

Reaction Kinetics of Propane Catalytic Combustion on Cr/ γ -Al₂O₃, Co/Cr/ γ -Al₂O₃, and Au/Cr/ γ -Al₂O₃

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Abstract—The kinetics of propane oxidation to carbon dioxide and water over Cr/ γ -Al₂O₃, Co/Cr/ γ -Al₂O₃, and Au/Cr/ γ -Al₂O₃ were investigated within the temperature range 563–593K at atmospheric pressure. The rate equations for all three catalysts were obtained in this research. A best-fit reduction-oxidation mechanism was found for the reaction. On the basis of the kinetic analysis, it is concluded that the existence of cobalt in Co/Cr/ γ -Al₂O₃ can increase the reducibility of chromium oxides; therefore, the reaction rate over Co/Cr/ γ -Al₂O₃ was more than that over Cr/ γ -Al₂O₃. Gold in Au/Cr/ γ -Al₂O₃ also enhanced the rate of propane oxidation; its initial activity was even higher than that of Co/Cr/ γ -Al₂O₃. However, due mainly to coking, there was a significant decay problem on the surface of Au/Cr/ γ -Al₂O₃ during the reaction. Moreover, the activation energies and the Arrhenius constants for the reduction and the oxidation steps on Cr/ γ -Al₂O₃ and Co/Cr/ γ -Al₂O₃ during complete propane oxidation were obtained. The promotion effect from cobalt oxides on chromium oxides with respect to the activation energies is discussed.

Key Words : Catalytic combustion, Chromium oxides, Propane, Oxidation, Gold, Cobalt

INTRODUCTION

In the past, a considerable number of studies have focused on the catalytic combustion of hydrocarbons (Spivey 1987; Rota *et al.*, 1996), for the purpose of developing atmospheric pollution control and more stringent environmental regulations. The advantage of catalytic combustion is that VOCs can be completely oxidized under relatively low temperatures, thus preventing the formation of NO_x. Moreover, the generation of solid or liquid wastes by a scrubbing process and by the adsorption or absorption processes can be avoided.

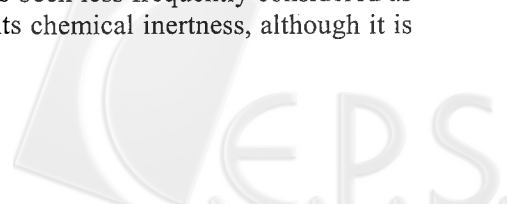
In previous studies, Morooka and Ozaki (1966) and Morooka *et al.* (1967) investigated the catalytic properties of various noble metals and transition metal oxides for the oxidation of hydrocarbons. They concluded that the catalytic activity of noble metals (*i.e.*, Pt, Pd) was higher than that of 1st raw transition metal oxides. However, at high temperatures between 773 and 1173K, Pt and Pd sinter easily, and a reduction of catalytic activity results. Furthermore, it is more expensive to use Pt and Pd as catalysts than to use 1st raw transition metal oxides. In addition, some compounds in VOC-containing streams can poison Pt and Pd. Therefore, the catalytic combustion activity

of transition metal oxides, which can avoid sintering at high temperature and exhibit activity that is not substantially lower than that of Pt or Pd, has been studied by many researchers. Prasad *et al.* (1980, 1982) found that mixtures of transition metal oxides exhibited better stability and activity than a single oxide did, and a binary mixture of chromium and cobalt oxides supported on alumina wash-coated ceramic substrates was the most active catalyst. They developed global kinetics for the catalytic combustion; however, the intrinsic reaction rate equation and the reaction mechanism were still not clear. Later, it was found in our research (Kang and Wan, 1994) that the cobalt phase in this chromium and cobalt oxide mixture was present primarily as CoAl₂O₄, which increased the reducibility and the catalytic oxidation activity of chromium oxide.

Because the rate equations and the reaction mechanisms for propane catalytic combustion over Cr/ γ -Al₂O₃ and Co/Cr/ γ -Al₂O₃ were not investigated in the past, one of the objectives of this research was to obtain the reaction rate equations and to study the reaction mechanisms on these catalysts. Moreover, the effect of gold on Cr/ γ -Al₂O₃ was explored in this research. Gold has been less frequently considered as a catalyst due to its chemical inertness, although it is

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a cheaper noble metal than Pt or Pd. The reason for using gold as a promoter is that gold oxides release oxygen and reduce to metal easily (Morooka and Ozaki, 1966; Lin *et al.*, 2002). The existence of gold may also further enhance the reducibility of chromium oxide. A similar idea has been applied to promote the activity of Co_3O_4 . It was found that Co_3O_4 co-precipitated with gold exhibited good catalytic activity for the complete oxidation of methane (Waters *et al.*, 1995).

EXPERIMENTAL

$\text{Cr}/\gamma\text{-Al}_2\text{O}_3$ and $\text{Co}/\text{Cr}/\gamma\text{-Al}_2\text{O}_3$ catalysts were prepared through the co-impregnation of aqueous solutions of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Riedel DeHaën) and $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Merck) on γ -alumina (Merck). The incipient-wetness impregnation method was applied. All of the samples were dried at 333K and calcined in air at 1073K for 4 h for the later characterization and reaction studies. The metal contents measured using a GBC 906 atomic absorption unit were 2.2 wt% of Cr in $\text{Cr}/\gamma\text{-Al}_2\text{O}_3$ and 2.2 wt% of Cr and 0.92 wt% of Co in $\text{Co}/\text{Cr}/\gamma\text{-Al}_2\text{O}_3$, respectively. The procedure for the preparation of $\text{Au}/\text{Cr}/\gamma\text{-Al}_2\text{O}_3$ was as follows: $\text{Cr}/\gamma\text{-Al}_2\text{O}_3$ was added into a 1N NaNO_3 solution with stirring; then, 1N of HNO_3 solution was used to adjust the pH of the solution to 6. After filtration, and drying at 333K, the sample was added into a 500 mL pH 6 chloroauric acid ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, Merck) solution. It was heated to 353K and maintained at this temperature for 16 h. After filtration, the resulted $\text{Au}/\text{Cr}/\gamma\text{-Al}_2\text{O}_3$ sample was washed with 500 mL de-ionized water to remove Cl^- ions, and then dried in air at room temperature. The metal contents of this resulted sample were 2.2 wt% of Cr and 1.9 wt% of Au in $\text{Au}/\text{Cr}/\gamma\text{-Al}_2\text{O}_3$.

