Kinetics of *iso*-Propanol Oxidation Catalyzed by TS-1 Membrane Reactor

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Titanium silicalite-1 (TS-1) tubular membrane was used as a catalytic active membrane reactor in the oxidation of *iso*-propanol with hydrogen peroxide. The TS-1 membrane prepared at 150°C showed the highest catalytic activity with the conversions above 90%. The kinetic parameters of the reaction were calculated and a simple column mathematical model was used to describe the catalytic activity of the membrane reactor.
Key words: Zeolite membrane, Titanium silicalite-1, Membrane reactor, Catalysis, Kinetics

1.INTRODUCTION

Titanium silicalite-1 (TS-1) zeolite is known to be an efficient catalyst for selective oxidation of organic. It had been employed in industrial processes of phenol hydroxylation [1]. Most of reports to date were emphasized on optimizing the synthesis route and improving the catalytic activity of TS-1 powder. However, two separation processes, catalyst separation from batch solution and product separation from substrates, were necessary in the case of TS-1 powder as catalyst. But if TS-1 membrane is used as membrane reactor, the catalysis reaction will occur in membrane layer when the reactants cross through the membrane layer from feed side to permeate side under the driving force of pressure and concentration gradient, the product will be obtained in the permeate side. Compared with TS-1 powder, the advantage of TS-1 membrane reactor is that the catalysis and separation processes are realized in a unit.

There are few reports on the supported TS-1 membranes. The TS-1/PDMS hybrid membrane prepared by filling TS-1 powders into organic PDMS membrane showed the catalytic activity and separation property [2-4]. TS-1 membrane prepared on a porous support by seeded growth method has no gas separation property [5].

To prepare supported TS-1 membrane by `in situ` method is a real challenge due to the difficulty in controlling the nucleation and crystallization on porous support. Our group has devoted to the preparation of TS-1 membrane for years. Nowadays, TS-1 membranes with catalytic activity for some oxidation reaction have been successfully prepared by hydrothermal thermal and microwave method [6-8].

The objective of this work was to investigate the catalytic kinetics of TS-1 membrane reactor for the oxidation of *iso*-propanol (IPA). To achieve this, TS-1 membranes were prepared, and the effects of reaction parameters were studied.

2. EXPERIMENT

TS-1 membranes were hydrothermally prepared on 10cm long tubular mullite supports (Nikkato, 12mm outer diameter, 1.5mm thickness and 1.3μm average pore size). Two series of membranes were prepared. The first series were achieved by crystallizing the synthesis gel with molar composition of SiO_2: (0.01-0.03) TiO_2: 0.35TPAOH: 28H_2O at 150, 160 and 170°C for certain time. They were coded as M1(T/t-X). T represents crystallization temperature, t crystallization time, and X the molar ratio of TiO_2/SiO_2 in synthesis gel. The second series were obtained by crystallizing the synthesis gel with molar composition of SiO_2: (0.003-0.02) TiO_2:0.17TPAOH: 120H_2O at 185°C for 48h. They were coded as M2(T/t-X), T, t and X have the same meaning as above. Tetraethyl orthosilicalite, titanium n-butoxide and Tetrapropylammonium hydroxide (TPAOH) were used as silicon, titanium sources and template, respectively After hydrothermal crystallization, the samples were took out from the autoclave, washed and dried, and then were calcined in air at 500 °C for 30 h.

X-ray diffraction (XRD) patterns of the powders and membranes were measured by a SHIMADZU XRD-6100 X-ray diffractometer with CuKα radiation. Fourier infrared (FT-IR) spectra were recorded by a JASCO FT/IR-610 spectrometer. Morphology observation was carried out with scanning electron microscopy (SEM, JEOL 6335F).

For the oxidation of IPA to acetone by TS-1 membrane reactor, the membrane was immersed in the feed solution composed of IPA, H_2O_2 and H_2O. Under the pervaporation (PV) condition, the catalysis reaction took place in membrane layer. Samples of feed and permeation were periodically analyzed by a Gas Chromatograph (SHIMADZU GC8A). The flux was calculated by weighing the permeate sample mass. The conversions of IPA was given : $C_{IPA}=(mol_{acetone})_{Permeate}/(mol_{acetone}+mol_{IPA})_{Permeate} \times 100$.

