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Sm-CeO_2/Zeolite Bifunctional Catalyst for Direct and Highly Selective Conversion of Bioethanol to Propylene

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Abstract: A series of Sm-CeO_2/Beta composites with various Beta contents were prepared by an incipient impregnation method, followed by calcination at 650 °C. They were characterized by XRD, N_2 adsorption, SEM, NH_3-TPD, CO_2-TPD and ^{27}Al MAS NMR. The Sm-CeO_2/Beta bifunctional catalysts exhibit eminent catalytic performances in the selective conversion of ethanol to propylene. In particular, the Sm-CeO_2/10%Beta catalyst with 10% Beta zeolite gives the highest C_3H_6 yield of 59.3%. A good match between Sm-CeO_2 and Beta accounts for its optimal result.

Keywords: bioethanol; Sm-CeO_2/Zeolite bifunctional catalyst; renewable propylene

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1. Introduction

Because of the ongoing shortage of petroleum and stricter environmental regulations, scientific awareness towards the development of alternative and renewable energy resources has increased. Due to its carbon-neutral renewable and abundant nature with low carbon emission, biomass has been generally recognized as one of the most feasible resources to produce biofuels (such as bioethanol). Although bioethanol is currently primarily employed as fuel or a fuel additive for motor vehicles, it is also a potential feedstock for the production of high value-added chemicals [1].

Propylene is a key building block for the chemical industry whose demand has been increasing in recent years [2]. There are many reports concerning the direct conversion of ethanol to propylene (ETP). The catalysts can be divided into three categories: zeolites, metal oxides and OX-ZEO (composite of metal oxide and zeolite). Zeolite catalysts, mainly ZSM-5 and modified ZSM-5, usually afford a propylene yield of 20–30% [3–12]. The metal oxides such as Y/CeO_2, Sc/In_2O_3, ZrO_2 and Y/ZrO_2 exhibit improved C_3H_6 yield of 30–44% [13–16]. Our group has reported that the composite catalyst of In_2O_3 (or Sc-In_2O_3) and zeolite Beta can give a high C_3H_6 yield of ca. 50% [17,18]. Recently, Xu and coworkers reported a 55% C_3H_6 yield over $ZnCeO_x$ and Beta composite [19]. However, to develop a catalyst exhibiting both high C_3H_6 yield and good stability is still a challenge.

Inspired by the prominent performances of OX-ZEO composite catalysts in the ETP reaction, in this work we have developed a new type of bifunctional catalyst composed of Sm-CeO_2 oxide and Beta zeolite which exhibits excellent catalytic performance. In particular, the Sm-CeO_2/10%Beta catalyst with 10% Beta shows a stable C_3H_6 yield of ca. 59% during continuous 120 h of reaction at 440 °C.

2. Results and Discussion

2.1. Structural and Textural Properties

The XRD patterns of SmCe/Beta catalysts with different Beta contents (Figure 1) reveal that these samples display single-phase reflections attributed to the cubic fluorite structure of CeO_2 (PDF #43-1002), with the peak positions slightly shifted to lower angles upon the Sm doping. All SmCe/Beta catalysts display larger lattice parameters than pure CeO_2 (Table 1). Taking into account the larger ionic radius of Sm^{3+} than Ce^{4+} (0.108 and 0.097 nm for the eight coordination, respectively), the above results imply that Sm^{3+} cations are doped into the crystal lattice of CeO_2. With the increase in Beta content from 2% to 20%, the surface areas of SmCe/Beta catalysts increase markedly from 30 to 124 m^2/g, and the micropore volumes rise from 0.004 to 0.032 cm^3/g (Table 1).

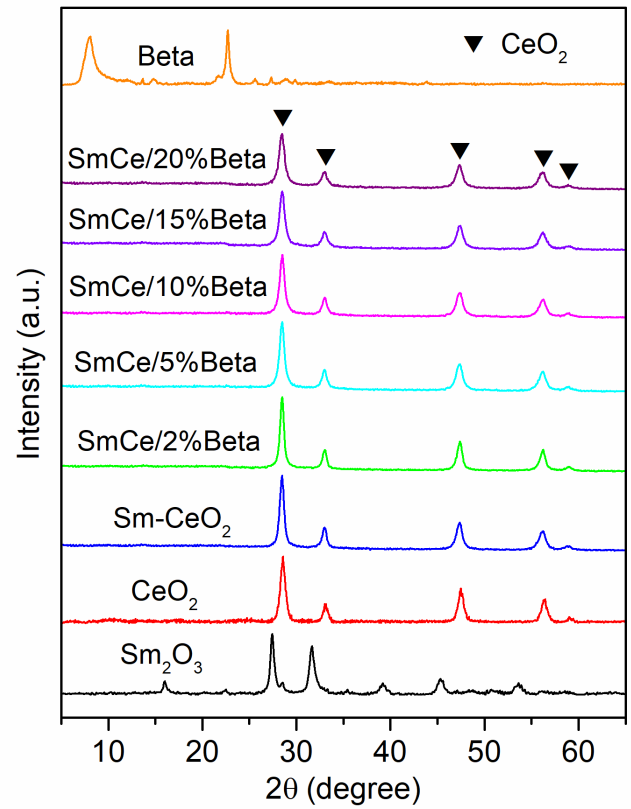

Figure 1. XRD patterns of SmCe/Beta catalysts with different Beta contents.