Propane combustion was carried out in a fixed bed differential type reactor (12-mm-o.d. quartz tube). The flow rates of propane, nitrogen and oxygen were controlled and read by mass controllers and meters (Brooks 5850 and 5878). The reaction temperatures were controlled in the range 563K-593K using a PID temperature controller. For the $\text{Cr}/\gamma\text{-Al}_2\text{O}_3$ and $\text{Co}/\text{Cr}/\gamma\text{-Al}_2\text{O}_3$ catalysts, each catalyst was pretreated under air flow at 803K for 2 h before each run. $\text{Au}/\text{Cr}/\gamma\text{-Al}_2\text{O}_3$ catalyst was pretreated under air flow at 803K for 2 h, then under N_2/H_2 (9/1) flow at 523K for 2 h for the reduction of gold compounds to gold metal. A Shimadzu GC-8A gas chromatograph with a Carboxy-2000 column was used to separate carbon dioxide, carbon monoxide, nitrogen and oxygen. Another Shimadzu GC-14A gas chromatograph with a SP-1700 column was used to separate carbon dioxide and propane.

In the reaction kinetic measurements, the catalyst

containing 0.0022 g of Cr and a total flow rate of 70 mL/min were used. The partial pressures of propane were adjusted within 0.01-0.1 atm and those of oxygen were adjusted within 0.2-0.5 atm. Due to the fact that the conversion of each reactant was maintained at less than about 8% in this research, the combustion rate of propane ($-r$) was calculated from the reaction rate in a differential reactor, $-r = FX/W$, where F is the mole flow rate of propane at the inlet, X is the propane conversion at the outlet, and W is the weight of chromium in the reactor.

RESULTS

Figure 1 shows propane conversions over $\text{Au}/\text{Cr}/\gamma\text{-Al}_2\text{O}_3$, $\text{Co}/\text{Cr}/\gamma\text{-Al}_2\text{O}_3$, and $\text{Cr}/\gamma\text{-Al}_2\text{O}_3$ at 593K, as a function of time on stream. Only products of carbon dioxide and water were observed at the outlet of the reactor. It was found that although $\text{Au}/\text{Cr}/\gamma\text{-Al}_2\text{O}_3$ exhibited the highest propane oxidation activity, the activity decayed during the reaction test. In order to check whether the decayed activity of $\text{Au}/\text{Cr}/\gamma\text{-Al}_2\text{O}_3$ can be recovered, a regeneration process, which was carried out under air flow at 803K for 2 h, was applied. Figure 2 shows that the activity can be recovered partially, although it was not as high as that of a fresh sample. However, it still decayed during the reaction at 593K. On the other hand, as shown in Fig. 1, $\text{Cr}/\gamma\text{-Al}_2\text{O}_3$ and $\text{Co}/\text{Cr}/\gamma\text{-Al}_2\text{O}_3$ needed an induction period to achieve a conversion at a steady state. There was no apparent decay problem during the reaction tests for these two catalyst systems.

The influence of propane partial pressure on the catalytic complete oxidation rate over $\text{Au}/\text{Cr}/\gamma\text{-Al}_2\text{O}_3$ at 593K and over $\text{Cr}/\gamma\text{-Al}_2\text{O}_3$ and $\text{Co}/\text{Cr}/\gamma\text{-Al}_2\text{O}_3$ at different reaction temperatures was examined, and the results are presented in Figs. 3 and 4, respectively. Only one temperature (*i.e.*, 593K) was used in the case of $\text{Au}/\text{Cr}/\gamma\text{-Al}_2\text{O}_3$ because of the decay problem of this catalyst. It had to be extra-plotted to time zero to obtain the initial rates for the later kinetic study. Therefore, it was found that at lower propane partial pressures, there were linear relationships between the reaction rate of propane and the propane partial pressure for all three catalyst systems. This suggests the existence of first-order reactions to propane partial pressure. Nevertheless, at higher propane partial pressures, all of the catalyst systems showed less dependence of the reaction rate on the propane partial pressures. The reaction rate orders gradually decreased to zero-orders when the propane partial pressures are increased. On the other hand, the influence of oxygen partial pressure on the catalytic complete oxidation rate over $\text{Au}/\text{Cr}/\gamma\text{-Al}_2\text{O}_3$, $\text{Cr}/\gamma\text{-Al}_2\text{O}_3$, and $\text{Co}/\text{Cr}/\gamma\text{-Al}_2\text{O}_3$ is presented in Figs. 5 and 6,

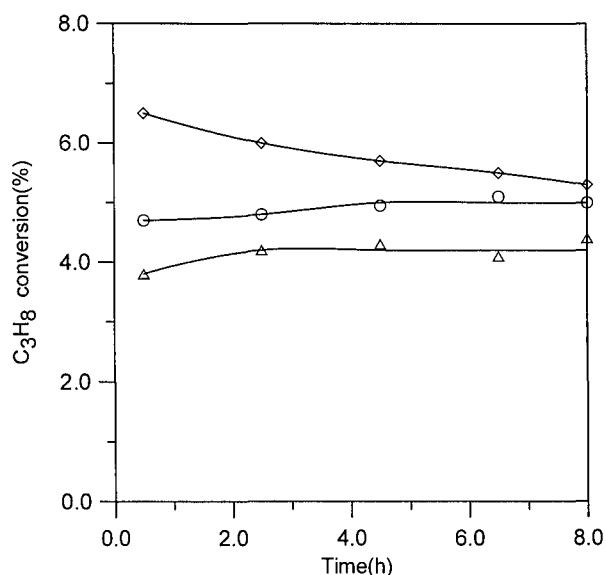


Fig. 1. The reaction extent as a function of the reaction time for (\diamond) Au/Cr/ γ -Al₂O₃, (\circ) Co/Cr/ γ -Al₂O₃, and (\triangle) Cr/ γ -Al₂O₃, a total flow rate = 70 mL/min, propane pressure = 0.006 atm, T = 593K, and 0.0022g Cr.

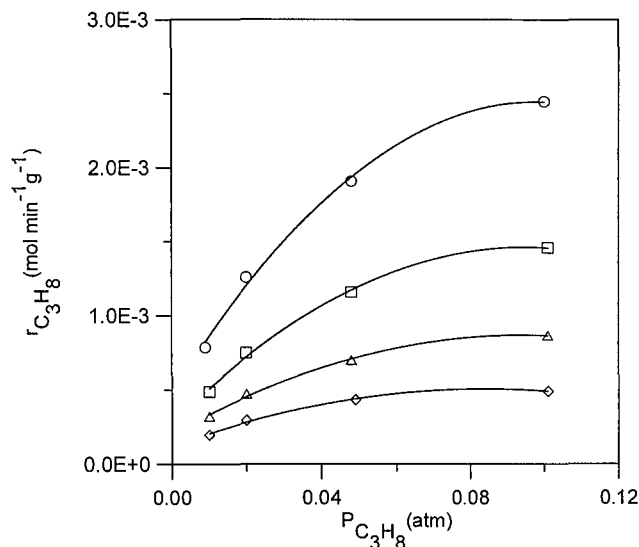


Fig. 3. Influence of propane partial pressure on the propane complete oxidation rate over Cr/ γ -Al₂O₃. Total flow rate = 70 mL/min, oxygen pressure = 0.2 atm: (\circ) 593K, (\square) 583K, (\triangle) 573K, and (\diamond) 563K.