In the case of TS-1 powder, 10wt% TS-1 powder based on the mass of IPA was used. The conversion of IPA was calculated by $C=(C_i-C_t)/C_i \times 100$, C_i and C_t were the concentration of IPA at initial and time *t*, respectively.

3. RESULTS AND DISCUSSION

Characterization of TS-1 membranes: All the TS-1 membranes show the typical XRD patterns of titanium silicalite-1 [9]. FT-IR spectra of TS-1 powders collected

from the bottom of autoclave show a characteristic shoulder peak of TS-1 at about 960-970 cm^{-1} [9]. These proved that TS-1 membrane was successfully prepared.

Effect of crystallization condition: The conversion of IPA as a function of molar ratio of TiO_2/SiO_2 in synthesis gel is presented in Fig.1. The crystallization temperature and the molar ratio of TiO_2/SiO_2 have great influence on membrane catalytic activity. Lower crystallization temperature benefits to the catalytic activity. For M1 and M2 series membranes, the conversion of IPA monotonically increases with increasing molar ratio of TiO_2/SiO_2 in synthesis gel. Thus, the highest conversion of 94% was obtained in the case of M1(150/72-0.03) membrane.
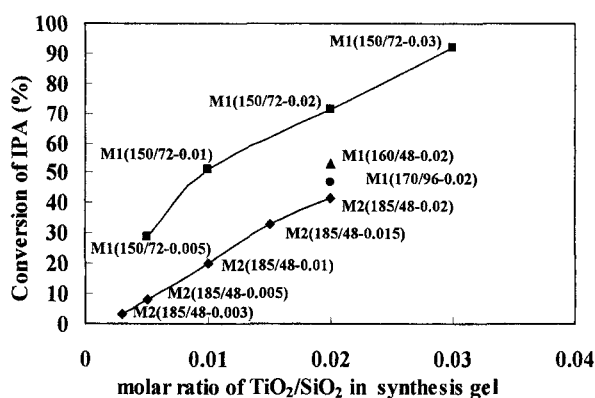

Fig.1 IPA conversion as a function of TiO_2/SiO_2 molar ratio in initial synthesis gel for M1 and M2 series membranes

Effect of reaction temperature: IPA conversion increased with increasing reaction temperature. M1(150/72-0.03) membrane exhibited higher activity than M2(185/48-0.02). The 100% IPA conversion was achieved at 55°C for 7h by TS-1 powder, and conversion of 94% was obtained for M1(150/72-0.03) membrane at 60°C for 8h. The conversion of IPA was less than 60% at 60°C after 13h for M2(185/48-0.02) membrane .

