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Selective Formation of Isobutane and Isobutene from Synthesis Gas over Zirconia Catalysts Prepared by a Modified Sol–Gel Method

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Zirconium oxide was synthesized by a modified sol–gel method, and was evaluated for the selective formation of isobutane and isobutene from synthesis gas. Due to increased basicity, zirconia from sol–gel preparation showed higher selectivities to *iso*-C_4's, while maintaining the same level of activity as zirconia prepared by calcination of zirconyl salts. The catalyst was further modified with Group I and II elements, and the activity tests showed increased *iso*-C_4 and decreased methane production for the catalysts doped with potassium, magnesium, calcium, or barium.

INTRODUCTION

With the recent enforcement of environmental regulations, there is a great need to search for alternative octane enhancers. Methyl *t*-butyl ether (MTBE) is one of the additives to replace aromatic compounds in gasoline. However, the production of MTBE is limited by a nationwide shortage of isobutane and isobutene (1). Thus, catalyst and process development for *iso*-C_4 synthesis becomes an important national objective.

Isosynthesis is the reaction that converts synthesis gas to isobutane and isobutene. Early research on isosynthesis was preformed by Pichler and Ziesecke (2), who reported that thorium oxide and zirconium oxide were the two most active single component isosynthesis catalysts. Since then, research groups worldwide have conducted extensive studies to improve the activity and selectivity of catalysts (3–20). Recent research has focused on zirconia catalysts because of their absence of radioactivity (3–10). With only a few exceptions, the catalysts reported in the literature were prepared by precipitating zirconyl cations with a base, usually an aqueous solution of sodium hydroxide or ammonium hydroxide. Various studies have shown that the selectivity of the isosynthesis reaction depends on the nature of active sites on the catalyst surface, such as oxygen vacancy (13, 14), acidity, and basicity (4, 21), and that these characteristics can be modified by different preparation procedures. Therefore, a synthesis method is needed to prepare zirconium oxide catalysts with high activity and selectivity.

A modified sol–gel procedure for catalyst preparation has received wide attention recently (22–26). The synthesis procedure was described by Dosch *et al.* (22) as follows:

$$M(OC_3H_7)_4 + NaOH \xrightarrow{\text{methanol}} \text{soluble intermediate}$$

$$(M = Ti, Zr, Nb, \text{or } Ta)$$

$$\text{soluble intermediate} \xrightarrow[\text{hydrolysis}]{\text{acetone + water}} NaHMO_x$$

$$NaHMO_x \xrightarrow{H+} HMO_x$$

$$HMO_x \xrightarrow{\text{calcination}} MO_2.$$

This method is referred to as a modified sol–gel method because it differs from the traditional sol–gel procedure in that a soluble intermediate is formed in a nonaqueous medium prior to hydrolysis. The metal oxides prepared by the modified sol gel method have several properties that make them promising catalyst materials, such as stabilized surface area, strong thermal stability, large ion exchange capacity, and dual ion exchange properties for cations and anions (23–25). Recent applications include waste water treatment (23), direct coal liquefaction (24), selective catalytic reduction of NO with NH_3 (25), and dehydrogenation of propane (26). In this study, zirconium oxides were synthesized by the modified sol–gel method, and were evaluated for the selective conversion of CO/H_2 to isobutane and isobutene. The effects of alkali and alkaline earth metals were also investigated.

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EXPERIMENTAL

Catalyst Preparation and Analysis

1. Commercial method for preparing ZrO_2. Zirconium oxide is commercially prepared by calcining zirconyl salts (e.g., chloride) at a temperature greater than 600°C (27, 28). A sample of zirconia (98%, Catalog No. Zr-0304 T 1/8, Merck Index 11, 10083) was purchased from Harshaw Chemical Co. The pellets were crushed and sieved to 0.25 mm particles, then calcined in air at 500°C for 4 h. The catalyst is referred to as ZrO_2 (H-0304). Previous work has shown that this commercial zirconia has similar isosynthesis characteristics as catalysts prepared by precipitation of zirconyl nitrate with ammonium hydroxide (10, 29). Therefore, ZrO_2 (H-0304) is used as a basis for comparison of our work with the literature.

