

KINETICS OF THE VAPOR-PHASE CATALYTIC OXIDATION OF *p*-METHOXYTOLUENE TO *p*-ANISALDEHYDE

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There are numerous studies concerned with vapor-phase oxidation of substituted toluenes, most of them focused on preparation of the corresponding carboxyl compounds.^{2,10)}

Although there have been several studies^{1,5,6)} devoted to preparation of the corresponding aldehydes, these processes have not been commercially successful. It seems to be a common feature that a coke (carbonaceous material) forms on the catalyst, reducing the oxidizing ability of the catalyst.

In our previous works,^{6,8,9)} we found a favorable catalyst in industry for the oxidation of *p*-methoxytoluene (PMT) to *p*-anisaldehyde (AA), and revealed information on the heat balance in a scale-down version of the expected final plant.

In the present paper, we develop the study of its kinetics, which should be industrially quite important.

1. Experiments

A metal-supported catalyst was prepared by a conventional impregnation method.⁶⁾ The active agents of the catalyst were V₂O₅, P₂O₅, K₂SO₄ and CuO at molar ratio 1:0.6:2:0.2, and the support was α -alumina particles of 3 mm ϕ having a BET surface of 37 m²/kg. The catalyst comprised 7.3 wt% of the active components supported on the α -alumina.

The kinetic experiments were conducted in a packed tube reactor made of 304 stainless steel, of 28.4 mm i.d. and 1.5 m height. The reactor was immersed in a fluidized sand bath which was used as the cooling medium for an exothermic reaction inside the tube reactor. The normal charges of active catalyst were 0.16, 0.32 and 0.56 kg, and the active catalyst was sandwiched between two inert packing layers as shown in Fig. 2. Air containing 0.73 vol% PMT was fed to the reactor at a total flow rate of 0.96 kg/(m²s). Since the pressure drops between inlet and outlet of the catalyst bed were about 5 to 14 kPa, isobaric operation throughout the bed was assumed. All the kinetic data were measured after steady state was reached. The experimental procedures and the gas

chromatographic analysis of the reactant and products are described elsewhere.^{8,9)}

The coke content on catalyst was measured by the thermogravimetric system.

2. Product Distribution and Reaction Scheme

The major products of PMT oxidation were AA and CO₂, and the minor products were formaldehyde, maleic acid and several unknown carboxylic acids.

Figure 1 shows the effect of process time on PMT conversion and AA yield at an operating condition. There was almost no change in catalyst activity after 10 days' operation. Separate experiments revealed that the coke content on the catalyst was kept at about 0.05 to 0.06 wt% all through the process time. Presumably, coke formation and coke combustion occur simultaneously and a quasi-stationary state is established after 10 days' operation.

On the other hand, increasing PMT feed concentration of more than 0.8 vol% decreased the conversion and AA yield with time. For instance, when using 0.83 vol% of PMT feed concentration, the coke content on the catalyst was 0.078 and 0.098 wt% at 11 and 20 days of process time, respectively. The catalyst particles used for 20 days were very fragile and showed preferential coking on the surface. This indicates catalyst decay caused by coke.

To remove the effect of coke on reaction kinetics, therefore, all the experiments were performed at a PMT feed concentration of 0.73 vol%, the most profitable for industrial operation.

Figures 2 and 3 are typical examples of axial temperature and concentration profiles at two different sand bath temperatures. The increase in CO₂ is almost linear with the axial distance, while the increase in AA is rapid near the inlet of the catalyst bed and very modest near the outlet. Based on such behavior, the reaction scheme shown in Fig. 4 was postulated.

3. Kinetic Model

Kinetic models for the oxidation of hydrocarbons are usually expressed by the Hougen-Watson for-

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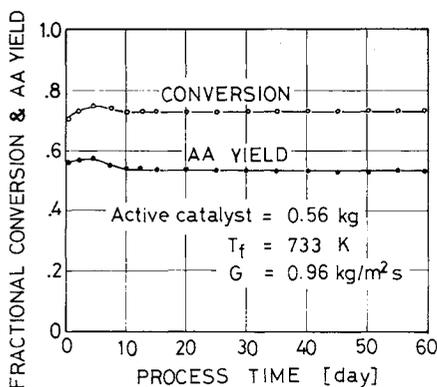


Fig. 1. Effect of process time on PMT conversion and AA yield.