Effect of IPA/H$_2$O$_2$ ratio: The effect of IPA/H$_2$O$_2$ ratio was studied at 50°C with 10wt% of IPA concentration in reaction solution (Fig.2). When the molar ratio of IPA/H$_2$O$_2$=2:1, H$_2$O$_2$ was completely consumed after 2h in the case of TS-1 powder, and the conversion of IPA was about 33%. In the case of M1(150/72-0.03) membrane, the needed time was only 0.5h. At IPA/H$_2$O$_2$=1:1, the conversion of IPA was about 70% after 2h in TS-1 powder system, while 90% after 0.5h and 94% after 1.5h in the case of M1(150/72-0.03) membrane. At IPA/H$_2$O$_2$=1:2, IPA conversion rate was further increased, and up to 100% after 1.8h for TS-1 powder system. However, for M1(150/72-0.03) membrane, the reaction rate and conversion of IPA had nearly no change similar to the case of IPA/H$_2$O$_2$=1. This indicated that the catalyst state as powder or membrane have different influence on the catalysis process.
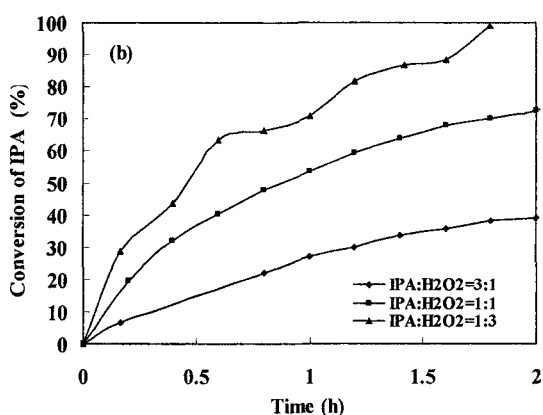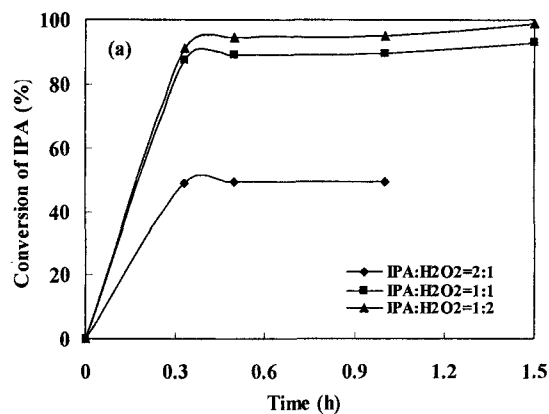

Fig.2 plots of IPA conversion versus reaction time for different molar ratio of IPA/H$_2$O$_2$ with (a) M1(150/72-0.03) membrane and (b) TS-1 powder

Apparent Kinetic parameters: The isolated method was used to obtain reaction order of IPA and H$_2$O$_2$ at 50°C in the case of TS-1 powder as catalyst. The obtained apparent reaction rate equation was

$$r=k(C^t_{IPA})^{0.84}(C^t_{H2O2})^{0.15} \qquad (1)$$

The apparent reaction activation energy and apparent reaction rate constant in the rang of 40-55°C were obtained from the fitted equation by Arrehenius method, they were $E_{app.}$= 86.1KJ/mol, k_o= 5.33×10^{13} and the correlation factor (R^2) was 0.995. In the case of M1(150/72-0.03) membrane, E_{app}=84.65KJ/mol, k_o= 8.82×10^{13} and R^2=0.953 in the range of 20-60°C. The linearity of fitted line was bad in the case of M2(185/48-0.02) membrane.

Column catalysis model: It has been known that the diffusion limitation of reactants in TS-1 pore channel decided the catalytic activity of TS-1 powder [10]. When TS-1 membrane was used under PV condition, the adsorption and desorption resistances of reactant in TS-1 channel will seriously influence its diffusion rate, and thus indirectly decide the catalytic activity. Combining all of these factors, the mathematic formulation of the reaction rate of IPA was established with the column model (Fig. 3) because the reaction occurs in the column channels of TS-1 framework structure.
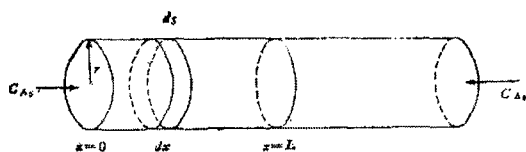
Fig. 3 illustration of column model

According 2th Fick law and the mass balance, mass transfer differential equation in dx volume can be described as:

$$-\pi r^2 D(\frac{dC_A}{dx})_x + \pi r^2 D(\frac{dC_A}{dx})_{x+dx} = \pi r^2 D\frac{d^2C_A}{dx^2}dx \quad (2)$$

$$\pi r^2 D\frac{d^2C_A}{dx^2}dx = 2\pi r dx k C_A \quad (3)$$

Boundary conditions are:

$x=0, \quad C_A=C_{Ao};$

$x=L, \quad dC_A/dx=0.$

The calculated reaction rate in channel with L dimension is:

$$\omega_L = \pi r^2 DC_{A0}\frac{h}{L}\tanh(h) \quad (4)$$

for n-order reaction, the reaction rate in unit volume catalyst is:

$$\omega = \frac{18}{d_p^2}\rho_B V_g DC_{Ao}h_n \tanh(h_n) \quad (5)$$

where $h_n = L\sqrt{\dfrac{2k_nC_{A0}^{(n-1)}}{rD}}$

d_p zeolite crystal particle size, ρ_B, stack density of TS-1 crystals in or on mullite support, V_g, specific micropore volume of TS-1 crystal which is close to that of silicalite-1 (0.19cm³/g), D, diffusion coefficient of reactant molecule in TS-1 channel; C_{A0}, initial concentration of reactant outside of zeolite pore; k_n, reaction rate constant; n, the intrinsic reaction order, r, radius of zeolite pore(0.55/2(nm)).

M1(150/72-0.03) membrane: SEM images clearly showed that the crystals ($\approx 1\mu m$) stacked loosely on or in support [6,7]. Furthermore this membrane has no separation ability for IPA/H₂O and acetone/H₂O systems under PV condition, which indicated that the mass transport was carried out by defects. In this case, the most possible factor deactivating the catalytic site is that the small amount of IPA molecule stacked on the pore opening, and thus inhibiting the reactant molecules to further enter the channel, which results in the catalyst deactivation. Here, the length of deactivation zone in zeolite channel was assumed as αL in Fig. 4.
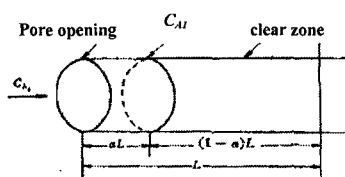

Fig. 4 illustration of deactivation in M1(150/72-0.03) membrane

The reaction rate in channel after and before deactivation are:

$$\omega_{deact} = \frac{[\pi r\sqrt{2rkD}\ \tanh[h_o(1-\alpha)]]C_{Ao}}{1+\alpha h_o \tanh[h_o(1-\alpha)]} \quad (6)$$

$$\omega_{bef} = C_{Ao}\pi r\sqrt{2\pi rkD}\ \tanh(h_o) \quad (7)$$

the catalytic efficiency is:

$$F = \frac{\omega_{deact}}{\omega_o} = \frac{1}{1+\alpha h_o \tanh[h_o(1-\alpha)]} \cdot \frac{\tanh[h_o(1-\alpha)]}{\tanh(h_o)} \quad (8)$$

in n-order reaction,

$$h_o = h_n = L\sqrt{\frac{2k_nC_{A0}^{(n-1)}}{rD}} \quad (9)$$

In experiment, $C^o_{IPA}=C^o_{H2O}\approx 1.65 mol/L$, and apparent reaction order obtained form TS-1 powder was near to 1. D belongs to the molecular with the lowest diffusion rate in the reaction solution. H₂O₂ has the similar chemophysical property to H₂O, which has much higher diffusion rate in silicalite-1 channel than that of IPA [11]. Here, the diffusion coefficient of IPA of 10^{-13} m²/s [11] was as D. The value of r was about 1μm from SEM, so the length of zeolite channel L was assumed 0.5μm in b-axis of crystals. The value of apparent k obtained from the plots of Log$r$~LogC$^t_{IPA}$ in 20-50°C was in the range of 0.1-7, which can be used as K_n in equation (9). So the the estimated value of $h_o=h_n\approx 10^5 \gg 2$, and $\tanh(h_o) \approx 1$. In this condition, equation (8) can be changed to the follows:

$$F = \frac{1}{1+\alpha h_o} \quad (10)$$

It can be deduced that only in the case of $\alpha \approx 0$, the highest catalysis efficiency would be achieved. That means that the number of IPA molecular stacking on the pore opening was low. That is, TS-1 membrane did not preferably adsorb the organic compound from water, and the concentration of organic in permeate side was near to that in feed side. PV separation experiments in the system of IPA/H₂O and acetone/H₂O just proved this, in which the concentration of organic in the permeated side was very close to that in the feed. So, this membrane exhibited high catalytic activity.

