

How sulphur really forms on the catalyst surface

The catalytic oxidation of hydrogen sulphide to sulphur plays a major role in the sulphur recovery process. The catalytic stages of a Claus unit produce about 30% of the total sulphur. The catalytic reaction is unique in being practically 100% selective, and it has been intensively investigated for many years in an effort to understand the nature of the active centres. Other research has been carried out to understand the kinetics of the reactions, as well as to elucidate the catalytic oxidation of H₂S to sulphur by oxygen. Nevertheless, many aspects of these catalytic reactions remain unexplored. Here, **T.K. Khanmamedov** of TKK Company and **R.H. Weiland** of Optimized Gas Treating, Inc., provide a new understanding of the reactions by appealing to the unique nature of sulphur itself.

The catalytic Claus process is central to gas processing plants and refineries that include amine desulphurisation and sulphur recovery units (SRUs). The SRU includes the thermal oxidation of H₂S in the gas phase with air (or air enriched oxygen) at high temperature with the formation of elemental sulphur, SO₂, water and some side products, such as COS, and CS₂.

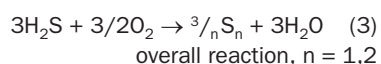
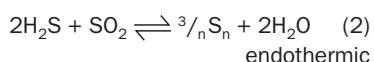
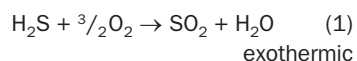
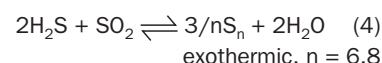


Figure 1 is a simplified diagram of the SRU. The thermal stage is followed by a waste heat boiler (WHB) producing high pressure steam, and a sulphur condenser where liquid sulphur is separated from the gas with the simultaneous generation of medium pressure steam. The gas from the condenser is heated (RH) and sent to catalytic reactors (CatBed) where the remaining H₂S and SO₂ react with each other to form sulphur. Also, some of the side products such as the COS and CS₂ produced in the thermal reactor are converted to H₂S in the first catalytic stage. A typical SRU consists of two or three catalytic reactors each served by its own sulphur condenser. The following reversible reaction occurs over activated alumina in a catalytic reactor:



Reactions (2) and (4) use the same reactants to produce different forms of sulphur and under different thermal conditions. Reaction (2) produces S or S₂ in the high temperature zone of the reaction furnace and is endothermic by nature (Fig. 2). Reaction (4) produces S₆ and S₈ at a much lower temperature in the catalytic beds and is exothermic. This leads to the unique thermodynamics for H₂S oxidation to sulphur shown in Figure 3¹.

There are numerous articles published and patents granted for the catalytic oxidation of H₂S to elemental sulphur in gas streams with low concentrations of H₂S. It is well known that regardless of the reaction path of H₂S oxidation to sulphur (e.g., “direct” versus “partial” oxidation), the thermodynamic limitation of reaction equilibrium of the overall reaction (3) must remain inviolate. Equilibrium thermodynamic limitations on chemical reactions are path independent. This is shown in Figs 2 and 3 which correspond to the equilibrium thermodynamics of reactions 2 and 4 over a wide range of temperatures and H₂S concentrations. Conversion of H₂S to sulphur depends strongly on temperature and on the concentration of H₂S in the feed gas. It can never exceed the level permitted by equilibrium thermodynamics, no matter how the reactions are carried out (i.e.,

Fig 1: Simplified diagram of sulphur recovery unit

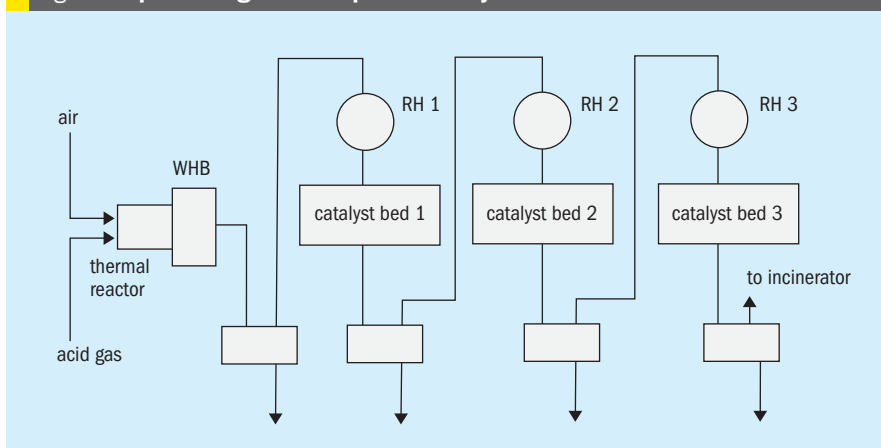


Fig 2: Thermodynamics of H₂S oxidation to sulphur: H₂S conversion vs temperature vs. concentration of H₂S in the acid gas

