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Effect of calcium salts on isosynthesis over ZrO$_2$ catalysts

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Abstract

The promoting effects of various calcium salts on the activity and selectivity of ZrO$_2$ in isosynthesis were studied in this work. Calcium salts were added into zirconia by mechanical mixing methods. Catalytic tests were performed under relatively mild operation conditions (673 K, 650 h^{-1}, 5.0 MPa). CaF$_2$ and CaSO$_4$ were found to be effective additives, which could remarkably enhance the i-C$_4$ selectivity in total hydrocarbons while maintaining the activity of pure ZrO$_2$ when being added into zirconia. However, Ca(NO$_3$)$_2$, Ca(BO$_2$)$_2$ and CaCl$_2$ wholly changed the distribution of hydrocarbons to favor the methanation. The results of temperature-programmed desorption (TPD) of NH$_3$ and CO$_2$ indicated that the performance of the catalysts depended on the acid–base properties of the catalysts. The appropriate amount of acid and base and the ratio of the basic to acidic sites on the catalysts are significant for the synthesis of i-C$_4$ hydrocarbons from CO hydrogenation. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Isosynthesis; Zirconia; Calcium salts; Promoting effect; Acid and base properties

1. Introduction

Isosynthesis is the reaction that converts synthesis gas (CO + H$_2$) to isobutene and isobutane (i-C$_4$). It was first reported by Pichler and Ziesecke [1–4] using several transition metal oxides (ThO$_2$, CeO$_2$) or mixed-oxide systems (ThO$_2$–Al$_2$O$_3$, ThO$_2$–ZnO and so on) to catalyze CO hydrogenation under very severe conditions (150–1000 atm). Zirconia has been shown to be active in the isosynthesis with high selectivity for isobutene [5]. It has the advantage over thoria because of no radioactivity. So recent investigations on the activity and selectivity of isosynthesis have been performed over zirconium dioxide-based catalysts.

Maruya et al. [6] studied the promoting effects of various oxide compounds. They found that the addition of highly electronegative oxide such as SiO$_2$ and Nb$_2$O$_5$ resulted in the decrease of isobutene and the increase of methane. ZrO$_2$ modified with NaOH could promote the selective formation of C$_4$ hydrocarbons (about 85%) while decreasing overall activity. They suggested that the electronegativity of the dopant oxide was significant for the formation of C$_4$ hydrocarbons, especially isobutene. This work was performed at very low conversions (0–5%).

Jackson and Ekerdt [7] investigated the effect of oxygen vacancies and acidity on the isosynthesis reaction conducted at 698 K and 35 atm. The oxygen vacancy availability was altered by the addition of dopants Y$_2$O$_3$ and CaO in varying concentrations. The acid–base strength of the catalysts was altered by additives including H$_2$SO$_4$, Sc$_2$O$_3$ and etc. The most active catalysts were those in which ionic conductivity was at a maximum, suggesting that vacancies in the crystal lattice play an important role in the reaction.

A balance of acidic and basic properties on ZrO_2 was suggested to be necessary for isobutene formation. But in a similar manner to the previous work by Pichler and Ziesecke over a 20% Al_2O_3/ThO_2 catalyst [1], methane was the predominant product with a low i-C_4 selectivity in total hydrocarbons.

Postula et al. [8] prepared zirconia-based catalysts by precipitation or hydrothermally method and tested the catalytic performance for the isosynthesis under modelatively mild reaction conditions (673 K, 50 atm, $CO/H_2 = 1$). The effects of sodium, titanium, cerium, and thorium additives were investigated. The highest yield of i-C_4 hydrocarbons was obtained over a precipitated 7 wt.% Ce–ZrO_2 at 150 s space time. The CO conversion was largely increased (about 35%) while a low i-C_4 selectivity was maintained as is for pure ZrO_2 (about 20%). It is therefore evident that the activity and selectivity in the isosynthesis are still challenging problems to be overcome.

We have reported a novel method (mechanical mixing method) to prepare promoted ZrO_2 [9]. The results of adding acidic or basic components into zirconia suggested that both the acidic and basic sites on the catalysts are necessary for the isosynthesis. In this paper, we report the promoting effect of calcium salts added into ZrO_2 by mechanical mixing method on the activity and selectivity in the isosynthesis. The selectivity to C_4 hydrocarbons especially i-C_4 fractions was

largely enhanced while a relatively high reactivity was maintained as pure ZrO_2. The surface acid–base properties required for the catalytic performance of zirconia in the isosynthesis are evaluated.

2. Experimental

2.1. Preparation of catalysts

Hydrous zirconia was prepared by adding dropwise a solution of $ZrOCl_2$ (0.15 mol/l) into the well-stirred ammonium solution (2.5%) at room temperature. The pH value during precipitation was carefully controlled at 10. The white precipitate formed was aged in the mother liquor for 3 h, followed by filtering and washing with deionized water until Cl^- was not detectable. The resultant paste was dried at 378 K overnight and calcined at 823 K for 1.5 h. A calcium salt was milled together with ZrO_2 and then the mixture was calcined again at 823 K for 1.5 h. The prepared catalysts are listed in Table 1. The calcium salts, $CaSiO_3$, $Ca(BO_2)_2$ and $Ca(AlO_2)_2$ were prepared according to the literature [10–12]. The others were purchased from Beijing Chemical Reagent Company. The crystal phase of prepared $CaSiO_3$ and $Ca(BO_2)_2$ were confirmed by XRD. But $Ca(AlO_2)_2$ was found to be a mixture of Al_2O_3 and CaO ($12CaO \cdot 7Al_2O_3$).

