Kinetic Promotion Effect of Hydrogen and Dimethyl Disulfide Addition on Propane Dehydrogenation over the \( \text{Pt–Sn–K/Al}_2\text{O}_3 \) Catalyst

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ABSTRACT: The kinetic effects of co-feeding of dimethyl disulfide (DMDS) and hydrogen on propane dehydrogenation (PDH) over the \( \text{Pt–Sn–K/Al}_2\text{O}_3 \) catalyst were investigated by the response surface method. The 3-level Box–Behnken design for 4 factors (reaction temperature, propene, hydrogen, and DMDS flow rate) was used to design the experiment. The initial propane conversion, propene selectivity, and coking amount were chosen as responses and the results were fitted by quadratic models. The fresh and coked catalysts were characterized by high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM-EDS), thermogravimetry (TG), \( \text{N}_2 \) physisorption, and Fourier-transform infrared spectroscopy (FT-IR). Analysis of variance (ANOVA) results showed that the DMDS flow rate is significant for propane conversion and coking amount while hydrogen flow rate is only significant for the conversion. By using the fitted model for the response surface, it is found that DMDS can significantly reduce the coking amount at the expense of propane conversion, and hydrogen weakly affects the selectivity and coking amount. The optimal conditions to achieve maximum conversion and selectivity and minimum coking amount are not consistent. The DMDS and hydrogen flow rate should be optimized to obtain the maximum economic profit out of the propane dehydrogenation (PDH) process.

1. INTRODUCTION

Propane dehydrogenation (PDH) has become one of the most important ways to increase propylene productivity.\(^1,2\) Pt-based catalysts are widely used in some commercialized processes, in which the PDH reaction is usually carried out at high temperatures, around \(540–640 \, ^\circ \text{C} \), due to the thermodynamic equilibrium limitation. The high temperature will lead to side reactions such as cracking, hydrogenolysis, and coking problem, and the catalysts need to be frequently regenerated.\(^3\)

To increase the profitability of the PDH process, most research efforts have been devoted to developing new catalysts with higher performance.\(^4\) It is found that achieving high dispersion of Pt is an effective strategy to maximize its activity and selectivity, which can be achieved by alloying with other metals,\(^5,6\) using different promoters and catalyst carriers.\(^7\) Catalysts with lower prices are also of research interest, and transition metals, carbonaceous materials, metal sulfides, and oxides have been reported as effective catalysts for PDH.\(^8\)

Several methods have been proposed to strengthen PDH more practically, which include (1) coupling with an exothermic reaction, e.g., selective hydrogen combustion, reverse water–gas shift reaction, oxychlorination, etc.;\(^11\) (2) using membrane reactors to separate the hydrogen during the reaction; (3) co-feeding gas additives, e.g., steam, hydrogen, and sulfide.\(^12,13\) The last method has been adopted in some commercialized PDH processes nowadays.

The positive role of hydrogen in the activity and selectivity of PDH has been experimentally observed by many authors.\(^14\) Some early possible explanations have been summarized by Saerens et al.,\(^15\) and their microkinetic modeling of PDH on Pt(111) results show that the promotion effect of hydrogen is because the increasing hydrogen partial pressure in the feed would lower the coverage of deeply dehydrogenated coke precursors on the surface, decrease the propene desorption...
strength, and increase the energy barrier for the dehydrogenation of propene. Xiao et al.\textsuperscript{16} also performed microkinetic modeling of PDH over the Pt catalyst and found that the adsorbate–adsorbate interactions must be considered in the modeling and that an optimum hydrogen/propane ratio existed for PDH, indicating that the kinetics of PDH on Pt is sensitive to the surface coverage of different surface species.

The influence of the sulfur species on PDH over the Pt catalyst was first reported by Rennard et al.\textsuperscript{17} who found that introduction of trace amounts of sulfur, H\textsubscript{2}S, or thiophene into the PDH feed would increase the propane selectivity to >94%. However, the catalysts exposed to sulfur are facile to deactivate due to the sintering of Jackson et al.\textsuperscript{18} showed that addition of sulfur in the catalyst preparation or in the PDH feed is effective for increasing the selectivity of the Pt/Al\textsubscript{2}O\textsubscript{3} catalyst, and their results indicate that the selectivity is not directly related to the sulfur amount accumulated on the surface. Wang et al.\textsuperscript{19} testified that a certain concentration of hydrogen sulfide can improve the selectivity and stability of a Pt/θ-Al\textsubscript{2}O\textsubscript{3} catalyst, but has a slightly adverse effect on the catalytic activity of the catalyst. The improved performance can be partially attributed to the electronic effect of the adsorbed sulfur species according to the density functional theory (DFT) calculation results. More recently, co-feeding of a high concentration of H\textsubscript{2}S in the PDH reactant is reported as a novel PDH process,\textsuperscript{20} in which transition metals or metal oxides can be used as catalysts. The oxidation state of the metal and the surface acidity of the metal oxide, and therefore their catalytic performance, could be changed by the sulfur species. Despite all of these research efforts, knowledge of the detailed kinetic effect of sulfur species and the underlying mechanism is still limited.

Few studies on the comprehensive effect of introducing various gas-phase additives into the PDH process have been reported. In this article, the effects of hydrogen and dimethyl disulfide, together with the reaction temperature and propylene flow rate, on the catalytic performance of a Pt–Sn catalyst were investigated by the response surface methodology (RSM) under the operation conditions of an industrial dehydrogenation reactor.