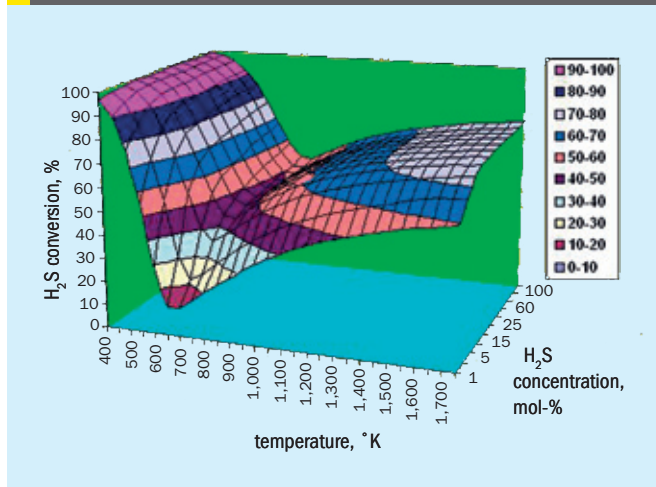
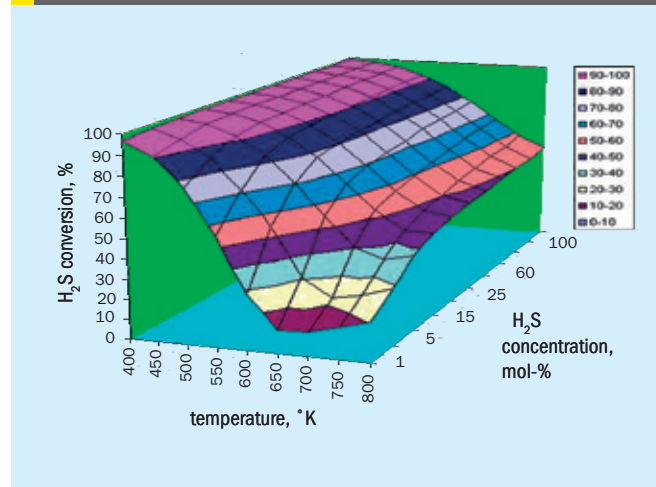


Fig 3: Thermodynamics of H₂S oxidation to sulphur: H₂S conversion vs temperature vs concentration of H₂S in the acid gas (temperature range of catalytic reactions)



in this case by either “direct” or “partial” oxidation). For example, for a gas stream containing 2 vol-% H₂S, the equilibrium limit for conversion of H₂S to sulphur in the temperature range 273°C to 300°C is 50% to 60% (Fig. 3), not 93% and higher as claimed in some patents and articles. A study of hydrogen sulphide oxidation in the presence of different catalysts inevitably leads one to the conclusion that all oxidation reactions of hydrogen sulphide to sulphur occur in-situ at active sites on the surface of the catalyst via the formation of SO₂ as well as by the further reaction of H₂S with the SO₂ already formed and still adsorbed on the surface. In reality, there is no such thing as “direct” catalytic oxidation of hydrogen sulphide to sulphur, despite the attractiveness of the concept. There are a number of publications in the scientific and patent literature that make claims of nearly 100% conversion of H₂S to sulphur using various catalysts with lean acid gases; however, all such claims violate the equilibrium conversion limitations dictated by the thermodynamics of reaction equilibrium – thermodynamics cannot be ignored.

There also seems to be some confusion

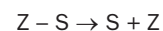
between the terms “conversion” (of hydrogen sulphide to sulphur) and “sulphur recovery”. Even with very high levels of H₂S conversion to sulphur, it does not follow that there is necessarily a high level of sulphur recovery. The recovery process itself occurs in the condensers, and it is quite hard to recover all sulphur from the reactor outlet in dilute systems using condensers of normal size or even using so-called super condensers.