Table 1
The physical and chemical properties of the catalysts

Catalysts	Content of Ca (%)[a]	Crystal phase	Particle size[b] (nm)	S_{BET} ($m^2 g^{-1}$)	Amount of acid sites[c] ($\mu mol\, g^{-1}$)	Amount of base sites[d] ($\mu mol\, g^{-1}$)
ZrO_2	0	M[e]	14.8	51.0	41.5	81.0
CaF_2–ZrO_2	16.7	M	19.2	39.4	56.5	127.1
$CaSO_4$–ZrO_2	9.1	M	14.4	42.2	67.2	131.6
$Ca_3(PO_4)_2$–ZrO_2	9.1	M	14.1	45.5	60.3	73.6
$CaSiO_3$–ZrO_2	9.1	M	13.6	47.8	68.2	91.1
$CaCO_3$–ZrO_2	9.1	M	13.7	46.1	41.8	86.0
$Ca(AlO_2)_2$–ZrO_2	9.1	M	14.7	43.1	47.0	87.9
CaO–ZrO_2	9.1	M	12.8	42.9	46.3	87.3
$Ca(NO_3)_2$–ZrO_2	9.1	M	13.1	44.7	19.1	197.7
$CaCl_2$–ZrO_2	9.1	M	13.6	40.6	56.6	36.1
$Ca(BO_2)_2$–ZrO_2	9.1	M	13.0	41.3	43.5	31.0

[a] Atom ratio of $Ca/(Zr + Ca)$.

[b] Calculated from the X-ray line broadening analysis (XLBA).

[c] Measured by NH_3-TPD.

[d] Measured by CO_2-TPD.

[e] Monoclinic phase.

2.2. Characterization

The crystal phase and particle size of the prepared catalysts were determined by powder X-ray diffraction (XRD), using a D8 advance powder diffractometer (Brüker Co., Germany) with Cu Kα radiation with a nickel filter. The peaks ($2\theta = 28$ and $31°$ for the ($\bar{1}$ 1 1) and (1 1 1) reflections, respectively) reflect the monoclinic phase. The peaks ($2\theta = 30°$ for the (1 1 1) reflection) in the XRD profile show the tetragonal phase.

The particle sizes determined by XRD was calculated from the half-width of the ($\bar{1}$ 1 1) reflection of monoclinic phase, after correction of the peak width for the contribution by instrumental broadening, using the Debye–Scherrer equation: $D_{hkl} = 0.89\lambda/B_{hkl}\cos\theta$. Measurement of surface area was performed on a CHEMBET-3000 using N_2 as adsorption gas. Before measurement, the samples were treated at 473 K in helium flow for 8 h.

The acid–base properties of the catalysts were measured by temperature-programmed desorption (TPD) of ammonia and carbon dioxide, respectively. TPD experiments were carried out in a flow apparatus. The sample (0.1 g) was treated at its calcined temperature in highly pure helium ($\geq$99.995%) flow for 3 h, and then saturated with a 1.0% NH_3/He mixture or highly pure CO_2 (99.99%) flow after cooling to 373 K. After flushed with He at 373 K for 1 h to remove physisorbed NH_3 or CO_2, the sample was heated to 823 K at a rate of 20 K/min in a helium flow of 60 cm³/min. The desorbed NH_3 or CO_2 was measured by a QMS (MSC200).

2.3. Reaction procedure

The hydrogenation of CO was carried out in a fixed-bed flow type pressurized stainless steel tubular reactor (i.d. 8 mm). The catalyst (2.1 g) was packed in the reactor and pretreated in a stream of N_2 at 673 K for 3 h. Then, syngas (CO/H_2 = 1) was introduced into the reactor and the reaction was conducted at temperatures in the range of 673–723 K at 5.0 MPa and 650 h⁻¹. The reactor effluent was reduced to atmospheric pressure and then injected into two on-line gas chromatographs. One equipped with TCD was used to separate CO, CH_4, CO_2, C_2, C_3, CH_3OH and CH_3OCH_3 through a GDX-101 column, and the other equipped with FID and a 30 m × 0.53 mm

Al_2O_3 capillary column was applied to separate hydrocarbons.

3. Results and discussion

3.1. The physical properties of catalysts

The crystal phase, specific surface area and particle size of the catalysts are summarized in Table 1. All the catalysts have a similar surface area (about 40–50 m²/g) and particle sizes (13–19 nm) calculated from the X-ray line broadening analysis (XLBA). The pure ZrO_2 prepared by precipitation was monoclinic as reported in the literatures [9,13].