2. Zirconium oxide prepared by the modified sol–gel method. Zirconium oxide was synthesized by the modified sol–gel method with the procedure developed by Dosch *et al.* (22), except that sodium hydroxide was replaced with an organic base. Tetramethylammonium hydroxide (25 wt% in methanol, Aldrich) was mixed with methanol (Mallinckrodt, 99.9%) to get a solution with 10 wt% tetramethylammonium hydroxide in methanol. Then zirconium isopropoxide (70 wt% in 1-propanol, Aldrich) was slowly added to the hydroxide solution to obtain a clear soluble intermediate. The intermediate was rapidly added to a 1 : 10 by volume solution of water (distillate and deionized) and acetone (Mallinckrodt, 99.8%). The slurry was continuously stirred until the particles were suspended in the solution. Finally, the precipitate was collected by filtering and drying in a vacuum at 80°C overnight. After being calcined in air for 4 h, the catalyst was crushed and sieved to 0.25-mm particles, and is referred to as ZrO_2 (Sol Gel).

3. Incorporation of alkali and alkaline earth metals. Alkali and alkaline earth metals were loaded by dissolving the respective hydroxides (lithium, sodium, potassium, rubidium, cesium, and barium) or nitrates (magnesium and calcium) in the tetramethylammonium hydroxide methanol solution, and following the above procedure. The alkali or alkaline earth metals were converted to oxides during calcination. The catalysts are referred to as Li–ZrO_2 (Sol Gel), Na–ZrO_2 (Sol Gel), K–ZrO_2 (Sol Gel), Rb–ZrO_2 (Sol Gel), Cs–ZrO_2 (Sol Gel), Mg–ZrO_2 (Sol Gel), Ca–ZrO_2 (Sol Gel), and Ba–ZrO_2 (Sol Gel), respectively.

4. Structures of the catalysts. Table 1 lists the compositions and structures of the catalysts. Small variations of apparent densities and surface areas are observed. The amount of dopant ranges from 0.4 to 0.9 wt% since previous work (2, 9) has shown that the maximum effect of alkali and alkaline earth metals was at a content below 1 wt%. The crystal phases are also shown in Table 1.

TABLE 1

Phase Structure, Composition, and Surface Area of the Catalysts

Catalyst	N_2 BET Surface Area, m^2/g	Amount of additives	Density, g/cc	Predominant phase structure[a]
ZrO_2 (H-0304)	27		1.7	M
ZrO_2 (Sol Gel)	24		2.1	T
Li–ZrO_2 (Sol Gel)	10	0.41 wt% Li	2.0	M
Na–ZrO_2 (Sol Gel)	18	0.48 wt% Na	2.3	T
K–ZrO_2 (Sol Gel)	32	0.52 wt% K	2.3	T
Rb–ZrO_2 (Sol Gel)	27	0.44 wt% Rb	2.0	M
Cs–ZrO_2 (Sol Gel)	22	0.93 wt% Cs	2.4	T
Ca–ZrO_2 (Sol Gel)	26	0.53 wt% Ca	2.3	T
Mg–ZrO_2 (Sol Gel)	25	0.46 wt% Mg	2.4	T
Ba–ZrO_2 (Sol Gel)	22	0.54 wt% Ba	2.3	T

[a] Predominate phase: estimated over 80%; M: monoclinic, T: tetragonal.

5. Acid–base properties. In this work, the base properties of the catalysts were measured by temperature programmed desorption (TPD) of carbon dioxide. TPD experiments were conducted at atmospheric pressure. Typically, a 200-mg sample was loaded into a quartz reactor and activated in a helium stream by heating to 550°C at a rate of 5°C/min and maintaining that temperature for 30 min. After the sample was cooled to 70°C, carbon dioxide was adsorbed. The sample was then flushed with helium at 70°C for 2 h to remove physisorbed carbon dioxide. TPD was performed from 70°C to 540°C at a heating rate of 5°C/min, and the effluent was monitored by a thermal conductivity detector.

