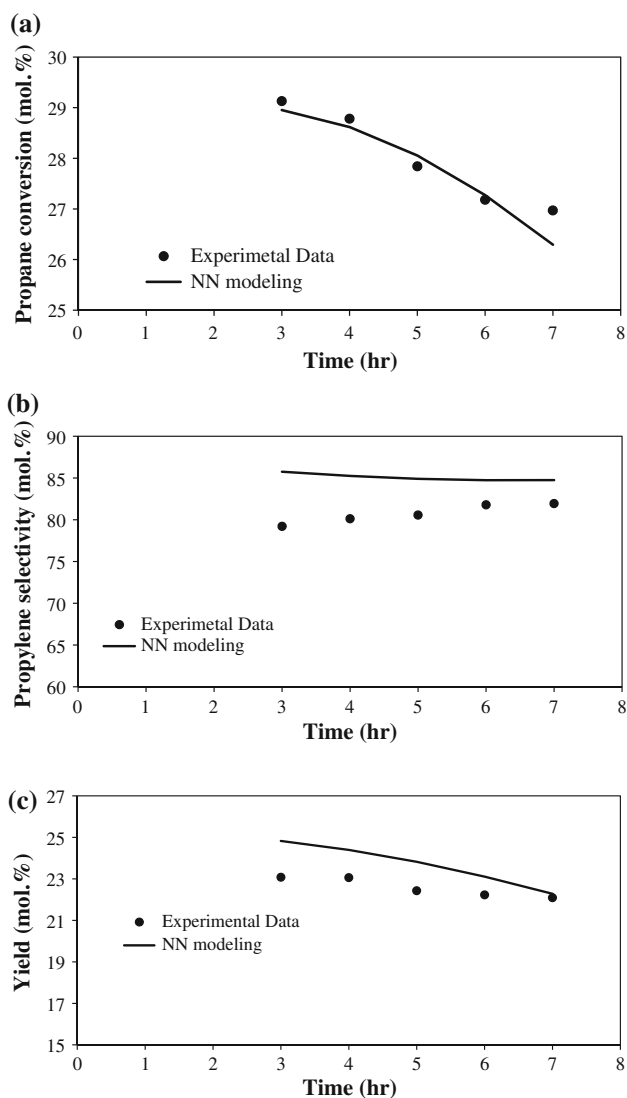


Fig. 4 ANN modeling and experimental comparison effects of methanol for **a** propane conversion, **b** propylene selectivity and **c** propylene yield on PDH over industrial Pt-Sn/ γ -Al₂O₃ catalyst in optimum amount of methanol addition at 575 °C

Table 8 Coke content of spent catalysts from TGA

<i>T</i> (°C)	Oxygenated additive	Wt% coke of catalyst
620	0.1 ml/h methanol	4.2
620	0.5 ml/h water	3.8
620	Non	8.0
600	0.05 ml/h methanol	3.2
600	Non	5.9
575	0.3 ml/h water	2.8
575	Non	4.6

coke deposition. Water and light oxygenates can also serve as catalyst modifier when used in low levels in the feed stream. They act as catalyst depressant. Pt-based catalysts

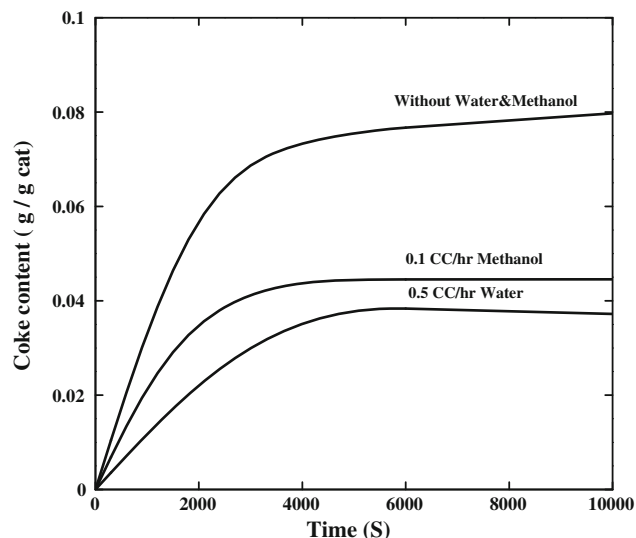


Fig. 5 Coke content versus time-on-stream(s) at 620 °C

are poisoned by high level of oxygenate by various mechanisms. They also deplete chlorine, essential for re-dispersion of sintered platinum, from the catalyst and increase the selectivity to carbon oxides. When used in appropriate levels, however, they could exhibit beneficial effects on catalyst performance without other adverse effects. In general, one can conclude that with increasing reaction temperature, the optimum amounts of oxygenated additives should be increased.

The results from TGA for selected spent catalyst samples are presented in Table 8 in terms of the coke content (g/g cat) of spent catalysts, indicating that without any added water or methanol, the coke content of the spent catalysts increased with increasing reaction temperature. Addition of water or methanol in optimum amounts significantly reduced the coke content of spent catalysts. Comparison of the coke content at 620 °C indicated that when water was added in the optimum amount, the reduction in the coke content of the spent catalyst was slightly more than when methanol was added in the optimum amount (Fig. 5).

Conclusions

PDH was carried out over an industrial Pt-Sn/ γ -Al₂O₃ catalyst with small amounts of water or methanol added to the feed. These oxygenated additives would maximize both the conversion of propane and the yield of propylene if they are added in the optimum amounts. Application of ANNs model can avoid difficulties like type of catalyst, uncertainty in porosity and mechanism of reaction, etc. in simulation of a catalyst activity. Based on different training

algorithms, MLP has been found as the best network with minimum training error for modeling of catalyst conversion and selectivity. The obtained results incorporate excellent capability of ANN in modeling. The estimated values of ANN agreed very well with the experimental values, even in the case where the experimental data seemed to contain some error and diversity. The optimum amounts of oxygenated additives increased with increasing reaction temperature. For a given temperature, the optimum amount of water was more than that for methanol. These trends were well predicted by the NN model and the results lead to the conclusion that the neural network is a powerful tool for the estimation of catalyst activity, selectivity and propylene yield for sufficient amounts of oxygenated additives.

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