# Green Chemistry

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## PAPER

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Direct conversion of bio-ethanol to propylene with high yield over the composite of In<sub>2</sub>O<sub>3</sub> and zeolite Beta

A series of In<sub>2</sub>O<sub>3</sub>-Beta composites with different content of zeolite Beta were prepared by deposition-precipitation method, followed by calcination at 700 °C, and their catalytic performance in conversion of ethanol to propylene (ETP) was investigated. The physicochemical properties of the as-synthesized materials were characterized by XRD, N<sub>2</sub> adsorption, SEM, NH<sub>3</sub>-TPD, CO<sub>2</sub>-TPD and a probe reaction. The combination of In<sub>2</sub>O<sub>3</sub> and zeolite Beta improves the propylene yield significantly. The optimal result was observed for the composite with Beta content of 20-50%, which gave ca. 50% yield of propylene. The role of Beta in In<sub>2</sub>O<sub>3</sub>-Beta composite catalyst is to promote the conversion of the intermediate of acetone to propylene via an additional reaction pathway, which accounts for the superior propylene yield of In<sub>2</sub>O<sub>3</sub>-Beta composite in comparison with In<sub>2</sub>O<sub>3</sub> (ca. 32%). The proximity of these two components (In<sub>2</sub>O<sub>3</sub> and zeolite Beta) plays a crucial role in achieving high vield of propylene the FTP reaction. for а

#### Introduction

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Fossil fuels are main energy sources to support human life and social development. The excessive exploitation of fossil fuels leads to the deterioration of environment and irreversible exhaustion of these resources. So there is an urgent need to accelerate the development and utilization of renewable energies. The use of biomass, as a sustainable energy, can alleviate the energy shortage problem. Bio-ethanol is usually produced from the fermentation of plants, and it is widely used as a platform molecule to produce many value-added chemicals such as ethylene, propylene, isobutene and so on.<sup>1–3</sup>

The reaction of ethanol to propylene (ETP) has been widely studied in recent years, as propylene is one of the most important raw materials to produce industrial commodities such as polypropylene, polyacrylonitrile, acrolein and acrylic acid. Zeolites (mainly MFI-type) and modified zeolites are generally employed for this reaction in previous studies.<sup>4–14</sup> Ethanol firstly dehydrates to ethylene, then ethylene goes through oligomerization-cracking way to get propylene.<sup>8,15,16</sup> Because of the randomness of oligomerization, the yield of propylene is just 20-30%, and the main by-products are ethylene, butenes and aromatic hydrocarbons. Moreover, coke is more prone to be produced on strong acid sites, leading to the fast deactivation of catalysts.<sup>4,9</sup> Mao's group prepared fluorinated nano-HZSM-5 and HZSM-5 zeolite comodified with alkaline and phosphorous, and found significantly better stability than for traditional HZSM-5.<sup>17,18</sup>

More recently, much attention has been transferred to metal oxide catalysts for the ETP reaction.<sup>19-23</sup> Iwamoto's group reported a propylene yield of 34% on Sc/In<sub>2</sub>O<sub>3</sub> for the ETP reaction in  $N_2$  atmosphere at 500 °C.<sup>19</sup> They also found that on Y/CeO<sub>2</sub>, the yield of propylene was constant at 30% for the ETP reaction in the presence of water during continuous experiment at 430 °C for 56 h.<sup>21</sup> Xia et al. prepared Y/ZrO<sub>2</sub> catalyst and achieved a yield for propylene of 44% for the ETP reaction at 450 °C and 1.11 MPa.<sup>23</sup> However, the exploration of a catalyst with both higher propylene yield and longer lifetime is still a tremendous challenge.

In the present study, we report for the first time the use of In<sub>2</sub>O<sub>3</sub>-Beta composite as a new efficient catalyst in the ETP reaction. Our results have shown that the combination of In<sub>2</sub>O<sub>3</sub> and zeolite Beta can improve the yield of propylene substantially. Moreover, the In2O3-Beta composite catalyst exhibits good stability in terms of propylene yield. The reasons for the remarkable propylene yield of In<sub>2</sub>O<sub>3</sub>-Beta composite were elucidated.

#### **Results and discussion**

#### Structural and textural properties

Fig. 1 shows the XRD patterns of In<sub>2</sub>O<sub>3</sub>-Beta composites with different zeolite Beta content. The intensities of In2O3 diffraction peaks (PDF#06-0416) gradually decrease and the peak width becomes broader with the decrease of In<sub>2</sub>O<sub>3</sub> content, indicating the smaller crystallite size of  $In_2O_3$  (Table 1). When the content of Beta is up to 20%, its characteristic peak at  $2\theta = 22.6^{\circ}$  can be discernible (Fig. 1c). When the content of Beta is up to 50%, its another characteristic peak at  $2\theta$  = 7.8° appears (Fig. 1f). The intensities of these two peaks

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(PDF#06-0416) increase gradually with increasing the Beta content.



