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Catalytic degradation of ethanol in an electric field

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ABSTRACT

We investigated novel catalytic reaction systems which were activated by an electric field. This is the first report for the synergetic effect of catalyst and electric field. These catalytic systems showed very high activity compared to conventional catalytic reaction systems. Although Pt supported on CeO_2 catalyst without an electric field showed no activity at 473 K, the addition of an electric field to the catalyst promoted the degradation of ethanol. Pt/CeO_2 catalyst was activated by the electric field and synergetic effect of Pt catalyst and electric field was observed. Thermal analyses showed that about 5–10% of input electrical power was wasted as a heat and about 90–95% was consumed for the endothermic reaction. Catalytic reactions in an electric field proceed under mild conditions and show a quick response.

1. Introduction

Most catalytic reactions require high temperatures for activation of reactant molecules. In relation to high-temperature catalytic processes, many problems exist such as deactivation of the catalyst and difficulty in using waste heat at low temperatures after heat exchange. That heat loss is part of the reason for depression of the total energy efficiency of chemical processes. For small commercial devices without a heat exchanger, waste heat cannot be recovered, thereby decreasing the total energy efficiency. Furthermore, for large chemical plants, wasted heat of high temperatures is recoverable using a heat exchanger, but wasted heat of temperatures lower than 573 K is difficult to recover. Therefore, low-temperature catalytic processes that function at lower temperatures such as 573 K are promising processes for high-energy efficiency.

We investigated catalytic reactions in an electric field as novel chemical processes to solve such problems. So far there has been no report for the hybrid process of an electric field and catalyst. As a utilization of electric power together with the catalyst, there are many reports. Hybrid reaction of the non-equilibrium plasma and catalyst is one such process. The reaction activates reactant molecules using electrons instead of application of heat [1]. So, it is expected to provide novel features such as lower reaction temperatures than existing catalytic reactions and higher conversion.

Various studies have examined for catalytic reactions in such plasma. Combined reactions of solid catalyst with DC corona [2–8], AC plasma [9], microwave plasma [10–17] were studied by many researchers. Some of these reported an interaction of the catalyst and active radical species supplied by the non-equilibrium plasma. Arc discharge and glid (or gliding) arc discharge are well known plasma reaction which has high efficiency, but the gas phase temperature is as high as 2000 K or much. So the combination of catalyst and arc/glid arc is impossible. Furthermore, as for other applications of an electricity for catalytic reactions, some other methods were reported such as electrically heated catalytic reactions [18–20], application of resonance oscillation of acoustic waves on the catalyst [21,22], and so on. So far, catalytic reactions in dense energetic field such as plasma and high-voltage electric fields were examined using various methods, but these have lower energy efficiency due to their high consumption of electric energy.

We have investigated catalytic reactions in an electric field (without plasma or electrical discharge) as a novel chemical process. The electric field requires less energy than a non-equilibrium electrical discharge, the reaction proceeds in milder conditions. We investigated catalytic degradation of ethanol in an electric field intended to increase catalytic activity in the low-temperature region.

Using ethanol as a reactant, we can obtain some information related to the respective mechanisms for activation of several bonds: C–C, C–O, O–H, and C–H:

$$C_2H_5OH \rightarrow CO + CH_4 + H_2, \quad \Delta H = 49.76\ \mathrm{kJ\,mol^{-1}} \qquad (1)$$

Ethanol is receiving much attention for use as an alternative fuel. Actually, ethanol can be produced easily through fermentation of biomass carbohydrates. For that reason, ethanol is anticipated as a clean energy source offering many possibilities. Furthermore, development of the effective use of ethanol as a fuel

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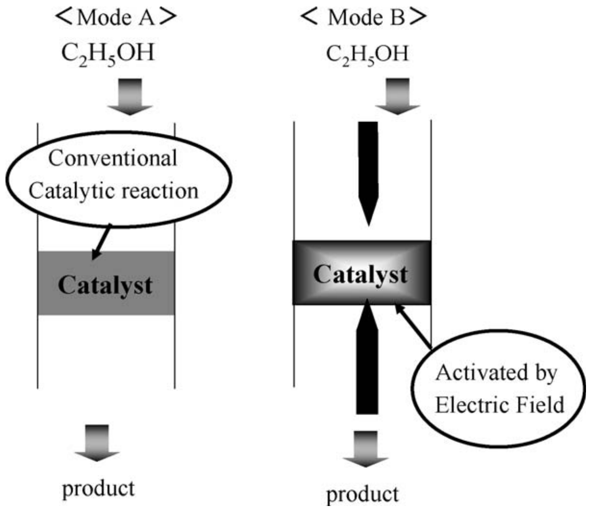

