Influences of preparation parameters on the structural and catalytic performance of zirconia in isosynthesis

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Abstract

The influences of precipitation pH, zirconium salt precursors and the calcination temperatures on the crystal structure and catalytic performance of zirconia in isosynthesis have been studied. The results indicated that the catalytic performance of zirconia in isosynthesis was strongly influenced by the pH of precipitating solution, zirconium salt precursors and the calcination temperatures, However, the crystal phase of zirconia was not so sensitively dependent on the pH. Monoclinic was always the main crystal phase when the value of pH was changed in the range of 6–14. Zirconia prepared from $Zr(NO_3)_4$, $ZrCl_4$, $ZrOCl_2$ were monoclinic/tetragonal, but monoclinic was the dominant phase. Zirconia prepared from $Zr(SO_4)_2$ was a mixture of tetragonal/amorphous. Even trace of SO_4^{2-} involved in the gel, the crystallization of zirconia was delayed, the phase transformation from tetragonal to monoclinic being inhibited. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Zirconia; Isosynthesis; Catalytic performance

1. Introduction

Isosynthesis is the reaction in which syngas is converted to branched chain hydrocarbons [1–3]. The term of isosynthesis has been particularly used in the synthesis of isobutane and isobutene by the hydrogenation of CO. Zirconium dioxide has been found to be an effective catalyst for this reaction [4–10]. It has been also reported that the structure of zirconia depends sensitively on the preparation conditions. Many material scientists have devoted their attentions [11–14] to the influence of preparation parameters on the structures of zirconia. Zirconia prepared under the specific conditions have been employed in isosynthesis [5,8,10]. The influence of preparation conditions on the catalytic performance in isosynthesis has not been evaluated in detail. Thus, we try to elucidate the dependence of the catalytic performance of zirconia in isosynthesis on the preparation conditions in this paper.

2. Experimental

2.1. Preparation of catalysts

Three series of zirconia were prepared. The gels of first series of zirconia were precipitated

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in the following sequences. For ZrO_2-1, a solution of $ZrOCl_2$ (0.15 M) was added dropwise into a stirred solution of NH_4OH (2.5%) (pH kept constant at 10). For ZrO_2-2, a solution of NH_4OH (2.5%) was added dropwise into a stirred solution of $ZrOCl_2$ (0.15 M) (pH changed from 3 to 10). For ZrO_2-3, a solution of NH_4OH (2.5%) and a solution of $ZrOCl_2$ (0.15 M) were added dropwise into a vessel with stirring (pH = 7). ZrO_2-4 was prepared at pH = 14, using KOH as basic precipitant. The precipitate was aged for 3 h, then was washed using deionized water thoroughly until no Cl^- was detected with 0.1 M $AgNO_3$ solution. Then the precipitate was filtered and dried at 353 K for 10 h, and calcined at 773 K for 3 h.

The second series of catalysts were prepared using different zirconium salt precursors: $Zr(SO_4)_2$, $Zr(NO_3)_4$, $ZrCl_4$, $ZrOCl_2$. Commercial ZrO_2 was also used to compare with the catalysts prepared from the above precursors. The precipitating procedure was same as that of ZrO_2-2 for the second series of zirconia, but the pH was changed from 3 to 7. The electron conductivity of the filtered liquor was checked to determine whether the anion was washed away thoroughly from the gel.

The third series of catalysts were prepared according to the procedure of ZrO_2-1, but they were calcined at 673 K, 723 K, 773 K, 823 K, 873 K, 923 K, 1073 K, respectively.

2.2. Characterization of catalyst structure

Bulk characterization of calcined zirconia was carried out by X-ray diffractometer(D/MAXRB) using CuKα radiation with a nickel filter. Measurement of surface area was performed on a CHEMBET-3000 using N_2 as adsorption gas.

2.3. Reaction procedure

The hydrogenation of CO was carried out using a flow-type fixed-bed pressurized tubular reactor at 623–723 K. The reactor consisted of an 8-mm i.d. stainless steel tube. In these experiments, 2 ml of a catalyst was packed in the reactor and pretreated in a stream of N_2 at 673 K for 2–3 h. The weight of the catalyst depended on its bulk density. After the pretreatment, a mixed gas of CO and H_2 (CO/H_2 = 1) was introduced into the reactor and the pressure was regulated to the desired pressure (5.0 MPa). The reactor effluent was introduced into two on line gas chromatographs (GC). One was used to separate CO, CH_4, CO_2, CH_3OH, CH_3OCH_3, C_2 and C_3 through a GDX-101 column and another was equipped with 2% squalane supported on aluminum oxide to separate C_4 isotherms and C_5^+ hydrocarbons.

