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Influence of precursors on the catalytic activity of alumina for bio-ethanol dehydration in microchannel reactors

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Abstract: In this paper, the catalytic activity of alumina for bio-ethanol dehydration was studied in a microchannel reactor. Five catalysts were prepared from precursors with different ratios of AlOOH (pseudo boehmite) and $Al(OH)_3$ (bayerite). The physicochemical properties of catalysts were characterised by X-Ray Diffraction (XRD) and Temperature Programmed Desorption (TPD). The influence of reaction temperature and space velocity was investigated. The results show that the catalyst prepared from precursor with AlOOH 46.3 mol% has the highest ethanol conversion and ethylene selectivity. An ethylene yield of 18.28 $g/(g_{cat}\cdot h)$ can be achieved, implying that the dehydration process can be intensified using microchannel reactors.

Keywords: activated alumina; precursor; bio-ethanol dehydration; microchannel reactor; global warming.

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1 Introduction

Ethylene is one of the major feedstock for the petrochemical industry and is derived mainly from steam-reforming of petroleum and natural gas. However, nowadays, with the shortage in natural resources and energy, and also with the skyrocketing prices of crude oil, production from a nonpetroleum, environment-friendly feedstock and development of novel, efficient ethylene production processes are considered as challenging research areas (Gucbilmez *et al.*, 2006; Pereira, 1999). Bio-ethanol is an attractive alternative feedstock for producing ethylene. It has many positive features with regard to the environment, and a majority of studies agree that compared to fossil fuels, bio-ethanol can decrease global warming and CO_2 emissions (von Blottnitz and Curran, 2007) because CO_2 gas can be recycled by growth of plants (Demain, 2009). Recently, researchers have suggested that bio-ethanol can offer more obvious and sustainable global warming advantages by utilising lignocellulosic materials and forest and agriculture residues (Petrou and Pappis, 2009), removing straw (Gabrielle and Gagnaire, 2008) as a raw material, avoiding the cultivation of energy plants on land rich in carbon, implementing a more integrated technology system production, efficiently utilising by-products (Borjesson, 2009; Petrou and Pappis, 2009) and increasing process efficiency.

The development of an efficient catalyst is the foundational and crucial step for heterogeneous catalytic reactions. In order to improve the efficiency of ethylene production via the catalytic ethanol dehydration process, catalysts with higher activity should be developed. Up to now, a large number of catalysts have been studied, which mainly consist of alumina or doped alumina (Bakoyannakis *et al.*, 2001; Clayborne *et al.*, 2004; Domok *et al.*, 2007; Golay *et al.*, 1999; Mitsuo *et al.*, 1981), zeolite (Nguyen and Le Van Mao, 1990; Oudejans *et al.*, 1982), alkali metal oxides or transition metal oxides (Berteau and Delmon, 1989; Di Cosimo *et al.*, 1998; El-Katatny *et al.*, 2000; Zaki, 2005), metal phosphate (Wan and Cheng, 1991), heteropoly acid (Saito and Niiyama, 1987; Varisli *et al.*, 2007) and others. As weak basic centres are needed for dehydration (Roca *et al.*, 1969), most alumina-based catalysts are doped by alkali metal or less acidic metal oxides to obtain high activities. Mitsuo *et al.* (1981) found that alumina containing 0.05 wt% Na_2O exhibited superior activity and selectivity. Wu and Marvil (1980) reported the application of γ-Al_2O_3 catalyst with KOH for the dehydration of saturated alcohol to produce the corresponding olefin. The Syndol catalyst based on MgO-Al_2O_3/SiO_2 developed by Halcon SD has been applied commercially (Kochar *et al.*, 1981). We previously reported a highly active and relatively stable TiO_2-doped alumina catalyst, and found that the catalyst doped with 10 wt% TiO_2 had higher activities than both undoped alumina and 20 wt% TiO_2-doped alumina, because 10 wt% Ti/γ-Al_2O_3 had more moderate acid centres than pure alumina and stronger acidity than 20 wt% Ti/γ-Al_2O_3 (Chen *et al.*, 2007).

Bakoyannakis *et al.* (2001) investigated the effect of the solvent medium on catalytic activity and found that the optimal solvent was pure water, due to its high surface hydroxylation and the presence of an increased number of surface Lewis acid sites. De Boer *et al.* (1967) studied the surface properties of two activated alumina, γ-Al_2O_3 and η-Al_2O_3, which were derived from boehmite and bayerite precursors, respectively. It was concluded that η-Al_2O_3 was more active, because the aluminium atoms at its surface were preferred to act as acid centres (Lewis-type) than those of γ-Al_2O_3. In their research, the chosen alumina hydroxides were calcined at 800°C to avoid narrow pores. However, the surface area of the catalyst was drastically decreased because of the high temperature.

Conventional reactors for ethanol dehydration are mainly fixed-bed reactors (Hu, 1983). However, for an intensively endothermic reaction, ‘cold-spots’ can be easily found in the fixed-bed reactor due to its relatively low heat transfer efficiency. Comparing with traditional reactors, microreactors possess many advantages due to small characteristic dimension of their internal structures (in the range of several hundred microns), including large surface-to-volume ratio, excellent heat and mass transfer capabilities, easy scaling up and on-site production, and so on. So far, microreactors have been widely applied in heterogeneous catalytic reactions (Kolb and Hessel, 2004), such as direct synthesis of hydrogen peroxide (Inoue *et al.*, 2007), alcohol reforming (Chen *et al.*, 2004; Christian *et al.*, 2006; Shin and Besser, 2007; Won *et al.*, 2006) and partial oxidation of toluene (Ge *et al.*, 2007).