Fig. 1. Schematic depictions of conventional catalytic reaction (Mode A) and a catalytic reaction in an electric field (Mode B).

is necessary considering the prospect of higher petroleum prices. More effective use of ethanol than simple combustion can be achieved through endothermic degradation of ethanol using low-temperature wasted heat. The thermal energy efficiency of the reaction can be improved by performing degradation at low temperature using waste heat.

In this study, by applying an electric field, we intended to achieve lower reaction temperatures and higher conversion than those of existing catalytic processes. Furthermore, effects of an electric field on the catalytic reaction were investigated using a reaction of ethanol decomposition. The conventional catalytic reaction (Mode A) and catalytic reaction in electric field (Mode B) were performed in this study. Schematic images of reaction systems used for this study are presented in Fig. 1.

2. Experimental

For use as the catalyst, we prepared several Pt catalysts supported on some oxides; among them, Pt catalyst supported on CeO_2 showed higher activity for the ethanol decomposition (shown in Supporting Information 1). Therefore, 5 wt% Pt/CeO_2 was used as the catalyst. The catalyst was prepared by impregnation. First, CeO_2(JRC) was soaked in distilled water, stirred and deaerated for 2 h at room temperature. Then, an aqueous solution of tetraamine-platinum(II) nitrate was added and stirred for 2 h. After evaporation to dryness, it was calcined at 973 K and crushed into particles of 355–500 μm.

In all experiments, a quartz tube was used as a flow-type reactor, as depicted in Fig. 2. Two stainless steel rods (2.0 mm o.d.) were inserted from each end of the quartz tube (4.0 mm i.d. and 6.0 mm o.d.) as electrodes for applying an electric field in the catalyst bed. In both cases of Mode A and Mode B, 100 mg of catalyst was charged in the quartz reactor. The catalyst was pretreated in situ in a hydrogen flow at 673 K before the reaction. Ethanol was supplied using a chemical pump (0.5 mmol min^{-1}), evaporated in a preheating zone (423 K), and carried into the reactor through a gas line (393 K) with Ar (40 cc min^{-1}). After the reaction, product gases were analyzed after passing a cold trap (2-butanol) using GC-FID and GC-TCD. For this study, conversion was calculated from product gases in each reaction:

$$\text{Conversion }(\%) = \frac{\text{Output carbon atoms in product gases (mol)}}{\text{Input carbon atoms in ethanol (mol)}} \times 100$$

Selectivity and carbon-based selectivity were defined as presented below:

$$\text{Selectivity }(\%) = \frac{\text{Product species (mol)}}{\text{Total of product gases (mol)}} \times 100$$

$$\text{C base selectivity }(\%) = \frac{\text{Carbon number} \times \text{product species (mol)}}{\text{Overall carbon number of product gases}} \times 100$$

A DC high-voltage power supply was used to generate the electric field in the catalyst bed. Changing input current controlled the electric field was controlled.

To observe the effects of heat generated by impressing an electric field, a thermograph (TH6200R; NEC San-ei Instruments Ltd.) was used to measure the catalyst bed temperature. Quartz, used as a reactor wall, does not enable infrared rays to penetrate well. For that reason, we measured the reactor skin temperature using a thermograph. We measured the reactor's inner temperature using a thermocouple. The correlation between the surface temperature and the inner catalyst bed temperature is presented in Supporting Information 2 and 3. The electrical power consumption applied to the electric field was measured and calculated using a digital oscilloscope (TDS3052B; Tektronix Inc.).