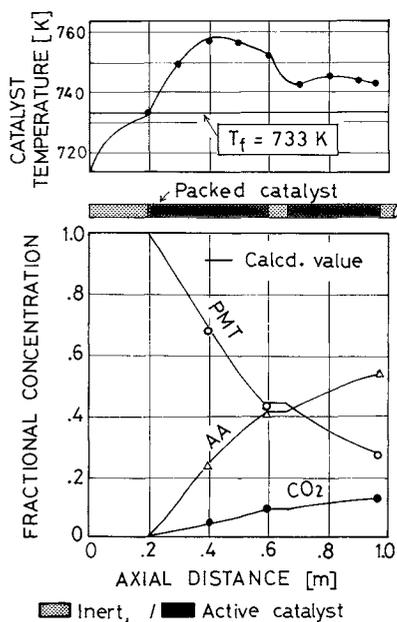


Fig. 2. Temperature and concentration profiles for $T_f = 733$ K.

mulation.⁴⁾ However, the reaction treated here was performed under a condition of very large excess of oxygen and high superficial gas velocity with a catalyst of very low surface area. In addition, the effectiveness factor could be assumed to be unity because in experiments using two sizes of catalyst particles, 3 mm ϕ and 5 mm ϕ , these two reaction rates were the same within an error of 5%. It may be natural, therefore, to use a simplified one-dimensional homogeneous model.³⁾ Consequently, the material balance can be written as follows:

$$-u_o(dy_P/dZ) = (k_1 + k_2 + k_4)y_P \quad \text{(PMT disappearance)} \quad (1)$$

$$u_o(dy_A/dZ) = k_1 y_P - k_3 y_A \quad \text{(AA formation)} \quad (2)$$

$$u_o(dy_C/dZ) = k_2 y_P + k_3 y_A \quad \text{(CO}_2 \text{ formation)} \quad (3)$$

$$y_P = 1.0 \quad \text{and} \quad y_A = y_C = 0 \quad \text{(at } Z = 0) \quad (4)$$

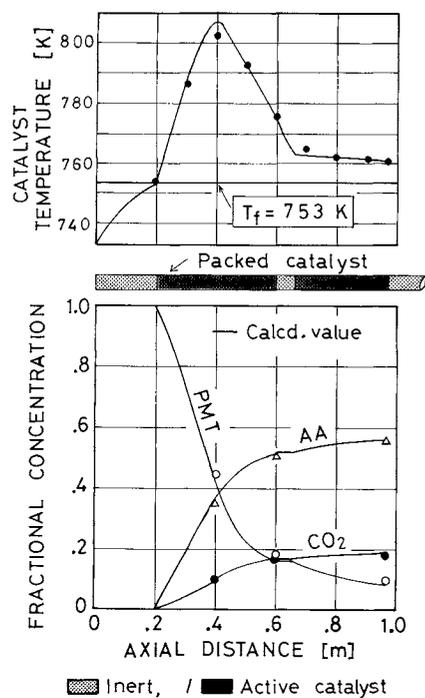


Fig. 3. Temperature and concentration profiles for $T_f = 753$ K.

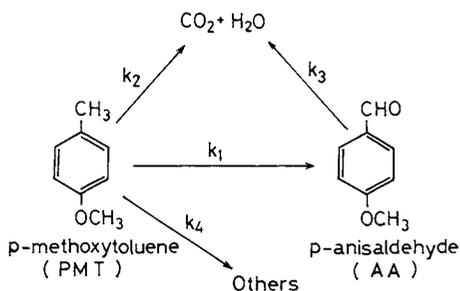


Fig. 4. Reaction scheme for oxidation of PMT.

and the heat balance can be expressed as

$$GC_{pg}(dT_g/dZ) = 4U(T_f - T_g)/d - \sum_j r_j \Delta H_j \quad (5)$$

4. Parameter Estimation at Steady State

To estimate adequate kinetic parameters under temperature profiles along bed height, we assumed that the rate constants vary with temperature according to the Arrhenius-type equation

$$k_i = \exp(S_i - \Delta E_i/RT) \quad (i = 1, 2, 3, 4) \quad (6)$$

First, eight unknown parameters in Eq. (6) were estimated from the set of Eqs. (1) to (4) by using the observed temperature profiles along bed height. The criterion, in this case, was that the function (ϕ) of Eq. (7) should be a minimum.

$$\phi = \sum_j \sum_i^N (y_{j, \text{obs}} - y_{j, \text{cal}})^2 \quad (j = P, A, C) \quad (7)$$

where the suffixes "obs" and "cal" denote the ob-

served and calculated values, respectively.