Quantitative comparison of the catalytic efficiency:
It should be noted that the values of some parameters in equation (5), which was use to describe the reaction rate, were different for M1(150/72-0.03) and M2(185/48-0.02) membranes. For both membranes, the intrinsic catalysis reaction was same, k_n and n were not changed; C_{A0} was constant in experiments. V_g and r were the constants of TS-1 crystal. D at the same experiment condition was constant. So, the reaction rate equation (5) can be changed as:

$$\omega \propto \frac{1}{d_p^2}\rho_B Dh_n \tanh(h_n) \quad (11)$$

Because $h_n \gg 2$ and $\tanh(h_n) \approx 1$, equation (11) was simplified as equation (12)

$$\omega \propto \frac{\rho_B L}{d_p^2} \quad (12)$$

For M1(150/72-0.03) membrane, the stack density ρ_B was not even from SEM observation. It was assumed that all the crystals were distributed in the column shell with 0.01cm thickness. The mass of TS-1 loaded on the support was about 0.45g, which was obtained by weighing the mass of the calcined membrane and the support, respectively. So

$$\rho_B(M1) = \frac{m}{V} = \frac{m}{\pi(r_{out}^2 - r_{int}^2)l} \qquad (13)$$

where l was the effective length of membrane, it usually was 0.63cm. r_{out}=1.2cm and r_{int}=1.19cm was support parameters. So, ρ_B *(M1)* $\approx 0.951 g/cm^3$.

For M2(185/48-0.02) membrane, the polycrystallinity dense layer was presumed as a single crystal, and ρ_B *(M2)* should be equal to the intrinsic density of crystal. Because the content of Ti in framework was much less than that of Si, the intrinsic density of TS-1 can be substituted with that of silicalite-1. It is known of 1.8g/cm³.

L represented that the effective length of zeolite channel. For M1(150/72-0.03) membrane, because the crystal size was about only 1um, it was reasonable to presume $L(M1)$=0.5um. For M2(185/48-0.02) membrane, just as the case of ρ_B, the polycrystallinity layer was considered as a single crystal. The effective length of zeolite channel that reactant molecule must pass through from feed side to permeate side was assumed as: $l=\delta A$. δ was tortuous factor for the two-dimension channel in MFI structure, and A was the thickness of polycrystallinity layer on support outer-surface. For solid catalyst δ was usually 2-4, A obtained by direct measurement was about 10-15um. When δ=2, A=10μm, $L(M2)$=20μm.

According SEM, the particle size of TS-1 crystal $d_p(M1)$=1μm for M1(150/72-0.03) membrane, and $d_p(M2)$=15μm for M2(185/48-0.02) membrane.

So $$M = \frac{\omega(M1)}{\omega(2)} = 2.97 \qquad (14)$$

Equation (14) showed that the molar or mass of obtained of acetone in permeated side in unite time for M1(150/72-0.03) membrane was 2.97 times higher than M2(185/48-0.02) membrane. This was proved by experiment. In Table I, the flux of product acetone for M1(150/72-0.03) membrane was about 2.5-3.5 times of M2(185/48-0.02) membrane. So the established reaction rate equation (5) based on column model can explain the experiment results.

Table I. the catalysis performance of TS-1 membrane under PV condition*

Membrane	Total flux(kg/m²h)	Acetone flux(kg/m²h)	Conversion of IPA(%)
M2-1	0.64	0.046	67
M2-2	0.61	0.036	64
M1-1	1.13	0.117	94
M1-2	1.17	0.117	92
M1-3	1.36	0.128	91

*Catalysis condition: 10wt% IPA solution, molar ratio of IPA/H₂O₂=1, $T_{reaction}$= 50°C.

4.CONCLUSION

Supported TS-1 membrane was prepared by `in situ` hydrothermal treatment method. Oxidation of iso-propanol was selected as probe reaction to test the catalytic activity of the obtained membranes. TS-1 membrane prepared at 150 °C showed the highest catalytic activity with the conversions above 90%, while TS-1 membrane prepared at 185°C had relatively low catalyyic activity. A column mathematical model was used to describe the discrepancy of catalytic activity between these two series membranes.

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