The current research is concerned with the effect of precursor on the activity of activated alumina for catalytic ethanol dehydration. The effects of reaction temperature and space velocity were investigated, and were found to obviously affect the yield of ethylene. The results can provide grounds for catalyst modification and process intensification.

2 Experimental procedure

2.1 Catalyst preparation

Dry powders consisting of AlOOH and $Al(OH)_3$ (Shandong Alumina Co.) were blended in aqueous solvents with a pH value maintained at 5. The obtained slurry was dried at 120°C. Then the solid was calcined at 500°C for 4 h to prepare Al_2O_3 with low crystallinity. Finally, the Al_2O_3 catalysts with the size of 50–65 mesh were was obtained after forming, crushing and sieving.

2.2 Catalyst characterisation

The catalyst powders were examined by X-Ray Diffraction (XRD) for the phase identification. The determination of the crystallinity was performed on an X'pert PRO diffractometer (PANalytical Inc.) equipped with Cu Kα radiation with an accelerating voltage of 40 kV and current of 200 mA. The patterns were recorded over the 2θ angle ranging from 10° to 70° at a scan rate of 4°/min.

The specific surface and the pore distribution of the crystals were determined by the nitrogen physisorption in ASAP2010 instruments (Micromeritics Instrument Corporation, USA). The samples were desiccated under 110°C for 1 h and then under vacuum conditions at 350°C for 4 h in order to remove the physically absorbed water. After that, the samples absorbed N_2 at liquid nitrogen temperature (–196°C). The specific surface was calculated by the Brunauer Emmett Teller (BET) method and the pore distribution by the Barrett-Joyner-Halenda (BJH) method, while the pore volume was determined on the basis of the maximum value of P/P_0.

The acidity and its distribution were analysed by NH_3 adsorption and NH_3-TPD. The amount of 0.14 g catalyst sample was placed into a stainless steel reactor, heated for 2 h at 450°C under He, and then at 100°C for impulse NH_3 adsorption. When saturated adsorption was achieved, the system was swept by He for 15 min. Then the temperature was programmed to increase to 450°C under the heating rate of 18°C/min. The desorbed NH_3 was analysed by a TCD detector.

2.3 Experimental set-up

The reaction of catalytic ethanol dehydration to ethylene was carried out in a microchannel reactor under atmospheric pressure. The catalysts were packed into channels of the microreactor in the form of pellets to fulfil the immobilisation. Through a micro liquid pump with a precision of 0.001 mL/min, a mixture of ethanol and water with an ethanol concentration of 93 wt% was pumped into a vaporiser kept at 220°C and then conveyed into the stainless steel microreacor. The microreactor contained 30 parallel channels with a width of 1000 μm, a depth of 1250 μm and a length of 30 mm (other specifications can be found in our previous work, Chen *et al.* (2007)). The reaction temperature inside the microreactor was controlled in the range of 300°C–460°C, the Weight Hourly Space Velocity (WHSV) based on the weight of ethanol was kept at 16–32 h^{-1} and the weight of the catalyst was kept at 0.6–0.8 g. The products were condensed via a cold trap with a mixture of ice and water; both the gas and the liquid were analysed by a gas chromatography (GC 4000A, Beijing West-East GC Co.), using a 406-organic-carrier column, H_2 as carrier gas and a TCD detector at an oven temperature of 110°C.

In this paper, WHSV is defined as the ratio of the hourly feed mass flow rate of ethanol to the catalyst weight. The ethanol conversion (X_{EtOH}), the selectivity of ethylene (S_E) and diethyl ether (S_{DEE}) are defined as follows:

$$X_{EtOH} = \frac{n_{EtOH,0} - n_{EtOH,1}}{n_{EtOH,0}} \times 100 \qquad (1)$$

$$S_E = \frac{n_{E,1}}{\Sigma v_i n_{i,1}} \times 100 \qquad (2)$$

$$S_{DEE} = \frac{2 n_{DEE1}}{\Sigma v_i n_{i,1}} \times 100 \qquad (3)$$

where:

$n_{EtOH,0}$ = denotes the molar flow rate (mmol/min) of ethanol in the feed
$n_{EtOH,1}$ = denotes the molar flow rate (mmol/min) of ethanol in the product
$n_{i,1}$ = denotes the molar flow rate of product *i* (*i* = ethylene, diethyl ether, ethane, C_3, C_4 byproducts)
v_i = denotes the stoichiometric ratio of product *i* to ethanol.