3. Results and discussion

3.1. The influence of precipitating pH

The XRD profiles of ZrO_2-1, 2, 3, are shown in Fig. 1a, b, c. Although the pH values of the precipitating solutions were different, the main crystal phase of the three samples was monoclinic. This is in agreement with Davis' result [11] in which monoclinic zirconia was produced from the materials precipitated in the pH range of 6.5 to 10.4. This result means that the crystal phase of zirconia was not so sensitive to the pH of precipitation. Even when the precipitate gel was aged in a KOH solution (pH 13–14) for several hours, the monoclinic phase was dominant (Fig. 1d). However, if the alkali metal ions (0.1% Na/Zr) were involved in the gel, the main crystal phase of the resulted zirconia was tetragonal (Fig. 1e).

The catalytic performance of ZrO_2, which were prepared at different pH, in the reaction of isosynthesis are shown in Table 1. As it can be seen, ZrO_2-3 which was prepared at pH = 6–7 showed highest activity, but the reaction selectivity to isobutene was obscured by its high activity comparing with other catalysts. The highest selectivity was obtained over ZrO_2-2, which was prepared in the pH range of 3 to 10.
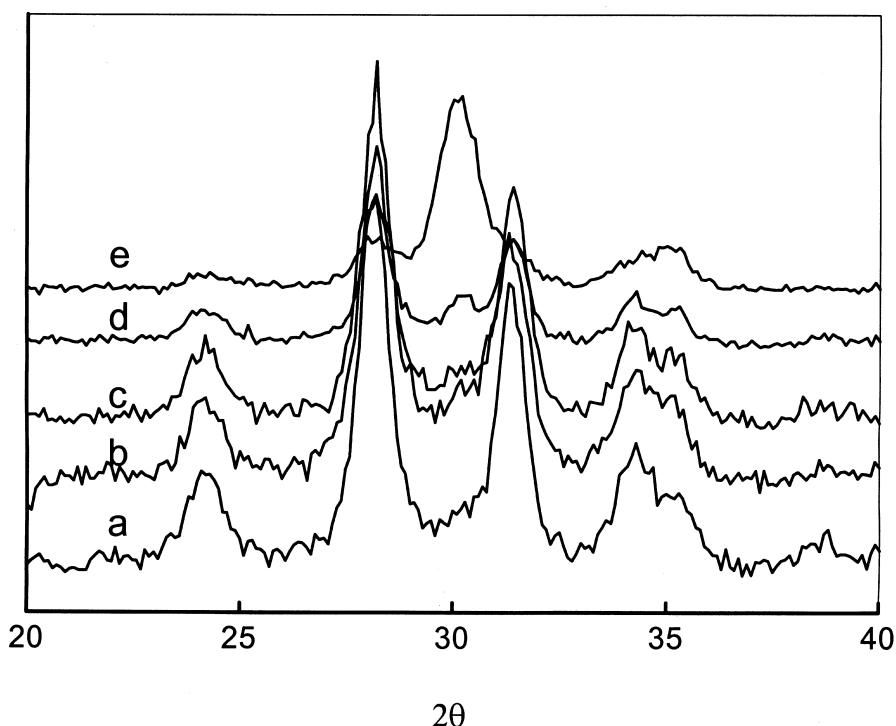
Fig. 1. XRD profiles of zirconia prepared at different precipitation pH. (a) ZrO_2-1(pH = 10), (b) ZrO_2-2 (pH = 3–10), (c) ZrO_2-3(pH = 6–7), (d) ZrO_2-4(pH = 14), (e) Na/ZrO_2.

By the comparison of the specific surface area of ZrO_2-1 (58 m^2/g), ZrO_2-2 (72 m^2/g), and ZrO_2-3 (64 m^2/g), it is clear that the difference in the activity was not caused by the specific surface area of the catalysts.

