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Influence of bulk oxygen diffusion on the kinetics of partial oxidation over molybdenum-containing catalysts

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Abstract

The relationship between bulk oxygen diffusion over oxide catalysts assisting the partial oxidation of acrolein and propylene, and reaction kinetics are discussed.

1. Introduction

Bruckman and Haber [1] and Ionescu et al. [2], who have written papers on the partial oxidation of hydrocarbons over molybdenum-containing catalysts, noted repeatedly the unusually bent temperature dependence of the main product formation rate. The products of the partial oxidation on such catalysts form stepwise via a redox mechanism, and oxygen in the catalyst bulk is very mobile. Using reactions of propylene and acrolein oxidation, we have tried to explain the bending of the temperature dependence by the effect of bulk oxygen diffusion.

2. Experimental

Propylene was oxidized over a multicomponent catalyst containing the oxides of Mo, Bi, Fe, Co, Ni, K and Si ($S_{BET} = 10\ m^2/g$). The catalyst, containing the oxides of Mo, V, Si ($S_{BET} = 70\ m^2/g$), was used for acrolein oxidation. Reaction kinetics was studied at 250–390°C in a flow-circulating system with the chromatographic analysis of reaction mixture components. Diffusion rate was measured using a vacuum static setup, equipped with a IPDO-2A mass-spectrometer, according to a procedure described elsewhere [3].

3. Experimental results

For both reactions, the rate of product accumulation (acrolein or acrylic acid) appears to depend on the C_{red}/C_{ox} ratio (C_{red} and C_{ox} are the stationary concentrations of reducing agent and oxygen, respectively). At a constant C_{red}/C_{ox} ratio, the first order with respect to the oxidized component is observed. With the temperature increase, the effect of C_{red}/C_{ox} ratio on reaction rates decreases. As soon as it becomes insignificant, the temperature dependence of the acrolein and acrylic acid formation rates (Figs. 1 and 2) exhibits a bend.

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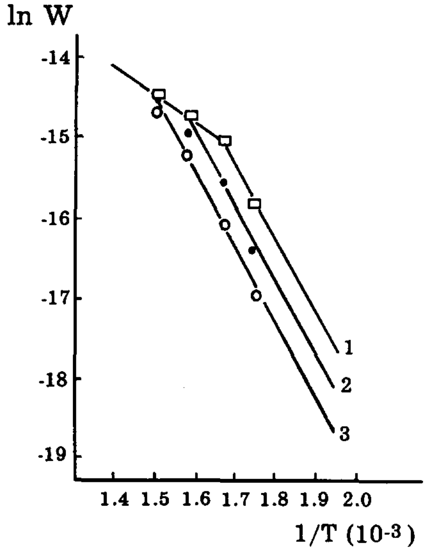

Fig. 1. Temperature dependencies of acrolein formation rates. Propylene conversion is 25% (curves: calculated; ○, ●, □, experimental). $C_{C_3H_6}=2.5\ 10^{-3}$ mol/L; $C_{C_3H_6}/C_{O_2}$: (1) 0.25; (2) 0.50; (3) 0.70.

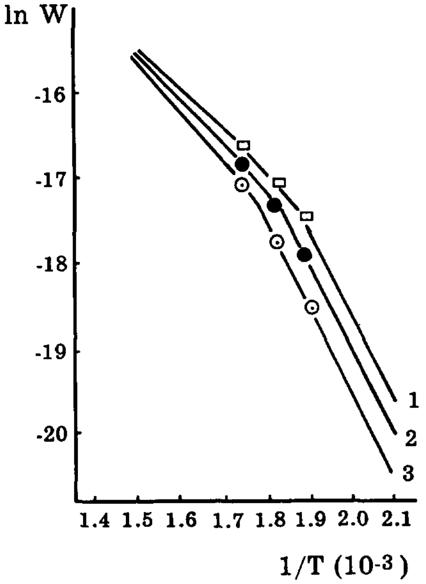

Fig. 2. Temperature dependencies of acrylic acid formation rates. Acrolein conversion is 25% (curves: calculated; ○, ●, □, experimental). $C_{C_3H_4O}=1.5\ 10^{-3}$mol/L; $C_{C_3H_4O}/C_{O_2}$: (1) 0.25; (2) 0.45; (3) 0.90.

4. Discussion

The rates of the formation of partial oxidation products can be expressed by the following equation:

$$W=\frac{K_{01}\,e^{-E_1/RT}\cdot C_{red}\cdot f(C_{pr})}{1+K_{02}\,e^{+E_2/RT}\cdot C_{red}/C_{ox}+f'(C_{pr})}$$

where $K_{01}\,e^{-E_1/RT}=K_1$ and $K_{02}\,e^{+E_2/RT}=K_2$ are the constants, C_{pr} are the concentrations of reaction products.

We have shown [4,5] that $K_1=K_{red}$, while K_2 is determined by the K_{red}/K_{ox} ratio. K_{red} and K_{ox} are the rate constants of catalyst reduction and reoxidation, respectively:

$$K_2=\frac{K_{0\,red}}{K_{0\,ox}}\,e^{-(E_{red}-E_{ox})/RT}$$

When $E_{ox}>E_{red}$, then $E_2=E_{red}-E_{ox}$ becomes negative, the exponent power in expression for K_2 becomes positive.

When the temperature increases, the rate of reoxidation increases faster than that of reduction. This changes the rate determining step. The catalyst surface reoxidation becomes the limiting step at low temperatures and its reduction is dominating at high temperatures. The bending of the temperature dependencies of the reaction rates seem to result from this phenomenon.

Bulk oxygen diffusion is of considerable importance at surface reoxidation [6,7]. For both catalysts, the activation rate was measured at various temperatures, the energy of activation and effective diffusion coefficients (D_{diff}) were calculated. The diffusion rate appears to increase with the temperature. Moreover, the temperature dependencies of the oxygen diffusion rates for both catalysts are very close to that obtained for this reaction at low temperatures. For the multicomponent catalyst, the activation energy of oxygen diffusion equals 15.4 kcal/mol, and that of acrolein formation equals 16.5 kcal/mol. For V–Mo catalyst, these values are 11.2 and 11.0, respectively. This coincidence suggests that bulk oxygen diffusion is a limiting reaction rate at low temperatures.

Reoxidation stops to limit the reaction, when the oxygen mobility attains a definite magnitude, determined by the C_{red}/C_{ox} value. At $C_{red}/C_{ox}\approx 0.25$ D_{diff} is 2 s^{-1} for both reactions (Figs. 1 and 2). With an increase of the C_{red}/C_{ox} ratio, the reduction rate increases as well. In order to prevent reoxidation from reaction limiting, the bulk oxygen mobility should be higher. This can be attained by a reaction temperature increase. The bending of the temperature dependence thus moves to higher temperatures, where $D_{diff} > 2\ s^{-1}$. Note, the $D_{diff} = 2\ s^{-1}$ is obtained at lower temperatures (250°C) on V–Mo–O catalyst than on the multicomponent one (330°C).

5. Conclusion

The bending of temperature dependencies, obtained on V–Mo–O and multicomponent catalysts, is determined by the bulk oxygen mobility. A definite level of mobility determines the temperature at which the limiting step changes.

6. References

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