2. MATERIALS AND METHODS

2.1. Preparation of the Catalyst. The Pt–Sn–K/Al\textsubscript{2}O\textsubscript{3} catalyst was prepared by the co-impregnation technique. The catalyst support was θ-alumina balls with a diameter of 1.6 mm. The Al\textsubscript{2}O\textsubscript{3} support was impregnated with a solution of H\textsubscript{2}PtCl\textsubscript{6}·6H\textsubscript{2}O (99.9%, Sinopharm), SnCl\textsubscript{2}·5H\textsubscript{2}O (99.9%, Sinopharm), and KCl (99.9%, Sinopharm). After the impregnation, the catalyst precursor was aged at room temperature for 12 h, dried at 110 °C for 8 h, and then calcined at 500 °C for 3 h with a heating rate of 2 °C/min. Before the testing of the catalyst, it was ground and sieved to particle sizes smaller than 0.125 mm.

2.2. Testing of the Catalyst. The propane dehydrogenation reaction was carried out in a fixed-bed reactor (μ-BenchCat, Altamira). In each experiment, 0.1 g of the catalyst sample was weighed and loaded into a quartz tube with an inner diameter of 6 mm. After checking the air tightness of the whole device, the reactor temperature was increased to 550 °C at a heating rate of 10 °C/min in pure argon atmosphere. Then the catalyst was reduced in pure hydrogen atmosphere for 100 min. After the reduction, the reactor temperature was raised to the setting reaction temperature. Then, the reaction mixture of propane (16 mL/min), hydrogen, dimethyl disulfide, and propylene was fed into the reactor in proportion, with argon introduced to maintain the total flow rate at 100 mL/min. The reaction time of each experiment was 240 min, and the conversion after a 5 min reaction was taken as the initial conversion. After the reactions, the spent catalysts were collected for characterization. The gas products of the propane dehydrogenation reaction (such as propane, propylene, ethane, ethylene, and methane) were detected by an online four-channel micro chromatograph (INFICON 3000). The conversion and propylene selectivity are calculated according to the following equations

\[
X = \frac{F_{\text{C}_3\text{H}_6\text{f}} - F_{\text{C}_3\text{H}_8\text{o}}}{F_{\text{C}_3\text{H}_6\text{f}}} \times 100% \tag{1}
\]

\[
S = \frac{F_{\text{C}_3\text{H}_8\text{o}}}{\sum_i n_i F_{i,o}} \times 100% \tag{2}
\]

where \(F_{\text{C}_3\text{H}_6\text{f}}\) is the feed flow rate of propane; \(F_{\text{C}_3\text{H}_6\text{f}}, F_{\text{C}_3\text{H}_8\text{o}},\) and \(F_{i,o}\) are the flow rates of propylene, propane, and other components \(i\) (e.g., methane, ethane, etc.) in the outlet; and \(n_i\) is the carbon number of component \(i\).

2.3. Characterization of the Coking Catalyst. The metal contents of the catalyst were determined using a Varian 710-ES (Varian) inductively coupled plasma atomic emission spectrometer (ICP-AES). Physiosorption of nitrogen was performed on a Micromeritics ASAP 2020 at 77 K. CO chemisorption experiments were carried out using an Autochem-II 2920 analyzer (Micromeritics). The scanning electron microscope and energy dispersive spectrometer (SEM-EDS) images were recorded using a JSM-6360LV to characterize the coke structure of the catalyst. Fourier-transform infrared spectroscopy (FT-IR) was used to characterize the coke structure of the catalyst. The instrument used was a Bruker EQUINOX-55 infrared spectrometer with a resolution of 4.0 cm\textsuperscript{-1} and a scanning range of 400–4000 cm\textsuperscript{-1}. The H/C ratio of coke deposited on the catalyst after reaction was characterized by elemental analysis with a vario El III elementar analyzer (Elementar, Germany).

2.4. Response Surface Method. The response surface method (RSM) is an effective method to estimate the interaction and even quadratic effects and find optimal and/or improved process conditions.\textsuperscript{22} The 3-level Box–Behnken design for 4 factors was used to design the experiment. For a practical PDH reactor, propane conversion, propene selectivity, and deactivation rate are deterministic for its performance. But, in the preliminary tests, low deactivation rates are obtained in the range of reaction conditions used here, which would lead to some uncertainties of the data analysis. Therefore, the initial propane conversion \((\alpha)\), propene selectivity \((\beta)\), and coke amount \((W_c)\) are selected to be the main responses. Since PDH reactors are often operated in series and under adiabatic conditions, the reactor inlet conditions of each reactor determine its yield. The reaction temperature \((T)\), propylene flow rate \((V_p)\), hydrogen flow rate \((V_h)\), and dimethyl disulfide flow rate \((\text{DMDS})\) were selected to be the operating conditions of an industrial dehydrogenation reactor.
\( V_j \) are chosen as factors. The experimental factors and their levels are shown in Table 1.