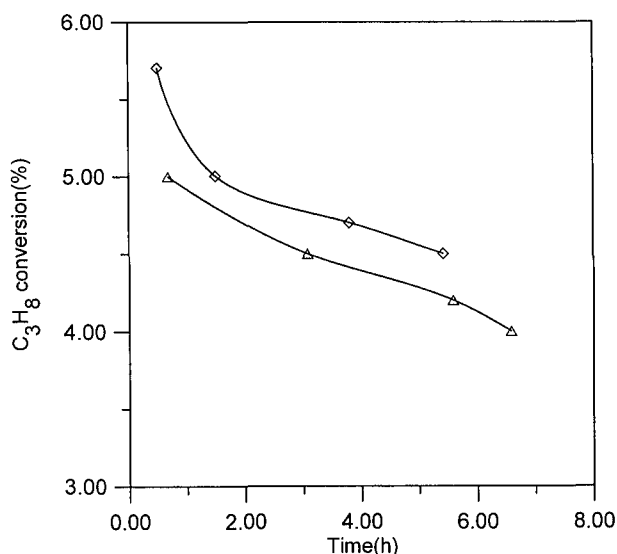


Fig. 2. Propane combustion conversion on Au/Cr/ γ -Al₂O₃ before and after regeneration. (\diamond) before regeneration, and (\triangle) after regeneration. The total flow rate = 70 mL/min, propane pressure = 0.01 atm, T = 593K, and 0.0022g Cr. Au/Cr/ γ -Al₂O₃ was regenerated at 803K under air flow for 2 h.

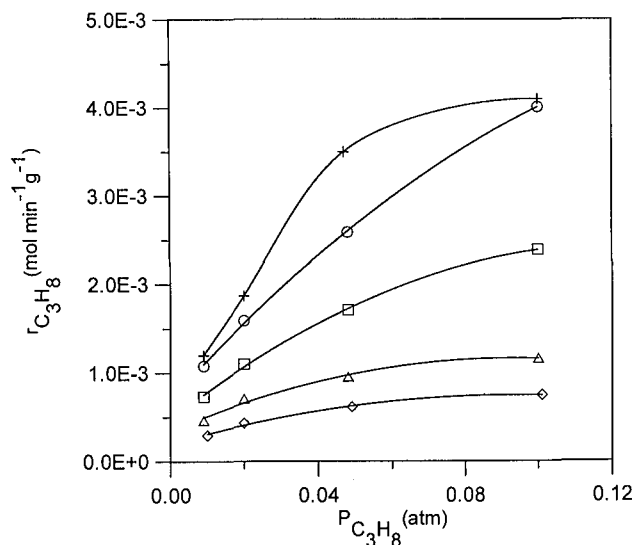


Fig. 4. Influence of propane partial pressure on the propane complete oxidation rate over Co/Cr/ γ -Al₂O₃ and Au/Cr/ γ -Al₂O₃. Total flow rate = 70 mL/min, oxygen pressure = 0.2 atm; Co/Cr/ γ -Al₂O₃: (\circ) 593K, (\square) 583K, (\triangle) 573K, and (\diamond) 563K; Au/Cr/ γ -Al₂O₃: (+) 593K.

respectively. Approximately linear relationships between the reaction rates and the oxygen partial pressures always existed in different catalyst systems at different temperatures. Nevertheless, the slopes of these linear lines are small, and the intercepts are not close to zero. These results indicate that the reaction rates over these three catalysts system may be close to zero order to oxygen partial pressure.

KINETIC MODEL DEVELOPMENT

The data of the reaction rates in relation to reactant partial pressures from different catalyst systems at different reaction temperatures are listed in Table 1, Table 2, and Table 3. The kinetic models and the rate equations were developed so as to fit these data

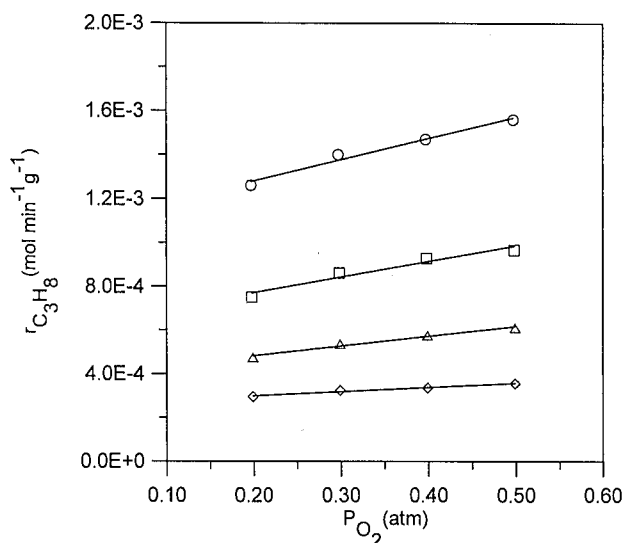


Fig. 5. Influence of oxygen partial pressure on the propane complete oxidation rate over Cr/ γ -Al₂O₃. Total flow rate = 70 mL/min, propane pressure = 0.02 atm: (○) 593K, (□) 583K, (△) 573K, and (◇) 563K.

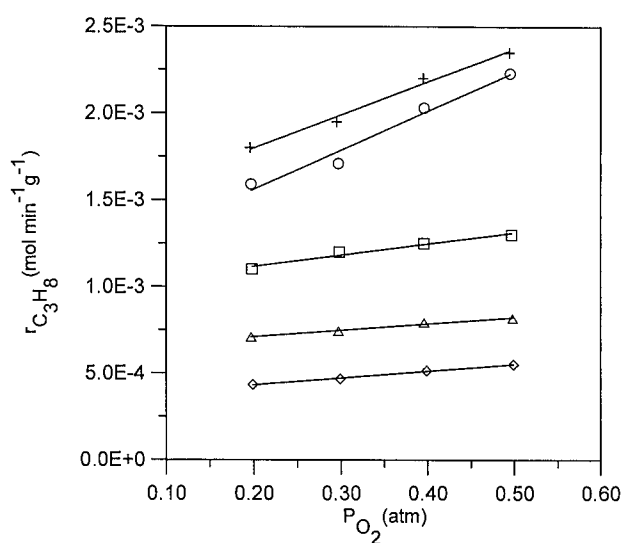


Fig. 6. Influence of oxygen partial pressure on the propane complete oxidation rate over Co/Cr/ γ -Al₂O₃ and Au/Cr/ γ -Al₂O₃. Total flow rate = 70 mL/min, propane pressure = 0.02 atm, Co/Cr/ γ -Al₂O₃: (○) 593K, (□) 583K, (△) 573K, and (◇) 563K; Au/Cr/ γ -Al₂O₃: (+) 593K.