Figure 1 shows the TPD of carbon dioxide for ZrO_2 (Sol–Gel), ZrO_2 (H-0304), K–ZrO_2 (Sol–Gel), and

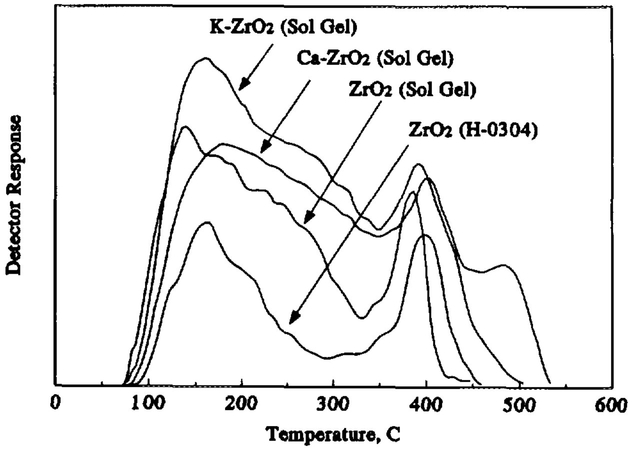


FIG. 1. Temperature programmed desorption of carbon dioxide. Heating rate 5°C/min.

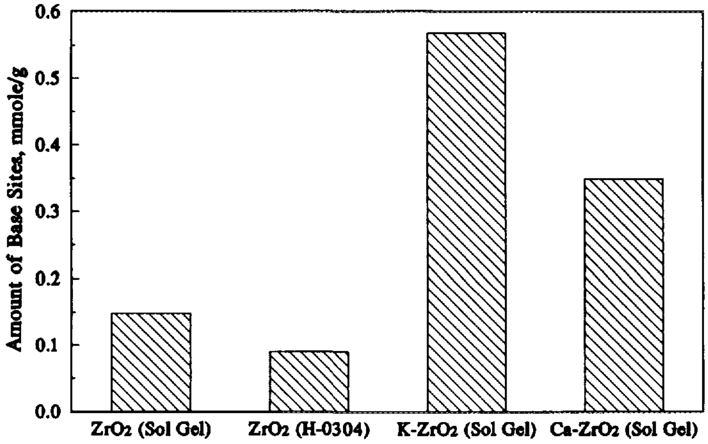


FIG. 2. Amount of base sites on the catalysts.

$Ca–ZrO_2$ (Sol–Gel). The desorption profiles indicate that base sites are present on the catalyst, and that the basicity of the catalyst is affected by the method of preparation; zirconium oxide prepared by the modified sol gel method shows stronger basicity than zirconium oxide prepared from calcination of zirconyl salts, and the incorporation of alkali and alkaline earth metals further increases the concentration of base sites on the catalysts. Of the four catalysts, $K–ZrO_2$ (Sol–Gel) shows the highest concentrations of base sites, as shown in Fig. 2. The increase in basicity cannot be attributed to the variation in surface area, since all four catalysts have about the same surface area as measured by N_2 BET (Table 1).

Previous work (26) has shown that zirconium oxides prepared from the modified sol–gel method also possess weak acid sites, and there are speculations that acid sites may be active for isosynthesis (6, 13). However, the acidity for zirconia from the modified sol–gel method is about the same as that for zirconia from calcination as determined from temperature programmed desorption of ammonia (the amounts of acid sites for ZrO_2 (Sol–Gel) and ZrO_2 (H-0304) are 0.171 mmol/g and 0.182 mmol/g, respectively). Therefore, the effects of acid sites will not results in differences in performance between the two catalysts.

APPARATUS AND PROCEDURE

The reactor unit used in this work is a CDS 900 fully automated reactor–gc system manufactured by Autoclave Engineers. A 20 in. long 1/2 in. i.d. stainless steel tubular reactor was located in the reactor oven which was heated to 180°C during reactions. A 6-in. section of the reactor was heated separately by a three-zone heater to maintain the reaction temperature. Reactants were fed to the reactor system in separate lines, and then preheated and mixed in a mixing chamber. Products were analyzed by an online gc equipped with parallel FID and TCD systems. The TCD system included two Porapak Q columns, a Molecular Sieve 5A column, and a palladium hydrogen transfer tube, while the FID system was equipped with a 50 m BP-1 capillary column. The separation was complete, except for 1-butene and isobutene, which were separated by an off-line Carle TCD/FID gc equipped with five separate columns and a hydrogen transfer system. Molecular sieve (5A) beds were installed in both carbon monoxide and hydrogen feed lines to remove residual moisture, and a zirconium oxide filter and an activated charcoal filter were also in the carbon monoxide line to remove carbonyls.