Table 1. Factors Settings for the Box–Behnken Design

| factor | level | \( T (\text{°C}) \) | \( V_1 \) (mL/min) | \( V_2 \) (mL/min) | \( V_3 \) (mL/min) |
|--------|-------|----------------|----------------|----------------|----------------|
|        | –1    | 575            | 0              | 6              | 10             |
| 0      | 610   | 2              | 8              | 16             |
| 1      | 645   | 4              | 10             |

The quadratic polynomial equation fitted by the ordinary least-square method of the experimental model can be expressed as

\[
Y_{\text{response}} = \beta_0 + \sum_{i=1}^{n} \beta_i x_i + \sum_{i=1}^{n} \beta_{ii} x_i^2 + \sum_{i=1}^{n} \sum_{j=1}^{n} \beta_{ij} x_i x_j
\]

where \( Y_{\text{response}} \) is the response; \( \beta_0, \beta_i, \beta_{ii}, \) and \( \beta_{ij} \) are the coefficient of the equation; and \( x_i \) and \( x_j \) (\( i \neq j \)) are the factor values, where the subscripts \( i \) and \( j \) denote different factors. Derringer’s desired function methodology was employed to optimize the propane dehydrogenation process conditions for the maximum (or minimum) \( Y_{\text{response}} \). The experimental design and data processing were done by MATLAB 2021b.

3. RESULTS AND DISCUSSION

3.1. Catalyst Properties. The ICP-AES results show that the catalyst contains 0.27 wt \% Pt, 0.13 wt \% Sn, 0.1 wt \% K, and a trace amount of Fe. The Brunauer–Emmett–Teller (BET) surface area of 90.1 m\(^2\)/g and volume-averaged pore diameter of 27.6 nm are determined from the physical adsorption of nitrogen. The distribution of elements in the catalyst particle is characterized by SEM-EDS mapping and is found to be well evenly distributed in the catalyst particles (Figure 1). A Pt dispersion of 70.15\% and an average particle size of 1.5 nm are determined by CO chemisorption. From HAADF-STEM images (Figure 2), the average particle size of the metal is 1.49 ± 0.3 nm, well in accordance with the results from CO chemisorption.

3.2. Coke Characterization Results. FT-IR, TGA, and elemental analysis were used to characterize the composition and properties of coke collected from experiments with different DMDS addition. The results are shown in Figure 3. Figure 3a,b shows the quantitative analysis results of coke accumulated on catalysts obtained by TG in different atmospheres. Figure 3d shows that the weight of the fresh catalyst hardly changes in N\(_2\) and air with the temperature rising. In nitrogen atmosphere, an obvious weight loss can be observed, which can be attributed to the volatile components in coke.\(^{23}\) The weight loss value determined by TG in air (shown in Figure 3b) is the total amount of coke, volatile and nonvolatile, and is usually higher than its counterpart obtained by TG in nitrogen atmosphere. The difference between these two kinds of weight losses becomes narrower with increase of DMDS addition amount, from 0.6\% at 0 ppm DMDS to near-identical at 9 and 18 ppm DMDS, which suggests that the formation of nonvolatile graphite-like coke could be prohibited with the co-feeding of a certain amount of DMDS in the feed. The elemental analysis results show that the cokes obtained with 0 and 3 ppm DMDS addition have H/C molar ratios of 0.47 and 0.71, respectively, which also verifies that the introduction of DMDS can influence the coking reaction on the catalyst surface by reducing the deep dehydrogenation reaction. Rennard\(^{17}\) reported that the introduction of H\(_2\)S can greatly improve the propylene selectivity of Pt/MgAl\(_2\)O\(_4\) and effectively inhibit the hydrogenolysis and coke formation on Pt particles, thus improving the anticoking performance of the catalyst. Wang et al.\(^{15}\) carried out DFT calculation of PDH over the Pt/Al\(_2\)O\(_3\) catalyst with co-feeding of H\(_2\)S and found that H\(_2\)S, the dominating sulfur species on Pt surfaces, can donate electrons to Pt atoms and has an adsorbate-adsorbate interaction with C3 hydrocarbons and could, therefore, improve the propylene selectivity and catalyst stability. The prominent influence of DMDS addition on the coking reaction suggests that DMDS may also be adsorbed on the active metal surface and influence its catalytic performance.

Figure 3c shows the FT-IR spectrum of the coked catalyst samples. There are several absorption peaks in the range of 600–3000 cm\(^{-1}\). The absorption peak at 1400–1450 cm\(^{-1}\) belongs to the branched-chain alkane skeleton vibration, the absorption peak at 1640–1680 cm\(^{-1}\) belongs to the olefin C=\(\text{C}\) vibration, and the absorption peak at 1500–1630 cm\(^{-1}\) belongs to the aromatic ring C==C skeleton vibration.\(^{24}\) Therefore, the infrared spectrum shows that the coke formed
Figure 3. Reaction temperature, 610 °C; C₃H₈/C₄H₈/H₂/DMDS feed flow rate = 16:0:8:(0, 3, 9, 16, 22) mL/min; reaction time, 240 min. (a) Spectra of TG in N₂; (b) spectra of TG in air; (c) FT-IR spectra; (d) fresh catalyst in N₂ and air.