It has been reported that the oxides of zirconium form three different phases: monoclinic, tetragonal, and cubic [14–16]. The monoclinic phase is stable below 1473 K, and the cubic phase is formed at temperatures above 2553 K. The presence of other doping metals in ZrO_2 and the parameters of precipitation play a role in determining the final crystal phase. Jackson and Ekerdt [7] found that the cubic crystal structure of zirconium dioxide could exist even at room temperature when ZrO_2 is doped with CaO or Y_2O_3 by coprecipitation. But in this work, the monoclinic phase was found to be the predominant for all the calcium salts promoted catalysts listed in Table 1. The fact that the cubic crystal structure was not observed might be due to the mechanical mixing method used to prepare promoted zirconia. In this method, the added Ca^{2+} probably exist on the surface of ZrO_2 and cannot enter the lattice to influence the crystal structure of ZrO_2. Maruya et al. [17] prepared zirconia with different crystal structure by controlling the pH of mother liquid for the precipitation from aqueous zirconium nitrate solution with aqueous ammonia. They found that the rate of formation of isobutene from CO and H_2 over ZrO_2 was proportional to the volume fraction of the monoclinic phase. However, the results of catalytic test listed in Table 2 would likely indicate that there are more significant factors controlling the performance of ZrO_2 for the same crystal structure of the catalysts in this study.

3.2. NH_3 and CO_2 TPD of catalysts

The acid and base characteristics of the catalysts are presented in Figs. 1 and 2 and Table 1. ZrO_2

Table 2
The catalytic performance of various calcium salts promoting ZrO_2 catalysts in the isosynthesis[a]

No.	Catalysts	CO conversion (%)	Selectivity of products (C mol%)			i-C_4/CH (C mol%)	$C_5{}^+$/CH (C mol%)	Yield of i-C_4 (C mol%)
			CO_2	CHO[b]	CH[c]			
1	ZrO_2	17.8	44.8	8.8	46.4	39.5	25.8	3.3
2	CaF_2–ZrO_2	18.4	39.1	9.0	51.9	50.5	20.5	4.8
2a	CaF_2–ZrO_2[d]	18.1	39.8	9.8	50.4	52.1	19.7	4.8
3	CaF_2–ZrO_2[e]	30.6	48.0	0.0	52.0	41.0	7.3	6.5
4	$CaSO_4$–ZrO_2	19.4	40.8	7.2	52.0	50.6	16.3	5.1
5	$Ca_3(PO_4)_2$–ZrO_2	19.3	45.3	3.5	51.2	39.4	15.2	4.0
6	$CaSiO_3$–ZrO_2	20.6	43.5	5.2	51.3	40.5	17.0	4.1
7	$CaCO_3$–ZrO_2	17.1	40.3	9.4	50.3	41.2	28.3	3.5
8	$Ca(AlO_2)_2$[f]–ZrO_2	18.0	41.8	9.0	49.2	40.8	27.1	3.6
9	CaO–ZrO_2	17.8	44.8	7.9	47.3	39.6	28.1	3.3
10	$Ca(NO_3)_2$–ZrO_2	12.4	45.7	7.9	46.4	14.5	9.1	0.8
11	$CaCl_2$–ZrO_2	4.5	40.0	0.0	60.0	2.0	0.0	0.1
12	$Ca(BO_2)_2$–ZrO_2	15.2	48.0	0.0	52.0	4.0	3.8	0.3

[a] Reaction conditions: 673 K, 5.0 MPa, GHSV $= 650\,h^{-1}$, $CO/H_2 = 1$, time on stream $= 1.5\,h$.
[b] $CH_3OH + CH_3OCH_3$.
[c] Hydrocarbons.
[d] Time on stream $= 5\,h$.
[e] Reaction temperature: 723 K.
[f] $Ca(AlO_2)_2$: a mixture of CaO and Al_2O_3 ($12CaO\cdot7Al_2O_3$).

has been well known as a bifunctional catalyst with both weak acid and base sites [18]. In this work, the weakly acidic and weakly basic properties of zirconia surface is indicated respectively by the desorption peaks of NH_3-TPD and CO_2-TPD at the temperatures lower than 573 K, respectively. No significant differences were observed on the strength of acid and base between the ZrO_2-based catalysts promoted by various
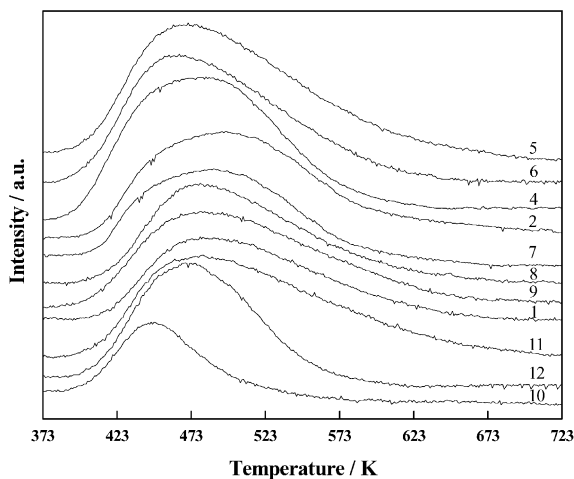