This article concerns the kinetics of H₂S oxidation to sulphur in the temperature range of operation of the catalytic beds. The well-known kinetic models for the catalytic Claus process over γ -Al₂O₃ do not include all the components necessary to distinguish the various forms of sulphur. For example, the first attempts to describe the kinetics of this reaction were made in 1976 and provided the following purely empirical kinetic expressions based on literature data^{2,3} see Figure 4.

Although the partial pressures of H₂S and H₂O were taken into account in these equations, the rate expressions themselves do not mirror the chemistry of sulphur formation on the catalyst surface. Furthermore, they do not reflect the role of the reverse

Claus reaction and they contain no element that would reflect the role of ratio H₂S/SO₂. Similarly, there are other published articles on the kinetics and mechanism of H₂S oxidation over different catalysts but the authors drew similar conclusions based on the same wrong concept. So, what is the wrong with these equations?

The central problem is that none of them refers to the real nature of sulphur. They are all derived from the same basic suggestion that the formation of mono-sulphur, S₁, on the surface of the catalysts includes a step of dissociative adsorption of H₂S on the surface of the catalyst. The S₁ attached to the active site then desorbs into the gas phase from the surface of the catalyst. In the last step of the mechanism, sulphur desorbs from the active site, Z:



This particular desorption step is completely contrary to the very nature of sulphur. The fact of the matter is, sulphur simply does not exist as S₁ in the temperature range of the processes that take place in any catalytic oxidation reactors for converting hydrogen sulphide to sulphur below 350°C⁷. Below this temperature sulphur exists only in the form of cyclic clusters S_n with n = 6 or 8. In short, the foregoing is emphatically not a plausible explanation for sulphur formation at the catalyst surface.

Kinetic schemes and models

Any plausible kinetic model of H₂S oxidation to sulphur by SO₂ or O₂ over any catalyst (γ -Al₂O₃, TiO₂ etc.) must reflect the real nature of the sulphur that forms in the

Fig 4: First empirical kinetic expressions for catalytic oxidation of H₂S

$$R_{H_2S} = -\frac{K \cdot p_{H_2S}}{1 + 0.1p_{H_2O}}$$

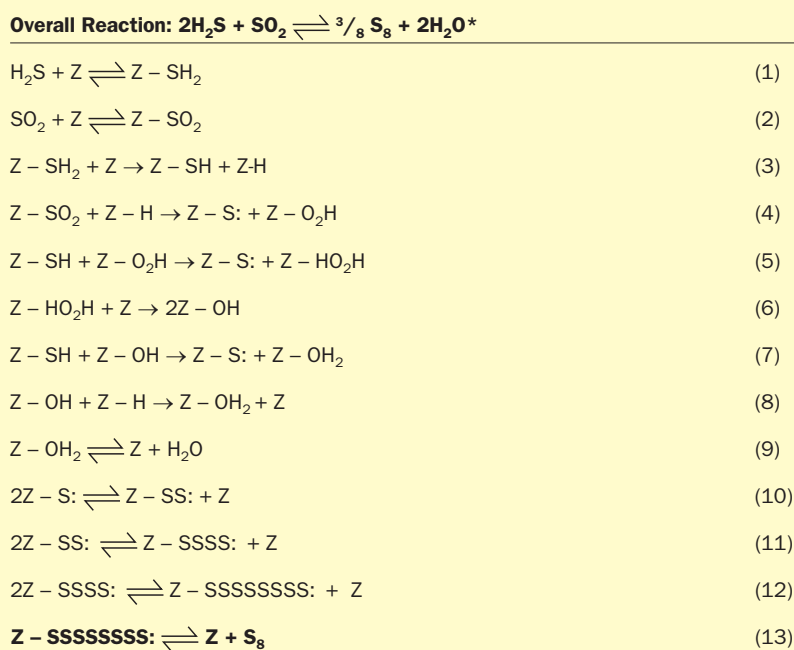
$$R_{H_2S} = -0.460 \exp(-7350/RT) \frac{p_{H_2S} p_{SO_2}^{0.5}}{1 + 0.16p_{H_2O}}$$

temperature zone of the catalytic process. Results of the first attempt to produce such a model were reported in 1988 when Khanmamedov⁴ described kinetic measurements of H₂S oxidation over an original TiO₂-based catalyst. The experiments were conducted in a specially designed reactor using catalyst pellets of a size that eliminated both diffusional limitations within the catalyst particles and any temperature gradient within the catalyst bed⁵. The main results of this study can be used as a tool to optimise H₂S catalytic oxidation processes.