Table 2. Design Matrix and Experimental Results

| experiment | T (°C) | V₁ (mL/min) | V₂ (mL/min) | V₃ (mL/min) | conversion (X) | selectivity (S) | weight of coke deposition (Wₜ) |
|------------|-------|--------------|--------------|-------------|----------------|----------------|-------------------------------|
| 1          | 575   | 0            | 8            | 16          | 2.59           | 97.92          | 1.61                          |
| 2          | 645   | 0            | 8            | 16          | 12.24          | 92.68          | 2.61                          |
| 3          | 575   | 4            | 8            | 16          | 18.32          | 99.89          | 1.90                          |
| 4          | 645   | 4            | 8            | 16          | 21.15          | 98.64          | 3.48                          |
| 5          | 610   | 2            | 6            | 10          | 16.21          | 99.38          | 2.61                          |
| 6          | 610   | 2            | 6            | 10          | 19.71          | 99.45          | 3.26                          |
| 7          | 610   | 2            | 6            | 22          | 15.08          | 99.41          | 2.20                          |
| 8          | 610   | 2            | 10           | 22          | 16.39          | 99.22          | 2.07                          |
| 9          | 575   | 2            | 8            | 10          | 15.11          | 99.84          | 1.86                          |
| 10         | 645   | 2            | 8            | 10          | 19.5           | 96.88          | 4.00                          |
| 11         | 575   | 2            | 8            | 22          | 12.96          | 99.81          | 0.80                          |
| 12         | 645   | 2            | 8            | 22          | 15.26          | 98.46          | 3.11                          |
| 13         | 610   | 0            | 6            | 16          | 6.87           | 97.14          | 1.50                          |
| 14         | 610   | 4            | 6            | 16          | 19.15          | 99.36          | 3.50                          |
| 15         | 610   | 0            | 10           | 16          | 10.24          | 98.27          | 1.51                          |
| 16         | 610   | 4            | 10           | 16          | 22.34          | 99.35          | 2.11                          |
| 17         | 575   | 2            | 6            | 16          | 14.47          | 99.83          | 0.91                          |
| 18         | 645   | 2            | 6            | 16          | 16.04          | 95.15          | 3.99                          |
| 19         | 575   | 2            | 10           | 16          | 14.81          | 99.85          | 1.54                          |
| 20         | 645   | 2            | 10           | 16          | 18.75          | 97.70          | 4.49                          |
| 21         | 610   | 0            | 8            | 10          | 11.53          | 98.26          | 1.69                          |
| 22         | 610   | 4            | 8            | 10          | 21.07          | 99.48          | 2.58                          |
| 23         | 610   | 0            | 8            | 22          | 9.74           | 98.90          | 0.87                          |
| 24         | 610   | 4            | 8            | 22          | 18.23          | 99.64          | 0.89                          |
| 25         | 610   | 2            | 8            | 16          | 17.19          | 99.80          | 2.29                          |
| 26         | 610   | 2            | 8            | 16          | 18.20          | 99.33          | 2.14                          |
| 27         | 610   | 2            | 8            | 16          | 16.17          | 98.89          | 1.84                          |
| 28         | 610   | 2            | 8            | 16          | 15.22          | 99.58          | 1.96                          |
| 29         | 610   | 2            | 8            | 16          | 19.33          | 99.14          | 2.44                          |
on the catalyst contains aromatic and aliphatic hydrocarbons, which is in line with the results reported by Wang et al.²⁵

### 3.3. Experimental Results and ANOVA Results

The experimental results are shown in Table 2. The ANOVA results of different responses are listed in Table 3. For the initial conversion response, α, all of the main factors are significant and follow the descending order reaction temperature (T) > hydrogen flow rate (V₂) > dimethyl disulfide flow rate (V₃) > propylene flow rate (V₁). To the coking amount response, reaction temperature (T), DMDS flow rate (V₃), and propylene flow rate (V₁) are significant at 0.05 significance level. Only reaction temperature (T) and propylene flow rate (V₁) are significant to the propene selectivity.

Propane dehydrogenation is a strong endothermic reaction. High temperature is advantageous for the increase of propane conversion from a thermodynamics point of view. In order to obtain a satisfying single-pass conversion, the dehydrogenation reaction needs to be carried out at a high temperature, which is also favorable for side reactions, e.g., cracking and coking. Therefore, this factor is significant to all the three responses. It is not strange that propylene, hydrogen, and DMDS flow rate have significant effects on the propane conversion since they can be readily adsorbed on the catalyst surface and play a role in the dehydrogenation reaction kinetics. The characterization results of the coking catalyst stated above also verify the effect of DMDS on coking reaction. These results indicate that the effect of DMDS flow rate on the PDH process could not be neglected. A counterintuitive finding is that the hydrogen flow rate is insignificant for the coking amount and selectivity. As a product of the dehydrogenation reaction, the kinetic effect of hydrogen flow rate is testified by its significant influence on the propane conversion. But, the products of the side reaction, e.g., ethylene, methane, coke etc., are usually formed through the complex reaction network including deep dehydrogenation, C−C breakage, etc., and the kinetic effect of hydrogen on these side reactions is weakened.

### 3.4. Response Surface Fitting Results

The response of the initial conversion is fitted with multiple linear models, including all four main effects and two-way interaction. The fitted model is as follows:

\[
\text{Conversion} = a + bT + cV_2 + dV_3 + eV_1 + fT \times V_2 + gT \times V_3 + hT \times V_1 + iV_2 \times V_3 + jV_2 \times V_1 + kV_3 \times V_1
\]

where T, V₂, V₃, and V₁ are the reaction temperature, hydrogen flow rate, dimethyl disulfide flow rate, and propylene flow rate, respectively. The ANOVA results of the fitted model are shown in Table 3.