Table 1. Textural properties of SmCe/Beta catalysts with different Beta contents.

Catalyst	Sm (wt%) [a]	Ce (wt%) [a]	S_{BET} (m^2/g)	V_{micro} (cm^3/g) [b]	a = b = c (nm) [c]
Sm-CeO_2	20.2	62.2	21	0	0.5420
SmCe/2%Beta	19.7	61.1	30	0.004	0.5420
SmCe/5%Beta	19.1	59.2	54	0.009	0.5420
SmCe/10%Beta	18.0	56.2	69	0.015	0.5420
SmCe/15%Beta	17.1	53.2	93	0.022	0.5419
SmCe/20%Beta	16.0	49.9	124	0.032	0.5419
Beta	-	-	546	0.183	-

[a] Detected by ICP; [b] Calculated by the *t*-plot method; [c] The lattice parameter of CeO_2 is 0.5411 nm.

Figure 2 shows the SEM images of various samples. For the SmCe/2%Beta and SmCe/10%Beta catalysts, zeolite Beta is unobservable owing to its low content, suggesting

that Beta was buried by Sm-CeO_2 particles. For the SmCe/20%Beta catalyst with higher Beta content, zeolite Beta with its surfaces covered by Sm-CeO_2 particles can be observed.

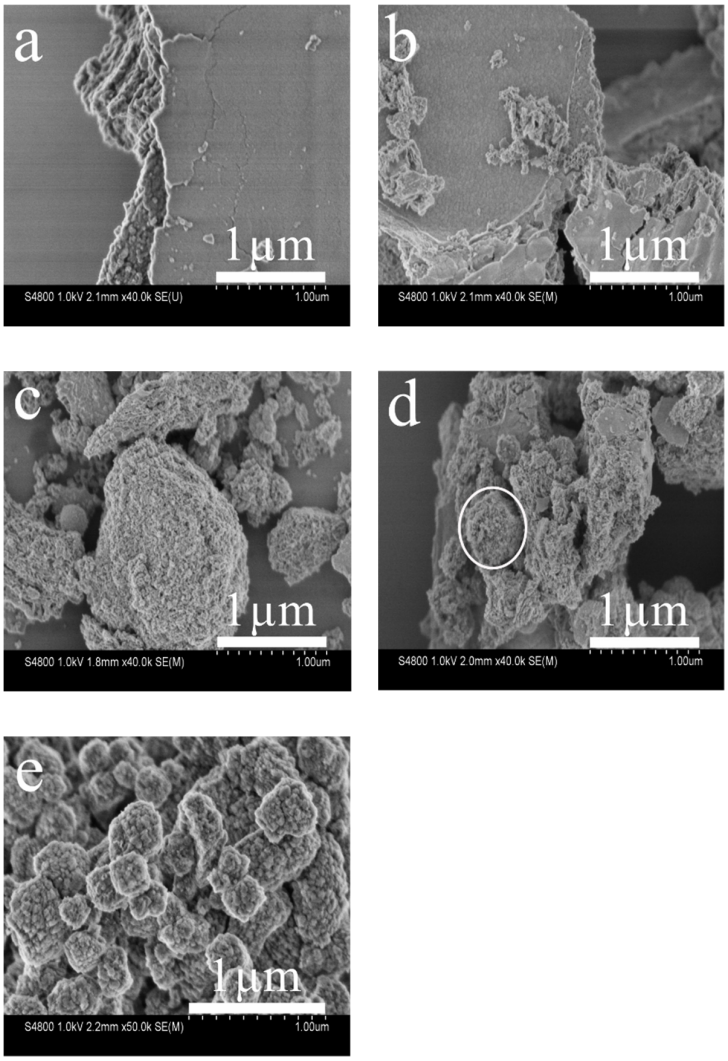

Figure 2. SEM images of different samples. (**a**) Sm-CeO_2, (**b**) SmCe/2%Beta, (**c**) SmCe/10%Beta, (**d**) SmCe/20%Beta, (**e**) Beta. The white circle area in Figure 2d represents zeolite Beta.

2.2. NH_3-TPD and CO_2-TPD

NH_3-TPD was used to probe the surface acidity, and the results are given in Figure 3 and Table 2. Sm-CeO_2 presents a broad desorption peak, whereas there are two desorption peaks for zeolite Beta. All SmCe/Beta catalysts give a broad peak of NH_3 desorption. As shown in Table 2, zeolite Beta has acid sites of 0.879 mmol/g, much greater than Sm-CeO_2 (0.118 mmol/g). With the increase in Beta content from 2% to 20%, the number of acid sites present on SmCe/Beta catalysts improves from 0.163 to 0.323 mmol/g. CO_2-TPD was employed to probe the surface basicity, and the results are presented in Figure 4 and Table 2. All catalysts show a broad peak of CO_2 desorption. The amount of basic sites on SmCe/Beta catalysts is similar.