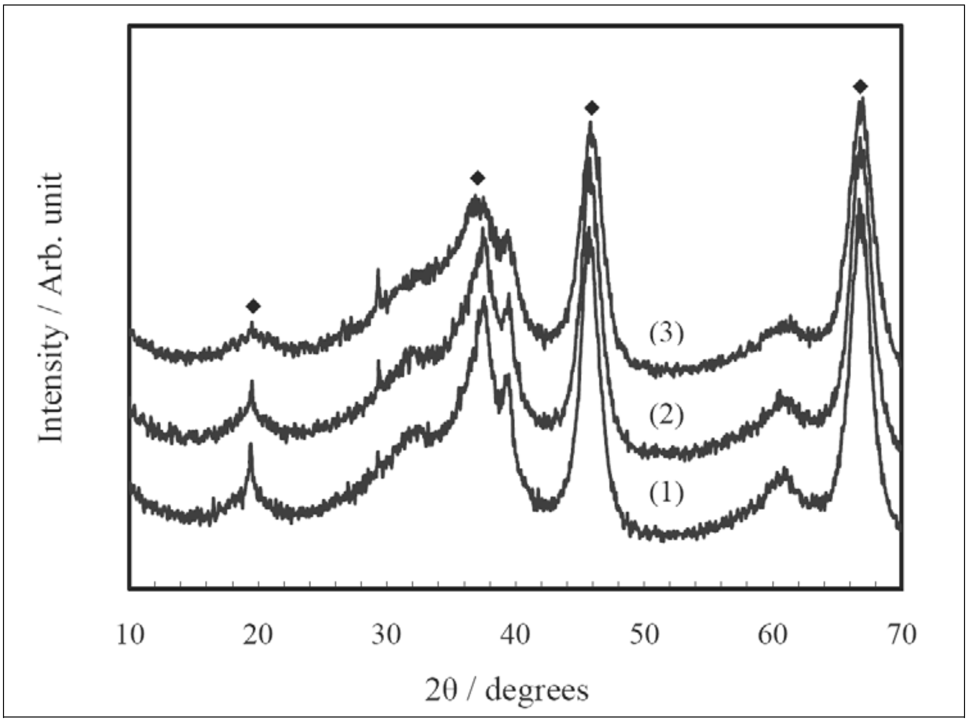
In order to eliminate the errors caused by catalyst deactivation, all the data were collected when the catalytic activity was stable, and the data under each reaction condition were repeated at least twice.

3 Results and discussion

3.1 Crystal phase

Figure 1 shows the XRD patterns of three different Al_2O_3 samples, all exhibiting wide diffraction peaks at 2θ of 19.7°, 37.2°, 45.9° and 66.8°. Since γ-Al_2O_3 and η-Al_2O_3 have similar crystal structures and thus exhibit almost the same characteristic peaks (Kim *et al.*, 2004), the two forms of activated alumina cannot be distinguished from the XRD patterns. However, as generally accepted, pseudo boehmite is calcined to γ-Al_2O_3 and bayerite to η-Al_2O_3 at 500°C (Digne *et al.*, 2002). Therefore, catalysts 1 and 3 should correspond to η-Al_2O_3 and γ-Al_2O_3, respectively, while catalyst 2 could be regarded as a mixture of the two Al_2O_3 forms.

Figure 1 XRD patterns of different Al_2O_3 samples



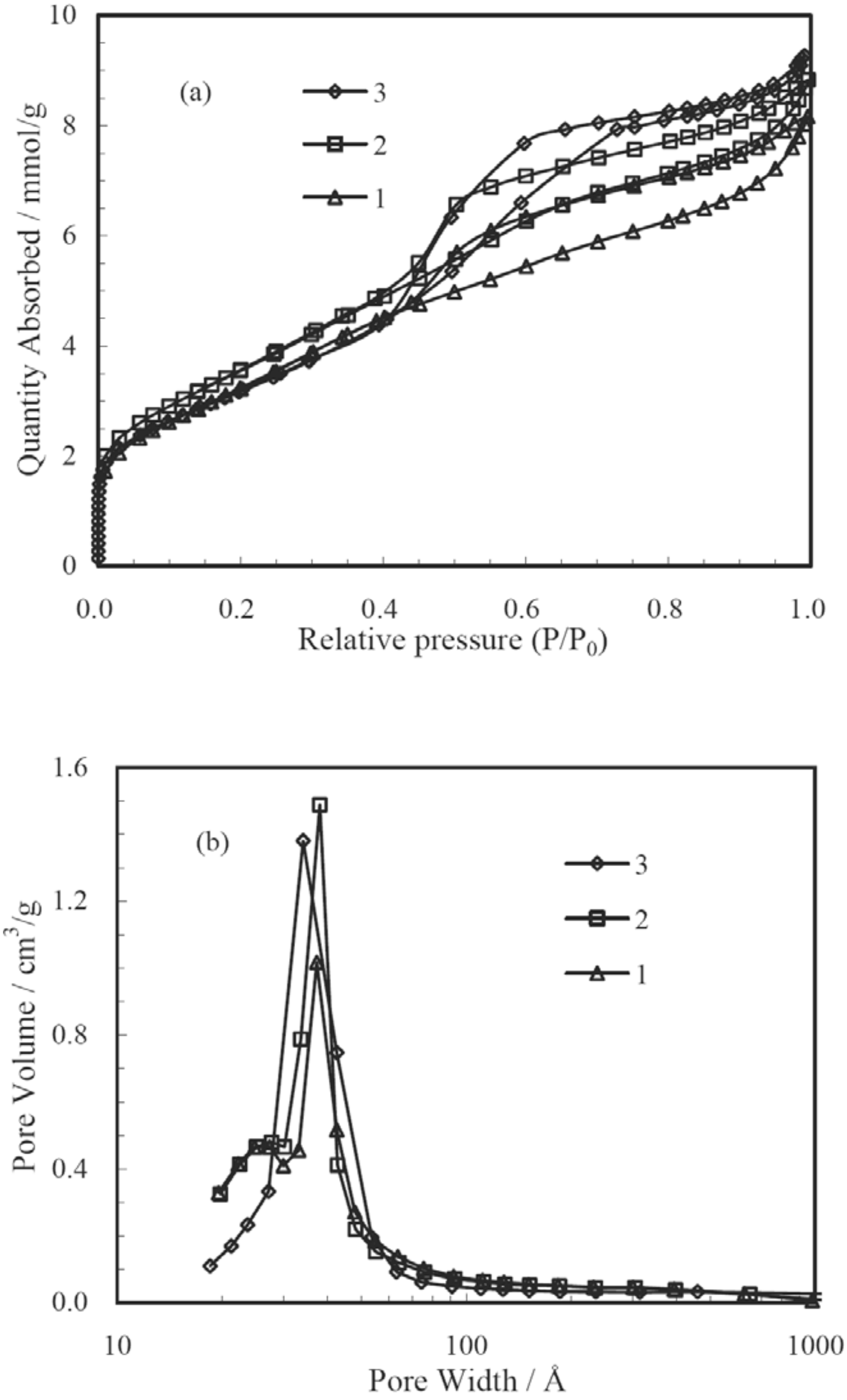
Note: AlOOH in the precursor (mol%): (1) 0, (2) 46.3, (3) 100.