Fig. 1 XRD patterns of  $In_2O_3$ -Beta composites with different Beta content. (a)  $In_2O_3$ , (b)  $In_2O_3$ -10%Beta, (c)  $In_2O_3$ -20%Beta, (d)  $In_2O_3$ -30%Beta, (e)  $In_2O_3$ -40%Beta, (f)  $In_2O_3$ -50%Beta; (g)  $In_2O_3$ -60%Beta, (h)  $In_2O_3$ -70%Beta, (i) Beta.

Fig. 2 displays the SEM images of different samples. The In2O3 particles are approximately sphere-shaped with diameters in the range of 30-70 nm (Fig. 2a). The Beta particles are approximately sphere-shaped with diameters in the range of 200-500 nm (Fig. 2e), much larger than In<sub>2</sub>O<sub>3</sub> particles. For the In<sub>2</sub>O<sub>3</sub>-20%Beta composite, only a few Beta particles can be observed (Fig. 2b), indicating that most of zeolite Beta were buried by  $In_2O_3$  nanoparticles when the Beta content is low. With the increase of Beta content up to 50%, most of the observed particles are zeolite Beta covered by In2O3 nanoparticles (Fig. 2c). It is noteworthy to point out that the density of Beta is much less than that of In<sub>2</sub>O<sub>3</sub> so that the volume of Beta is much larger than that of In<sub>2</sub>O<sub>3</sub>, although Beta and In<sub>2</sub>O<sub>3</sub> have the same weight in the In<sub>2</sub>O<sub>3</sub>-50%Beta composite. For the In2O3-70%Beta composite, almost all the observed particles are zeolite Beta with the presence of tiny In<sub>2</sub>O<sub>3</sub> particles on the surface of Beta (Fig. 2d). The sizes of In<sub>2</sub>O<sub>3</sub> particles in In<sub>2</sub>O<sub>3</sub>-20%Beta, In<sub>2</sub>O<sub>3</sub>-50%Beta and In<sub>2</sub>O<sub>3</sub>-70%Beta composites are 34.3, 16.4 and 14.3 nm, respectively, which are smaller than pure  $In_2O_3$  (55.2 nm). This observation is consistent with the XRD result (Table 1).



The textural properties of the samples are listed in Table 1.

Fig. 2 SEM images of (a)  $In_2O_3,$  (b)  $In_2O_3\text{-}20\%\text{Beta},$  (c)  $In_2O_3\text{-}50\%\text{Beta},$  (d)  $In_2O_3\text{-}70\%\text{Beta}$  and (e) Beta.

**Table 1** Textural properties of  $In_2O_3$ -Beta composites with<br/>different Beta content

	$S_{\text{BET}}$	$V_{\rm micro}^{a}$	V <sub>meso</sub>	$V_{\text{total}}^{b}$	Crystallite
Sample	$(m^2 g^{-1})$	$(cm^3 g^{-1})$	$(cm^3 g^{-1})$	$(cm^3 g^{-1})$	size <sup>c</sup> (nm)
In <sub>2</sub> O <sub>3</sub>	22	0	0.186	0.186	56.8
In <sub>2</sub> O <sub>3</sub> -10%Beta	84	0.015	0.165	0.180	33.2
In <sub>2</sub> O <sub>3</sub> -20%Beta	117	0.020	0.169	0.189	32.4
In <sub>2</sub> O <sub>3</sub> -30%Beta	167	0.046	0.197	0.243	26.7
In <sub>2</sub> O <sub>3</sub> -40%Beta	228	0.060	0.235	0.295	19.9
In <sub>2</sub> O <sub>3</sub> -50%Beta	268	0.075	0.243	0.318	16.7
In <sub>2</sub> O <sub>3</sub> -60%Beta	327	0.102	0.270	0.372	15.9
In <sub>2</sub> O <sub>3</sub> -70%Beta	371	0.114	0.279	0.393	15.8
Beta	546	0.183	0.316	0.499	_

<sup>*a*</sup> Calculated by *t*-plot method. <sup>*b*</sup> Total pore volume adsorbed at  $P/P_0 = 0.99$ . <sup>*c*</sup> The crystallite size of In<sub>2</sub>O<sub>3</sub> determined using Scherrer equation.

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**Fig. 3** Product distribution over  $In_2O_3$ -Beta composites for ethanol conversion. Reaction conditions: reaction temperature, 460 °C; WHSV of ethanol, 0.2 h<sup>-1</sup>; time-on-stream, 3 h.