Fig. 1. NH_3-TPD profiles of the catalysts. (1) ZrO_2, (2) CaF_2–ZrO_2, (4) $CaSO_4$–ZrO_2, (5) $Ca_3(PO_4)_2$–ZrO_2, (6) $CaSiO_3$–ZrO_2, (7) $CaCO_3$–ZrO_2, (8) $Ca(AlO_2)_2$–ZrO_2, (9) CaO–ZrO_2, (10) $Ca(NO_3)_2$–ZrO_2, (11) $CaCl_2$–ZrO_2, (12) $Ca(BO_2)_2$–ZrO_2.
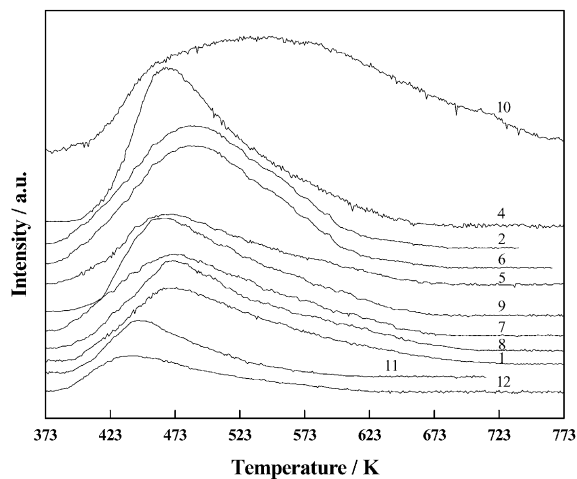
Fig. 2. CO_2-TPD profiles of the catalysts. (1) ZrO_2, (2) CaF_2–ZrO_2, (4) $CaSO_4$–ZrO_2, (5) $Ca_3(PO_4)_2$–ZrO_2, (6) $CaSiO_3$–ZrO_2, (7) $CaCO_3$–ZrO_2, (8) $Ca(AlO_2)_2$–ZrO_2, (9) CaO–ZrO_2, (10) $Ca(NO_3)_2$–ZrO_2, (11) $CaCl_2$–ZrO_2, (12) $Ca(BO_2)_2$–ZrO_2.

calcium salts and pure ZrO_2 (Figs. 1 and 2). However, the amount of acidic and basic sites markedly varied with the type of calcium salt added (see Table 1). Calcium salts such as CaF_2 and $CaSO_4$ increased the amount of both acidic and basic sites on ZrO_2 when added into zirconia. Some calcium salts ($CaCO_3$, CaO, and $Ca(AlO_2)_2$) maintained the amount of acidic and basic sites. $Ca(NO_3)_2$ clearly decreased the amount of acidic sites on ZrO_2, while $Ca(BO_2)_2$ and $CaCl_2$ remarkably decreased the amount of basic sites on ZrO_2.

3.3. Catalytic performance of the catalysts

Table 2 lists the performance of the catalysts promoted by various calcium salts in the isosynthesis at 673 K. The blank reactivity of the stainless steel tube surface was also measured at the same reaction conditions following the same reaction procedure as the catalytic tests of the catalysts. Methane was the primary product and neither C_4^+ hydrocarbons nor oxygenated products were detected in the blank experiment (less than 1% CO conversion).

It can be seen that about 12–20% of CO was converted into 46–52% hydrocarbons, 4–9% CH_3OH + CH_3OCH_3 and 40–48% CO_2 at 673 K over most catalysts shown in Table 2. Very small amount of water was also formed in the products. Experimentally it was quite difficult to be quantitatively measured. It was shown that the catalysts were very stable; e.g. over CaF_2–ZrO_2 catalyst, the performance of the catalyst after 5 h on stream (Table 2, no. 2a) was nearly the same as that after 1.5 h on stream (Table 2, no. 2) at 673 K. It could be demonstrated that over the catalyst CaF_2–ZrO_2 (no. 3), as an example, increasing reaction temperature to 723 K resulted in an increase of CO conversion to about 30% and the disappearance of CH_3OH and CH_3OCH_3 products without change in CO_2/hydrocarbons ratio. Figs. 3 and 4 show the product distribution of hydrocarbons. Schulz–Flory distribution was not followed for the hydrocarbons except over $CaCl_2$ promoted ZrO_2 and the deviations would be due to the formation of large amounts of C_4 and C_5^+ hydrocarbons (78–85% in total for most catalysts listed in Table 2). The formation of large percentage of heavier hydrocarbons (C_5^+ fractions) would be attributed to the higher pressure used, because increasing pressure shifted the product distribution toward heavier hydrocarbons. Previous work [1,8,13]
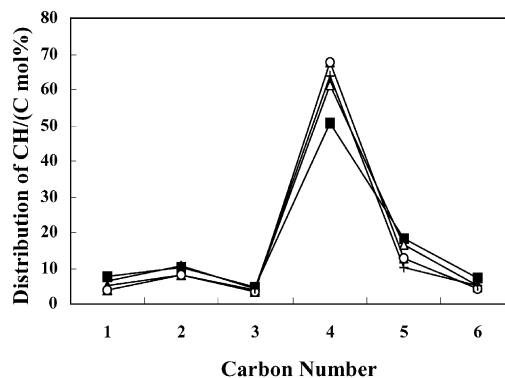

Fig. 3. Distribution of hydrocarbon products for calcium salts promoted ZrO_2 catalysts. (■) ZrO_2, (▲) $CaSO_4$–ZrO_2, (△) CaF_2–ZrO_2, (+) $Ca_3(PO_4)_2$–ZrO_2, (○) $CaSiO_3$–ZrO_2.