| Source | Sum of Squares (X) | Sum of Squares (S) | Sum of Squares (W) | DF | F-value | p-value |
|--------|--------------------|--------------------|--------------------|----|---------|---------|
| Model  | 517.88             | 61.83              | 23.34              | 14 | 19.27   | 6.50    | <0.0001 | 0.0003  | 0.0006  |
| A-T    | 50.76              | 25.90              | 14.21              | 1  | 26.44   | 44.67   | 55.47   | 0.0001  | <0.0001 | <0.0001 |
| B-V₁   | 374.64             | 14.50              | 1.82               | 1  | 195.17  | 25.00   | 7.09    | <0.0001 | 0.0002  | 0.0185  |
| C-V₂   | 17.33              | 1.06               | 0.01               | 1  | 9.03    | 1.83    | 0.02    | 0.0095  | 0.1974  | 0.8798  |
| D-V₃   | 19.94              | 0.39               | 3.06               | 1  | 10.39   | 0.66    | 11.94   | 0.0061  | 0.4287  | 0.0039  |
| AB     | 11.63              | 3.98               | 0.08               | 1  | 6.06    | 6.86    | 0.33    | 0.0274  | 0.0202  | 0.5758  |
| AC     | 1.40               | 1.60               | 0.00               | 1  | 0.73    | 2.76    | 0.02    | 0.4068  | 0.1189  | 0.8997  |
| AD     | 1.09               | 0.65               | 0.01               | 1  | 0.57    | 1.12    | 0.03    | 0.4632  | 0.3083  | 0.8691  |
| BC     | 0.01               | 0.32               | 0.49               | 1  | 0.00    | 0.56    | 1.91    | 0.9491  | 0.4665  | 0.1884  |
| BD     | 0.28               | 0.06               | 0.19               | 1  | 0.14    | 0.10    | 0.74    | 0.7104  | 0.7573  | 0.4046  |
| CD     | 1.20               | 0.02               | 0.15               | 1  | 0.62    | 0.03    | 0.59    | 0.4425  | 0.8669  | 0.4538  |
| A²     | 10.43              | 8.05               | 1.17               | 1  | 5.44    | 13.88   | 4.57    | 0.0352  | 0.0023  | 0.0506  |
| B²     | 32.39              | 3.69               | 0.71               | 1  | 16.87   | 6.36    | 2.78    | 0.0011  | 0.0244  | 0.1179  |
| C²     | 0.17               | 0.21               | 0.79               | 1  | 0.09    | 0.37    | 3.08    | 0.7718  | 0.5535  | 0.1011  |
| D²     | 0.03               | 1.02               | 0.09               | 1  | 0.02    | 1.75    | 0.36    | 0.9000  | 0.2066  | 0.5559  |
| Residual | 26.87             | 8.12               | 3.59               | 14 | 0.67    | 5.95    | 5.71    | 0.7208  | 0.0502  | 0.0538  |
| Lack of fit | 16.87       | 7.61               | 3.35               | 10 | 0.67    | 5.95    | 5.71    | 0.7208  | 0.0502  | 0.0538  |
| Pure Error | 10.00       | 0.51               | 0.23               | 4  | 0.67    | 5.95    | 5.71    | 0.7208  | 0.0502  | 0.0538  |
| Total  | 544.76            | 69.95              | 26.92              | 28 | 0.67    | 5.95    | 5.71    | 0.7208  | 0.0502  | 0.0538  |

Figure 4. Conversion response surface for (a) T−V₂ (V₁ = 2 mL/min, V₃ = 16 mL/min) and (b) T−V₃ (V₁ = 2 mL/min, V₂ = 8 mL/min).
The coefficient of determination ($R^2$) is 0.9498 and the lack-of-fit test is not significant. These statistics validate the fitting model for initial conversion. The optimal conversion process conditions for maximum propane conversion were obtained as follows: the reaction temperature $T$, 614.9°C; propylene flow $V_1$, 4 mL/min; hydrogen flow $V_2$, 10 mL/min; and DMDS flow rate $V_3$, 10 mL/min. The optimal conditions are close to either high or low levels of each factor.

The conversion response surfaces for $T−V_2$ and $T−V_3$ are shown in Figure 4. It is clear that increase of temperature and hydrogen flow rate has a positive influence on propane conversion, while increase of propene and DMDS flow rate has a negative effect.

$$X = -435.5904 + 1.3427 \times T + 20.3262 \times V_1$$
$$- 3.1666 \times V_2 + 12.7735 \times V_3 - 0.0244 \times T \times V_1$$
$$+ 0.0085 \times T \times V_2 - 0.0025 \times T \times V_3$$
$$- 0.0113 \times V_1 \times V_2 - 0.0219 \times V_1 \times V_3$$
$$- 0.0456 \times V_2 \times V_3 - 1.0354 \times 10^{-3} \times T^2$$
$$- 0.5587 \times V_1^2 + 0.0402 \times V_2^2 - 1.9329 \times 10^{-1} \times V_3^2$$
$$
(4)
$$

The fitted model for propene selectivity ($S$) is as follows:

$$S = -139.3626 + 0.9371 \times T - 6.6491 \times V_1$$
$$- 4.4112 \times V_2 - 1.4247 \times V_3 + 0.01424 \times T \times V_1$$
$$+ 0.009047 \times T \times V_2 + 0.001917 \times T \times V_3$$
$$- 0.0715 \times V_1 \times V_2 - 0.009896 \times V_1 \times V_3$$
$$- 0.005317 \times V_2 \times V_3 - 0.009099 \times T^2$$
$$- 0.1885 \times V_1^2 - 0.04538 \times V_2^2 + 0.0109 \times V_3^2$$
$$
(5)
$$

The model is satisfactory for its regression statistics, $R^2 = 0.8752$, and not significant for the lack-of-fit test. The optimal conditions for maximizing the propene selectivity are temperature $T$, 587.4°C; propylene flow rate $V_1$, 0.13 mL/min; hydrogen flow rate $V_2$, 6.2 mL/min; and DMDS flow rate $V_3$, 19.54 mL/min. The low level of temperature, high level of DMDS flow rate, and a proper hydrogen flow rate are advantageous for maximizing the propene selectivity.