<b>Table 2</b> Acidic and basic properties of the cataly
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	Amount of acidic sites (mmol $g^{-1}$ )			Conversion of	Amount of basic
			cumene cracking	sites	
Sample	weak <sup>a</sup>	strong <sup>b</sup>	total	<b>(%</b> )	$(\text{mmol g}^{-1})$
In <sub>2</sub> O <sub>3</sub>	0.065	0	0.065	0	0.051
In <sub>2</sub> O <sub>3</sub> -10%Beta	0.135	0.054	0.189	4.1	0.083
In <sub>2</sub> O <sub>3</sub> -20%Beta	0.223	0.072	0.295	16.3	0.078
In <sub>2</sub> O <sub>3</sub> -30%Beta	0.254	0.098	0.352	25.5	0.079
In <sub>2</sub> O <sub>3</sub> -40%Beta	0.314	0.129	0.443	30.7	0.082
In <sub>2</sub> O <sub>3</sub> -50%Beta	$0.359(0.233)^c$	$0.158(0.085)^c$	$0.517(0.318)^{c}$	$38.4(4.7)^{c}$	$0.068(0.062)^{c}$
In <sub>2</sub> O <sub>3</sub> -60%Beta	0.389	0.184	0.573	48.9	0.066
In <sub>2</sub> O <sub>3</sub> -70%Beta	0.397	0.192	0.589	55.3	0.073
Beta	0.515	0.364	0.879	78.2	0.063

<sup>a</sup> NH<sub>3</sub> desorbing between 80 and 250°C. <sup>b</sup> NH<sub>3</sub> desorbing between 250 and 500°C.

<sup>c</sup> The values inside the bracket are the data measured after the stability test.

 $In_2O_3$  shows a small BET surface area (22 m<sup>2</sup> g<sup>-1</sup>) and no micropores, which means  $In_2O_3$  is a dense phase. The mesopore volume of 0.186 cm<sup>3</sup> g<sup>-1</sup> is contributed from voids between the  $In_2O_3$  particles. Different from  $In_2O_3$ , zeolite Beta has a very large surface area (546 m<sup>2</sup> g<sup>-1</sup>) and co-existence of micropores and mesopores with pore volume of 0.183 and 0.316 cm<sup>3</sup> g<sup>-1</sup>, respectively. With the increase of Beta content, the surface area and pore volume of  $In_2O_3$ -Beta composites become larger. It can be concluded from Table 1 that the surface areas of  $In_2O_3$ -Beta composites mainly result from zeolite Beta, and the micropore volumes of  $In_2O_3$ -Beta composites arise from zeolite Beta.

#### Acid and base properties

The surface acidity of  $In_2O_3$ -Beta composites was measured by NH<sub>3</sub>-TPD, and the results are given in Fig. S1 and Table 2. As shown in Fig. S1,  $In_2O_3$  exhibits only one broad small peak desorbing from 80 to 250 °C, suggesting that  $In_2O_3$  has no strong acid sites. Zeolite Beta possesses two large desorption

peaks. The low temperature peak at 150 °C and the high temperature peak at 311 °C correspond to the weak and strong acid sites of Beta. The NH<sub>3</sub>-TPD profiles of In<sub>2</sub>O<sub>3</sub>-Beta composites display the feature with combination of Beta and  $In_2O_3$ . With the increase of Beta content, the amount of acid sites (weak, strong and total, respectively) becomes larger (Table 2). Cumene cracking is a typical Brønsted acid-catalyzed reaction.<sup>24,25</sup>  $In_2O_3$  is inactive for cumene cracking, indicating that there are no Brønsted acid sites on In<sub>2</sub>O<sub>3</sub>, i.e. In<sub>2</sub>O<sub>3</sub> is a Lewis acid catalyst. When zeolite Beta was composited with  $In_2O_3$ , the conversion of cumene over  $In_2O_3$ -Beta composites increases with increasing the Beta content, which is a consequence of enhanced Brønsted acidity. In addition, the surface basicity of In2O3-Beta composites was measured by CO2-TPD, and the results are given in Fig. S2 and Table 2. One broad CO<sub>2</sub> desorption peak was observed for all samples. The amount of basic sites on In<sub>2</sub>O<sub>3</sub>-Beta composites does not differ significantly, ranging from 0.066 to 0.083 mmol  $g^{-1}$  (Table 2).

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The data in Table 2 shows that there is a much greater number of acidic sites than of basic sites on  $In_2O_3$ -Beta composites.