Table 1. Experimental data of the propane combustion rate on Cr/ γ -Al₂O₃ at different reactant partial pressures.

T (K)	$r_{C_3H_8}$ (mol·min ⁻¹ ·g ⁻¹ Cr)			P_{O_2} (atm)	$P_{C_3H_8}$ (atm)
	Measured	Eley-Rideal ^a	Reduction-Oxidation ^b		
593	7.87E-4 ^c	5.93E-4	6.96E-4	0.198	0.009
	1.26E-3	1.07E-3	1.22E-3	0.197	0.020
	1.91E-3	1.73E-3	1.90E-3	0.196	0.048
	2.45E-3	2.24E-3	2.39E-3	0.195	0.100
	1.40E-3	1.61E-3	1.40E-3	0.297	0.020
	1.47E-3	2.15E-3	1.51E-3	0.397	0.020
	1.56E-3	2.69E-3	1.59E-3	0.497	0.020
583	4.89E-4	4.06E-4	4.68E-4	0.199	0.010
	7.50E-4	6.65E-4	7.48E-4	0.198	0.020
	1.16E-3	1.07E-3	1.15E-3	0.198	0.048
	1.46E-3	1.37E-3	1.44E-3	0.197	0.101
	8.61E-4	10.01E-4	8.64E-4	0.298	0.020
	9.29E-4	13.37E-4	9.36E-4	0.398	0.020
573	9.66E-4	16.46E-4	9.85E-4	0.498	0.020
	3.22E-4	2.67E-4	2.98E-4	0.199	0.010
	4.74E-4	4.25E-4	4.68E-4	0.199	0.020
	7.00E-4	6.50E-4	7.00E-4	0.199	0.048
	8.67E-4	8.06E-4	8.56E-4	0.198	0.101
	5.36E-4	6.38E-4	5.47E-4	0.299	0.020
563	5.75E-4	8.52E-4	5.97E-4	0.399	0.020
	6.11E-4	10.65E-4	6.32E-4	0.499	0.020
	1.97E-4	1.59E-4	1.80E-4	0.200	0.010
	2.95E-4	2.48E-4	2.81E-4	0.199	0.020
	4.34E-4	3.72E-4	4.20E-4	0.199	0.049
	4.92E-4	4.53E-4	5.09E-4	0.199	0.101
563	3.24E-4	3.72E-4	3.29E-4	0.299	0.020
	3.36E-4	4.96E-4	3.60E-4	0.399	0.020
	3.56E-4	6.21E-4	3.82E-4	0.499	0.020

^a Propane combustion rate predicted by the Eley-Rideal model.

^b Rate predicted by the Reduction-Oxidation model.

^c Read as 7.87×10^{-4} .

Table 2. Experimental data of the propane combustion rate on Co/Cr/ γ -Al₂O₃ at different reactant partial pressures.

T (K)	$r_{C_3H_8}$ (mol·min ⁻¹ ·g ⁻¹ Cr)			P_{O_2} (atm)	$P_{C_3H_8}$ (atm)
	Measured	Eley-Rideal ^a	Reduction-Oxidation ^b		
593	1.08E-3 ^c	0.76E-3	0.93E-3	0.198	0.009
	1.59E-3	1.46E-3	1.71E-3	0.197	0.020
	2.95E-3	2.58E-3	2.85E-3	0.194	0.048
	4.01E-3	3.62E-3	3.77E-3	0.192	0.100
	1.71E-3	2.21E-3	1.91E-3	0.297	0.020
	2.03E-3	2.94E-3	2.03E-3	0.396	0.020
	2.23E-3	3.54E-3	2.02E-3	0.495	0.019
583	7.33E-4	5.33E-4	6.03E-4	0.199	0.009
	1.10E-3	0.97E-3	1.09E-3	0.198	0.020
	1.71E-3	1.61E-3	1.76E-3	0.197	0.048
	2.39E-3	2.11E-3	2.27E-3	0.195	0.100
	1.20E-3	1.46E-3	1.23E-3	0.298	0.020
	1.25E-3	1.95E-3	1.31E-3	0.397	0.020
	1.30E-3	2.44E-3	1.37E-3	0.497	0.020
573	4.65E-4	3.94E-4	4.21E-4	0.199	0.010
	7.08E-4	6.09E-4	6.53E-4	0.199	0.020
	9.53E-4	8.91E-4	9.57E-4	0.198	0.048
	1.16E-3	1.08E-3	1.16E-3	0.198	0.101
	7.43E-4	9.13E-4	7.68E-4	0.298	0.020
	7.92E-4	12.19E-4	8.42E-4	0.398	0.020
	8.17E-4	15.25E-4	8.95E-4	0.498	0.020
563	2.95E-4	2.42E-4	2.72E-4	0.199	0.010
	4.33E-4	3.77E-4	4.19E-4	0.199	0.020
	6.14E-4	5.63E-4	6.17E-4	0.199	0.049
	7.44E-4	6.82E-4	7.41E-4	0.199	0.101
	4.67E-4	5.67E-4	4.94E-4	0.299	0.020
	5.14E-4	7.56E-4	5.43E-4	0.399	0.020
	5.50E-4	9.46E-4	5.78E-4	0.499	0.020

^a Propane combustion rate predicted by the Eley-Rideal model.

^b Rate predicted by the Reduction-Oxidation model.

^c Read as 1.08×10^{-3} .

Table 3. Experimental data of the propane combustion rate on Au/Cr/ γ -Al₂O₃ at different reactant partial pressures.

T (K)	$r_{C_3H_8}$ (mol·min ⁻¹ ·g ⁻¹ Cr)			P_{O_2} (atm)	$P_{C_3H_8}$ (atm)
	Measured	Eley-Rideal ^a	Reduction-Oxidation ^b		
593	1.21E-3 ^c	0.88E-3	1.03E-3	0.197	0.009
	1.80E-3	1.64E-3	1.89E-3	0.196	0.020
	3.50E-3	2.74E-3	3.10E-3	0.193	0.047
	4.10E-3	3.76E-3	4.15E-3	0.192	0.100
	1.95E-3	2.47E-3	2.11E-3	0.295	0.020
	2.20E-3	3.31E-3	2.24E-3	0.395	0.020
	2.35E-3	3.98E-3	2.22E-3	0.494	0.019

^a Propane combustion rate predicted by the Rideal model.

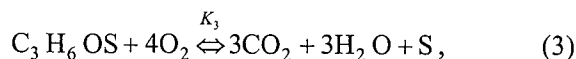
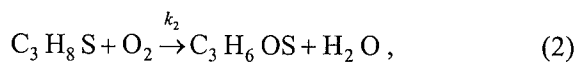
^b Rate predicted by the Reduction-Oxidation model.