Table 2. NH_3-TPD and CO_2-TPD results of SmCe/Beta catalysts with different Beta contents.

Catalyst	NH_3-TPD Result (mmol/g)			CO_2-TPD Result (mmol/g)		
	Weak [a]	Strong [b]	Total	Weak [d]	Moderate [e]	Total
Sm-CeO_2	0.036	0.082	0.118	0.042	0.069	0.111
SmCe/2%Beta	0.053	0.110	0.163	0.070	0.080	0.150
SmCe/5%Beta	0.069	0.124	0.193	0.072	0.082	0.154
SmCe/10%Beta	0.083	0.150	0.233	0.072	0.083	0.155
SmCe/15%Beta	0.113	0.186	0.299	0.080	0.085	0.165
SmCe/20%Beta	0.120	0.203	0.323	0.077	0.083	0.160
Beta [c]	0.515	0.364	0.879	-	0.060	0.060

[a] NH_3 desorbing between 80 and 200 °C; [b] NH_3 desorbing between 200 and 500 °C; [c] For zeolite Beta, NH_3 molecules desorbing between 80 and 250 °C correspond to weak acidity, and those desorbing between 250 and 500 °C correspond to strong acidity; [d] CO_2 desorbing between 80 and 200 °C; [e] CO_2 desorbing between 200 and 500 °C.

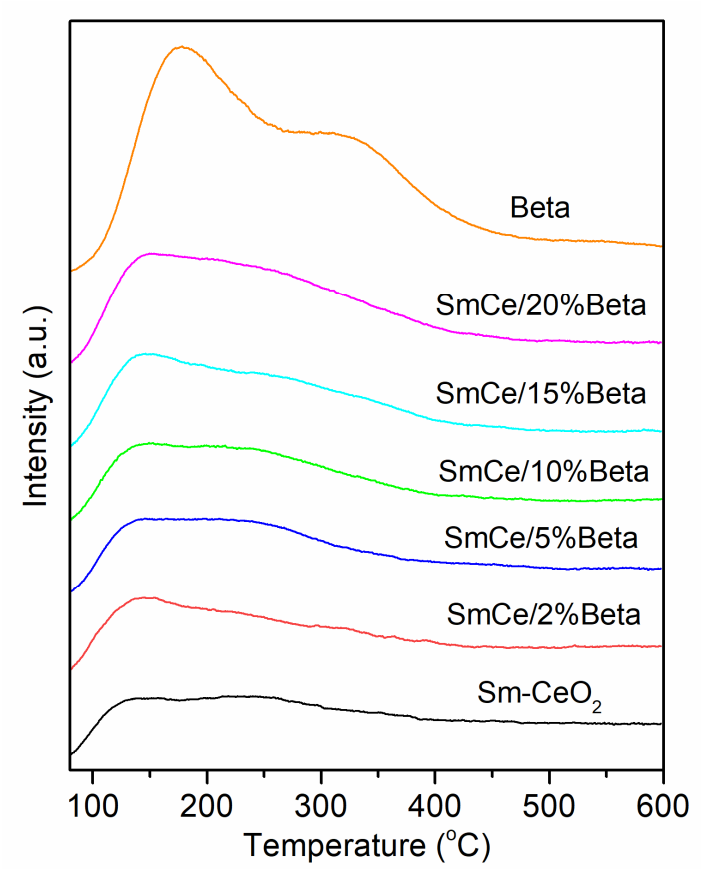

Figure 3. NH_3-TPD profiles of SmCe/Beta catalysts with different Beta contents.

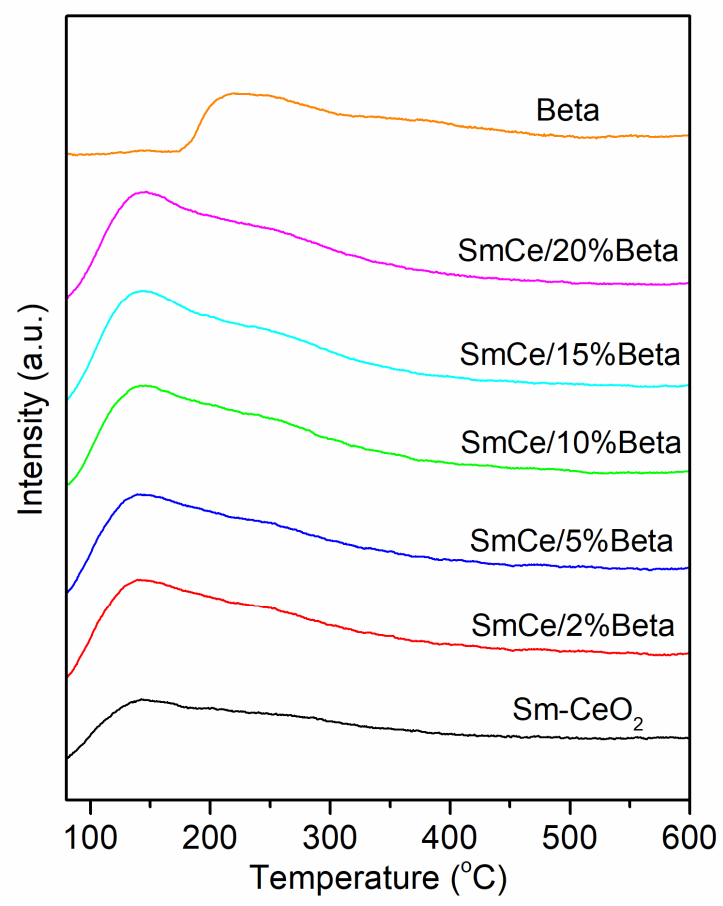

Figure 4. CO_2-TPD profiles of SmCe/Beta catalysts with different Beta contents.