#### Catalytic performance

#### Effect of zeolite Beta content

All catalysts give 100% ethanol conversion under the reaction conditions studied in this work. Nevertheless, the product distribution is significantly dependent on the catalyst composition. Fig. 3 shows the product distribution on In<sub>2</sub>O<sub>3</sub>-Beta composites at 460 °C after 3 h of the reaction. The  $In_2O_3$ catalyst gives a 32.1% yield of propylene. Besides that, there are 25.6% yield of  $C_4H_8$  (almost entirely isobutene) and 30.1% yield of CO<sub>x</sub> (ca. 95% CO<sub>2</sub> and 5% CO). CO2 is concurrently produced along with propylene and isobutene during the conversion of ethanol.<sup>19,26</sup> Minor by-products are acetone,  $C_2H_4$ ,  $CH_4$  and  $C_2$ - $C_4$  paraffins. However, the catalytic results on zeolite Beta are different from those on In<sub>2</sub>O<sub>3</sub>. Ethylene accounts for 59.7% of products, which is stemmed from ethanol dehydration. And 16.0% yield of BTX (benzene, toluene and xylenes) is generated via successive steps of ethylene oligomerization, cracking and/or cyclization and hydrogen transfer reactions over Brønsted acid sites of zeolite Beta.<sup>27–29</sup> Moreover, there are 13.8% yield of  $C_2$ - $C_4$  paraffins formed by olefins hydrogenation and/or hydrogen transfer reactions.<sup>27–29</sup> Only a small amount of propylene (5.2%) is produced. It is expected that the formation of  $C_3H_6$  on zeolite Beta follows the same reaction pathway as that on other acidic zeolites such as SAPO-34 and ZSM-5, i.e. trimerization of  $C_2H_4$ followed by  $\beta$ -scission.<sup>15,16,30</sup> Zeolite Beta gives a yield of C<sub>4</sub>H<sub>8</sub> as low as 2.6%. No acetone and very small amount of  $CO_x$ (1.8%) were observed. When  $In_2O_3$  is composited with zeolite Beta, the yield of  $C_3H_6$  is enhanced significantly. The  $C_3H_6$  yield on  $In_2O_3$ -10%Beta is 39.0%. When the Beta content in  $In_2O_3$ -Beta composites is between 20% and 50%, the yield of  $C_3H_6$  is similar, reaching as high as ca. 50%. But a further increase in zeolite Beta content brings about a decrease in  $C_3H_6$  yield. The  $C_3H_6$  yield on the In<sub>2</sub>O<sub>3</sub>-70%Beta catalyst with 70% Beta is decreased to 38.2%. It should be mentioned that butenes (C<sub>4</sub>H<sub>8</sub>) formed over In<sub>2</sub>O<sub>3</sub>-Beta composites are primarily isobutene (> 80%).

The reaction pathways for the catalytic conversion of ethanol to propylene over In2O3-based oxides have been proposed by Iwamoto and co-workers, <sup>19,22,31</sup> as shown in Scheme 1. Ethanol dehydrogenation to acetaldehyde is catalyzed by both acidic and basic sites through a concerted mechanism, followed by formation of acetone from acetaldehyde through ketonization catalyzed by basic sites. At last, acetone is hydrogenated to isopropanol and then isopropanol is converted to propylene through dehydration process. The dehydration of isopropanol to propylene is catalyzed by acidic sites. It should be mentioned that hydrogen is produced during the process of ethanol to acetaldehyde  $(CH_3CH_2OH = CH_3CHO + H_2)$  and acetaldehyde to acetone  $(2CH_3CHO + H_2O = CH_3COCH_3 + CO_2 + 2H_2)$ . On the other hand, the intermediate of acetone can be also converted to isobutene via aldolization and cracking catalyzed by Lewis acidbase pairs on In<sub>2</sub>O<sub>3</sub>-based oxides, as suggested by Sun et al.<sup>32</sup>

(Scheme 1). The conversion of acetone to propylene or isobutene is a slow step.<sup>19,26,32</sup> Therefore, the products of  $C_3H_6$ and  $i-C_4H_8$  are generated though the same intermediate of acetone, i.e., the conversion of acetone to  $C_3H_6$  and  $i-C_4H_8$  are two parallel procedures. The production of  $C_3H_6$  and  $i-C_4H_8$ competes with each other. Correlation of C<sub>3</sub>H<sub>6</sub> yield (Fig. 3) with surface acidity and basicity (Table 2) suggests that different acidity of the catalysts is responsible for different  $C_3H_6$  yield achieved on the catalysts since these catalysts have similar amount of basic sites. As the amount of acidic sites increases from 0.065 to 0.295 mmol  $g^{-1}$ , the yield of  $C_3H_6$  is obviously increased. When the amount of acidic sites is between 0.295 and 0.517 mmol  $g^{-1}$ , the C<sub>3</sub>H<sub>6</sub> yield is similar. A further increase of acidity from 0.517 to 0.879 mmol  $g^{-1}$  leads to an evident decline in C<sub>3</sub>H<sub>6</sub> yield, which is due to the fact that too many acidic sites (i.e. higher content of zeolite Beta in the composites) favors the formation of BTX and C<sub>2</sub>H<sub>4</sub>.



Scheme 1 Reaction pathways for ethanol conversion to propylene and isobutene over  $In_2O_3$ -based oxides.