^c Read as 1.21×10^{-3} .

statistically. An SAS package was applied to carry out regression. Several mechanisms (a Langmuir-Hinshelwood type with molecular adsorption on a single site, oxygen dissociation adsorption, an Eley-Rideal type for adsorption, and a reduction-oxidation type) were examined. The approach steps used to justify a proposed mechanism were as follows: First, several rate equations were derived by assuming different rate-determining-steps in the proposed mechanism. Second, linear regression of the consequent equations was conducted to obtain the reaction rate constants and the adsorption equilibrium constants at

different temperatures. Finally, when any of the derived constants from regression was negative, that rate equation was eliminated from further consideration.

It was found from this research that the rate equations derived from the Eley-Rideal and the reduction-oxidation mechanisms could satisfactorily fit the kinetic data from different catalyst systems at different reaction temperatures. The following is the Eley-Rideal mechanism, while propane is adsorbed on the surface and oxygen reacts with the adsorbed propane directly to form carbon dioxide:



where S represents the active site on the catalyst surface. When reaction (2) is the rate-determining step and the remaining two steps are assumed fast to reach equilibrium, the following rate equation for the consumption of propane can be derived:

$$r_{\text{C}_3\text{H}_8} = \frac{C_t K_1 k_2 P_{\text{C}_3\text{H}_8} P_{\text{O}_2}}{\left[1 + K_1 P_{\text{C}_3\text{H}_8} + \frac{P_{\text{CO}_2}^3 P_{\text{H}_2\text{O}}^3}{K_3 P_{\text{O}_2}^4} \right]}. \quad (4)$$

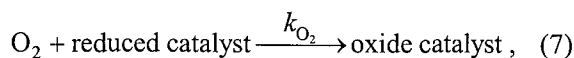
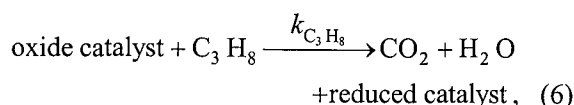
Because reaction (3) is highly exothermic, the equilibrium constant K_3 should be a very large number. The last term in the denominator of Eq. (4) can be neglected. Therefore, Eq. (4) can be simplified as

$$r_{\text{C}_3\text{H}_8} = \frac{C_t K_1 k_2 P_{\text{C}_3\text{H}_8} P_{\text{O}_2}}{[1 + K_1 P_{\text{C}_3\text{H}_8}]}. \quad (5)$$

It should be noted that there is a linear relationship between the reaction rate and the partial pressure of oxygen in Eq. (5). When the partial pressure of propane is low, because the value of the denominator is close to 1, the reaction rate is first order to the partial pressure of propane. On the other hand, when the partial pressure of propane is high and causes the value of $K_1 P_{\text{C}_3\text{H}_8}$ to be much larger than 1, due to cancellation of the terms of the propane partial pressures, the reaction rate is zero order to the

propane partial pressure. It is apparent that Eq. (5) satisfies most of the relationships between the reaction rates and the partial pressures shown in Figs. 3 to 6. Therefore, the Eley-Rideal mechanism is one of the mechanisms that can explain the reaction kinetics in this research. From linear regressions on the inverse rate expression of Eq. (5), the propane adsorption equilibrium constants and the apparent oxidation rate constants ($C_t k_2$) from each catalyst system at different temperatures were obtained and are listed in Table 4. The predicted reaction rates from these parameters at different partial pressures of propane and oxygen are shown in Tables 1-3.

For the reduction-oxidation mechanism, the proposed reaction sequence is as follows:



where $k_{\text{C}_3\text{H}_8}$ and k_{O_2} are the rate constants for the reduction and re-oxidation reactions, respectively. Elementary reactions are assumed in this mechanism. Therefore, if θ is the fractional coverage of the reduced catalyst surface at any time, then the rate equations for the consumption of oxygen and propane can be formulated as follows:

$$r_{\text{O}_2} = k_{\text{O}_2} P_{\text{O}_2} \theta, \quad (8)$$

$$r_{\text{C}_3\text{H}_8} = k_{\text{C}_3\text{H}_8} P_{\text{C}_3\text{H}_8} (1 - \theta). \quad (9)$$

Furthermore, for complete oxidation of one mole of propane, the stoichiometric oxygen required is five moles; thus,

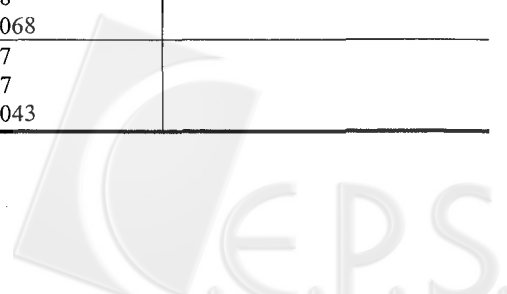
Table 4. Equilibrium constants and rate constants on Cr/ γ -Al₂O₃, Co/Cr/ γ -Al₂O₃, and Au/Cr/ γ -Al₂O₃ at different reaction temperatures from the Eley-Rideal mechanism.

T (K)	Constants	Cr/ γ -Al ₂ O ₃	Co/Cr/ γ -Al ₂ O ₃	Au/Cr/ γ -Al ₂ O ₃
593	K_1^a	25.7	15.97	19.9
	k_a^b	0.41	0.49	0.585
	k_s^c	0.016	0.031	0.029
583	K_1	27.4	23.2	
	k_a	0.26	0.36	
	k_s	0.0095	0.016	
573	K_1	34.3	41.42	
	k_a	0.18	0.28	
	k_s	0.0052	0.0068	
563	K_1	38.4	39.67	
	k_a	0.11	0.17	
	k_s	0.0029	0.0043	

^a Propane adsorption equilibrium constant K_1 , atm⁻¹.

^b Apparent rate constant $k_a = C_t K_1 k_2$, mol·min⁻¹·g⁻¹·atm⁻².

^c Specific rate constant $k_s = C_t k_2$, mol·min⁻¹·g⁻¹·atm⁻¹.



$$r_{O_2} = 5r_{C_3H_8} \quad (10)$$

By substituting Eqs. (8) and (9) into Eq. (10), one can obtain the expression θ . The rate equation of propane consumption can be derived by simply substituting θ into Eq. (9):

$$r_{C_3H_8} = \frac{k_{O_2} k_{C_3H_8} P_{C_3H_8} P_{O_2}}{k_{O_2} P_{O_2} + 5k_{C_3H_8} P_{C_3H_8}}, \quad (11)$$

which is the Mars-van Krevelen rate expression for the complete oxidation of propane. It can be found that the rate order to propane can be adjusted between zero and one, depending on the ratio of the partial pressure of propane to that of oxygen. When the partial pressure of oxygen is significantly higher than that of propane, the rate order of oxygen becomes close to zero. These qualitative aspects seem to fit the results shown in Figs. 3-6. Therefore, from linear regressions on the inverse expression of Eq. (11), the rate constants for oxidation and for reduction on each catalyst at different temperatures were

obtained and are listed in Table 5. The predicted reaction rates from these rate constants at different partial pressures of propane and oxygen are also shown in Tables 1-3.