3.2 Structure

As shown in Figure 2(a), the N_2 adsorption-desorption isotherms of the catalysts at the liquid nitrogen temperature are found to have reversible isotherms of type IV and exhibiting close hysteresis loops of type H2, and the P/P_0 at the closure points is 0.4. At a high P/P_0 value, the shape of the hysteresis loops indicates that catalysts 1 and 2 have similar ink-bottle structured pores, whereas catalyst 3 exhibits equivalent condensation and evaporation pressures from P/P_0 at 0.75 to 1.0. Furthermore, the N_2 saturation capacity of catalyst 3 is higher than 1 and 2, indicating that the total pore volume within catalyst 3 is the largest.

Figure 2(b) and Table 1 show that the three catalysts have similar mean pore radii and all are mesoporous in nature, but their peak shapes and pore size distribution regions are different: catalyst 3 shows a unimodal pore distribution with pore sizes concentrated at 3–5 nm, while catalysts 1 and 2 show dimodal distributions with pore sizes concentrated at 2–4 nm. The pores of the catalysts are small; however, the surface areas for γ-Al_2O_3 and η-Al_2O_3 in Table 1 are much higher than the value obtained in de Boer's experiment (*i.e.*, 55 m^2/g and 65 m^2/g, respectively) (de Boer *et al.*, 1967).

Figure 2 N_2 adsorption-desorption isotherms and BJH pore volume of three Al_2O_3 catalysts



Note: AlOOH in the precursor (mol%): (1) 0, (2) 46.3, (3) 100.

Table 1 Structural properties and BJH pore distribution

Catalyst	*AlOOH (mol%*[a]*)*	*Pore distribution (%)* 1.5–2 nm	2–3 nm	3–4 nm	4–5 nm	5–10 nm	A_{BET} (m^2/g)	V_P (cm^3/6)	r_p (nm)
1	0	7.25	27.17	30.14	14.57	13.31	268.44	0.2831	3.79
2	46.3	7.00	27.41	42.80	11.32	11.43	292.25	0.3061	3.77
3	100.0	2.45	17.44	41.15	28.17	10.90	259.24	0.3215	3.89

Note: [a] Refers to the AlOOH mol% in the precursor.

3.3 Surface acidity of catalysts

Figure 3 shows the results of NH_3-TPD for the catalysts. The dispersed and overlapped desorption spectra of three different kinds of Al_2O_3 can be clearly observed, showing that the distribution of surface acidity intensities is nonuniform, and acid centres with different intensities are difficult to differentiate. From a qualitative viewpoint, Berteau and Delmon (1989) proposed a classification: T_m in the range of 20°C–200°C corresponds to the weak acid sites; T_m in the range of 200°C–400°C corresponds to the moderate acid sites; T_m higher than 400°C is associated with strong acid sites. According to this classification, most of the acid sites in all three samples can be ascribed to moderate acid sites, which are regarded as the main activity sites for the alcohol dehydration reaction (Berteau and Delmon, 1989). As shown in Table 2, among the three catalysts, catalyst 3 has the most weak acid sites and the minimum moderate acid sites.

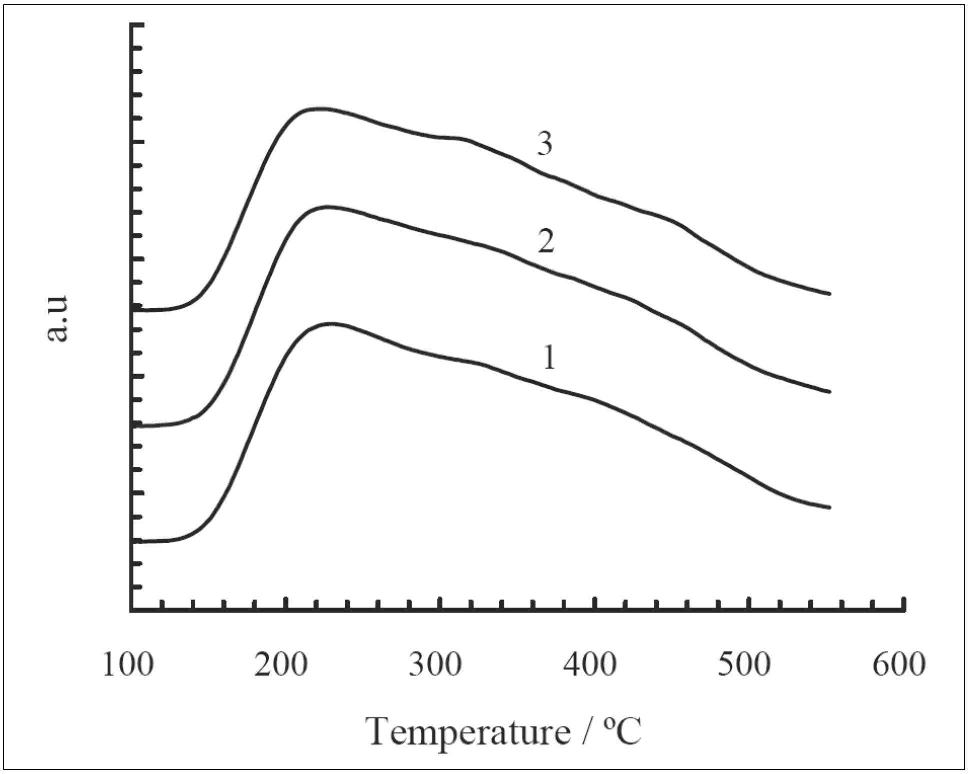
Table 2 Acid properties of Al_2O_3 catalysts with different pseudo boehmite contents