Carbon monoxide (Matheson, 99.5%) and hydrogen (Airco, 99.995%) were stored in gas cylinders located in a ventilation hood. Roughly 20 g of catalysts were loaded in the reactor. The reactor was pressurized to reaction pressure at room temperature with nitrogen, and then heated to reaction temperature at a rate of 5°C/min and maintaining at that temperature for 4 h before reactants were continuously fed into the system and nitrogen feed was discontinued. A base condition of 450°C and 70 atm was chosen in this work since early research (2) showed increased alcohol and ether production at lower temperatures or higher pressures, and increased methane production at higher temperatures. Equal moles of carbon monoxide and hydrogen were fed, and data were taken at 2 h time on stream. No deactivation was observed over 20 h time on stream.

RESULTS AND DISCUSSIONS

Isosynthesis over Zirconium Oxides

Figure 3 shows CO conversion over ZrO_2 (Sol–Gel) and ZrO_2 (H-0304) as a function of CO/H_2 GHSV. Under the same temperature and pressure, CO conversions decrease as expected with increasing GHSV. The activity of ZrO_2 (Sol–Gel) is slightly higher than that of ZrO_2 (H-

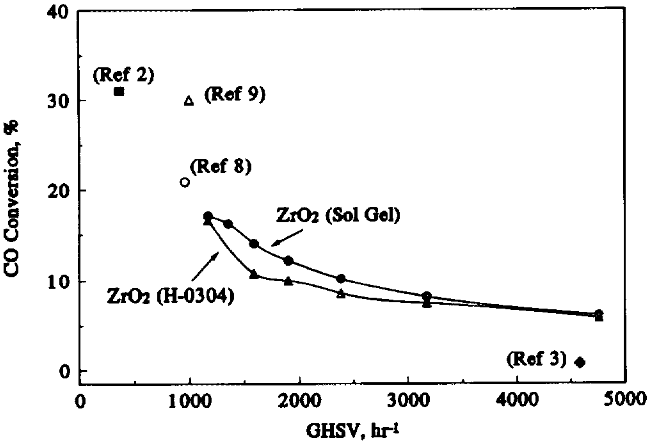


FIG. 3. A comparison of activities for ZrO_2 (H-0304), ZrO_2 (Sol–Gel), and ZrO_2 in the literature. CO/H_2 = 1 in the feed: ●, 450°C, 70 atm, ZrO_2 (Sol–Gel); ▲, 450°C, 70 atm, ZrO_2 (H-0304); ZrO_2 in the literature: ■, 450°C, 150 atm, Ref. 2; ◆, 425°C, 36 atm, Ref. 3; ○, 450°C, 70 atm, Ref. 8; △, 450°C, 20 atm, Ref. 9.

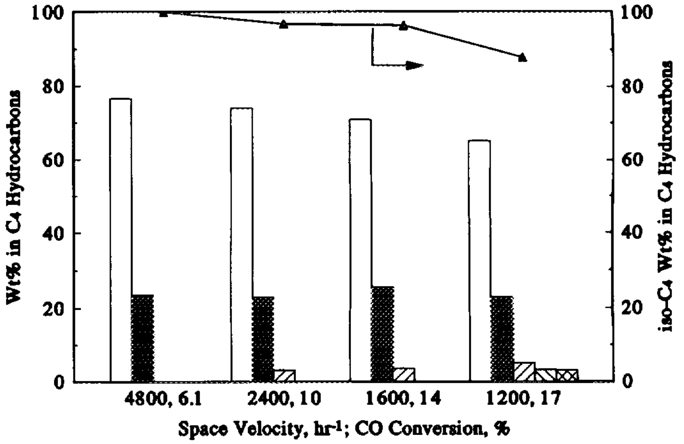


FIG. 5. C_4 hydrocarbon distributions over ZrO_2 (Sol–Gel) at various levels of CO conversions: □, isobutene; ■, isobutane; ▨, 1-butene + *n*-butane; ▧, *tans*-2-butene; ⊠, *cis*-2-butene; ▲, *iso*-C_4 wt% in total C_4's.