2.3. Catalytic Performances

Figure 5 shows the product distribution of the ETP reaction over SmCe/Beta catalysts after 5 h on stream. All catalysts afford 100% conversion of ethanol. The Sm-CeO_2 catalyst only gives a low propylene yield of 6.2%. The main products on Sm-CeO_2 are acetone (22.7%), ethylene (37.4%) and CO_x (12.9%, mostly CO_2), C_2-C_4 paraffins (7.8%) and BTX (benzene, toluene and xylenes, 7.4%). Zeolite Beta also affords a propylene yield as low as 9.1%. The main products on Beta are ethylene (59.1%), BTX (12.7%) and C_2-C_4 paraffins (9.7%). However, the integration of Sm-CeO_2 oxide with zeolite Beta brings about a significantly enhanced yield of propylene. The catalytic performance of SmCe/Beta catalysts depends largely on the content of Beta. When the Beta content increases from 2% to 10%, the propylene yield improves from 54.2% to 59.3%, which is in line with the enhanced amount of acid sites present on the catalysts (Table 2). In the meantime, the yields of acetone, ethylene and C_2-C_4 paraffins diminish. A further increase in the content of Beta to 20% results in the decline of the C_3H_6 yield to 47.8%. The reason is that more acid sites present on SmCe/15%Beta and SmCe/20%Beta facilitate the formation of ethylene and BTX. Thus, the SmCe/10%Beta catalyst with 10% Beta exhibits the maximum yield of C_3H_6. By correlating the acidity and basicity characterizations with catalytic performance of SmCe/Beta catalysts with different Beta contents, it is clear that since the catalyst basicity is similar (0.150–0.165 mmol/g), its acidity is much more crucial for the highly selective conversion of ethanol to propylene. Thus, an appropriate amount of acid sites in SmCe/10%Beta are responsible for its best performance.

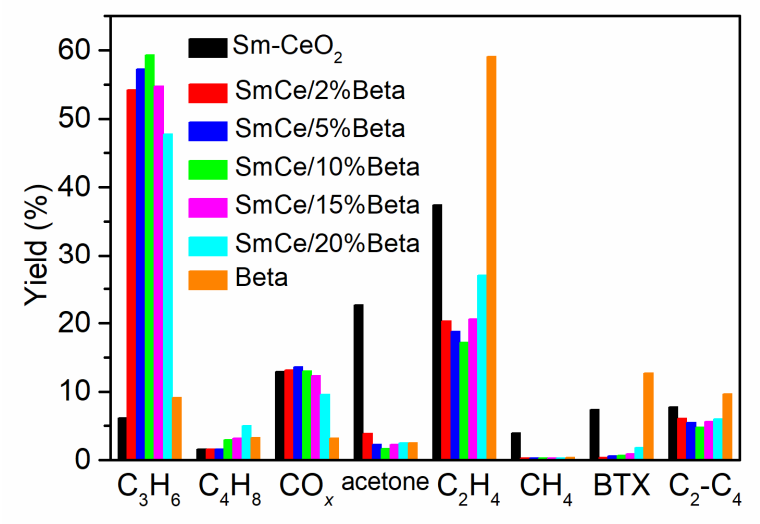

Figure 5. Product distribution for the ETP reaction over SmCe/Beta catalysts with different Beta contents. Reaction conditions: 440 °C; WHSV of ethanol 0.52 h^{-1}; ethanol:H_2O:N_2 = 10:10:80 (molar ratio); time on stream 5 h.

For the conversion of ethanol to propylene over the Y-CeO_2 catalyst, Hayashi et al. [13] suggested that the reaction pathway was ethanol → acetaldehyde → ethyl acetate → acetone → 2-propanol → propylene, i.e., the acetone route. The acetone intermediate undergoes Meerwein–Ponndorf–Verley (MPV) reduction by ethanol, producing 2-propanol. The subsequent dehydration of produced 2-propanol catalyzed by acid sites yields propylene. Compared with other zeolites, zeolite Beta possesses unique acid properties related to local defects. Beta was reported to exhibit remarkable behavior in the MPV reaction [20–23]. The catalytic activity is associated with Lewis acid aluminum atoms which are only partially bonded to the framework [20,21]. It is generally accepted that the conversion of the acetone intermediate to propylene is the rate-determining step of the ETP reaction [14,24]. Taking into account the aforementioned research results [13,14,20–24], we think that the function of zeolite Beta in SmCe/Beta catalysts is to enhance both the conversion of acetone produced on Sm-CeO_2 to 2-propanol via the MPV reaction and the dehydration of generated 2-propanol to propylene, i.e., promoting the conversion of the acetone intermediate to propylene. Hence, the selective conversion of ethanol to propylene is enhanced significantly.