Sample	*AlOOH (mol%*[a]*)*	N_{acid} *(mmol/g)*	*Acid distribution (10^{-5} mol/g)* Weak	Moderate	Strong	*Acid-sites density (n*[b]*/m^2)*
1	0	0.2218	4.854	9.984	7.337	4.97×10^{13}
2	46.3	0.2217	4.852	9.986	7.333	4.57×10^{13}
3	100.0	0.2210	4.855	9.946	7.301	5.13×10^{13}

Notes: [a] refers to the AlOOH mol% in the precursor; [b] refers to the number of molecules.

The effect of different AlOOH content levels on the acid properties can be referred to in Table 2. With the increase in the AlOOH content in the precursor, the total number of acid sites per gram of catalyst decreases, indicating that η-Al_2O_3 has greater acidity over γ-Al_2O_3, in agreement with the well-known properties of these transition aluminas (Maciver *et al.*, 1963; Satterfield, 1980; Sohlberg *et al.*, 2001). As initial rates of conversion correlate well with the total number of acidic sites (Jiratova and Beranek, 1982), we can predict that the level of AlOOH in the precursor could influence the activity of the dehydration reaction by regulating the acid properties. Table 2 also reveals that the acid-site density of catalyst 2 is much less than that of catalyst 3 due to its large BET surface area.

Figure 3 TPD spectra of ammonia absorbed on Al_2O_3



Note: AlOOH in the precursor (mol%): (1) 0, (2) 46.3, (3) 1.

3.4 *Catalyst activity test*

3.4.1 *Effect of reaction temperature*

Two reactions can occur in parallel during the dehydration process:

$$C_2H_5OH = C_2H_4 + H_2O \qquad +44.9\ \text{kJ/mol} \tag{4}$$

$$2C_2H_5OH = C_2H_5OC_2H_5 + H_2O \qquad -25.1\ \text{kJ/mol.} \tag{5}$$

The products of ethanol dehydration are mainly ethylene and diethyl ether generated from an intramolecular reaction (Equation 4) and an intermolecular reaction (Equation 5), respectively. As shown in Figure 4, at low temperature, not only the activity of the catalysts is poor, but the selectivity of ethylene is also low because a large proportion of ethanol is converted to diethyl ether. In addition, both are improved gradually when the temperature increases. The opposite trends of the selectivities of ethylene and diethyl ether with the increase of the reaction temperature can be explained from the thermodynamic and kinetic viewpoints. On the one hand, thermodynamically, the reaction to produce ethylene is endothermic with $\Delta H_0 > 0$, and the reaction to produce diethyl ether is exothermic with $\Delta H_0 < 0$, indicating that at higher temperatures, the former reaction is more favourable according to Van't Hoff's equation. On the other hand, from a kinetic viewpoint, intermolecular dehydration (Equation 5) requires lower activation energy than the intramolecular reaction (Equation 4) (de Boer *et al.*, 1967). As

Arrhenius's equation suggests, higher temperatures favour the reaction demanding high activation energy. Thus the selectivity of ethylene production is improved at higher reaction temperatures as well.

As shown in Figure 4(a), catalyst 1 (η-Al_2O_3) performs better than catalyst 3 (γ-Al_2O_3), which is in accordance with de Boer's (1967) findings. This can be explained by the fact that the number of acid sites on catalyst 1 is higher than that on catalyst 3, and that catalyst 1 has more moderate acid sites. Besides that, catalyst 1 exhibits dimodal pore distribution, which may possibly provide a wider pore size region for the dehydration process despite the fact that the peaks of the two catalysts are very close to each other.

The other three catalysts also shown in Figure 4(a), catalysts 2, 4 and 5, can be considered as the mixtures of γ-Al_2O_3 and η-Al_2O_3. It can be noticed that ethanol conversion over these three catalysts are all better than those of catalyst 1 and 3. Among them, catalyst 2 prepared from a precursor with 46.3 mol% AlOOH shows the highest activity. At 440°C, ethanol conversion for catalyst 2 is about 95.27%, whereas it is only 93.60% and 92.45% for catalysts 1 and 3, respectively. Although the pore sizes of catalyst 2 concentrate on the range of 2–4 nm, and Asaoka and Sendo (1985) have pointed out that small pores in the catalyst would lead to a low diffusion rate of the reactant, its high activity proves that the negative effects of the small size can be neglected. As it has no significant advantage in either total acid sites or moderate acid sites as compared to catalyst 1, and both catalysts show similar peak shapes, we can speculate that catalyst 2 may have more Lewis-type acid sites, which are responsible for its high activity (Arai *et al.*, 1968), which still requires further characterisation. Moreover, it has the largest surface area, which may play a positive role in improving the activity as well.