The results in Fig. 3 reveals that the combination of appropriate amount of zeolite Beta (20-50%) with In<sub>2</sub>O<sub>3</sub> can improve the  $C_3H_6$  yield markedly for the conversion of ethanol to propylene, but obviously diminish the yield of butenes (mainly isobutene). According to the reaction pathways shown in Scheme 1, the reason could be attributed to enhanced dehydration of isopropanol to propylene caused by higher amount of acid sites, thus promoting the conversion of acetone to propylene. The possibility of conversion of acetone to isobutene is declined accordingly. To verify our hypothesis, we employed  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, which is a good catalyst for isopropanol dehydration to propylene,<sup>33–35</sup> as a substitution of zeolite Beta to prepare In<sub>2</sub>O<sub>3</sub>-50%Al<sub>2</sub>O<sub>3</sub> composite. This catalyst possesses 0.365 mmol  $g^{-1}$  of acid sites, which is slightly higher than that of In<sub>2</sub>O<sub>3</sub>-30%Beta. Unexpectedly, the yields of C<sub>3</sub>H<sub>6</sub> and C<sub>4</sub>H<sub>8</sub> over the In<sub>2</sub>O<sub>3</sub>-50%Al<sub>2</sub>O<sub>3</sub> composite are similar to those over  $In_2O_3$  (Fig. S3), suggesting that this hypothesis is not true.

Dolejšek et al.<sup>36</sup> found that acetone can be converted to propylene through the intermediate of allene ( $C_3H_4$ ) catalyzed by Brønsted acid sites on HZSM-5. According to the literature,<sup>36</sup> it could be inferred that the role of zeolite Beta in  $In_2O_3$ -Beta composites is to provide an additional reaction

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pathway to convert the intermediate of acetone to propylene, thus enhancing the formation of propylene from ethanol. To verify this, we chose acetone as reactant to compare the catalytic performance of In2O3, In2O3-50%Beta and In2O3-50%Al<sub>2</sub>O<sub>3</sub>. As mentioned above,  $H_2$  is produced during the process of ethanol to acetone. Therefore, we added some H<sub>2</sub> in the feed. The conversion of acetone for these catalysts is ca. 98%. The product distribution on three catalysts at 460 °C after 3 h of the reaction is shown in Fig. 4. It is clear that the yield of C<sub>3</sub>H<sub>6</sub> over In<sub>2</sub>O<sub>3</sub>-50%Beta composite is substantially higher than that over  $In_2O_3$ , whereas the yield of  $C_4H_8$  (mainly isobutene) is markedly lower than that over In<sub>2</sub>O<sub>3</sub>. This result strongly suggests that zeolite Beta in  $In_2O_3$ -50%Beta composite can promote the conversion of acetone to propylene significantly. Accordingly, the possibility of conversion of acetone to isobutene is diminished. The yields of  $C_3H_6$  and  $C_4H_8$  over both  $In_2O_3$  and  $In_2O_3$ -50%Al<sub>2</sub>O<sub>3</sub> composite do not differ significantly. This result indicates that  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> in In<sub>2</sub>O<sub>3</sub>-50%Al<sub>2</sub>O<sub>3</sub> composite can not enhance the conversion of acetone to propylene due to the lack of Brønsted acid sites on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, since  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is inactive for cumene cracking at 300 °C (not shown here). When the Beta content in In<sub>2</sub>O<sub>3</sub>-Beta composites is low (In<sub>2</sub>O<sub>3</sub>-10%Beta), the promoting effect of zeolite Beta on the conversion of acetone to propylene is relatively small due to lower amount of Brønsted acid sites. Thus, the propylene yield over In<sub>2</sub>O<sub>3</sub>-10%Beta for the ETP reaction is also relatively low. However, when the Beta content in In<sub>2</sub>O<sub>3</sub>-Beta composites is high (In<sub>2</sub>O<sub>3</sub>-60%Beta and In<sub>2</sub>O<sub>3</sub>-70%Beta), the propylene yield for the ETP reaction is also relatively low. The reason is that too many Brønsted acid sites favors the formation of BTX and C<sub>2</sub>H<sub>4</sub>. As a result, the optimum yield of propylene is achieved on In<sub>2</sub>O<sub>3</sub>-Beta composites with 20-50% Beta.



The effect of the proximity of these two components  $(In_2O_3)$ and zeolite Beta) on the catalytic performance was also investigated. We prepared three In<sub>2</sub>O<sub>3</sub>-50%Beta catalysts with different distance between In<sub>2</sub>O<sub>3</sub> and zeolite Beta using different preparation methods. The product distribution on three catalysts at 460 °C after 3 h of the reaction is shown in Fig. 5. As the proximity of two components increases (Fig. 5a to Fig. 5c), the yield of  $C_3H_6$  rises substantially. Meanwhile, the yields of C<sub>2</sub>H<sub>4</sub> and BTX dramatically decrease. The results in Fig. 5 suggest that the proximity of two components  $(In_2O_3 and$ zeolite Beta) plays a crucial role in giving a high yield of C<sub>3</sub>H<sub>6</sub> for the ETP reaction. Propylene can be produced via two pathways from ethanol over In<sub>2</sub>O<sub>3</sub>-Beta composites. Conversion of ethanol on the surface of  $In_2O_3$  forms acetone. Then a part of acetone molecules are converted to  $C_3H_6$  on In<sub>2</sub>O<sub>3</sub>. Another part of acetone molecules move to the surface of zeolite Beta to produce C<sub>3</sub>H<sub>6</sub> catalyzed by Brønsted acid sites. The nearer distance between In2O3 and Beta will facilitate the fast diffusion of acetone molecules from In<sub>2</sub>O<sub>3</sub> to zeolite Beta, thus enhancing the conversion of acetone to propylene on the surface of zeolite Beta. That is to say, the second reaction pathway to produce propylene from ethanol is promoted. Consequently, the  $C_3H_6$  yield is higher for the ETP reaction.