reported a similar trend with increasing pressure. But in this work, the undesired products (C_5^+ hydrocarbons) were largely decreased (about 25% in total hydrocarbons) on pure ZrO_2 (Table 2, no. 1) compared with that reported in the literatures (≥50%) under the similar reaction conditions. The C_5^+ selectivity in total hydrocarbons could even be significantly decreased over ZrO_2 promoted by some calcium salts listed in Table 2 (nos. 2–6) while a relatively high CO conversion and i-C_4 selectivity could be maintained. The i-C_4 selectivity in total hydrocarbons (i-C_4/CH) over some of the catalysts shown in Table 2 (nos. 1–9) was nearly two times as high as that over 7 wt.% Ce–ZrO_2
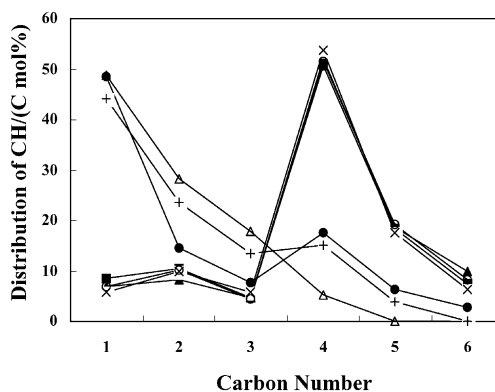

Fig. 4. Distribution of hydrocarbon products for calcium salts promoted ZrO_2 catalysts. (■) ZrO_2, (▲) $CaCO_3$–ZrO_2, (○) CaO–ZrO_2, (×) $Ca(AlO_2)_2$–ZrO_2, (●) $Ca(NO_3)_2$–ZrO_2, (+) $Ca(BO_2)_2$–ZrO_2, (△) $CaCl_2$–ZrO_2.

catalyst reported by Postula (about 20%) [8]. The only difference in the reaction conditions between these two cases was that the space velocity of $650 \, h^{-1}$ for the reaction in Table 2 was much higher than that of $50 \, h^{-1}$ for the reaction studied by Postula. When reaction temperature increases or space velocity (h^{-1}) decreases, for most of the catalysts shown in Table 2, the i-C_4 selectivity in total hydrocarbons fell to about 35–41% and the CO conversion raised to about 30%, approaching the value of 35% reported by Postula. Therefore, ZrO_2 as well as some of the promoted ZrO_2 in Table 2 are promising catalysts for isosynthesis.

The effects of various calcium salts additives on the isosynthesis over ZrO_2 could be divided into three groups based on the C_4 selectivity in total hydrocarbons: (i) the calcium salts such as CaF_2, $CaSO_4$, $CaSiO_3$, and $Ca_3(PO_4)_2$ are able to produce a clearly positive effect on the selectivity of hydrocarbons when added into ZrO_2. The C_4 selectivity in total hydrocarbons increased (Fig. 3) meanwhile the CO conversion was surely maintained. Moreover, this effect did not cause more CO_2 production (see Table 2). Furthermore, the two salts of $CaSO_4$ and CaF_2 caused a clearly increase in the i-C_4 selectivity in total hydrocarbons (i-C_4/CH), but the other two salts of $CaSiO_3$ and $Ca_3(PO_4)_2$ maintained it with an increase of linear C_4 hydrocarbons (n-C_4). Nevertheless, the salts such as $CaSO_4$, CaF_2 obviously made an enhancement of i-C_4 yield while $CaSiO_3$, $Ca_3(PO_4)_2$ salts kept i-C_4 yield over ZrO_2. (ii) $CaCO_3$, CaO and $Ca(AlO_2)_2$ did not produce any distinct variation in the performance of ZrO_2 in the isosynthesis (see Table 2 and Fig. 4). (iii) $Ca(NO_3)_2$, $Ca(BO_2)_2$ and $CaCl_2$ showed an adverse effect on the C_4 formation. $Ca(NO_3)_2$ and $Ca(BO_2)_2$ slightly decreased the CO conversion while $CaCl_2$ strongly lowered it. These three additives completely changed the distribution of hydrocarbons. Methane became the predominant product and the C_4 selectivity in total hydrocarbons was far lower than that over pure ZrO_2 (Fig. 4).

It is well known that oxygen vacancies could be created to preserve lattice neutrality when a metal oxide with lower valence than Zr^{4+} was added into zirconia. Jackson and Ekerdt [7] doped zirconia with CaO and Y_2O_3 in varying concentrations to investigate the effect of oxygen vacancies on the isosynthesis reaction carried out at 673–698 K, 3.5 MPa, $CO/H_2 = 1$. They suggested that the oxygen vacancies in the

crystal lattice play an important role in the isosynthesis. But in our experiments, the oxygen vacancies could not explain the distinct differences in the activity and selectivity of the zirconia-based catalysts because the Ca content of various catalysts listed in Table 2 was almost at the same level (about 9.1 mol%) except for CaF_2–ZrO_2 catalysts (16.7 mol%).