0304), and it is in the same range with those reported in the literature, as is also shown in Fig. 3. Hydrocarbons (alkanes and alkenes) and carbon dioxide are the main products. For all the experiments in this work, the amount of ethylene and propylene is about equal to the amount of ethane and propane in the product. The reactions are catalytic, since hydrocarbons are not thermodynamically favorable products from CO/H_2 at equilibrium, and no reactions were observed to occur without using the catalysts.

Several major differences are observed between isosynthesis and Fischer–Tropsch synthesis: First, although both reactions form hydrocarbons from CO/H_2, isosynthesis in this work is selective to C_4 hydrocarbons. A discontinuity at carbon number 4 is observed on an Anderson–Schulz–Flory plot for zirconium oxides (Fig. 4), which is contrary to the straight line expected for F-T synthesis. Second, only traces of methanol, isobutanol, dimethylether, and water were detected in the product stream under the reaction conditions of this work.

Another deviation of isosynthesis from traditional polymerization reaction is the selective formation of branched C_4 hydrocarbons. Figures 5 and 6 are the distributions among C_4 hydrocarbons for ZrO_2 (Sol–Gel) and ZrO_2 (H-0304), respectively. Isobutane and isobutene account for most butanes and butenes, and zirconia prepared from the modified sol–gel method is more selective to isobutane and isobutene than that prepared from calcination of zirconyl salts.

The high selectivity to *iso*-C_4 over the sol–gel-prepared catalysts can be explained as due to the surface characteristics of the catalysts. As suggested by Jackson and Ekerdt

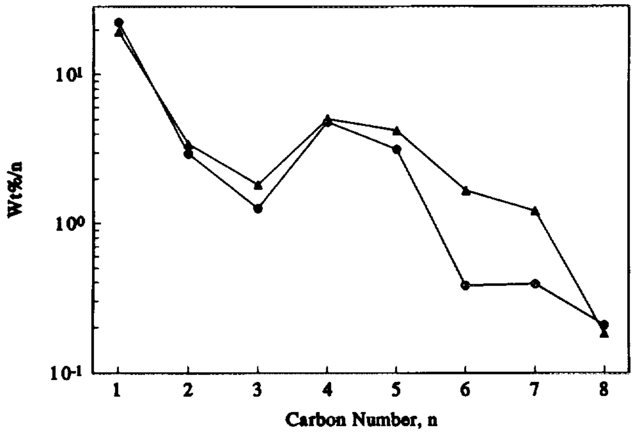


FIG. 4. Anderson–Schulz–Flory distribution of hydrocarbon products. 450°C, 70 atm, CO Conversion 17%, CO/H_2 = 1 in the Feed: ●, ZrO_2 (Sol–Gel); ▲, ZrO_2 (H-0304).

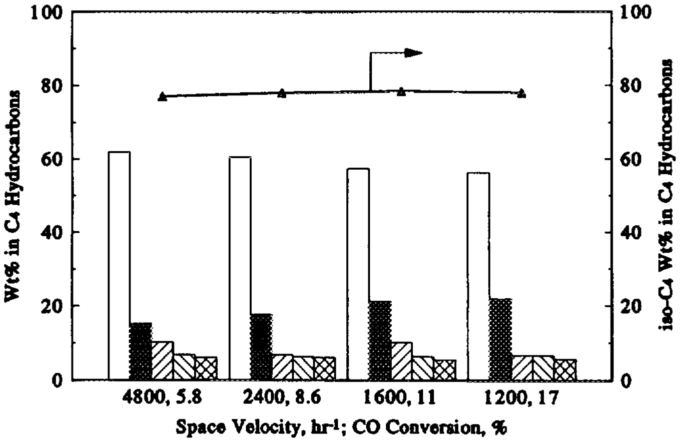
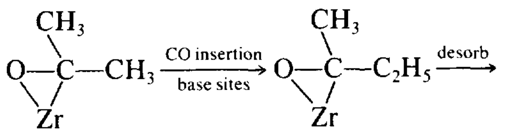


FIG. 6. C_4 hydrocarbon distributions over ZrO_2 (H-0304) at various levels of CO conversions: □, isobutene; ■, isobutane; ▨, 1-butene + *n*-butane; ▧, *trans*-2-butene; ⊠, *cis*-2-butene; ▲, *iso*-C_4 wt% in total C_4's.