**Fig. 4** Product distribution over  $In_2O_3$ ,  $In_2O_3$ -50%Beta and  $In_2O_3$ -50%Al<sub>2</sub>O<sub>3</sub> catalysts for acetone conversion. Reaction conditions: reaction temperature, 460 °C; acetone:H<sub>2</sub>O:H<sub>2</sub>:N<sub>2</sub> = 5:11:8:76, molar ratio; WHSV of acetone, 0.12 h<sup>-1</sup>; time-on-stream, 3 h.

**Fig. 5** Influence of the proximity of  $In_2O_3$  and zeolite Beta on catalytic behaviors of the  $In_2O_3$ -Beta (1:1 mass ratio) composite catalysts for ethanol conversion. (a) Stacking of 40-60 mesh  $In_2O_3$  and 40-60 mesh Beta. (b)  $In_2O_3$  and Beta powders were fully mixed in an agate mortar and then sieved to 40-60 mesh. (c) Prepared by deposition-precipitation method (see Experimental section), sieved to 40-60 mesh.

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Reaction conditions: reaction temperature, 460  $^{\circ}$ C; WHSV of ethanol, 0.2 h<sup>-1</sup>; time-on-stream, 3 h.

#### Effect of reaction conditions

We chose  $In_2O_3$ -50%Beta composite as a representative catalyst to investigate the effect of reaction temperature on the product distribution for the ETP reaction, and the results are shown in Fig. 6. The  $C_3H_6$  yield increases from 43.9% to 50.0% with an increase in reaction temperature from 440 °C to 460 °C, which is mainly due to the decrease in yields of  $C_2H_4$ ,  $C_4H_8$ ,  $CO_x$ ,  $C_2$ - $C_4$  paraffins and BTX. A further increase in reaction temperature leads to the decrease in  $C_3H_6$  yield, which is mainly due to the increase in yields of  $CO_x$ ,  $CH_4$  and  $C_2$ - $C_4$  paraffins. The  $C_3H_6$  yield at 500 °C is similar to that at 480 °C. Thus the highest yield of  $C_3H_6$  is obtained at 460 °C. In addition, with increasing the reaction temperature from 440 °C to 500 °C, the CH<sub>4</sub> yield also increases slightly (from 0.8% to 2.6%), but the BTX yield drops slightly (from 4.6% from 1.9%).



Fig. 6 Influence of reaction temperature on product distribution over  $In_2O_3$ -50%Beta composite for ethanol conversion. Reaction conditions: WHSV of ethanol, 0.2 h<sup>-1</sup>; time-on-stream, 3 h.



We further investigated the effect of space velocity (WHSV) on the product distribution over  $\ln_2O_3$ -50%Beta composite for the ETP reaction at 460 °C, and the results are shown in Fig. 7. In these experiments, WHSV was adjusted by varying the weight of the  $\ln_2O_3$ -50%Beta composite catalyst, while other reaction conditions were kept unchanged. Higher WHSV value implies shorter residence time. As discussed above, acetone is the intermediate for the conversion of ethanol to propylene, and its conversion to propylene is a slow step. Hence, higher propylene yield will be expected at longer residence time. When the WHSV value drops from 0.8 h<sup>-1</sup> to 0.2 h<sup>-1</sup>, the C<sub>3</sub>H<sub>6</sub> yield increases from 45.2% to 50.0%, but the acetone yield drops obviously from 9.8% to 1.7%. The yield of C<sub>4</sub>H<sub>8</sub> (mainly isobutene) declines slightly, whereas that of BTX increases slightly.

#### **Catalyst stability**

The stability of the  $In_2O_3$ -50%Beta composite in terms of propylene yield was also evaluated, and the results are shown in Fig. 8. The ethanol conversion keeps 100% during 105 h of time-on-stream operation at 460 °C. The yield of  $C_3H_6$  remains stable at around 50% during the initial 43 h. After that, the yield of  $C_3H_6$  diminishes slowly and that of acetone increases concurrently, which is due to the loss of active sites for acetone-to-propylene conversion. The  $C_3H_6$  yield is still above 40% after 81 h of the reaction and it drops to around 34% after 105 h of the reaction. Accordingly, the acetone yield increases from around 4% after 43 h time-on-stream to 25% after 105 h time-on-stream. The yield of BTX decreases slightly from around 4% at the initial 1 h to 0.5%, and that of  $C_2-C_4$  paraffins decreases slightly from around 6% to 4%. Meanwhile, the yields of other products remain almost constant.