The significant effect of 10-30 vol-% water vapour in the feed that Khanmamedov observed led to a substantial decrease in the rate of oxidation of H₂S to sulphur. The practically 100% selectivity of the catalytic Claus reaction with the formation of only a very few products – S₆ (S₈) and H₂O, and the limited number of components in the feed (H₂S and SO₂ only) obviated the need to simplify the kinetic model. This circumstance made it easy to derive a kinetic equation⁶. Contrary to the earlier work of others on the kinetics of catalytic H₂S oxidation, the fact of the formation of the thermodynamically stable clusters S₆ and S₈ was explicitly taken into account in this work.

It was established that the best description of the observed results over a wide temperature range was based on the following stoichiometric equations of the reaction stages. For the first time, Khanmamedov proposed new steps in the mechanism paths for elemental sulphur formation on catalyst surfaces in sulphur production units (Claus process, partial oxidation of H₂S etc.), which formed the basis for the development of new kinetic models^{4,9}. The new mechanisms and kinetic models are based on the fact that in the temperature range of operation of these catalytic reactors, elemental sulphur does not exist in the mono-atomic form but only as the 6- and 8-membered rings, S₆ and S₈. Therefore production of sulphur takes place with the intermediate formation of di-, tetra-, hexa- and hepta-sulphur species on the surface of the catalysts with further formation and simultaneous desorption of cyclic S₆ and S₈ into the gas phase. Formation of elemental sulphur on the surface of different catalysts in the Claus process is shown in the table below. Similar reaction mechanisms should be considered for elemental sulphur formation in any other type of catalytic process for oxidation of H₂S to sulphur. By using the principle of quasi stationarity of the

Table 1: Steps in the mechanism for the catalytic oxidation of H₂S by SO₂



Z – Active site on the catalyst’s surface

* Similar reactions take place for S₆ formation but via shorter path.

concentrations of intermediate chemical compounds (activated complexes) and the condition of quasi-equilibrium of adsorption-desorption, the kinetic model of this reaction was derived by using the kinetic stages shown in Table 1.

In the authors’ opinion it is logical to assume that the formation of cyclic clusters of S₈ and S₆ occur on the same active sites of the catalyst that are responsible for the adsorption of H₂S, SO₂ (O₂) and H₂O. Indeed, this can be observed by using special techniques such as in-situ spectroscopy.

The thermodynamically reversible nature of the Claus reaction⁹ was considered while developing the kinetic equation. Accordingly it was assumed that the reverse Claus reaction takes place on the same active catalyst sites with participation of S₈, S₆ and H₂O.

Assuming that step (3) is limiting for the overall reaction, the rate of conversion of H₂S can be calculated as:

$$W = W_3 = K_3[\text{Z} - \text{SH}_2][\text{Z}] = K_1K_{p1}[\text{H}_2\text{S}][\text{Z}]^2$$

The assumption that step (3) is reaction rate limiting is based on an earlier publication³ in which much weaker adsorption of H₂S on the surface of γ-Al₂O₃ was reported than for SO₂. Thus the total concentration of H₂S adsorbed on active sites is low and because

of this the reaction step involving H₂S then would tend to be rate limiting. This step as rate limiting is also supported by the results of the response method carried out by Khanmamedov on TiO₂-based catalysts.

Quasi-steady state concentrations of intermediates can be determined under the assumption that the time rate of change of the concentrations of (adsorbed) intermediates is so slow as to be essentially zero. The expressions for the concentrations of various intermediates result from writing rate equations for the intermediates according to the elementary stoichiometry of the reactions in Table 1 and setting the time derivatives to zero, see Figure 5.

Assuming adsorption equilibrium in steps (1), (2), (9) and (13), and after replacing concentrations by appropriate component partial pressures, the kinetic model for the catalytic Claus reaction is shown in Figure 6.

The calculation of the kinetic parameters has been carried out using kinetic data and values for enthalpy, entropy and exponents on activation energies were obtained.

The final kinetic model of the Claus catalytic reaction is as follows (mole/L min) see Figure 7.