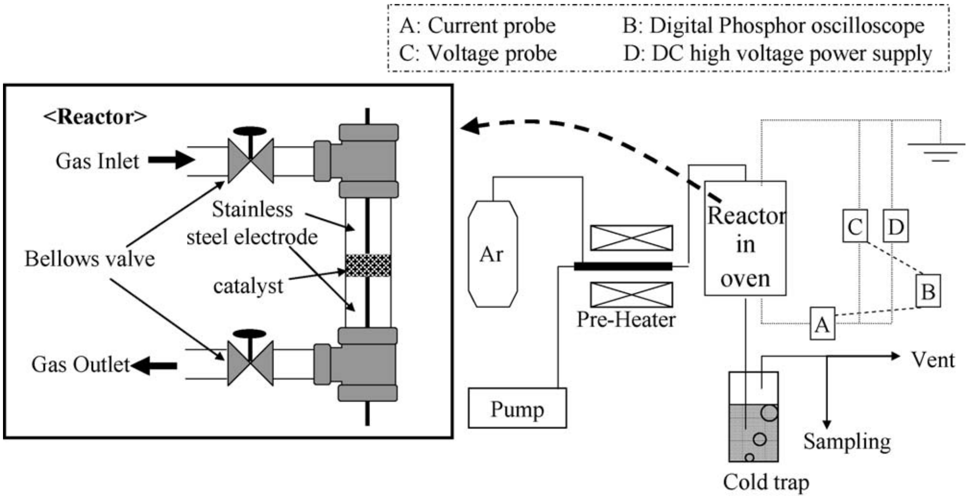

Fig. 2. Reaction apparatus.

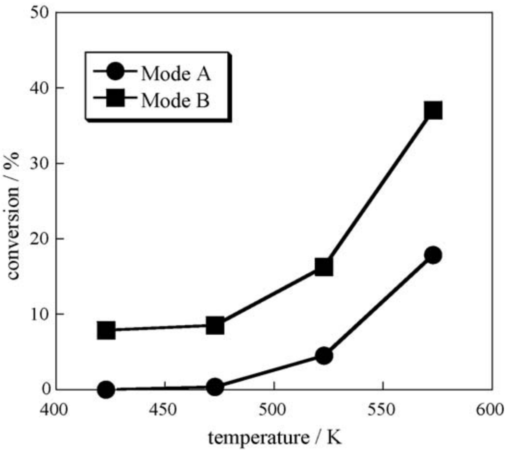

Fig. 3. Effects of the electric field for ethanol degradation at various temperatures with 5 wt% Pt/CeO_2 catalyst.

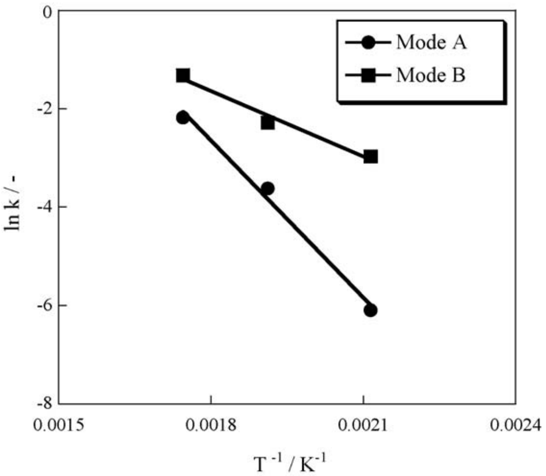

Fig. 4. Arrhenius plot for the degradation of ethanol with and without an electric field.

3. Results and discussion

3.1. Effect of electric field on the catalytic reaction

First, we examined the effect of application of an electric field on catalytic degradation of ethanol. In these experiments, the catalyst bed height was 4 mm, and the gap distance of each electrode was 5 mm, so the catalyst bed did not contact with the upper electrode (not electrified in the catalyst bed because of a disconnected circuit).

Fig. 3 portrays ethanol conversion by the catalytic reaction without an electric field (Mode A) and by the catalytic reaction in the electric field (Mode B) under various temperatures. From Fig. 3, conversion of Mode A was 0.0, 0.4, 4.5, and 17.8%, at 423, 473, 523, and 573 K, respectively, and conversion of Mode B was 7.7, 8.8, 16.2, and 37.1%. Consequently, in the presence of an electric field, conversion increased at all temperatures. Conversion of Mode B at 423 K was close to the conversion of Mode A at about 525 K. Therefore, the electric field can decrease the reaction temperature by about 100 K.