The typical selectivity response surface is shown in Figure 5. It can be seen that the decrease of $T$ is advantageous to the increase of propene selectivity and the selectivity deteriorates greatly when the temperature is close to 640°C. It should be...
noticed that the decrease of propene and the increase of propane conversion are usually concomitant, except for some conditions under low temperature (the right bottom corner of the response surface). Although, compared with temperature and propene flow rate, hydrogen and DMDS flow rate are not significant for propene selectivity, they do have a mild influence on the propene selectivity.

The fitted model for coking amount (W*) is as follows

\[
W_* = 123.7806 - 0.4185 \times T + 0.2295 \times V_1 - 0.7566 \times V_2 + 0.0414 \times V_3 + 0.0021 \times T \times V_1 - 0.000464 \times T \times V_2 + 0.000202 \times T \times V_3 - 0.0875 \times V_1 \times V_2 - 0.0181 \times V_1 \times V_3 - 0.01625 \times V_2 \times V_3 + 0.000347 \times T^2 - 0.08279 \times V_1^2 + 0.08721 \times V_2^2 - 0.0033 \times V_3^2
\]

The regression statistics \( R^2 = 0.8471 \) and insignificance for lack-of-fit test validate the regression model. To minimize the coking amount, the optimal conditions are found to be temperature \( T \), 575 °C; propylene flow rate \( V_1 \), 0 mL/min; hydrogen flow rate \( V_2 \), 7 mL/min; and DMDS flow rate \( V_3 \), 22 mL/min. The coking amount of the final catalyst can be as low as 0.8%.

The coking amount response surfaces for \( T-V_2 \) and \( T-V_3 \) are shown in Figure 6. It can be seen that decrease of \( T \) and increase of DMDS are advantageous to prohibit the formation of coking. Unfortunately, these optimal conditions are not beneficial for the increase of propane conversion. Optimal hydrogen flow rates exist under different temperatures to reduce the coking amount.

According to the response surface fitting results, the effects of temperature and propene flow rate on the reactor performance are clear. But, in industrial applications, these two factors are actually not adjustable for a given propene productivity. The maximum reaction temperature is limited due to the existence of severely side reactions, heterogeneous and/or homogeneous, and therefore constrains the increase of the productivity of propene. The existence of propene is totally disadvantageous and its selective removal from the reactant on the site is highly desirable to increase the propene productivity.

The kinetic promotion effect of hydrogen is verified because it can increase the propane conversion. But it only has a mild effect on the propene selectivity and coking amount. In previous studies, Saerens et al.15 show that the co-feeding of hydrogen can reduce the coverage of the coke precursor for deep dehydrogenation on the catalyst surface and the adsorption strength of propylene and increase the energy barrier of propylene dehydrogenation, which could release more free active sites and improve the catalytic activity on the Pt(111) surface. Xiao et al.16 further reveal that the kinetic effect of hydrogen is related to the coordination environment of Pt. They find that a nonreverse Horiuti–Polanyi mechanism accounts for more than half of the propylene yield at the under-coordinated active site and a high hydrogen addition amount would increase the free 4-fold hollow sites of Pt and lead to a dominant role of deep dehydrogenation in the kinetics. These findings are in line with part of the results obtained here, e.g., the positive role of hydrogen flow rate on the activity.

A superficial difference between the reported results and ours lies in the effect of hydrogen on the coking reaction. It is reasonable to deduce that the reduction of coke precursor on the catalyst surface would lead to less formation of coke when hydrogen is co-fed. But this positive role of hydrogen in coking is not found here. One of the possible explanations is that the formation of carbon atoms is adopted as representative of the coking reaction in reference,15 which is not consistent with the major composition of coke, the hydrocarbons formed from oligomerization, obtained here (see Section 3.2). Other explanations include the difference of catalyst composition and the experimental conditions.

The insignificant influence of hydrogen on propene selectivity and coking suggests that the reaction order of hydrogen may be close to zero. This finding is consistent with our previous results of a weak kinetic effect of hydrogen on the coking kinetics,26 which originates from the weak adsorption of hydrogen, compared to the C3 hydrocarbon intermediate, on the surface. Although the effect of hydrogen flow rate on propene selectivity and coking is not significant in the whole experimental range, it can be seen from Figure 5a that increase in the hydrogen flow rate is helpful for improving the propene selectivity under a low reaction temperature range, under which the surface coverage of the hydrogen species would be higher and may have a mild influence on the selectivity.

Some previously reported PDH kinetics are listed in Table 4. These results show that hydrogen usually has a negative impact on the propane consumption rate. However, the results obtained here show that the conversion of propane increases with the increase of the feed hydrogen flow rate in a certain range. Therefore, kinetic models that can fully address these results are still anticipated.

The addition of a certain amount of DMDS can reduce the activity of the catalyst, but only slightly improve the selectivity of propylene, which is in agreement with the DFT results of Wang et al.12 When DMDS enters the reaction system, it will be cracked to form sulfur species and adsorbed on the catalyst surface. The sulfur species adsorbed on the metal surface makes Pt in the electron-rich state, which promotes the desorption of propylene and inhibits the deep dehydrogenation reaction, thus improving the selectivity of propylene. But, at the same time, the adsorbed sulfur species also occupied a
small number of active sites of the catalyst, resulting in the decrease of catalyst activity.