It has been known that zirconia has both acid and base properties. Many examples of the acid–base bifunction of zirconia have been re-

ported and discussed [15,16]. Pichler and Ziesecke [1] reported that ThO_2 and ZrO_2 have higher selectivity to iso-C_4 than Al_2O_3, ZnO, UO_2, CeO_2 in isosynthesis. The acid–base bifunctional behavior of ThO_2 and ZrO_2 has been proved by the H–D exchange between methyl group of adsorbed 2-propanol-d_8 and surface OH group [15]. It was therefore inferred that the

Table 1
The catalytic performance of zirconia prepared at different precipitation pH in isosynthesis[a]

Catalysts (pH)	CO conv. (%)	Selectivity (C mol%)			Distribution of hydrocarbons (C mol%)								
		CO_2	DME + CH_3OH	CH	CH_4	C_2H_6	C_2H_4	C_3H_8	C_3H_6	ΣC_4	i-C_4H_{10}	i-C_4H_8	i-C_4/C_4
ZrO_2-1 (10)	20.4	52.2	6.7	41.1	25.4	17.4	5.6	8.5	8.2	34.9	1.0	30.0	88.8
ZrO_2-2 (3–10)	15.8	58.2	13.7	28.1	17.9	6.6	7.0	2.8	6.1	59.6	0	59.6	100
ZrO_2-3 (6–7)	80.3	40.3	0	59.7	16.3	25.8	3.5	17.2	15.8	21.3	0.4	7.5	36.8
ZrO_2-4 (14)[b]	56.8	49.0	1.3	49.7	21.4	27.7	0	21.6	10.9	18.4	1.0	7.2	44.6

[a]Reaction conditions: 673 K, 5.0 MPa, GHSV: 700/h.
[b]GHSV: 500/h.

acid–base bifunctional property of ThO_2 and ZrO_2 was responsible for the high selectivity to iso-C_4. The amount of acid and base sites on the catalyst surface would be influenced by the precipitating pH and other preparation conditions. Feng et al. [10] have proved that the selectivity for isobutene in isosynthesis depends strongly on the ratio of basic to acidic sites on the surface of catalysts, and the catalysts with a higher ratio of basic to acid sites were more selective to isobutane and isobutene. It can be speculated that the acidic and basic properties of zirconia would be influenced by the precipitating pH. The catalytic performance of these catalysts may be related to their different acid and basic properties, although it is not clear that how the pH of the solution influences the acidic and basic properties of zirconia. ZrO_2-3, which was prepared under pH = 6–7, probably had a larger amount of acid–base sites on the surface than that of other catalysts, so it was more

active. ZrO_2-2 may have a highest ratio of basic to acidic sites among these four catalysts, thus, it had a highest selectivity to isobutene.

3.2. The influence of zirconium salt precursors

Srinivasan and Davis [12] have reported that the zirconium salt precursor had a tremendous influence on the resulted crystal structure of the calcined materials. Therefore, it can be supposed that the catalytic performance of zirconium dioxide in isosynthesis would be also influenced by the zirconium salt precursors. The XRD profiles of zirconia prepared from different precursors are shown in Fig. 2. It can be seen that zirconia prepared from $Zr(SO_4)_2$ was a mixture of tetragonal/amorphous, and zirconia prepared from $Zr(NO_3)_4$, $ZrCl_4$, $ZrOCl_2$ were monoclinic/tetragonal, but monoclinic was the dominant phase. Commercial zirconia was completely monoclinic. The effects of SO_4^{2-} on the
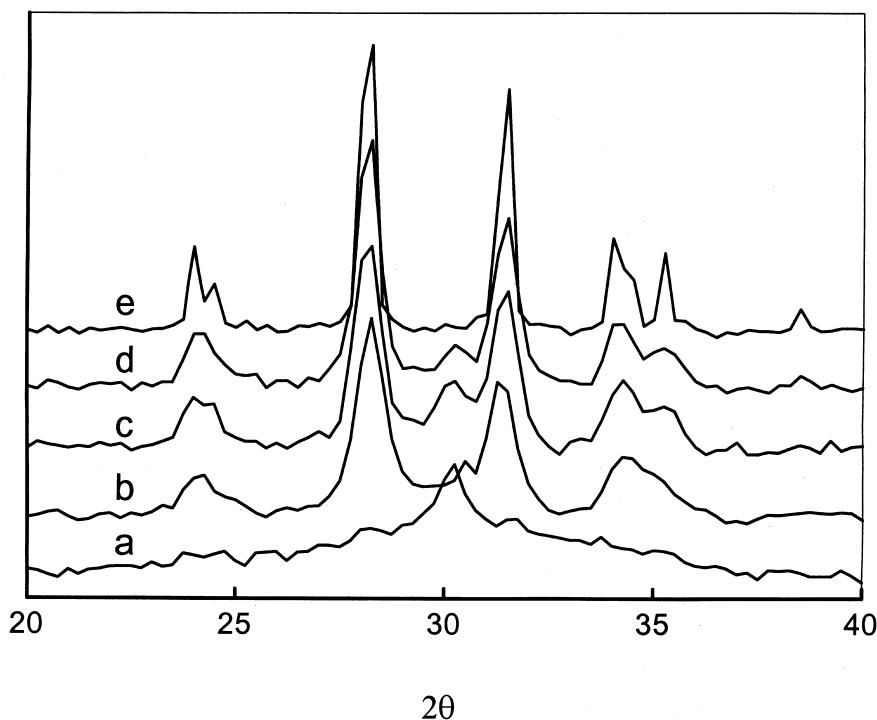