We presume that ethanol degradation is a first-order reaction, because it is catalytic pyrolysis of uni-molecule. On the basis of this assumption, the reaction rate constant (LHSV base) of each reaction mode was calculated. Fig. 4 shows an Arrhenius plot of each reaction mode. From the slope of each plot, the activation energy was calculated. The activation energy of Mode A was about 89 kJ mol^{-1}; that of Mode B was about 36 kJ mol^{-1}. Therefore, the electric field depressed activation energy by about 53 kJ mol^{-1} in this reaction.

Table 1 depicts the product distribution of each reaction mode. The product distribution of Mode B resembles that of Mode A, but it is slightly different. The main products of this reaction are hydrogen, CO, methane and CO_2. As byproducts, trace amount of C2 hydrocarbons and trapped some liquid products (not analyzed) were generated.

Presuming that this reaction proceeds as a theoretical equation, the product distribution ratio of hydrogen and CO and methane was 1:1:1. However, the product distribution in this research is hydrogen-rich against the theoretical ratio. That result suggests that a liquid component, such as that of acetaldehyde in a liquid trap at the end of reactor (not analyzed in this research), was generated. Mostly, methane and CO were 1:1 in the results.

The waveform in Mode B was observed using a digital oscilloscope (shown in Supporting Information 4). Respective profiles of current and voltage were flat. The voltage applied to the gap for the electric field was about 150 V. We measured the consumption of electricity using an oscilloscope, and it was 404–662 mW (shown in Table 2). Consequently, Mode B proceeded under very mild conditions from these data.

From the standard enthalpy of combustion of products, the total endothermic reaction enthalpy was calculated by following equation:

$$\text{Endothermic reaction enthalpy } (\mathrm{J\,min^{-1}}) = \sum \Delta_C H \ (\text{product}) - \Delta_C H \ (\text{reactant})$$

Table 2 shows the electric energy consumption, the endothermic reaction enthalpy and the difference of enthalpy between

Table 1
Formation rates of products and selectivity to products on the catalytic degradation of ethanol without (Mode A) and with (Mode B) an electric field.

Temperature/K	Mode A				Mode B			
	H_2	CO	CH_4	CO_2	H_2	CO	CH_4	CO_2
Formation rate/mmol min^{-1}								
423	0.007	0.000	0.000	0.000	0.098	0.033	0.037	0.009
473	0.028	0.000	0.004	0.000	0.108	0.035	0.042	0.008
523	0.1	0.018	0.024	0.004	0.169	0.067	0.081	0.014
573	0.2	0.074	0.090	0.014	0.319	0.153	0.182	0.036
Selectivity/%								
423	100.0	0.0	0.0	0.0	55.3	18.5	21.0	5.1
473	87.6	0.0	12.4	0.0	56.0	18.2	21.9	4.0
523	63.5	14.2	19.2	3.1	50.9	20.4	24.4	4.4
573	50.4	20.7	25.0	4.0	46.2	22.1	26.4	5.2

Table 2
Energy balances on the catalytic degradation of ethanol under various temperatures with/without electric field.

Temperature/K	Conversion/%	Electric power/mW	E_1[a]/J min^{-1}	E_2[b]/J min^{-1}	ΔE_{ef}[c]/J min^{-1}
Without an electric field					
423	0.0	0	0	2.0	
473	0.4	0	0	8.9	
523	4.5	0	0	24.1	
573	17.8	0	0	36.3	
With an electric field					
423	7.9	662	39.7	16.3	14.3
473	8.5	473	26.2	20.0	11.1
523	16.3	428	25.7	28.1	4.0
573	37.1	403	24.2	43.1	6.8

[a] E_1 is the consumption of electric power (converted from mW to J min^{-1}).
[b] E_2 is the endothermic reaction enthalpy ($=\sum\Delta H_{products} - \Delta H_{reactant}$).
[c] ΔE_{ef} is the difference of $E_{2(\text{without electric field})}$ and $E_{2(\text{with electric field})}$ at the same temperature, i.e., at 573 K, 6.8 = 43.1 − 36.3.