The co-feeding of DMDS in the reactant can significantly reduce the coking amount of the catalyst and change the coke properties. These results can be attributed to the adsorption of sulfur species on the metal surface as discussed above. Besides this, it should be noticed that the sulfur species adsorbed on the Al₂O₃ support may have a more expected impact on the reaction process. In industrial processes, some Fe species may accumulate on the catalyst, which is very active for coking and needs to be removed during catalyst regeneration. Meanwhile, it is demonstrated that the addition of sulfur species will compound with Fe atoms via the Fe-O-S bond and change its activity for dehydrogenation and the coking reaction in the PDH process. The existence of Fe is harmful to the catalyst, but the sulfur addition could reduce this problem.

4. CONCLUSIONS

In summary, the addition of DMDS in the PDH process can significantly reduce the amount of coking, prohibit the formation of graphite-like cokes, and improve the propene selectivity at the expense of propane conversion. The promotion effect of hydrogen on PDH is to increase propane conversion. It is not significant for selectivity and coking amount according to ANOVA results. The quadratic models for conversion, selectivity, and coking amount responses are fitted. The optimal conditions for each response are obtained through these models and they are found to be contradictory to each other. These results suggest that the PDH kinetics is sensitive to the surface coverages of different adsorbed species, which could be influenced by the introduction of DMDS and hydrogen, leading to different reaction performances and coking properties. The reduction of coking amount and change of the coke properties with the co-feeding of DMDS could indicate the modification of sulfur species on the active metal structure, which is disadvantageous for the catalytic activity. To obtain the maximum economic profit of the PDH process, the addition amount of DMDS and hydrogen should be optimized by balancing the catalyst activity, propylene selectivity, and coking amount.

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Notes
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■ REFERENCES

(1) Wang, G.; Zhu, X.; Li, C. Recent Progress in Commercial and Novel Catalysts for Catalytic Dehydrogenation of Light Alkanes. Chem. Rec. 2020, 20, 604–616.
(2) Sattler, J. J. H. B.; Ruiz-Martinez, J.; Santillan-Jimenez, E.; Weckhuysen, B. M. Catalytic dehydrogenation of light alkanes on metals and metal oxides. Chem. Rev. 2014, 114, 10613–10653.
(3) Lian, Z.; Si, C.; Jan, F.; Zhi, S.; Li, B. Coke Deposition on Pt-Based Catalysts in Propane Direct Dehydrogenation: Kinetics, Suppression, and Elimination. ACS Catal. 2021, 11, 9279–9292.
(4) Chen, S.; Chang, X.; Sun, G.; Zhang, T.; Xu, Y.; Wang, Y.; Pei, C.; Gong, J. Propane dehydrogenation: catalyst development, new chemistry, and emerging technologies. Chem. Soc. Rev. 2021, 50, 3315–3354.
(5) Searles, K.; Chan, K. W.; Burak, J. A. M.; Zemlyanov, D.; Safonova, O.; Copéret, C. Highly Productive Propane Dehydrogenation Catalyst Using Silica-Supported Ga-Pt Nanoparticles Generated from Single-Sites. J. Am. Chem. Soc. 2018, 140, 11674–11679.
(6) Wang, G.; Zhang, H.; Wang, H.; Zhu, Q.; Li, C.; Shan, H. The role of metallic Sn species in catalytic dehydrogenation of propane: Active component rather than only promoter. J. Catal. 2016, 344, 606–608.
(7) Shi, L.; Deng, G. M.; Li, W. C.; Miao, S.; Wang, Q. N.; Zhang, W. P.; Lu, A. H. Al₂O₃ Nanosheets in Pentacoordinate Al³⁺ Ions Stabilize Pt-Sn Clusters for Propane Dehydrogenation. Angew. Chem., Int. Ed. 2015, 54, 13994–13998.
(8) Saelee, T.; Namuangruk, S.; Kungwan, N.; Junkawa, A. Theoretical Insight into Catalytic Propane Dehydrogenation on Ni(111). J. Phys. Chem. C 2018, 122, 14678–14690.
(9) Carrero, C. A.; Schloegl, R.; Wachs, I. E.; Schomaecker, R. Critical Literature Review of the Kinetics for the Oxidative Dehydrogenation of Propane over Well-Defined Supported Vanadium Oxide Catalysts. ACS Catal. 2014, 4, 3357–3380.
(10) Carter, J. H.; Bere, T.; Pitchers, J. R.; Hewes, D. G.; Vandecaveye, B. D.; Kiely, C. J.; Taylor, S. H.; Hutchings, G. J. Direct and oxidative dehydrogenation of propane: from catalyst design to industrial application. Green Chem. 2021, 23, 9747–9799.
(11) Shan, Y. L.; Sui, Z. J.; Zhu, Y.; Zhu, J. H.; Zhou, X. G.; Chen, D. Boosting Size-Selective Hydrogen Combustion in the Presence of Propene Using Controllable Metal Clusters Encapsulated in Zeolite. Angew. Chem., Int. Ed. 2018, 57, 9770–9774.
(12) Wang, H.-Z.; Zhang, W.; Jiang, J.-W.; Sui, Z.-J.; Zhu, Y.-A.; Ye, G.-H.; Chen, D.; Zhou, X.-G.; Yuan, W.-K. The role of H₂S addition on Pt/Al₂O₃ catalyzed propane dehydrogenation: a mechanistic study. Catal. Sci. Technol. 2019, 9, 867–876.
(13) Shan, Y.; Sui, Z.; Zhu, Y.; Chen, D.; Zhou, X. Effect of steam addition on the structure and activity of Pt–Sn catalysts in propane dehydrogenation. Chem. Eng. J. 2015, 278, 240–248.
(14) Otroschenko, T.; Kondratenko, E. V. Effect of hydrogen and supported metal on selectivity and on-stream stability of ZrO₂-based catalysts in non-oxidative propane dehydrogenation. Catal. Commun. 2020, 144, No. 106068.
(15) Saerens, S.; Sabbe, M. K.; Galvita, V. V.; Redekop, E. A.; Reyniers, M.-F.; Marin, G. B. The Positive Role of Hydrogen on the Dehydrogenation of Propane on Pt(111). ACS Catal. 2017, 7, 7495–7508.
(16) Xiao, L.; Shan, Y.-L.; Sui, Z.-J.; Chen, D.; Zhou, X.-G.; Yuan, W.-K.; Zhu, Y.-A. Beyond the Reverse Horiiuti—Polanyi Mechanism in...
Propane Dehydrogenation over Pt Catalysts. *ACS Catal.* 2020, 10, 14887−14902.