(4), *iso*-C_4 hydrocarbons are formed by stepwise chain growth, and a step that leads to the formation of *iso*-C_4 hydrocarbons is an CO insertion on a η^3-enolate, as follows:



iso-C_4 hydrocarbons.

The reaction is catalyzed by base sites (4, 13). Temperature-programmed desorption of carbon dioxide shows an increased concentration of base sites for sol–gel zirconia, which results in increased *iso*-C_4 formation through CO insertion reaction.

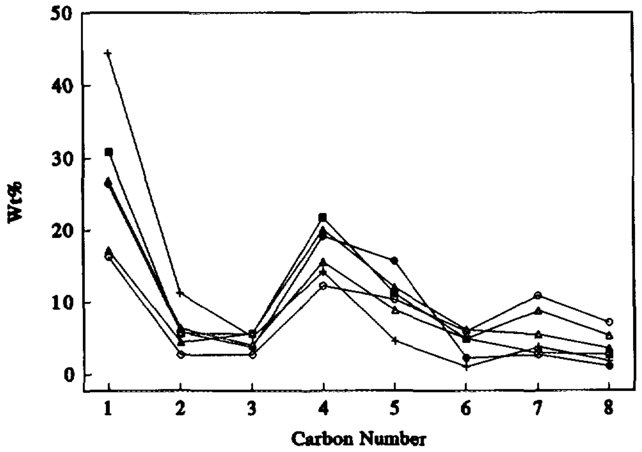


FIG. 8. Effects of alkali metals on hydrocarbon distributions. 450°C, 70 atm, GHSV of CO/H_2 = 1200 h^{-1}, CO/H_2 = 1 in the feed: +, Li-ZrO_2 (Sol-Gel); △, Na-ZrO_2 (Sol-Gel); ▲, K-ZrO_2 (Sol-Gel); ○, Rb-ZrO_2 (Sol-Gel); ■, Cs-ZrO_2 (Sol-Gel); ●, ZrO_2 (Sol-Gel).

Effects of Alkali and Alkaline Earth Metals

The effects of alkali metals (lithium, sodium, potassium, rubidium, and cesium) and alkaline earth metals (magnesium, calcium, and barium) were studied. Incorporation of alkali metals shows increased isobutane and isobutene weight percent in total C_4's (Fig. 7). However, the effect on methane and C_4 weight percent in hydrocarbons is not the same for all alkali metals (Fig. 8). Decreased methane and increased C_4 production over K–ZrO_2 (Sol–Gel) are observed, while the presence of lithium, sodium, rubidium, or cesium results in either increased methane production or decreased C_4 production. On the other hand, all alkaline earth metals investigated in this work improve the overall selectivity of the catalyst. C_4 hydrocarbon distributions are not changed significantly by the presence of alkaline earth metals (Fig. 9), but increased C_4 and decreased methane in hydrocarbons are observed (Fig. 10) for Mg–ZrO_2 (Sol–Gel), Ca–ZrO_2 (Sol–Gel), and Ba–ZrO_2 (Sol–Gel).

The improvement of catalyst performance over potassium, magnesium, calcium, and barium can be explained by enhancement of base sites on these catalysts. Potassium and calcium are the two dopants that show the largest improvement on *iso*-C_4 production. Figure 1 shows a comparison of basicity among K–ZrO_2 (Sol–Gel), Ca–ZrO_2 (Sol–Gel), and ZrO_2 (Sol–Gel), and Fig. 2 shows the concentration of base sites on these catalysts. As can been seen in both figures, K–ZrO_2 (Sol–Gel) and Ca–ZrO_2