In order to corroborate our hypothesis, we first chose 2-propanol as the reactant to investigate catalytic properties of Sm-CeO_2, SmCe/10%Beta and Beta. All catalysts afford 100% conversion. As presented in Figure 6, the propylene yield is much higher on SmCe/10%Beta than Sm-CeO_2 (76.3% vs. 44.5%), which is due to an obviously greater number of acid sites present on the former catalyst than the latter one (Table 2). Zeolite Beta gives a high propylene yield of 68.8%. Clearly, the results in Figure 6 indicate that the Beta component in the SmCe/10%Beta catalyst enhanced the dehydration of 2-propanol to propylene significantly.

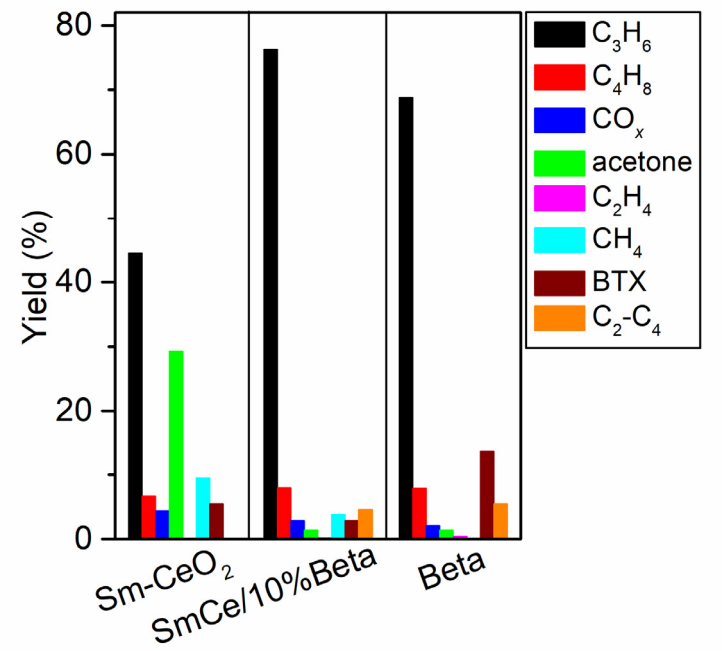

Figure 6. Product distribution over Sm-CeO_2, SmCe/10%Beta and Beta catalysts for 2-propanol conversion. Reaction conditions: 440 °C; 0.3 g SmCe/10%Beta, 0.27 g Sm-CeO_2 or 0.03 g Beta; 2-propanol :H_2O:H_2:N_2 = 5:11:8:76 (molar ratio), total flow 13.1 mL/min; time on stream 5 h.

It is important to point out that the MPV reduction of acetone by ethanol (namely CH_3COCH_3 + CH_3CH_2OH = $CH_3CHOHCH_3$ + CH_3CHO) is inclined to proceed towards the left side due to the fact that the dehydrogenation of 2-propanol is easier than that of ethanol [25]. However, the coupled dehydration of 2-propanol to propylene will favor the shift of the above MPV reaction to the right side due to the immediate removal of 2-propanol. In order to demonstrate the promoting role of Beta component in SmCe/Beta composites for the MPV reduction of acetone by ethanol separately, we selected the reduction of cyclohexanone by 2-butanol as a model MPV reaction to evaluate the activities of Sm-CeO_2, SmCe/10%Beta and Beta. As seen in Table 3, Sm-CeO_2 gives a very low conversion of cyclohexanone (0.5%), whereas the SmCe/10%Beta catalyst presents a conversion as high as 35.9%. The higher conversion observed on SmCe/10%Beta is associated with higher activity of Beta component in the catalyst (30.0% conversion). Based on the results in Table 3, it can be therefore rational to deduce that Beta component in the SmCe/10%Beta catalyst significantly enhanced the MPV reaction between acetone and ethanol separately. In conclusion, the results in Figure 6 and Table 3 have validated our conjecture.

Table 3. Results of MPV reduction of cyclohexanone with 2-butanol [a].

Catalyst	Sm-CeO_2	SmCe/10%Beta	Beta	SmCe/10%ZSM-5	ZSM-5
Conv. (%)	0.5	35.9	30.0	0.6	0.2

[a] Reaction conditions: 150 °C; 0.1 g SmCe/10%Beta or SmCe/10%ZSM-5, 0.09 g Sm-CeO_2, 0.01 g Beta or ZSM-5; 5 mmol cyclohexanone, 50 mmol 2-butanol; reaction time 1 h.