Fig. 2. The XRD profiles of zirconia prepared from different Precursors. (a) ZrO_2–S, (b) ZrO_2–O, (c) ZrO_2–Cl, (d): ZrO_2–N, (e) commercial ZrO_2.

crystallization and phase transformation of zirconia are well in agreement with the result of Wu and Yu [14]. They concluded that the presence of sulfur atoms in hydrated zirconia hindered the t–m phase transformation. In our experiments, even the gel was washed thoroughly and no SO_4^{2-} was detected using XPS, but the effect of SO_4^{2-} on the crystal structure of zirconia was still existing. It means that even trace of SO_4^{2-} involved in the gel can delay the crystallization of zirconia, and disturbs the phase transformation from tetragonal to monoclinic.

The catalytic performance of zirconia prepared from $Zr(SO_4)_2$ was quite different from others (Table 2). Isobutane was favored due to its higher Lewis acid strength for the zirconia prepared from $Zr(SO_4)_2$. Highest selectivity to isobutene was obtained over the catalysts prepared from $Zr(NO_3)_4$. Since Cl^- has been proved to be a poison, the selectivity to isobutene over Zirconia prepared from $ZrCl_4$ or $ZrOCl_2$. was lower than that of zirconia prepared from $Zr(NO_3)_4$. Over commercial ZrO_2, neither isobutane nor isobutene was produced, perhaps because it was calcined at a higher temperature, which was speculated from its intensive monoclinic profiles. Higher calcination temperatures lead to more intensive monoclinic profiles. Meanwhile, the surface property of the catalyst calcined at a high temperature is not favorable to the formation of isobutane and isobutene.

The dependence of catalytic performance to the calcination temperatures will be discussed in Section 3.3.

3.3. The influence of calcination temperatures

The XRD results of zirconia calcined in air at different temperatures are shown in Fig. 3. Zirconia calcined at 573 K was amorphous. When the temperature was increased to 673 K, a significant formation of monoclinic phase appeared, and the intensity of XRD profiles due to monoclinic phase increased with the increase of calcination temperature. The dominant crystal phase of the samples calcined from 673–1073 K was all monoclinic. Higher calcined temperature leads to better crystallization.

The catalytic performance of the samples calcined at 673–1073 K is listed in Table 3. As it can be seen, the catalyst calcined at 873 K have a highest selectivity to isobutene. The catalysts calcined at lower temperature are more active due to their higher surface area (673 K 126 m^2/g, 773 K 50 m^2/g, 823 K 38 m^2/g, 973 K 13.3 m^2/g, 1073 K 9.4 m^2/g). The product distribution changed regularly with the increase in calcination temperatures (Fig. 4). The catalysts, which have higher selectivity to DME and methanol, are also favored to the formation of isobutene. It implies that DME or methanol is an intermediate to form isobutene. Maruya et al.

Table 2
The catalytic performance of zirconia prepared from different precursors[a]

Catalysts[b]	CO conv. (%)	Selectivity (C mol%)			Distribution of hydrocarbons (C mol%)								
		CO_2	DME + CH_3OH	CH	CH_4	C_2H_6	C_2H_4	C_3H_8	C_3H_6	ΣC_4	i-C_4H_{10}	i-C_4H_8	i-C_4/C_4
ZrO_2-C[c]	19.3	44.7	1.8	53.5	32.1	29.3	3.7	17.5	10.0	7.3	0	0	0
ZrO_2-S	9.5	58.4	0	41.6	31.8	27.9	7.7	15.5	0	17.2	17.2	0	100
ZrO_2-Cl	17.7	50.4	6.7	42.9	31.5	17.3	4.7	7.4	14.2	25.0	2.7	9.7	49.6
ZrO_2-O	21.7	56.6	0	43.4	35.2	19.8	4.0	8.7	11.1	21.1	0	12.3	58.3
ZrO_2-N	15.4	57.0	19.6	23.4	25.5	13.7	0	10.9	6.3	43.6	4.3	39.3	100

[a]Reaction conditions: 673 K, 5.0 MPa, GHSV: 800/h.