Comparing the predicted reaction rates shown in Tables 1-3, one can find that the values from the reduction-oxidation mechanism are always closer to the observed values than are those from the Eley-Rideal mechanism. Therefore, it can be concluded from this research that the Mars-van Krevelen model, derived from the reduction-oxidation mechanism, better fits the kinetic data of propane complete oxidation on supported chromium oxides than does the Eley-Rideal model. Figures 7 and 8 show that the rate data from the experiments agree with those estimated using the rate Eq. (11). The mean deviation error is about 3.5%(Cr/ γ -Al₂O₃), 8.3%(Co/Cr/ γ -Al₂O₃), and 5.9%(Au/Cr/ γ -Al₂O₃), respectively. The random distribution around the diagonal equivalent line of the empirical and the calculated values of rate suggests that this rate equation derived from reduction-oxidation mechanism describes the experimental results quite well.

Table 5. Rate constants on Cr/ γ -Al₂O₃, Co/Cr/ γ -Al₂O₃, and Au/Cr/ γ -Al₂O₃ at different reaction temperatures from the reduction-oxidation mechanism.

T (K)	k_{O_2} (mol·min ⁻¹ ·g ⁻¹ ·atm ⁻¹)			$k_{C_3H_8}$ (mol·min ⁻¹ ·g ⁻¹ ·atm ⁻¹)		
	Cr/ γ -Al ₂ O ₃	Co/Cr/ γ -Al ₂ O ₃	Au/Cr/ γ -Al ₂ O ₃	Cr/ γ -Al ₂ O ₃	Co/Cr/ γ -Al ₂ O ₃	Au/Cr/ γ -Al ₂ O ₃
593	0.0808	0.1410	0.1550	0.0989	0.1240	0.137
583	0.0473	0.0803		0.0623	0.0826	
573	0.0272	0.0364		0.0412	0.0594	
563	0.0160	0.0230		0.0251	0.0386	

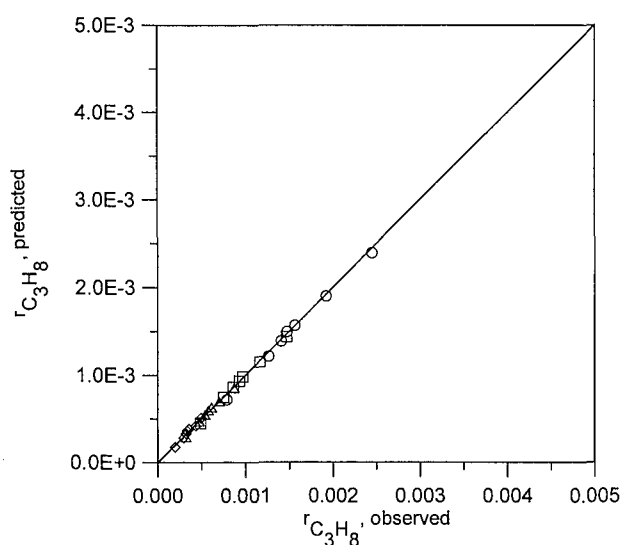


Fig. 7. Comparison of the predicted and the observed values of the C₃H₈ complete oxidation rate on Cr/ γ -Al₂O₃: (○) 593K, (□) 583K, (△) 573K, and (◇) 563K.

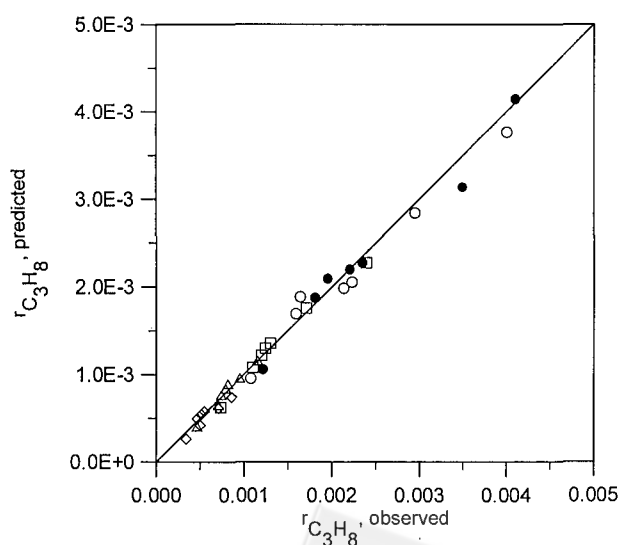


Fig. 8. Comparison of the predicted and the observed values of the C₃H₈ complete oxidation rate on Co/Cr/ γ -Al₂O₃ and Au/Cr/ γ -Al₂O₃. Co/Cr/ γ -Al₂O₃: (○) 593K, (□) 583K, (△) 573K, and (◇) 563K; Au/Cr/ γ -Al₂O₃ (●) 593K.

The temperature dependence of k_{O_2} and $k_{C_3H_8}$, listed in Table 5, can be expressed as

$$k_{O_2} = A_1 \exp(-E_{a1} / RT), \quad (12)$$

$$k_{C_3H_8} = A_2 \exp(-E_{a2} / RT), \quad (13)$$

where E_{a1} and E_{a2} are the activation energies, and A_1 and A_2 are the Arrhenius constants. From the plots of $\ln k$ vs. the reciprocal of the reaction temperature (shown in Fig. 9), the parameters in Eqs. (12) and (13) were estimated as $A_1 = 1.36 \times 10^{12}$ mol/(min·g·atm), $E_{a1} = 36$ kcal·mol⁻¹, $A_2 = 1.16 \times 10^{10}$ mol/(min·g·atm) and $E_{a2} = 30$ kcal·mol⁻¹ for Cr/ γ -Al₂O₃. The linear correlation factors, R^2 , of these two lines (shown in Fig. 9) were 0.999 and 0.999, respectively, which suggests good linear relationships ($R^2 = 1$ represents a perfect linear relationship). Moreover, the parameters were estimated as $A_1 = 2.34 \times 10^{14}$ mol/(min·g·atm), $E_{a1} = 41$ kcal·mol⁻¹, $A_2 = 2.86 \times 10^8$ mol/(min·g·atm), and $E_{a2} = 25$ kcal·mol⁻¹ for Co/Cr/ γ -Al₂O₃. The linear correlation factors, R^2 , of the two lines are 0.989 and 0.998, respectively, which also suggests good linear relationships.