ZSM-5 is a kind of zeolite with MFI structure, which is generally employed as a solid acid catalyst. The product distribution of the ETP reaction over SmCe/10%ZSM-5, Sm-CeO_2 and ZSM-5 catalysts is compared in Figure 7. The propylene yield on the SmCe/10%ZSM-5 catalyst is 21.8%, evidently higher than that on Sm-CeO_2 (6.2%) and ZSM-5 (16.4%). This result implies that the integration of Sm-CeO_2 and zeolite ZSM-5 can also obviously enhance the ETP reaction. Interestingly, the SmCe/10%ZSM-5 catalyst

gives a much lower propylene yield than SmCe/10%Beta. As expected, when using 2-propanol as the reactant, the SmCe/10%ZSM-5 catalyst exhibits much higher propylene yield than Sm-CeO_2 (77.8% vs. 44.5%, Figure 8), which is due to the fact that ZSM-5 is highly active for the dehydration of 2-propanol to propylene (63.1% yield). This observation suggests that zeolite ZSM-5 component in the SmCe/10%ZSM-5 catalyst promoted the dehydration of 2-propanol to propylene markedly. However, both SmCe/10%ZSM-5 and Sm-CeO_2 display very low conversion for the MPV reaction between cyclohexanone and 2-butanol (0.6% and 0.5%, respectively, Table 3). It is thus inferred that the ZSM-5 component in the SmCe/10%ZSM-5 catalyst cannot promote the MPV reduction of acetone by ethanol obviously, unlike in the case of the Beta component in the SmCe/10%Beta catalyst. Importantly, this is the main reason responsible for the far lower yield of propylene observed on SmCe/10%ZSM-5 than SmCe/10%Beta.

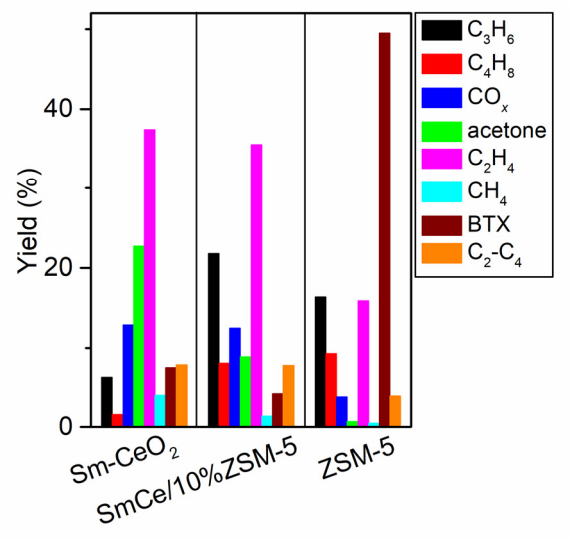

Figure 7. Product distribution for the ETP reaction over SmCe/10%ZSM-5, Sm-CeO_2 and ZSM-5 catalysts. Reaction conditions: 440 °C; WHSV of ethanol 0.52 h^{-1}; ethanol:H_2O:N_2 = 10:10:80 (molar ratio); time on stream 5 h. Note that all catalysts give 100% conversion.

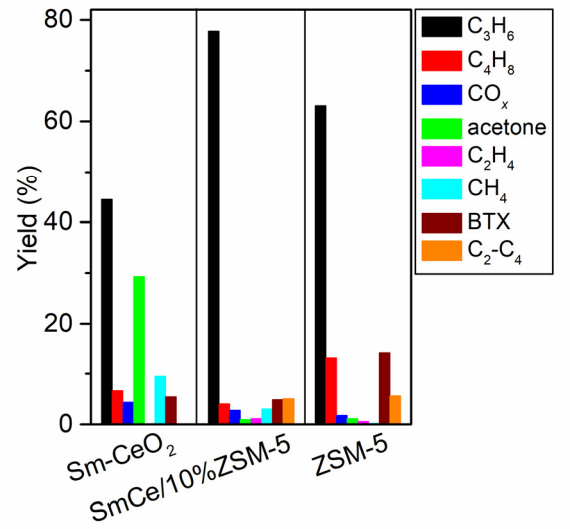

Figure 8. Product distribution over Sm-CeO_2, SmCe/10%ZSM-5 and ZSM-5 catalysts for 2-propanol conversion. Reaction conditions: 440 °C; 0.3 g SmCe/10%ZSM-5, 0.27 g Sm-CeO_2 or 0.03 g ZSM-5; 2-

propanol:H_2O:H_2:N_2 = 5:11:8:76 (molar ratio), total flow 13.1 mL/min; time on stream 5 h. Note that all catalysts give 100% conversion.

The proximity effect of two components (i.e., Sm-CeO_2 and Beta) on the catalytic performance was also studied, and the results are illustrated in Figure 9. We prepared three SmCe/10%Beta catalysts with different distances between Sm-CeO_2 and Beta. With the increase in the proximity between two components (Figure 9a–c), the propylene yield augments dramatically. Meanwhile, the yields of acetone, CO_x, BTX and C_4H_8 (mostly isobutene) decline. Ethanol is first converted to acetone on Sm-CeO_2, then acetone is converted to propylene on zeolite Beta. The nearer distance between two components will benefit the faster diffusion of acetone from Sm-CeO_2 to Beta, where acetone underwent the MPV reduction by unreacted ethanol to yield 2-propanol, followed by the dehydration of generated 2-propanol to propylene. Consequently, the selective conversion of ethanol to propylene is markedly improved.