Fig. 8 Stability test for the ETP reaction over  $\ln_2O_3$ -50%Beta composite. Reaction conditions: reaction temperature, 460 °C; WHSV of ethanol, 0.2 h<sup>-1</sup>.

The  $In_2O_3$ -50%Beta composite collected before and after the stability test were characterized by XRD. As shown in Fig. 9, no differences in the diffraction patterns were seen for fresh and spent catalysts, demonstrating the maintenance of phase

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structure after the stability test. <sup>27</sup>Al MAS NMR was used to characterize the  $In_2O_3$ -50%Beta composite collected before and after the stability test, and the results are shown in Fig. 10. For both fresh and spent catalysts, only an intense signal at 54 ppm, which is assigned to tetrahedral coordinated framework Al,<sup>37,38</sup> was seen. The absence of the signal at 0 ppm attributed to extra-framework Al in octahedral coordination<sup>37,38</sup> for both fresh and spent catalysts suggests that no dealumination occurred during the long-term experiment. The <sup>27</sup>Al NMR signal of spent catalyst is obviously broader than that of fresh one. This can be attributed to coke species interacting with the AlO<sub>4</sub> groups of the zeolite framework.<sup>39,40</sup>

Coking is generally responsible for the catalyst deactivation in acid-catalyzed conversion of ethanol.<sup>4,9,26</sup> The TG analysis shows that 4.7 wt% coke was detected on the In<sub>2</sub>O<sub>3</sub>-50%Beta composite after 105 h time-on-stream. Raman spectroscopy was used to investigate the nature of deposited carbon, and the result is shown in Fig. S4. The G-band and D-band were observed at 1609 and 1374  $\text{cm}^{-1}$ , respectively, for spent  $\ln_2 O_3$ -50%Beta composite. This observation is indicative of graphitic and amorphous carbon deposition.<sup>41,42</sup> As presented in Table 2, the amount of acid sites on In2O3-50%Beta obviously decreases from 0.517 to 0.318 mmol  $g^{-1}$  after the stability test, whereas the amount of basic sites remains almost unchanged. Coke deposition is responsible for the decrease in acidity. In contrast, the conversion of In<sub>2</sub>O<sub>3</sub>-50%Beta for cumene cracking decreases more significantly from 38.4% to 4.7% after the stability test, suggesting that coke is more readily to deposit on Brønsted acid sites.<sup>43,44</sup> Due to the decrease in acidity, the intermediate of acetone can not be converted in time. Thus, the yield of acetone increases and that of propylene decreases.



Fig. 9 XRD patterns of  $In_2O_3$ -50%Beta composite before and after the stability test.



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Fig. 10  $^{27}$ Al MAS NMR spectra of In<sub>2</sub>O<sub>3</sub>-50%Beta composite before and after the stability test.

#### Conclusions

We report for the first time the excellent catalytic performance of In2O3-Beta composite in the reaction of ethanol to propylene (ETP). The propylene yield is strongly dependent on the composite composition, i.e. acidity of the catalyst. The optimal result is achieved on the catalyst with 20-50% Beta, which can afford around 50% propylene yield. The superior propylene yield of In<sub>2</sub>O<sub>3</sub>-Beta composite compared to  $In_2O_3$  (around 32%) is due to the fact that zeolite Beta in  $In_2O_3$ -Beta composite catalyst enhances the conversion of the intermediate of acetone to propylene via an additional reaction pathway. The proximity of these two components (In<sub>2</sub>O<sub>3</sub> and zeolite Beta) plays a crucial role in giving a high yield of propylene for the ETP reaction. The yield of propylene over the  $In_2O_3$ -50%Beta composite remains stable at around 50% for 43 h at 460 °C and a space velocity of 0.2 h<sup>-1</sup>. This work affords a new strategy for the design of a high-performance catalyst by combining  $\ensuremath{\mathsf{In}_2\mathsf{O}_3}$  and zeolite for the ETP reaction.

#### Experimental

#### **Catalyst preparation**

A series of  $\ln_2O_3$ -x%Beta composite catalysts (x% = 10%, 20%, 30%, 40%, 50%, 60%, 70%) were prepared via depositionprecipitation method, where x% represents the weight percentage of H-Beta in the catalysts. 1.5 g H-Beta zeolite (Si/Al molar ratio = 14, Nankai University Catalyst Co., Ltd.) was dispersed in 250 mL deionized water and the pH value was adjusted to 9 with aqueous ammonia (3 mol L<sup>-1</sup>). Then aqueous ammonia (3 mol L<sup>-1</sup>) and a calculated amount of aqueous  $\ln(NO_3)_3$  (0.2 mol L<sup>-1</sup>) were simultaneously added dropwise into the above Beta suspension under vigorous stirring. During the whole precipitation process, the pH value was kept constant at 9 until the  $\ln(NO_3)_3$  solution was used up. The obtained suspension was aged for 24 h at room temperature, washed with deionized water and dried at 100 °C overnight. Finally, the product was calcined at 700 °C in air

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flow for 6 h. For comparison,  $In_2O_3$  was prepared in the same way without use of H-Beta zeolite.  $In_2O_3$ -50%Al<sub>2</sub>O<sub>3</sub> with 50 wt%  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> in the catalyst was prepared in the same way using  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (268 m<sup>2</sup> g<sup>-1</sup>, Alfa Aesar) as a substitution of H-Beta zeolite.