"with" and "without an electric field". The differences of reaction enthalpy with/without an electric field were 14.3, 11.1, 4.0, 6.8 J min^{-1} at 423, 473, 523, 573 K, respectively, where the electric energy consumptions were 39.7, 26.2, 25.7, 24.2 J min^{-1} at each temperature. Table 2 shows that endothermic enthalpy increases concomitantly with the temperature increase.

Thermal balance analysis was performed using a thermograph with the working curve of surface temperature of quartz tube and inner bed temperature. Impressing an electric field, the surface temperature of the quartz tube increased slightly, and the observed increase of the catalyst bed temperature was about 5–10 K, as presented in Supporting Information 2 and 3.

From the temperature of the catalyst bed and working curve, the electric power used for heating the catalyst was calculated for various temperatures and input powers. About 5–10% of input power was wasted in heating and about 90–95% was consumed in the reaction, as shown in Supporting Information 5. The result shows that, in Mode B, the effect of direct heating of the catalyst is very small; most of the consumed electric power might be a dark current by electrical conduction (dark discharge), which enhanced catalytic activity.

A cyclic turning on and off test of impressing electric field for 20 min in the conventional catalytic reaction at 523 K was examined to investigate the responsiveness of Mode B. Fig. 5 shows the conversion of ethanol under the cyclic turning on and off condition; Fig. 6 portrays the product distribution. In Figs. 5 and 6, ON represents impressing of an electric field (equal to Mode B) and OFF represents not impressing the electric field (equal to Mode A).

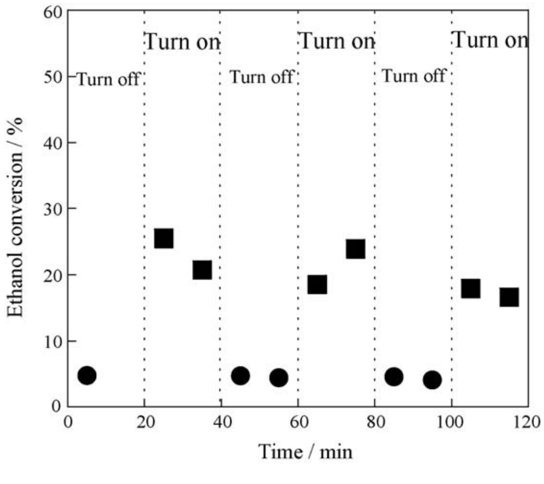

Fig. 5. Cyclic turning on and off test for the electric field at 543 K with 5 wt% Pt/CeO_2 catalyst.

Fig. 5 shows that conversion was about 20% while the electric field was impressed and about 5% when the electric field was not impressed. Conversion switched into each reaction mode as the electric field was turned on. From Fig. 6, selectivity to products also switched into each reaction mode as the electric field turned on. Regarding the switching impression of the electric field, negative effects on the reaction, such as deterioration of catalytic activity and the catalyst itself, were not observed. These results show that Mode B has quick response with impression of an electric field. As described above, we examined the products only for H_2, CO, CO_2, CH_4, and C2 hydrocarbons. The cyclic turning on and off results demonstrate that the hydrogen to CO or CH_4 ratio becomes close to 1 in the turning on condition, which indicates the decrease of the formation of dehydrogenated products trapped in the liquid trap.

3.2. Effect of input current

In reaction Mode B, effects of changing of the input current at the same temperature as the controlling parameter of an electric field were examined. At 573 K, three patterns of reaction at no current (Mode A) and 3.0 and 8.0 mA of current in Mode B were examined for the time course of 90 min. Impressing of an electric field was started at 0 min in each run. The results are shown in Fig. 7: the conversions on reaction patterns were about 16% at 0.0 mA, about 30% at 3.0 mA, about 45% at 8.0 mA. Regarding Mode B, increasing the input dark current (by dark discharge) promotes the catalytic degradation of ethanol.