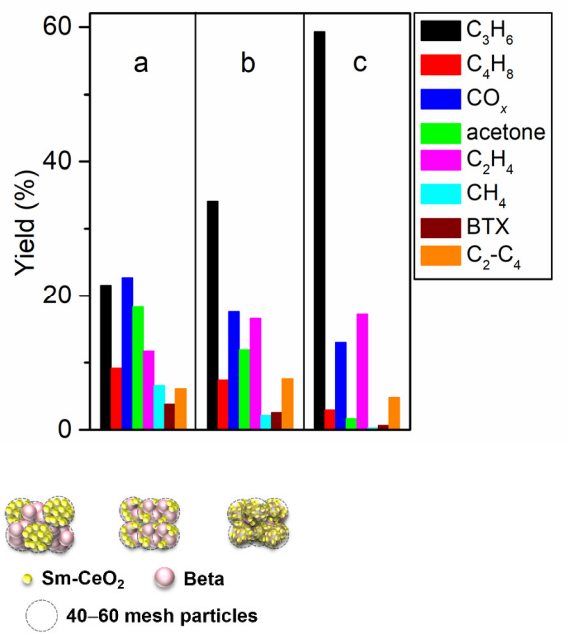

Figure 9. Effect of the proximity of Sm-CeO_2 and zeolite Beta on catalytic performance of the SmCe/10%Beta catalysts for the ETP reaction. (**a**) Stacking of 40–60 mesh Sm-CeO_2 and 40–60 mesh Beta. (**b**) Sm-CeO_2 and Beta powders were first mixed in an agate mortar and then sieved to 40–60 mesh. (**c**) Prepared by an incipient impregnation method, sieved to 40–60 mesh. Reaction conditions: 440 °C; WHSV of ethanol 0.52 h^{-1}; ethanol:H_2O:N_2 = 10:10:80 (molar ratio); time on stream 5 h.

We further investigated the stability of the best SmCe/10%Beta catalyst in terms of propylene yield for a longer time, which was evaluated at 440 °C continuously for 120 h. The ethanol conversion was 100% during the total duration. As presented in Figure 10, after a short induction period, the propylene yield maintains at about 59%, displaying good stability. The SmCe/10%Beta catalyst collected before and after the stability test was characterized by means of XRD and ^{27}Al MAS NMR. It is clear that there is no difference in the diffraction patterns of fresh and spent catalysts,

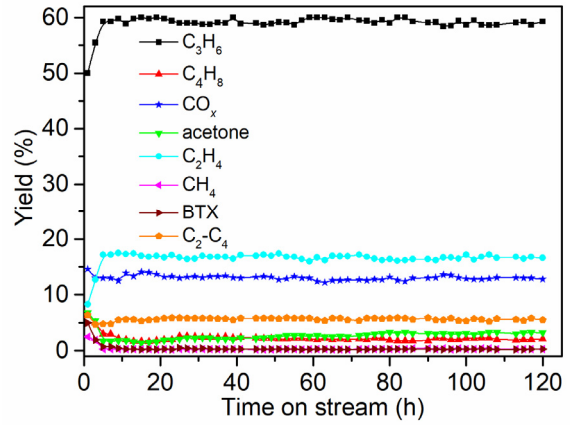

Figure 10. Long-term test of the SmCe/10%Beta catalyst for the ETP reaction. Reaction conditions: 440 °C; WHSV of ethanol 0.52 h^{-1}; ethanol:H_2O:N_2 = 10:10:80 (molar ratio).

Suggesting that the cubic fluorite structure is well retained (Figure S1). Only a strong signal at 54 ppm attributed to tetra-coordinated framework Al was observed for both fresh and spent catalysts (Figure S2), suggesting that no dealumination appeared during 120 h of reaction. Clearly, the results in Figures S1 and S2 indicate that the catalyst structure is well maintained during the long-term test.

The catalytic performance of our best catalyst (SmCe/10%Beta) in this work is compared with other typical catalysts reported in the literature. Table S1 lists the propylene yield together with the reaction conditions. As far as both propylene yield and catalyst stability are concerned, the SmCe/10%Beta catalyst is superior to the reported catalysts.

3. Materials and Methods

3.1. Catalyst Preparation

A series of Sm-CeO_2/*x*%Beta catalysts (labelled as SmCe/*x*%Beta) were prepared by an incipient impregnation method using $Sm(NO_3)_3 \bullet 6H_2O$ and $Ce(NO_3)_3 \bullet 6H_2O$ as the precursors, where *x*% represents the mass percent of H-Beta in the catalysts. The Sm/Ce molar ratio was fixed to 0.3. Zeolite H-Beta (Si/Al molar ratio of 14) was purchased from Nankai University Catalyst Co., Ltd. After drying under an infrared lamp, the sample was calcined at 650 °C in air flow for 5 h. For comparison, the Sm-CeO_2 catalyst was synthesized using the same procedure but without adding zeolite H-Beta. We also prepared the SmCe/10%ZSM-5 catalyst in the same way as SmCe/10%Beta, during which H-ZSM-5 with a Si/Al molar ratio of 15 obtained by calcination of NH_4-ZSM-5 (CBV3024E, Zeolyst) at 450 °C for 4 h was used.