DISCUSSION

From this research, it is found a better fit of the rate model can be derived from the reduction-oxidation mechanism than from the Eley-Rideal mechanism. This indicates that the adsorption of

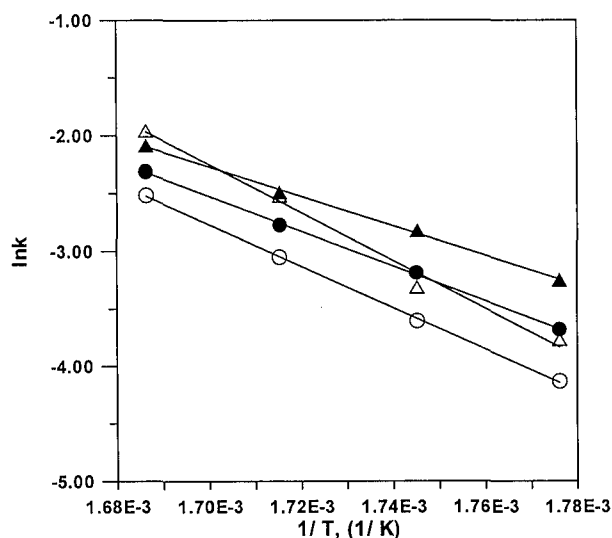


Fig. 9. Arrhenius plots of (●) the re-oxidation rate constants on Cr/ γ -Al₂O₃, (○) the reduction rate constant on Cr/ γ -Al₂O₃, (▲) the re-oxidation rate constant on Co/Cr/ γ -Al₂O₃, and (△) the reduction rate constant on Co/Cr/ γ -Al₂O₃.

propane is no longer a key step for the complete oxidation of propane on these supported chromium oxides catalysts, under the reaction conditions studied. The reason for this is that the surface reaction step and the product desorption step proceed fast. Therefore, propane and the reaction products no longer accumulate on the active sites, and the reaction kinetics are not hindered.

Both cobalt and gold on chromium oxides promote catalytic activity for the oxidation of propane. It can be found in Table 5 that all of the rate constants from Co/Cr/ γ -Al₂O₃ and Au/Cr/ γ -Al₂O₃ catalyst systems are larger than those from Cr/ γ -Al₂O₃. It is believed that there are different active sites on Au/Cr/ γ -Al₂O₃ for the reactions. One is on the surfaces of pure chromium oxides, and the other is on the surfaces of mixed metal and metal oxides of gold and chromium. Therefore, it was observed in this research that there initially was high catalytic activity of Au/Cr/ γ -Al₂O₃. This activity decayed and dropped to about that of Cr/ γ -Al₂O₃, due to coking on the active sites from mixed metal and metal oxides of gold and chromium. However, the catalytic activity of the regenerated catalyst was not as good as that of the fresh one. This was due to sintering of the gold particles during the regeneration process at high temperature.

The plots in Fig. 9 show that the activation energy (*i.e.*, 25 kcal·mol⁻¹) for the reduction of metal oxides on Co/Cr/ γ -Al₂O₃ is lower than that (*i.e.*, 30 kcal·mol⁻¹) on Cr/ γ -Al₂O₃, and that the activation energy (*i.e.*, 41 kcal·mol⁻¹) for oxidation of the reduced active sites on Co/Cr/ γ -Al₂O₃ is higher than that (*i.e.*, 36 kcal·mol⁻¹) on Cr/ γ -Al₂O₃. These results indicate that the catalytic active sites on Co/Cr/ γ -Al₂O₃ can be reduced more easily during the propane combustion reaction than those on Cr/ γ -Al₂O₃, and that the reduced site is more difficult to be re-oxidized. It is concluded from this research that the catalytic active sites of Cr/ γ -Al₂O₃ and Co/Cr/ γ -Al₂O₃ are from chromium oxides and promoted chromium oxides on the surface. This is because, in our previous research (Kang and Wan, 1994), we found that only chromium oxides in these two catalysts rather than cobalt compounds in Co/Cr/ γ -Al₂O₃ can be reduced during temperature programmed reduction (TPR by hydrogen) experiments. Cobalt may bond with alumina to form cobalt aluminate in Co/Cr/ γ -Al₂O₃. Due to the interaction between chromium and cobalt aluminate, the reduction temperature for chromium oxides in Co/Cr/ γ -Al₂O₃ during TPR was lower than that for Cr/ γ -Al₂O₃. Therefore, the lower activation energy for the reduction of Co/Cr/ γ -Al₂O₃ during propane combustion in this research is consistent with our previous TPR results. Moreover, it can be found from the research results of Morooka and Ozaki (1966) and Morooka *et al.*

(1967) that cobalt oxides are more easily reduced than chromium oxides; in contrast, reduced cobalt oxides are more difficult to be re-oxidized than reduced chromium oxides. Therefore, for a binary oxide system in which cobalt oxides are doped into chromium oxides, the reduction temperature for chromium oxides may drop due to the influence of cobalt oxides; on the other hand, the re-oxidation temperature for the reduced chromium oxides may rise. Although instead of cobalt oxides, cobalt aluminate in Co/Cr/ γ -Al₂O₃ is proposed in this research. The lower and the higher activation energies for the reduction and the oxidation reactions on Co/Cr/ γ -Al₂O₃ than those on Cr/ γ -Al₂O₃ indicate a similar interaction between cobalt aluminate and chromium oxides in Co/Cr/ γ -Al₂O₃ to that between cobalt oxides and chromium oxides of a binary oxide system.

It can be found from this research that the Arrhenius constant for the reduction of metal oxides on Co/Cr/ γ -Al₂O₃ is much lower than that on Cr/ γ -Al₂O₃. Note that the Arrhenius constant is proportional to the number of active sites on the catalyst surface available for the reaction. A lower value for the Arrhenius constant on Co/Cr/ γ -Al₂O₃ suggests a smaller number of active sites for the reaction. This implies that the majority of the reaction between propane and Co/Cr/ γ -Al₂O₃ occurs on the active sites of mixed metal oxides of Co and Cr on the surface. Due to the limited amount of cobalt (0.92 wt%) in Co/Cr/ γ -Al₂O₃, the Arrhenius constant is low for the reaction on Co/Cr/ γ -Al₂O₃.

It can be observed in Table 5 that the rate constants for oxidation of the reduced active sites on Co/Cr/ γ -Al₂O₃ are always higher than those on Cr/ γ -Al₂O₃ at the same reaction temperature, although the addition of cobalt should have lowered the activity of Co/Cr/ γ -Al₂O₃ for this reaction due to the increase of activation energy. The higher value of the Arrhenius constant on Co/Cr/ γ -Al₂O₃ can explain this. However, it must be noted that the Arrhenius constant for the oxidation of the reduced active sites on Co/Cr/ γ -Al₂O₃ is higher than that on Cr/ γ -Al₂O₃; in contrast to that for the reduction of metal oxides. It is believed that dissociation of propane on the active sites of the catalyst surface occurs during the reaction. The dissociated propane may produce hydrogen for the reduction of metal oxides on Cr/ γ -Al₂O₃ and on Co/Cr/ γ -Al₂O₃. The other products (e.g., carbons, hydrocarbons, and hydride) might spill onto the surrounding area around the active sites on the catalyst surface. This spilled area may be treated as new sites on the catalyst surface for the oxidation reaction. Nevertheless, the number of these new sites is not related to θ value (fraction of reduced metal oxides) in Eq. (8); rather, it is lumped into the value of A_1 in Eq. (12) and causes a higher value of k_{O_2} in Eqs. (8)

and (12). Therefore, the more dissociation of propane that occurs, the higher value of k_{O_2} should be obtained. In other words, the dissociation activity of propane on Co/Cr/ γ -Al₂O₃ should be higher than that on Cr/ γ -Al₂O₃. The increase in the number of products generated by this dissociation reaction certainly increases the frequency factor (i.e., the Arrhenius constant) of the later oxidation reaction kinetics.