3.4. Influence of acid–base properties on the performance of the catalysts

Figs. 5–9 show the correlations between the performance of the various calcium salts promoted ZrO_2 catalysts shown in Table 2 and the amount of acidic and basic sites on the catalysts (Table 1). Fig. 5 shows the relationship of the activity and n-C_4 selectivity in total hydrocarbons to the amount of acidic sites on various calcium salts promoted ZrO_2 catalysts except $CaCl_2$–ZrO_2. It can be seen that the activity and n-C_4 selectivity increased with an increase in the amount of acidic sites on ZrO_2 promoted by various calcium salts. The lower activity over $CaCl_2$–ZrO_2 is expected because Cl^- has been reported to be a poison for isosynthesis [19,20]. The adverse effect of Cl^- on isosynthesis was further demonstrated by the test reaction using 9.1 mol% NH_4Cl–ZrO_2 catalyst prepared by mechanical mixing method as $CaCl_2$–ZrO_2. The

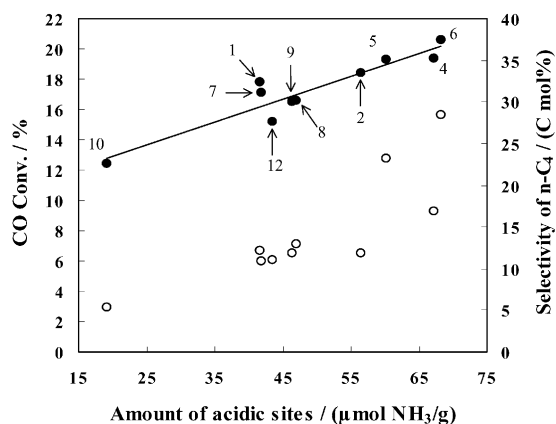Fig. 5. Relationship of CO conversion and n-C_4 selectivity in total hydrocarbons with amount of acidic sites on the catalysts. (1) ZrO_2, (2) CaF_2–ZrO_2, (4) $CaSO_4$–ZrO_2, (5) $Ca_3(PO_4)_2$–ZrO_2, (6) $CaSiO_3$–ZrO_2, (7) $CaCO_3$–ZrO_2, (8) $Ca(AlO_2)_2$–ZrO_2, (9) CaO–ZrO_2, (10) $Ca(NO_3)_2$–ZrO_2, (12) $Ca(BO_2)_2$–ZrO_2. (●) CO conversion, (○) n-C_4 selectivity in total hydrocarbons.
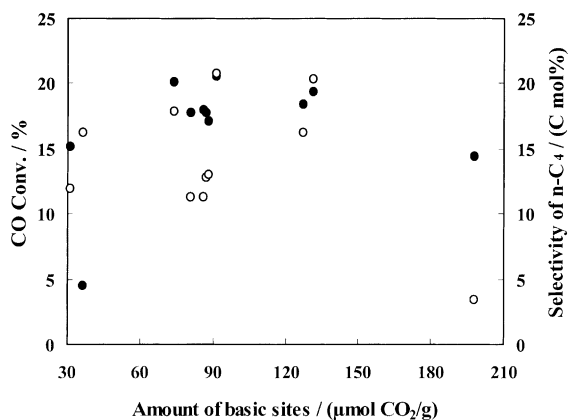
Fig. 6. Relationship of CO conversion and n-C_4 selectivity in total hydrocarbons with amount of basic sites on the catalysts. (●) CO conversion, (○) n-C_4 selectivity in total hydrocarbons.

Fig. 8. Relationship of i-C_4 selectivity in total hydrocarbons with amount of basic sites on the catalysts.

CO conversion was 6% with a low i-C_4 selectivity in total hydrocarbons (about 12%) over NH_4Cl–ZrO_2. On the other hand, the basic sites of catalysts do not seem to have any relationship to the activity and n-C_4 selectivity, as shown in Fig. 6. This would suggest that CO is more easily adsorbed and activated on acidic sites of ZrO_2 than basic sites, as reported by Su et al. [9]. The fact that n-C_4 selectivity in total hydrocarbons increased with the increase of the amount of acidic sites and not basic sites on the catalysts would likely
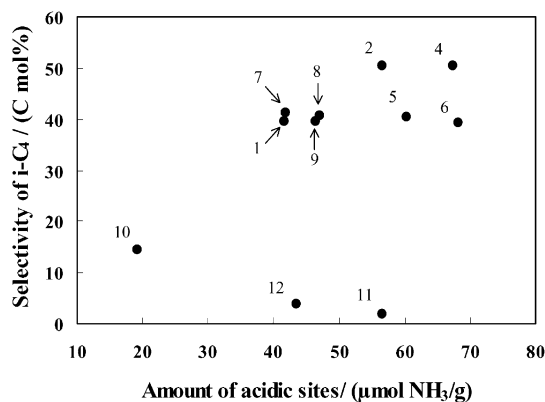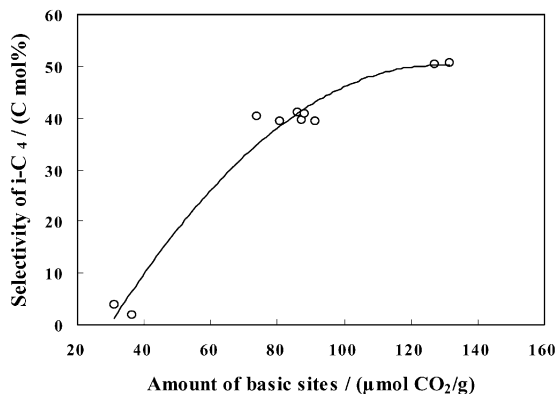
indicate that n-C_4 is more probably formed on the acidic sites of the catalysts.