3.2. Characterization of Catalyst

Powder X-ray diffraction (XRD) patterns were recorded on a D2 PHASER X-ray diffractometer using nickel-filtered Cu Kα radiation at 30 kV and 10 mA (Brucker, Madison, WI, USA). Sm and Ce content was determined by inductively coupled plasma (ICP) atomic emission spectroscopy using an Optima 8000 apparatus (Perkin–Elmer, Waltham, MA, USA). The BET surface areas and pore volumes of the catalysts were determined from N_2 adsorption at −196 °C on a Micromeritics Tristar 3000 apparatus (Micromeritics, Atlanta, GA, USA). Prior to measurement, all samples were degassed at 300 °C under vacuum for 5 h. Field-emission scanning electron microscopy (FESEM) images were taken using a Hitachi S-4800 instrument (Hitachi, Tokyo, Japan). ^{27}Al magic-angle spinning nuclear magnetic resonance (^{27}Al MAS NMR) characterization was performed on an AVANCE III 400WB spectrometer (Brucker, Rheinstetten, Germany). The spectra were acquired at a resonance frequency of 104.3 MHz. The sample was hydrated for 3 days in a desiccator filled with a saturated NaCl solution before the measurement. Temperature-

programmed desorption of NH_3 (NH_3-TPD) and temperature-programmed desorption of CO_2 (CO_2-TPD) characterizations were carried out on an AutoChem II instrument (Micromeritics, Atlanta, GA, USA) loaded with 0.2 g of sample (40–60 mesh). The sample was in situ pretreated at 550 °C in N_2 flow for 1 h. Afterwards, ammonia was adsorbed at 80 °C for 2 h under 10 vol.% NH_3/He flow (30 mL/min) or CO_2 was adsorbed at 80 °C for 2 h under 5 vol.% CO_2/He flow (30 mL/min). Subsequently, the flow was changed to He flow (30 mL/min) and swept for 2 h. Finally, the sample was heated in He flow (30 mL/min) to 600 °C at a rate of 10 °C/min.

3.3. Catalytic Tests

The catalytic reaction of ethanol to propylene was performed in a fixed-bed flow microreactor at 440 °C under ambient pressure [17]. The catalyst (0.3 g) was pretreated in N_2 flow at 500 °C for 1 h prior to reaction. A gas mixture of ethanol (AR, Sinopharm, 10 mol%), H_2O (10 mol%) and N_2 (80 mol%) was fed to the catalyst bed with a weight hourly space velocity (WHSV) of ethanol of 0.52 h^{-1}. The process of 2-Propanol dehydration was carried out in the same microreactor at 440 °C under ambient pressure. Prior to reaction, the catalyst was pretreated in N_2 flow at 500 °C for 1 h. The composition of feed gas was 2-propanol:H_2O:H_2:N_2 = 5:11:8:76 (molar ratio), and the total flow was 13.1 mL/min. The hydrocarbon reaction products including hydrocarbon oxygenates were analyzed periodically on-line with a gas chromatograph (GC) equipped with an FID and a PoraPLOT Q capillary column (50 m × 0.32 mm × 10 μm). CH_4 and CO_x (CO and CO_2) 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 using the standard normalization method on the basis of carbon atom balance. The selectivity to one specific product is defined as the ratio of the number of carbon moles in this product to the total number of carbon moles in all products. The yield to one specific product is defined as the ratio of the number of carbon moles in this product to the total number of carbon moles in all products and unreacted ethanol or 2-propanol. Generally, the carbon mass balance can be achieved up to 98%.

The MPV reaction between cyclohexanone and 2-butanol was carried out in an autoclave reactor (25 mL) equipped with a magnetic stirrer. Cyclohexanone (5 mmol), 2-butanol (50 mmol) and catalyst (preactivated at 400 °C for 1 h) were placed in the reactor. Then, the reactor was sealed and purged three times with N_2. The reaction was conducted at 150 °C for 1 h under stirring (at 600 rpm). The products were analyzed by a GC equipped with an FID and an SE-30 capillary column (30 m × 0.25 mm × 0.25 μm).

4. Conclusions

In this work we report a new finding that the Sm-CeO_2/Beta bifunctional catalysts exhibit excellent catalytic performances in the ETP reaction. Sm-CeO_2 catalyzed the conversion of ethanol to acetone, and zeolite Beta catalyzed the conversion of the acetone intermediate to propylene. A good match between Sm-CeO_2 and Beta makes the Sm-CeO_2/10%Beta catalyst with 10% Beta display the optimal propylene yield of 59.3%. The C_3H_6 yield over Sm-CeO_2/10%Beta keeps stable at around 59% for 120 h at 440 °C and a space velocity of 0.52 h^{-1}.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/catal12040407/s1, Figure S1. XRD patterns of SmCe/10%Beta before and after the stability test; Figure S2. ^{27}Al MAS NMR spectra of the SmCe/10%Beta catalyst before and after the stability test; Table S1. Propylene yield of some catalysts for the ETP reaction in reported literature

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