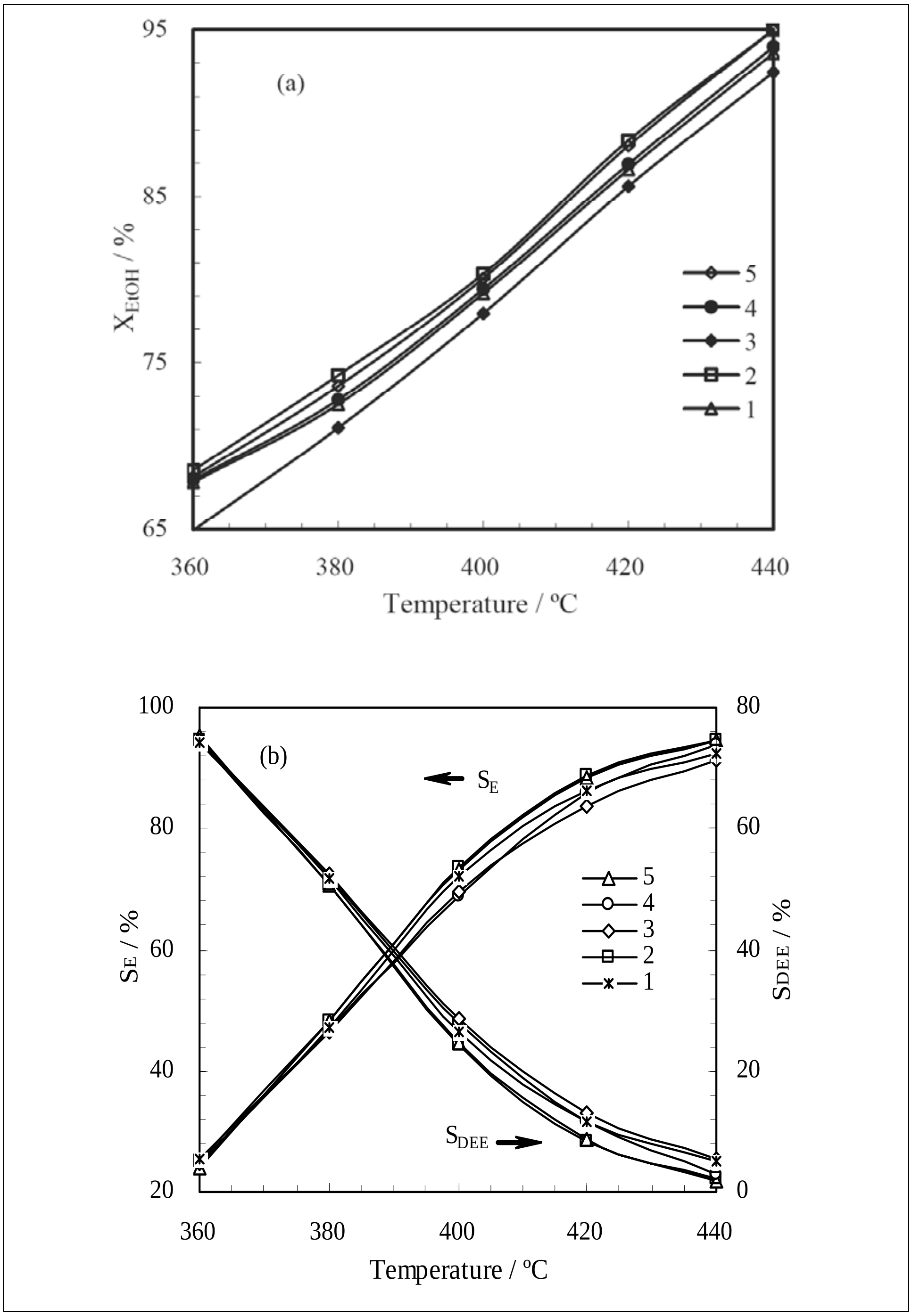
The selectivity curves of the two main dehydration products are shown in Figure 4(b), and some typical results are also listed in Table 3. It is evident that among the five catalysts, catalyst 3 shows the lowest selectivity towards ethylene and the highest selectivity to diethyl ether. This phenomenon can be ascribed to the higher acid-site density over the surface of this catalyst, on which two adjacent ethanol molecules have more chances to collide with each other to form diethyl ether (de Boer *et al.*, 1967).

The conversion and selectivities over five catalysts at 380°C are shown in Figure 5. This figure explicitly exhibits that catalyst 2, with 46.3 mol% AlOOH in the precursor, behaves best among the five catalysts not only in the conversion of ethanol but also in the selectivity to ethylene.

3.4.2 Effect of space velocity

Figure 6 depicts the conversion curves of catalyst 2 with respect to reaction temperature as well as space velocity. With the increase of space velocity, the residence time decreases, causing the conversion of ethanol and the selectivity of ethylene to decline accordingly. The conversion and selectivity of ethanol can reach 98.69% and 96.97% at 460°C and a WHSV of 14 h^{-1}. The yield of ethylene of 18.28 g/(g_{cat}·h) can be achieved at a WHSV of 32 h^{-1}, indicating that the mass transfer performance can be effectively improved.