According to Morooka and Ozaki (1966) and Morooka *et al.* (1967), gold oxides are even more easily reduced than cobalt oxides; on the other hand, gold is more difficult to be re-oxidized. Indeed, it can be found in Table 5 that the rate constant for the reduction on Au/Cr/ γ -Al₂O₃ at 593K is higher than that on Co/Cr/ γ -Al₂O₃. The existence of gold on Au/Cr/ γ -Al₂O₃ increases the reduction activity of chromium oxides. Moreover, the rate constant for oxidation on Au/Cr/ γ -Al₂O₃ is also higher than that on Co/Cr/ γ -Al₂O₃. This means that more dissociation of propane may occur on Au/Cr/ γ -Al₂O₃. These dissociation products on the surface need oxygen for oxidation. Nevertheless, it is apparent that there was not enough oxidation activity on Au/Cr/ γ -Al₂O₃ for their total removal. The accumulation of some of the dissociation products on the catalyst surface caused a coking problem on Au/Cr/ γ -Al₂O₃.

CONCLUSION

From the results of this study, it is concluded that the reaction rate model derived from the reduction-oxidation or Mars-van Krevelen mechanism can explain very well about the complete oxidation of propane on Co/Cr/ γ -Al₂O₃, Au/Cr/ γ -Al₂O₃, and Cr/ γ -Al₂O₃, respectively. The rate equation can be expressed as

$$\text{rate} = \frac{k_{O_2} k_{C_3H_8} P_{C_3H_8} P_{O_2}}{k_{O_2} P_{O_2} + 5k_{C_3H_8} P_{C_3H_8}}$$

The rate constants for reduction and for oxidation on each catalyst were obtained through regression. It was found that both cobalt and gold on chromium oxides promoted catalytic activity. Therefore, at the same reaction temperature, all of the rate constants for the Co/Cr/ γ -Al₂O₃ and Au/Cr/ γ -Al₂O₃ catalyst systems are larger than those for Cr/ γ -Al₂O₃. The initial activity of Au/Cr/ γ -Al₂O₃ was even higher than that of Co/Cr/ γ -Al₂O₃. Nevertheless, there was a coking problem on Au/Cr/ γ -Al₂O₃. The activity of the regenerated Au/Cr/ γ -Al₂O₃ was lower than that of the fresh sample, due to gold sintering during regeneration at high temperature.

The activation energies and the Arrhenius constants for the reduction and the oxidation reactions

on Co/Cr/ γ -Al₂O₃ and Cr/ γ -Al₂O₃ were obtained in this research. It was found that a lower activation energy for the reduction and a higher activation energy for the oxidation on Co/Cr/ γ -Al₂O₃ than those on Cr/ γ -Al₂O₃. These promotion effects of cobalt oxides on chromium oxides are consistent with the previous results obtained by Kang and Wan (1994).

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NOMENCLATURE

A_1	Arrhenius constant for the oxidation of metal in Eq. (12), mol · min ⁻¹ · g ⁻¹ · atm ⁻¹
A_2	Arrhenius constant for the reduction of metal oxide in Eq. (13); mol · min ⁻¹ · g ⁻¹ · atm ⁻¹
C_t	total number of active sites on the catalyst
E_{a1}	activation energy for the oxidation of metal, kcal · mol ⁻¹
E_{a2}	activation energy for the reduction of metal oxides, kcal · mol ⁻¹
F	mole flow rate of propane, mol · min ⁻¹
K_1	propane adsorption equilibrium constant in Eq. (5), atm ⁻¹
K_3	equilibrium constant of reaction (3)
k_2	rate constant of the surface reaction in the Eley-Rideal mechanism
k_a	$C_t K_1 k_2$, the apparent rate constant in Eq. (5), mol · min ⁻¹ · g ⁻¹ · atm ⁻²
$k_{C_3H_8}$, k_{O_2}	rate constants in the reduction-oxidation mechanism, mol · min ⁻¹ · g ⁻¹ · atm ⁻¹
k_s	$C_t k_2$, the specific rate constant in Eq. (5), mol · min ⁻¹ · g ⁻¹ · atm ⁻¹
$P_{C_3H_8}$	partial pressure of propane, atm
P_{CO_2}	particle pressure of carbon dioxide, atm
P_{H_2O}	partial pressure of water vapor, atm
P_{O_2}	partial pressure of oxygen, atm

$r_{C_3H_8}$	reaction rate of propane, mol · min ⁻¹ · g ⁻¹ Cr
r_{O_2}	reaction rate of oxygen, mol · min ⁻¹ · g ⁻¹ Cr
S	active site on the catalyst surface
T	reaction temperature, K
W	weight of chromium
X	propane conversion

Greek symbol

θ	fractional coverage of the reduced active sites on the catalyst surface
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丙烷在 Cr/ γ -Al₂O₃，Co/Cr/ γ -Al₂O₃ 及 Au/Cr/ γ -Al₂O₃ 上 之催化燃燒反應動力研究

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摘 要

本研究是在反應溫度 563-593K 及一大氣壓條件下，研究丙烷在 Cr/ γ -Al₂O₃，Co/Cr/ γ -Al₂O₃，及 Au/Cr/ γ -Al₂O₃ 上之催化燃燒反應動力機制，並已結論出經由觸媒之還原及氧化機制所推導出之反應速率方程式是最適合於各反應動力實驗數據。該機制顯示出添加 Co 之 Co/Cr/ γ -Al₂O₃ 觸媒，其被丙烷還原之速率遠高於 Cr/ γ -Al₂O₃，因此丙烷在 Co/Cr/ γ -Al₂O₃ 上之催化燃燒速率遠快於 Cr/ γ -Al₂O₃ 上。添加 Au 之 Au/Cr/ γ -Al₂O₃ 其初始反應活性甚至高於 Co/Cr/ γ -Al₂O₃，但該觸媒有結碳及失活的缺點。本研究已由反應速率常數與溫度之關係推導出在 Cr/ γ -Al₂O₃ 及 Co/Cr/ γ -Al₂O₃ 上之活化能及速率常數，因此添加 Co 而增加 Co/Cr/ γ -Al₂O₃ 活性之原因，將藉由這些活化能數據在文中詳加討論。