On the other hand, the effect of enhancing the amount of acidic sites of the catalysts on i-C_4 formation was not significant, as shown in Fig. 7. Although $CaSiO_3$–ZrO_2 and $Ca_3(PO_4)_2$–ZrO_2 catalysts possessed more acidic sites than CaF_2–ZrO_2 catalyst, i-C_4 selectivity in total hydrocarbons over $CaSiO_3$–ZrO_2 and $Ca_3(PO_4)_2$–ZrO_2 (about 40%) was far lower than that of CaF_2–ZrO_2 catalyst (50.5%). Feng et al. [13] also reported that the catalysts with strong acidity but minimal basicity, such as SiO_2–ZrO_2 (sol–gel), is less selective for i-C_4 hydrocarbons. Maruya and coworkers also indicated the importance of basic sites

Fig. 7. Relationship of i-C_4 selectivity in total hydrocarbons with amount of acidic sites on the catalysts. (1) ZrO_2, (2) CaF_2–ZrO_2, (4) $CaSO_4$–ZrO_2, (5) $Ca_3(PO_4)_2$–ZrO_2, (6) $CaSiO_3$–ZrO_2, (7) $CaCO_3$–ZrO_2, (8) $Ca(AlO_2)_2$–ZrO_2, (9) CaO–ZrO_2, (10) $Ca(NO_3)_2$–ZrO_2, (11) $CaCl_2$–ZrO_2, (12) $Ca(BO_2)_2$–ZrO_2.
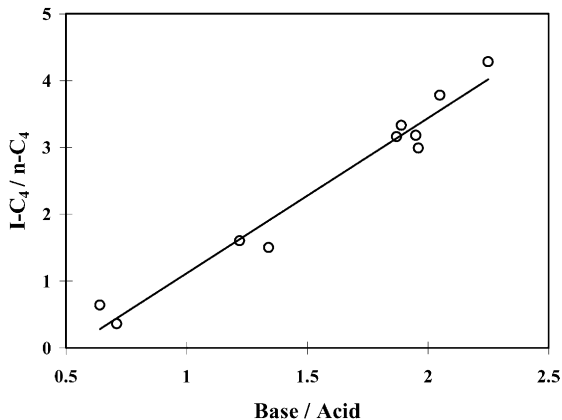

Fig. 9. Relationship of ratio of i-C_4/n-C_4 with ratio of base/acid on the catalysts.

of the catalysts in the isosynthesis [21]. Fig. 8 shows the relationship of i-C_4 selectivity in total hydrocarbons to the amount of basic sites on the catalysts. The higher the amount of basic sites on the catalysts, the higher i-C_4 selectivity in total hydrocarbons was obtained. That the i-C_4 selectivity in total hydrocarbons increased with an increase in the amount of basic sites on zirconia modified by various calcium salts except for $Ca(NO_3)_2$ suggested that the basic sites of the catalysts are significant for the formation of isobutene and isobutane in the isosynthesis [9,17]. The observed increase in the i-C_4 selectivity in total hydrocarbons over CaF_2–ZrO_2 and $CaSO_4$–ZrO_2 catalysts shown in Fig. 7 could not be attributed to the increase in the amount of acidic sites because the amount of basic sites were also enhanced. $CaSiO_3$–ZrO_2 and $Ca_3(PO_4)_2$–ZrO_2 catalysts showed no apparent effect on the i-C_4 selectivity in total hydrocarbons compared with pure ZrO_2 because the amount of basic sites were not apparently increased (see Table 1), although they possessed more acidic sites than ZrO_2.

It has been reported that the isosynthesis reaction involves two distinct chain growth steps, CO insertion into adsorbed aldehyde and aldol condensation between methoxide and enolate [22]. The condensation reaction was suggested to be responsible for the deviations from Schulz–Flory product distributions (see Figs. 3 and 4) in the isosynthesis [23,24], since this only contributes to the C_3^+ hydrocarbons because of lack of C_1 enolate. The surface acid and base properties on ZrO_2 could influence these two chain growth reactions [7,17]. In this study, the observed decrease in the C_4 selectivity in total hydrocarbons over $Ca(NO_3)_2$–ZrO_2 catalyst (shown in Fig. 4) would be due to the marked decrease in the amount of acidic sites on ZrO_2 (see Table 1) to retard the chain growth steps for the large portion of lighter hydrocarbons (C_1, C_2 fractions) in the productions (about 65% in total hydrocarbons). The lower C_4 selectivity in total hydrocarbons over $CaCl_2$ and $Ca(BO_2)_2$ promoted ZrO_2 shown in Fig. 4 could be attributed to the large decrease in the amount of basic sites on ZrO_2 (see Table 1). This would likely suggest that both the acidic and basic sites on ZrO_2 are important for the chain propagation to form heavier hydrocarbons (C_4^+ fractions). A large decrease in the amount of acidic or basic sites on ZrO_2 would change the distribution of hydrocarbons to favor methanation.