Using this equation, the calculated results were found to match the experi-

Fig 5: Expressions for intermediates concentrations based on stoichiometry

$$[ZOH] = \frac{K_4 K_{P_2}}{K_8} [SO_2][Z]; \quad [ZH] = \frac{K_3 K_{P_1} [H_2S][Z]}{2K_4 K_{P_2} [SO_2]}$$

$$[ZSH] = \frac{K_8 K_3 K_{P_1} [H_2S]}{2K_7 K_4 K_{P_2} [SO_2]} [Z]; \quad [ZO_2H] = \frac{K_7 K_4 K_{P_2}}{K_5 K_8} [SO_2][Z]$$

$$[ZHO_2H] = \frac{K_5 K_{P_1}}{2K_7 K_8} [H_2S][Z]; \quad [Z-S] = \frac{\sqrt{3} K_3^{0.5} K_{P_1}^{0.5}}{2K_{10}^{0.5}} [H_2S]^{0.5} [Z]$$

$$[Z] = \frac{1}{1 + K^I [H_2S] + K^{II} [H_2S]^{0.5} + K^{III} [SO_2] + K^{IV} \frac{[H_2S]}{[SO_2]} + K_{P_9}^{-1} [H_2O] + K_{P_{13}}^{-1} [S_8]}$$

Fig 6: Kinetic model for Claus catalysis expressed by partial pressures

$$W = \frac{K_1 K_{P_1} P_{H_2S}}{[1 + K^I P_{H_2S} + K^{II} P_{H_2S}^{0.5} + K^{III} P_{SO_2} + K^{IV} \frac{P_{H_2S}}{P_{SO_2}} + K_{P_9}^{-1} P_{H_2O} + K_{P_{13}}^{-1} P_{S_8}]^2}$$

Here, W is the rate of H₂S conversion in reaction (3), are adsorption equilibrium constants for Steps (1), (3), (9) and (13), and K^I, K^{II}, K^{III} and K^{IV} are constants, obtained from the following simplifications:

$$K^I = [K_{P_1} + \frac{K_3 K_{P_1}}{K_6}]; \quad K^{II} = K_{P_2} K_4 (1 + \frac{K_7}{K_5 K_8}) + \frac{1}{K_8}$$

$$K^{IV} = [(\frac{K_3 K_{P_1}}{K_{10}})^{0.5} + (\frac{K_3 K_{P_1}}{K_{11}})^{0.5} + (\frac{K_3 K_{P_1}}{K_{12}})^{0.5}]$$

Because K₆ >> K₃, K₅ >> K₇ and K₄ >> K₃, after simplification of K^I, K^{II} and K^{III} the following results:

$$K^I = K_{P_1}; \quad K^{II} = K_{P_2} K_4; \quad K^{III} = \frac{K_3 K_{P_1}}{2K_4 K_{P_2}}$$

mental data to within ± 20-35%. A correlation between the rates of the reactions and the partial pressures of H₂S, H₂O and S₈, and the ratio H₂S:SO₂ reflected changes in the reaction path and the possible influ-

ence of the reverse reaction. The previously suggested kinetic models did not correlate with the ratio H₂S:SO₂ and the partial pressure of S₈, but depended only on the value of the partial pressure of H₂O.

In a completely parallel manner, the oxidation of H₂S to sulphur in a very dilute acid gas (3 vol-% H₂S) using oxygen over a Ti-based catalyst⁹ the following set of steps in the mechanism steps was proposed as shown in Table 2.

It is assumed that the two parallel reactions (1) and (2) take place on the surface of the catalyst. The final rate equation for this reaction, derived using similar assumptions to those already used above, yield (mole /L min), see Figure 8.

Numerical values of the coefficients for the particular titanium-based catalyst were regressed from experimental data using method of least squares, and by solving of differential reaction rate equations using Runge-Kutte integration method, shown in Figure 9.

The overall results were in fair agreement with a large amount of experimental data⁹ and they reflected the practically observed inhibiting effects of water vapour and dependence on the ratio H₂S/O₂. Constants in the kinetic model were found to be as shown in Table 3.