(17) Rennard, R. J.; Freal, J. The role of sulfur in deactivation of PtMgAlO4 for propane dehydrogenation. *J. Catal.* 1986, 98, 235−244.

(18) Jackson, S. D.; Leeming, P.; Grenfell, J. The Effect of Sulfur on the Nonsteady State Reaction of Propane over a Platinum/Alumina Catalyst at 873 K. *J. Catal.* 1994, 150, 235−244.

(19) Watanabe, R.; Hirata, N.; Miura, K.; Yoda, Y.; Fushimi, Y.; Fukuhara, C. Formation of active species for propane dehydrogenation with hydrogen sulfide co-feeding over transition metal catalyst. *Appl. Catal., A* 2019, 587, No. 117238.

(20) Sharma, L.; Jiang, X.; Wu, Z.; Baltrus, J.; Rangarajan, S.; Baltrusaitis, J. Elucidating the origin of selective dehydrogenation of propane on γ-alumina under H2S treatment and co-feed. *J. Catal.* 2021, 394, 142−156.

(21) Watanabe, R.; Hirata, N.; Yoda, Y.; Fushimi, Y.; Fukuhara, C. Effect of Support Species on Performance of Transition Metal-based Catalysts for Propane Dehydrogenation with Co-feeding of H2S. *J. Jpn. Pet. Inst.* 2020, 63, 228−237.

(22) Lažić, Ž. R. *Design of Experiments in Chemical Engineering: A Practical Guide*; Wiley: Germany, 2004.

(23) Larsson, M.; Hultén, M.; Blekkan, E. A.; Andersson, B. The Effect of Reaction Conditions and Time on Stream on the Coke Formed during Propane Dehydrogenation. *J. Catal.* 1996, 164, 44−53.

(24) Ibarra, J. V.; Royo, C.; Monzón, A.; Santamaría, J. Fourier transform infrared spectroscopic study of coke deposits on a Cr2O3-Al2O3 catalyst. *Vib. Spectrosc.* 1995, 9, 191−196.

(25) Wang, H.-Z.; Sun, L.-L.; Sui, Z.-J.; Zhu, Y.-A.; Ye, G.-H.; Chen, D.; Zhou, X.-G.; Yuan, W.-K. Coke Formation on Pt−Sn/Al2O3 Catalyst for Propane Dehydrogenation. *Ind. Eng. Chem. Res.* 2018, 57, 8647−8654.

(26) Li, Q.; Sui, Z.; Zhou, X.; Zhu, Y.; Zhou, J.; Chen, D. Coke Formation on Pt−Sn/Al2O3 Catalyst in Propane Dehydrogenation: Coke Characterization and Kinetic Study. *Top. Catal.* 2011, 54, 888−896.

(27) Lobera, M. P.; Téllez, C.; Herguido, J.; Menéndez, M. Transient kinetic modelling of propane dehydrogenation over a Pt−Sn−K/Al2O3 catalyst. *Appl. Catal., A* 2008, 349, 156−164.

(28) Chen, G.; Yang, Y.; Rong, S. Study on the intrinsic kinetics of propane dehydrogenation over Pt-Sn/Al2O3 catalyst. *Chem. React. Eng. Technol.* 1998, 14, 130−137.

(29) Li, Q.; Sui, Z.; Zhou, X.; Chen, D. Kinetics of propane dehydrogenation over Pt−Sn/Al2O3 catalyst. *Appl. Catal., A* 2011, 398, 18−26.

(30) Wang, J.; Reyniers, M.-F.; Marin, G. B. Influence of Dimethyl Disulfide on Coke Formation during Steam Cracking of Hydrocarbons. *Ind. Eng. Chem. Res.* 2007, 46, 4134−4148.

(31) Sun, Y.-n.; Tao, L.; You, T.; Li, C.; Shan, H. Effect of sulfation on the performance of Fe2O3/Al2O3 catalyst in catalytic dehydrogenation of propane to propylene. *Chem. Eng. J.* 2014, 244, 145−151.