These trends suggest that the input dark current is an important parameter to enhance catalytic activities. Increased input current means increased dark current and the number of electrons in the reaction field from the observation with an oscilloscope. Therefore,

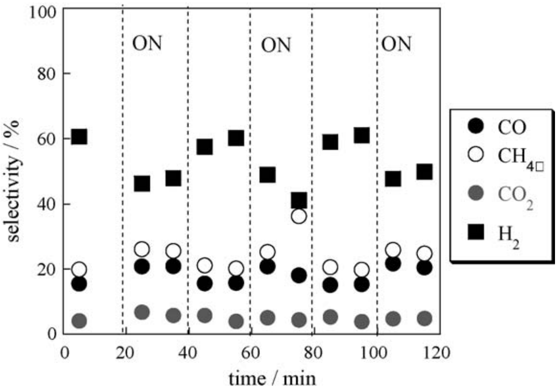

Fig. 6. Selectivity to products under the cyclic test (corresponding to Fig. 5).

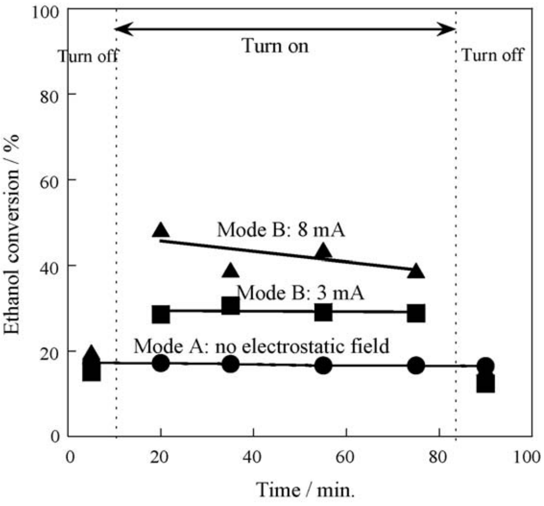

Fig. 7. Effect of the input dark current on ethanol degradation in an electric field.

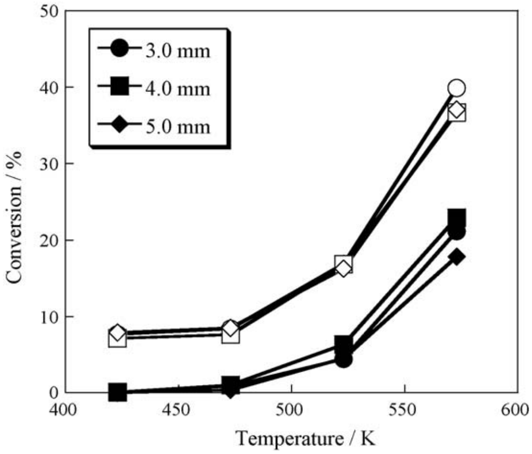

Fig. 8. Effect of the gap distance on catalytic degradation of ethanol in an electric field: for closed symbols: Mode A; open symbols: Mode B.

catalytic conversion was promoted in the electric field. The reason for the promoting effect is still unclear.

3.3. Effect of gap distance

To examine the effects of gap distance, three patterns of reaction, with gap distances of 3.0, 4.0, and 5.0, were obtained. Fig. 8 portrays ethanol conversion for each gap distance condition. The catalyst bed height was 4 mm in this study. Therefore, the relation of the upper electrode and catalyst bed was changed by the gap distance. For 3.0 mm, the upper electrode was embedded in the catalyst bed. For 4.0 mm, the upper electrode contacted the top surface of the catalyst bed. For the case of 5.0 mm, the upper electrode did not touch the catalyst bed. Lower electrode was in contact with the bottom-end of catalyst bed for all the conditions.

Fig. 8 shows that conversions for all patterns of gap distances exhibit the same trend. The conversions of Mode B were, respectively, about 7, 8, 16, and 36% at 423, 473, 523, and 573 K. These results show that these synergetic effects of the catalyst and electric field are unaffected by the gap distance.

4. Conclusions

We investigated catalytic degradation of ethanol in an electric field intended to increase catalytic activity in a low-temperature area. In the presence of an electric field, ethanol conversion increased at all temperatures.

Thermal analyses showed that about 5–10% of input power was wasted heat and about 90–95% was consumed in the endothermic reaction. Results suggest that, in catalytic reactions in an electric field, the dark current by an electric field enhanced catalytic activity, not only the effects of heating. Catalytic reactions in an electric field proceed under mild conditions and show a quick response.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cattod.2009.03.027.

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