Figure 4 Effect of reaction temperature on (a) conversion of ethanol and (b) selectivity of ethylene and diethyl ether over different catalysts filled in the microchannel reactor

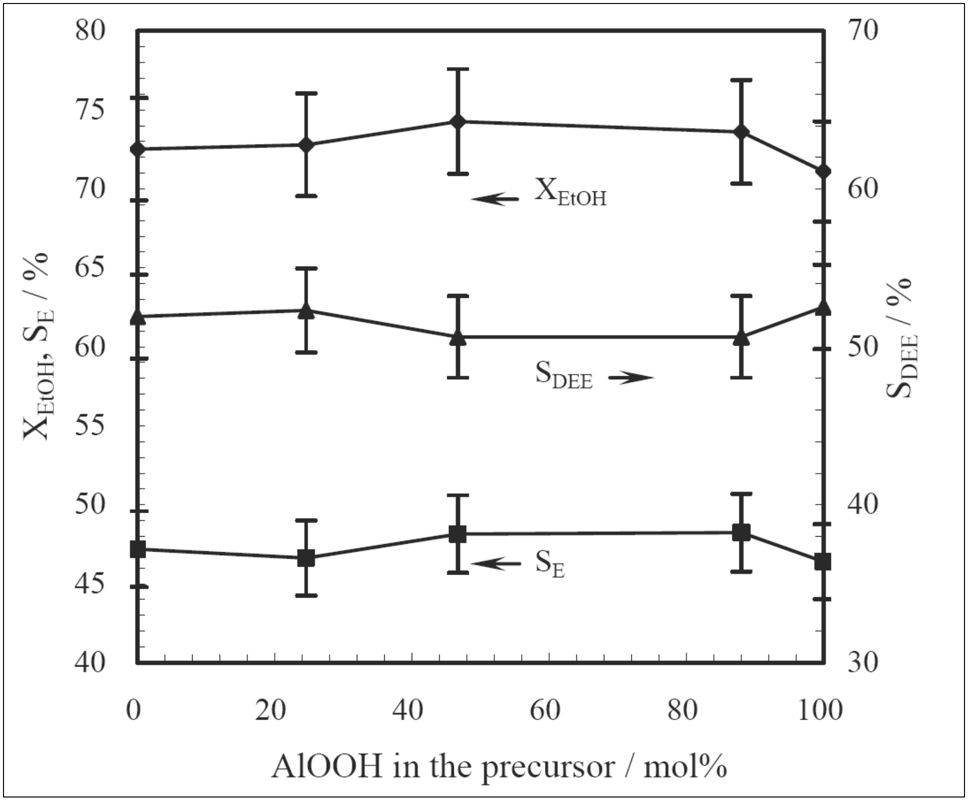


Notes: WHSV: 26 h^{-1}; feed: 93.8 wt% ethanol. AlOOH in the precursor (mol%): (1) 0, (2) 46.3, (3) 100, (4) 24.6, (5) 88.0.

Table 3 Selectivities of ethylene (E) and diethyl ether (DEE) over five catalysts at different temperatures

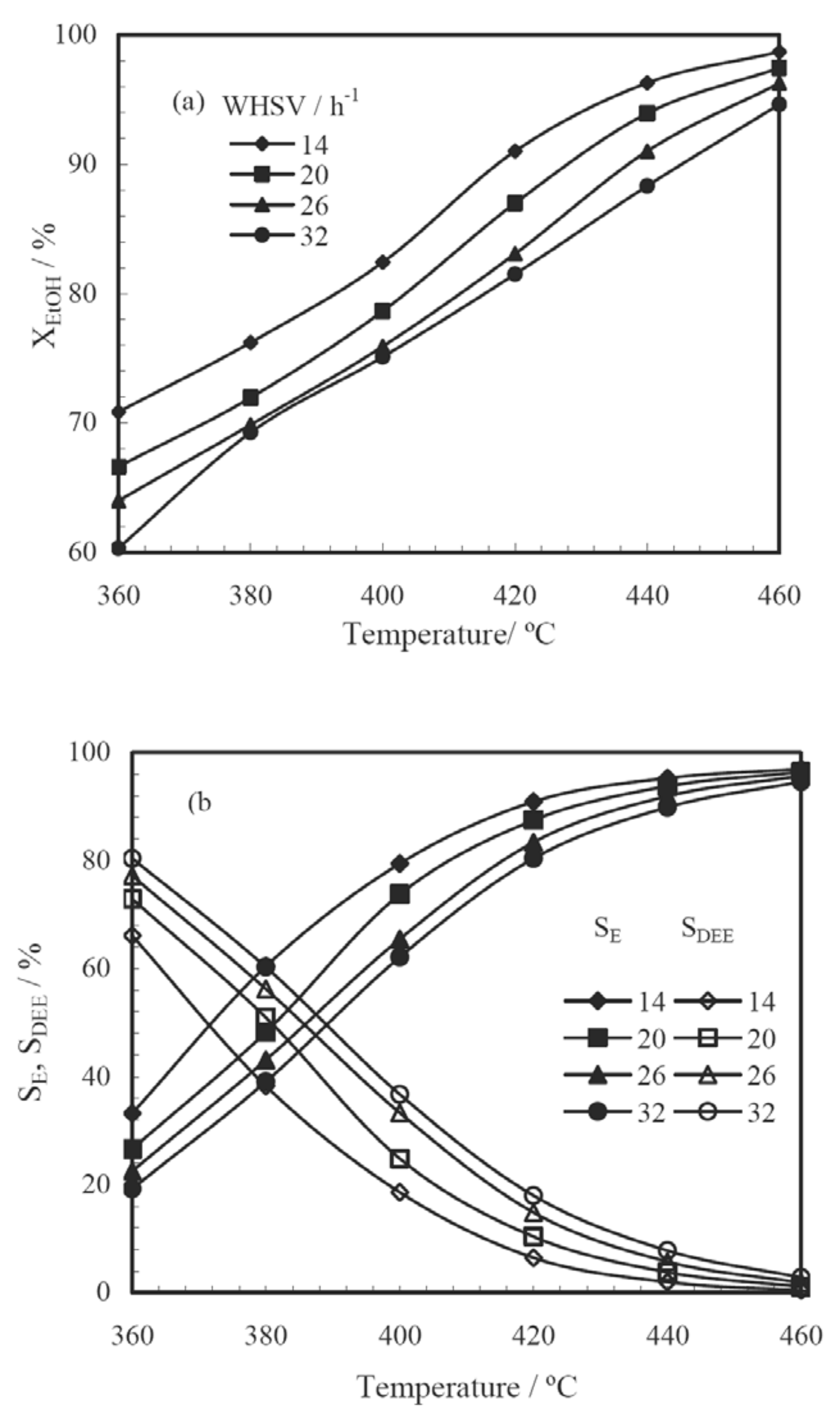
Sample	*A1OOH content (mol%)*	*S_E (%)*			*S_{DEE} (%)*		
		400°C	*420°C*	*440°C*	*400°C*	*420°C*	*440°C*
1	0	72.11	86.11	92.49	26.29	11.71	4.97
2	46.7	73.57	88.93	94.50	24.28	8.18	2.16
3	100.0	69.46	83.87	91.21	28.49	13.21	5.26
4	24.6	69.89	85.72	94.01	28.01	11.67	2.84
5	88.0	73.08	88.45	94.44	24.78	8.55	1.82