#### Catalyst characterization

X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance X-ray diffractometer using nickel-filtered Cu K $\alpha$ radiation at 40 kV and 40 mA. The BET surface areas and pore volumes of the samples were analyzed by N<sub>2</sub> sorption at -196 °C using a Quantachrome Autosorb iQ2 instrument. Before analysis, all samples were degassed in vacuum at 300 °C for 10 h. Field-emission scanning electron microscopy (FE-SEM) images were recorded on a Nova NanoSEM 450 instrument.

<sup>27</sup>Al magic-angle spinning nuclear magnetic resonance (<sup>27</sup>Al MAS NMR) characterization was performed on an AVANCE III 400WB instrument at a resonance frequency of 104.3 MHz. The samples were hydrated in a desiccator over a saturated NaCl solution for 3 days prior to the measurements. Thermogravimetric (TG) analysis was performed in air flow on a TA SDT Q600 apparatus to determine the amount of coke deposited on the catalyst after the stability test. The nature of deposited carbon was investigated by Raman spectra recorded on a HORIBA Jobin Yvon XploRA spectrometer with an exciting wavelength of 532 nm.

Surface acidity was measured by NH<sub>3</sub> temperatureprogrammed desorption (NH<sub>3</sub>-TPD) on a Micromeritics AutoChem II instrument loaded with 0.15 g sample (40-60 mesh). The sample was pretreated in He flow at 550 °C for 1 h, and cooled to 80 °C. The flow was switched to 10% NH<sub>3</sub>/He (30 mL min<sup>-1</sup>) and kept for 2 h, and then swept by He (30 mL min<sup>-1</sup>) for 1.5 h. Finally, the sample was heated in He (30 mL min<sup>-1</sup>) to 550 °C at a rate of 10 °C min<sup>-1</sup>. Surface basicity was measured by CO<sub>2</sub> temperature-programmed desorption (CO<sub>2</sub>-TPD) with the same instrument loaded with 0.15 g sample (40-60 mesh). The sample was pretreated in He flow at 550 °C for 1 h, and cooled to 80  $^{\circ}$ C. The flow was switched to 5% CO<sub>2</sub>/He (30 mL min<sup>-1</sup>) and kept for 2 h, and then swept by He (30 mL min<sup>-1</sup>) for 1.5 h. Finally, the sample was heated in He (30 mL  $min^{-1}$ ) to 550 °C at a rate of 10 °C  $min^{-1}$ . Cumene cracking, catalyzed only by Brønsted acid sites,<sup>24</sup> was used as a model reaction to measure the Brønsted acidity. The reaction was carried out at 300 °C in a pulsed microreactor loaded with 0.03 g catalyst (40-60 mesh). The catalyst was preheated at 450 °C for 1 h in He flow before reaction. Helium was used as the carrier gas at a flow rate of 40 mL min<sup>-1</sup>. The amount of cumene injected for each test was 1 µL.

#### **Catalytic testing**

The reaction of ethanol to propylene was carried out in a flowtype fixed-bed microreactor under atmospheric pressure. To obtain the gas reactant (ethanol: $H_2O:N_2$  =10:10:80, molar ratio), two  $N_2$  flows were passed through two glass evaporators filled with ethanol and H<sub>2</sub>O, respectively., then were mixed and passed through the catalyst. Unless otherwise stated, the reaction temperature was 460 °C, the catalyst load was 0.8 g (40–60 mesh), and the weight hourly space velocity (WHSV) of ethanol was 0.2 h<sup>-1</sup>. Prior to the reaction, the catalyst was pretreated in N2 flow at 500 °C for 1 h. The hydrocarbon reaction products including hydrocarbon oxygenates were analyzed periodically on-line with a gas chromatograph (GC) equipped with a FID and a PoraPLOT Q capillary column (50 m × 0.32 mm × 10  $\mu$ m). CH<sub>4</sub> and CO<sub>x</sub> (CO and CO<sub>2</sub>) were analyzed on-line by another GC equipped with a TCD and a 3 m long TDX–01 packed column. Before analyzing by TCD, the products were passed through a cold trap at -3 °C to remove the majority of water. The yield and selectivity were calculated on the carbon basis.

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### A table of contents entry

The superior propylene yield of  $In_2O_3$ -Beta composite (*ca.* 50%) for conversion of ethanol to propylene compared to  $In_2O_3$  (*ca.* 32%) is due to the fact that zeolite Beta in the composite enhances the conversion of the intermediate of acetone to propylene via an additional reaction pathway.