The minimization was performed by the Sequential Simplex method,⁷⁾ and the parameters estimated are listed in Table 1.

There are still five unknown thermodynamic parameters, U , ΔH_1 , ΔH_2 , ΔH_3 and ΔH_4 , in Eq. (5). The values of ΔH_1 , ΔH_2 and ΔH_3 were calculated from the change in enthalpies of formation of compounds and the remaining two unknown parameters U and ΔH_4 were estimated from the set of Eqs. (1) to (6). These thermodynamic parameters are listed in Table 1.

The solid lines in Figs. 2 and 3 represent the calculated values based on Table 1. The slight difference between observed and calculated data in Fig. 3 are caused by the neglect of thermal axial dispersion effect.

5. Application of Reaction Kinetics to a Multitubular Packed Bed Reactor

As is obvious from Figs. 2 and 3, the inert layer inserted between two active catalyst layers plays an important role in the cooling of reactant gas. Some trials replacing the position of the inert layer have been carried out in a multitubular packed bed reactor consisting of 52 tubes⁹⁾ at a sand bath temperature of 733 K. The life span of the catalyst was made longer than six months by placing the inert layer from 0.36 to 0.42 m in axial distance to compensate for a local high temperature along the bed height. In these trials, the temperature and concentration profiles could be explained by the kinetics presented here for the first three months, while for the remaining three months, the selectivity of AA gradually decreased.

According to the calculations based on Table 1, k_1 and k_4 were almost unchanged for six months, while k_2 and k_3 increased about 1.2 times during the final three months. This is caused by the sintering and partial dispersion of the catalytic agents owing to high temperature.

Conclusions

The catalyst decay depended on the PMT feed concentration. A concentration of more than 0.8 vol% was unsuitable because of catalyst decay due to successive coke deposits. However, in the case of a feed concentration of 0.73 vol% the catalyst maintained its activity at a constant level for a long period without successive coke deposits.

A kinetic model was developed from the product distribution, and the kinetic and thermodynamic parameters were determined on the assumption of a one-dimensional homogeneous model. The parameters obtained were useful for the interpretation of all the experimental data, and were made available for

Table 1. Estimated kinetic and thermodynamic parameters

k_i value [1/s]	r_i [mol/(m ³ s)]
$k_1 = \exp(15.09 - 88509/RT)$	$r_1 = k_1 y_P C_P^0$
$k_2 = \exp(11.10 - 81852/RT)$	$r_2 = k_2 y_P C_P^0$
$k_3 = \exp(19.28 - 124850/RT)$	$r_3 = k_3 y_A C_P^0$
$k_4 = \exp(29.25 - 185090/RT)$	$r_4 = k_4 y_P C_P^0$

$\Delta H_1 = -222$ kJ/mol, $\Delta H_2 = -4354$ kJ/mol, $\Delta H_3 = -4132$ kJ/mol,
 $\Delta H_4 = -628$ kJ/mol, $U = 78.4$ W/(m²K)

the design of an expected final plant.

Nomenclature

C_P^0	= initial concentration of PMT	[mol/m ³]
C_{pg}	= specific heat capacity of air	[J/(kg·K)]
d	= inside diameter of reactor tube	[m]
ΔE_i	= activation energy for reaction i	[J/mol]
G	= total flow rate based on cross-section area of tube	[kg/(m ² s)]
ΔH_i	= heat of reaction for reaction i	[J/mol]
k_i	= first-order kinetic constant of the reaction i ($i = 1, 2, 3, 4$)	[1/s]
N	= number of sets of discrete data	[—]
R	= universal gas constant	[J/(mol·K)]
r_i	= elementary rate based on catalyst volume	[mol/(m ³ s)]
S_i	= logarithm of pre-exponential factor for reaction i	[—]
T_f	= temperature of fluidized sand bath	[K]
T_g	= reactant gas temperature inside tube	[K]
U	= overall heat transfer coefficient between packed bed and fluidized sand bath at internal tube surface	[W/(m ² K)]
u_0	= superficial velocity of gaseous mixture based on empty tube	[m/s]
y_j	= fractional concentration of component j on a carbon-accounted-for basis	[—]
Z	= axial distance	[m]
<Subscripts>		
A	= <i>p</i> -anisaldehyde	
C	= carbon dioxide (CO ₂)	
P	= <i>p</i> -methoxytoluene	

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