Figure 5 Effect of the composition of the precursor on the conversion of ethanol, and selectivity of ethylene and diethyl ether



Notes: Temperature: 380°C; WHSV: 26h^{-1}; feed: 93.8 wt% ethanol.

Figure 6 Effect of WHSV on (a) ethanol conversion and (b) selectivity of ethylene and diethyl ether over catalyst 2 filled in the microchannel reactor

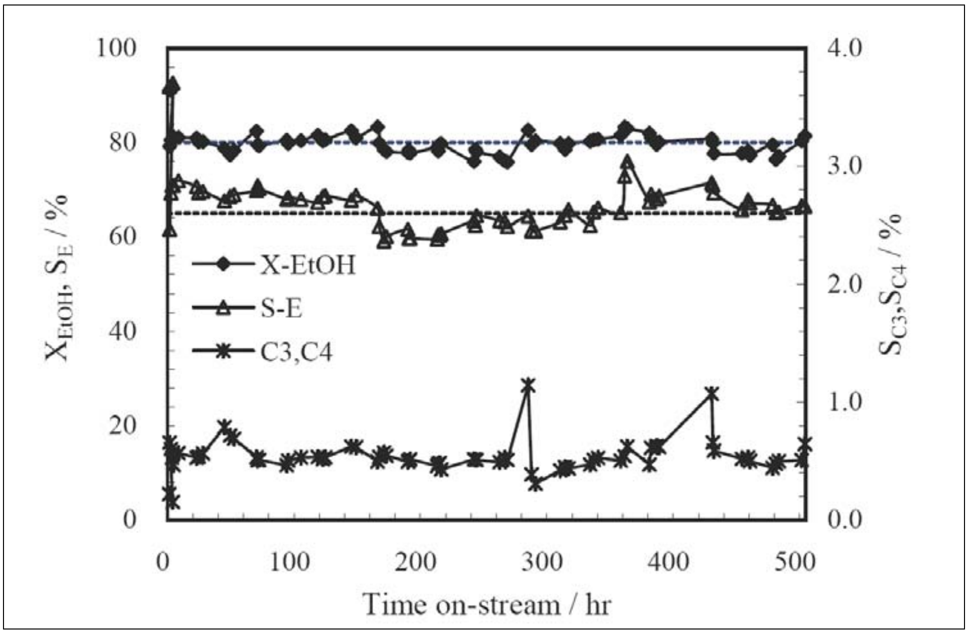


Note: Feed: 93.8 wt% ethanol.

3.4.3 Catalyst stability

The stability of the activity of catalyst 2 was tested under a reaction temperature of 365°C, as shown in Figure 7. Although the pore sizes of the selected catalyst were concentrated on a region as small as 2–4 nm, the conversion of ethanol and the selectivity of ethylene were almost constant over 500 h on stream. The selectivity of polymer byproducts such as C_3 and C_4 was found to be very low. The weight of the catalyst also showed no significant change before and after the reaction. Thus, it seems that activated Al_2O_3 catalysts are not prone to poisoning, especially not to fouling by polymerisation and carbon deposits, as suggested by Winfield (1960).

Figure 7 The life time of catalyst 2 prepared from the precursor with 46.3 mol% AlOOH



Notes: Reaction temperature: 365°C; WHSV: 3.15 h^{-1}; feed: 93.8 wt% ethanol.

4 Conclusions

This paper describes an experimental characterisation of the physicochemical properties of activated Al_2O_3 made from precursors containing different ratios of pseudo boehmite and bayerite and their catalytic activities for the dehydration of ethanol to ethylene in a microchannel reactor. The results demonstrate that the optimal catalyst is the one made from 46.3 mol% AlOOH and 53.7 mol% $Al(OH)_3$ as it gives a relatively high conversion of ethanol and selectivity towards ethylene. An ethylene yield of 18.28 $g/(g_{cat}\cdot h)$ can be achieved, indicating that the mass transfer process can be effectively intensified via microreactors and thereby the bio-ethanol-to-ethylene process can be miniaturised.

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