Nunan et al. [25,26] investigated in detail the mechanism of formation of higher alcohols from CO hydrogenation over cesium-doped Cu/ZnO catalysts. It was suggested that there are two competitively primary carbon chain growth types, linear chain growth via C_1 addition steps and aldol condensation via β addition steps, which lead to linear primary alcohols and branched primary alcohols, respectively. The presence of cesium promoted the formation of the branched product by promoting the β additions than the linear chain growth. If isobutene was assumed to be produced by the dehydration of the primary product, isobutanol [22], our results would be consistent with the mechanism suggested by Nunan [26]. Fig. 9 shows the relationship of the ratio of i-C_4 to n-C_4 to the ratio of basic to acidic sites of the catalysts. The fact that the ratio of i-C_4 to n-C_4 hydrocarbons increased with increase in the ratio of basic to acidic sites would indicate that n-C_4 and i-C_4 are formed on different active sites on ZrO_2 through the dehydration of C_4 alcohols produced from C_3 intermediates via the two competitive chain growth steps [26]; n-C_4 hydrocarbons are more probably produced on the acidic sites via linear chain growth step, while i-C_4 hydrocarbons are formed primarily on the basic sites of ZrO_2 via aldol condensation step [17]. The ratio of basic sites to acidic sites on ZrO_2 would influence the proportion of the two chain growth steps in the isosynthesis reaction and therefore determine the ratio of i-C_4 to n-C_4 hydrocarbons in the C_4 fractions.

4. Conclusions

The performance of the zirconia-based catalysts varied with the calcium salts added. CaF_2 and $CaSO_4$ proved to be effective promoters, which could remarkably enhance the i-C_4 selectivity in total hydrocarbons and meanwhile surely maintain the activity of pure ZrO_2, giving the highest yield of i-C_4 hydrocarbons.

The surface acidic–basic properties play an important role in determining the performance of the catalysts in the isosynthesis. The acidic sites are responsible for the activation of CO to start the reaction and the formation of n-C_4 hydrocarbons. However, the basic sites are significant for the formation of i-C_4 hydrocarbons. The ratio of basic to acidic sites on the catalysts would determine the percentage of

i-C_4 in total C_4 hydrocarbons. The observed promoting effect of CaF_2 and $CaSO_4$ would be due to the increase in both acidic and basic sites on ZrO_2 while maintaining an appropriate ratio of basic to acidic sites as pure ZrO_2. The appropriate amount of acid and base and the ratio of the basic to acidic sites on the catalysts are significant for the direct synthesis of i-C_4 hydrocarbons from CO hydrogenation.

Acknowledgements

References

[1] H. Pichler, K.H. Ziesecke, Brennst. Chem. 30 (1949) 1.
[2] H. Pichler, K.H. Ziesecke, Brennst. Chem. 30 (1949) 13.
[3] H. Pichler, K.H. Ziesecke, Brennst. Chem. 30 (1949) 60.
[4] H. Pichler, K.H. Ziesecke, Brennst. Chem. 30 (1949) 333.
[5] T. Maehashi, K. Maruya, K. Domen, K. Aika, T. Onishi, Chem. Lett. (1984) 747.
[6] K. Maruya, T. Maehashi, T. Haraoka, S. Narui, Y. Asakawa, K. Domen, T. Onishi, Bull. Chem. Soc. Jpn. 61 (1988) 667.
[7] N.B. Jackson, J.G. Ekerdt, J. Catal. 126 (1990) 31.
[8] W.S. Postula, Z.T. Feng, C.V. Philip, A. Akgerman, R.G. Anthony, J. Catal. 145 (1994) 126.
[9] C.L. Su, J.R. Li, D.H. He, Z.X. Cheng, Q.M. Zhu, Appl. Catal. A: General 202 (2000) 81.
[10] D.K. Smith, A.J. Majumdar, J. Am. Ceram. Soc. 44 (1961) 405.
[11] D.M. Roy, R.R. Neurgaonkav, T.P. O'Holleran, R. Roy, Am. Ceram. Soc. Bull. 56 (1977) 1023.
[12] Muki Kagaku no Gousei II, Maruzen Press, Tokyo, 1977.
[13] Z.T. Feng, W.S. Postula, A. Akgerman, R.G. Anthony, Ind. Eng. Chem. Res. 34 (1995) 78.
[14] J.D. Mccullough, K.N. Trueblood, Acta. Crystallogr. 12 (1959) 507.
[15] P. A Evans, R. Stevens, J.G.P. Binner, Trans. J. Br. Ceram. Soc. 83 (1984) 39.
[16] H.G. Scott, J. Mater. Sci. 10 (1975) 1527.
[17] K. Maruya, T. Komiya, T. Hayakawa, L.H. Lu, M. Yashima, J. Mol. Catal. A: Chem. 159 (2000) 97.
[18] B.Q. Xu, T. Yamaguchi, K. Tanabe, Chem. Lett. (1988) 1663.
[19] T. Tatsumi, H. Matsuhashi, K. Arata, Bull. Chem. Soc. Jpn. 69 (1996) 1191.
[20] H. Nakabayashi, Chem. Lett. (1996) 945.
[21] L.H. Lu, T. Hayakawa, T. Ueda, M. Hara, K. Domen, K. Maruya, Chem. Lett. (1998) 65.
[22] S.C. Tseng, N.B. Jackson, J.G. Ekerdt, J. Catal. 109 (1988) 284.
[23] N.B. Jackson, J.G. Ekerdt, J. Catal. 126 (1990) 46.
[24] T.J. Mazanec, J. Catal. 98 (1986) 115.
[25] J.G. Nunan, C.E. Bogdan, K. Klier, K.J. Smith, C.W. Young, R.G. Herman, J. Catal. 113 (1988) 410.
[26] J.G. Nunan, C.E. Bogdan, K. Klier, K.J. Smith, C.W. Young, R.G. Herman, J. Catal. 116 (1989) 195.