Table 3: Kinetic model constants

K _{P1} = 7.0 exp(-12.35 10 ³ /T)
K _{P2} = 3.5 exp(-9.25 10 ³ /T)
K _{P7} = 4.0 exp(-11.1 10 ³ /T)
K _{P8} = 2.2 exp(-15.7 10 ³ /T)
K _{P12} = 1.5 exp(-16.2 10 ³ /T)
K ₂ = 1.5 exp(-2.5 10 ³ /T)
K ₆ = 4.7 exp(-3.7 10 ³ /T)
K ₉ = 7.0 exp(-5.7 10 ³ /T)
K ₁₀ = 3.4 exp(-7.5 10 ³ /T)
K ₁₁ = 6.0 exp(-3.2 10 ³ /T)

A similar approach can be used for the known Shift-Claus[®] process¹⁰.

Fig 7: The final kinetic model of the Claus catalytic reaction, mole/Lt-min

$$W = \frac{\exp(6.251 - 32498/T)}{[1 + \exp(4050.8/T - 4.539) P_{H_2S} + \exp(6.297 - 1293.7/T) P_{SO_2} + \exp(4.6 * 10^{-2} - 1956.02) P_{H_2S} / P_{SO_2} + \frac{P_{H_2S}}{\exp(6.251 - 3249.8/T) P_{H_2S}^{0.5} + \frac{P_{H_2O}}{\exp(4902.4/T - 3.31)} + \frac{P_{S_8}}{\exp(37804/T - 4.80)}}]^2}$$

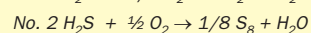
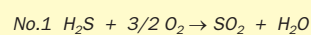
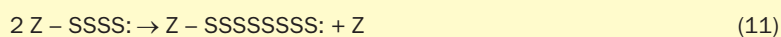
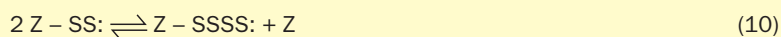
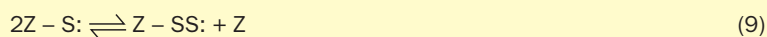
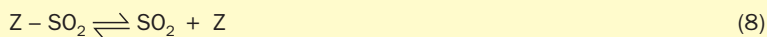
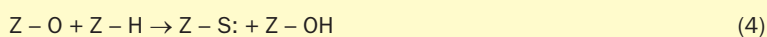
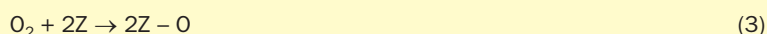
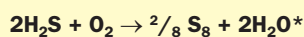
Fig 8: Final rate equation for parallel reactions 1 and 2

$$W = \frac{K_2 K_{p_1} P_{H_2S} - K_2 K_{p_1} K''' \frac{P_{H_2S}^2}{P_{O_2}}}{[1 + K_{p_1} P_{H_2S} + K' P_{H_2S}^{0.5} + K_{p_2}^{0.5} P_{O_2}^{0.5} + K'' \frac{P_{H_2S}}{P_{O_2}^{0.5}} + K_{p_7}^{-1} P_{H_2S} + K_{p_{12}}^{-1} P_{S_8} + K_{p_8}^1 P_{SO_2}]^2}$$

Fig 9: Coefficients for titanium catalyst were calculated by Runge-Kutte method

$$K' = 2k_2^{0.5} \cdot k_2^{0.5} \quad K'' = \frac{k_2 \cdot k_{p_1}}{k_4 \cdot k_{p_2}^{0.5}}$$

$$K''' = \frac{k_2 k_{p_1}}{k_6 k_{p_2}} + \frac{k_9 k_2 k_{p_1}}{k_{10} k_6 k_{p_2}} + \frac{k_9 k_2 k_{p_1}}{k_{11} k_6 k_{p_2}}$$

 Table 2: Mechanism for oxidation of dilute H₂S by oxygen


Z – Active center of the catalyst's surface

* – Similar reactions take place for S₆ formation but via shorter path.

Conclusion

A mechanism path for catalytic oxidation of hydrogen sulphide to sulphur has been discussed. The mechanism involves the formation of S₆ and S₈ that desorb from the catalyst's active sites with simultaneous formation of stable cyclic elemental sulphur. Kinetic models that identify the main peculiarities of catalytic oxidation in the Claus reaction and the oxidation of H₂S with oxygen have been suggested. The underlying fundamentals of these kinetic models can be used for comparison with the activities of different catalytic systems, for optimisation of the process for the reactors of different design and for determining model parameters for each catalyst. ■

Acknowledgment

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