[b]ZrO_2-C is commercial zirconia, ZrO_2-S, ZrO_2-Cl, ZrO_2-O, ZrO_2-N were prepared from $Zr(SO_4)_2$, $ZrCl_4$, $ZrOCl_2$ and $Zr(NO_3)_4$, respectively.
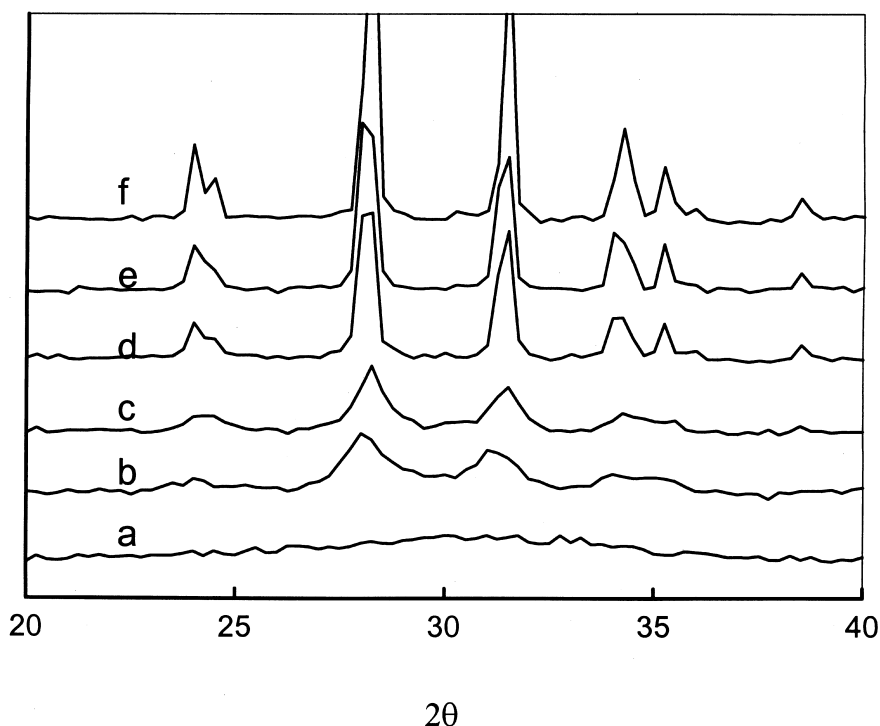
[c]GHSV: 500/h.

Fig. 3. The XRD profiles of zirconia calcined at different temperatures. (a) 573 K, (b) 673 K, (c) 773 K, (d) 873 K, (e) 973 K, (f) 1073 K.

[17] have studied the effects of DME addition to CO hydrogenation over zirconia and mixed oxide catalysts. It was found that the isobutene selectivity in C_4 hydrocarbons was higher in the presence of DME than that in the absence. One of the roles of DME is possibly to interact with surface hydroxyl groups and produce methoxy species and methanol. Methoxy species on zir-

conia have been considered [18] as intermediates to form isobutene from CO hydrogenation.

It has been proved that the activity of zirconia-based catalyst was improved by adding acidic components, however the selectivity for isobutene was increased greatly by basic additives [19]. Thus, the dependence of the activities and selectivities of the reaction on the calcina-

Table 3

The catalytic performance of zirconia calcined at different temperatures[a]

Calcination temperature (K)	CO conv. (%)	Selectivity (C mol%)			Distribution of hydrocarbons (C mol%)								
		CO_2	DME +MeOH	CH	CH_4	C_2H_6	C_2H_4	C_3H_8	C_3H_6	ΣC_4	i-C_4H_{10}	i-C_4H_8	i-C_4/C_4
673[b]	38.7	53.2	1.8	45.0	29.6	23.5	0	20.0	5.4	21.5	2.0	8.1	47.3
723	22.5	47.4	4.5	48.1	28.9	22.8	0	16.8	0.0	31.5	9.7	8.7	58.6
773	16.9	53.2	1.9	44.9	21.2	11.8	6.0	14.1	5.9	41.0	4.7	36.3	100
823	10.6	60.6	13.8	25.6	25.1	17.1	0	9.1	0	48.6	0	48.6	100
873	10.7	55.6	19.0	25.4	23.5	6.1	7.1	3.3	5.2	54.8	0	54.8	100
973	16.3	50.1	19.4	30.5	45.7	13.5	0	8.5	0	32.3	0	32.3	100
1073	11.2	57.2	1.5	41.3	47.1	16.2	4.6	8.2	6.3	17.6	0	17.6	100

[a]Reaction conditions: 673 K, 5.0 MPa, GHSV: 700/h.
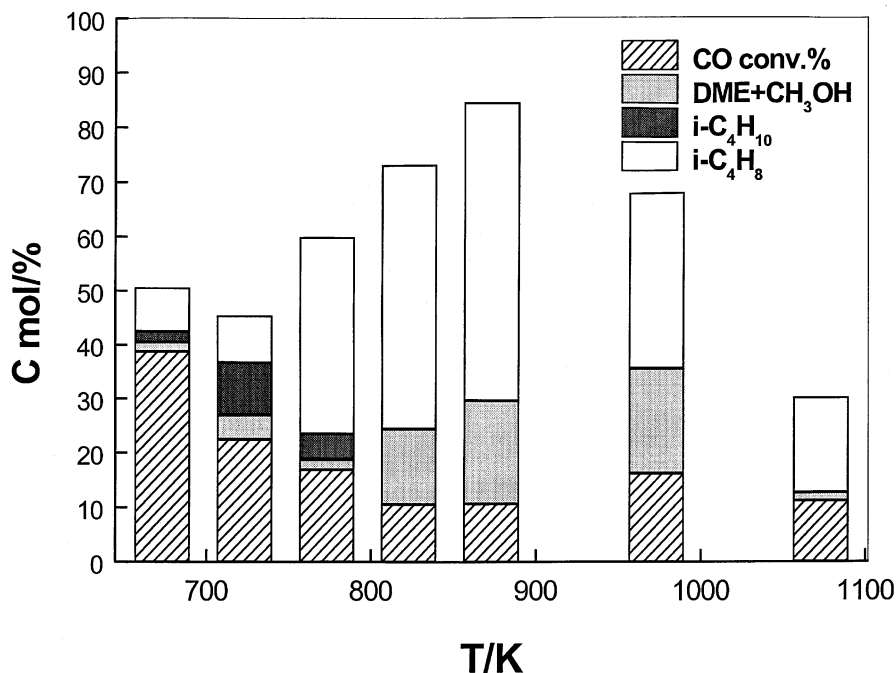[b]GHSV: 1000/h.

Fig. 4. The catalytic performance of zirconia calcined at different temperatures.

tion temperatures implies that the acidic and basic properties of zirconia may be changed with the change of calcination temperatures. Jackson and Ekerdt [8] have studied the changes of acidity and basicity of zirconnia with the variation of the calcinatiobn temperatures. They found that zirconia treated at 1023 K in flowing oxygen possessed a maximum amount of strong basic sites, and a maximum amount of strong acidic sites was obtained when zirconia was calcined at 973 K. It can be reasonably estimated that the acidity and basicity of zirconia is not only dependent on the calcination temperature. The samples which are prepared in different process may be also responsible for the different acidic and basic properties even they are calcined at same temperature. In our experiments, the catalysts calcined at 873 K were most favorable for the formation of isobutene. Since the lattice constant of zirconia changes considerably with the change of calcination temperature [18], it is reasonably concluded that the distance between acid site (Zr^{4+}) and basic

site (O^{2-}) on the surface of zirconia calcined at 873 K is most suitable to form isobutene.

4. Conclusions

Zirconia precipitated at pH = 6–7 (ZrO_2-3) had highest activity in isosynthesis than the catalysts prepared at pH = 10(ZrO_2-1), pH = 3–10(ZrO_2-2), and pH = 14(ZrO_2-4). However, ZrO_2-2, which was precipitated in a solution of pH being changed from 3 to 10, was most selective to the formation of isobutene.

The influences of different zirconium salt precursors on the catalytic performance of zirconia in isosynthesis were caused by the involvement of precursor anions in the hydroxide gel. It was found that even trace amounts of SO_4^{2-} affects the structure and catalytic performance of the catalysts strongly.

The product distribution of isosynthesis over zirconia calcined at different temperatures changed regularly with the increase of calcina-

tion temperatures. The formation of isobutane was favored over the catalysts calcined at 773–973 K. The highest selectivity for isobutene was obtained over the catalyst that was calcined at 873 K.

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