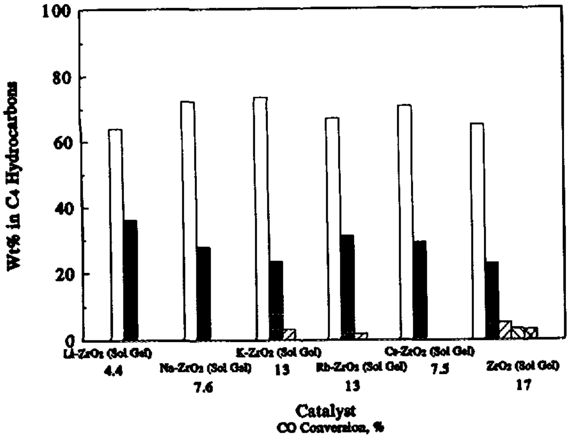


FIG. 7. A comparison of C_4 hydrocarbon distributions and CO conversions over LiZrO_2 (Sol-Gel), Na-ZrO_2 (Sol-Gel), K-ZrO_2 (Sol-Gel), Rb-ZrO_2 (Sol-Gel), Cs-ZrO_2 (Sol-Gel), and ZrO_2 (Sol-Gel). 450°C, 70 atm, GHSV of CO/H_2 = 1200 hr^{-1}, CO/H_2 = 1 in the feed: □, isobutene; ■, isobutane; ▨, 1-butene + *n*-butane; ▧, *trans*-2-butene; ☒, *cis*-2-butene.

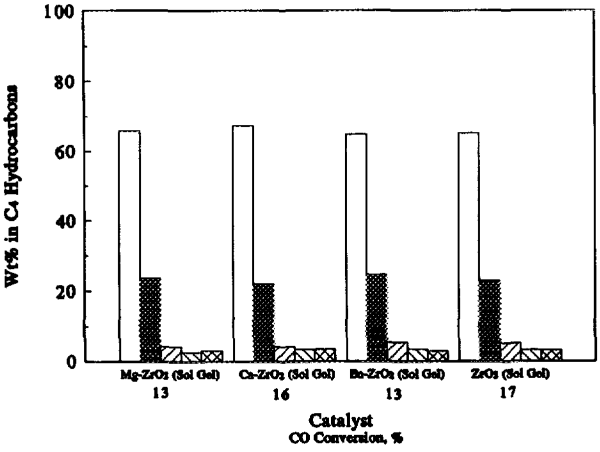


FIG. 9. A comparison of C_4 hydrocarbons distributions and CO conversions over Mg–ZrO_2 (Sol Gel), Ca–ZrO_2 (Sol Gel), Ba–ZrO_2 (Sol Gel), and ZrO_2 (Sol Gel). 450°C, 70 atm, GHSV of CO/H_2 = 1200 h^{-1}, CO/H_2 = 1 in the feed: □, isobutene; ■, isobutane; ▨, 1-butene + *n*-butane; ▧, *trans* – 2 – butene; ☒, *cis*-2-butene.

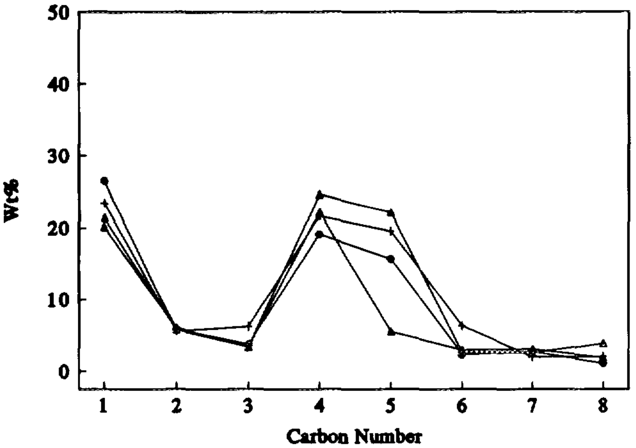


FIG. 10. Effects of alkaline earth metals on hydrocarbon distributions. 450°C, 70 atm, GHSV of CO/H_2 = 1200 h^{-1}, CO/H_2 = 1 in the feed: +, Mg–ZrO_2 (Sol–Gel); △, Ca–ZrO_2 (Sol–Gel); ▲, Ba–ZrO_2 (Sol–Gel); ●, ZrO_2 (Sol–Gel).

(Sol–Gel) have a stronger basicity than ZrO_2 (Sol–Gel), which results in the improvement in isosynthesis selectivity.

The effects of potassium and calcium on zirconia prepared by precipitation were studied by Pichler and Ziesecke (2), Jackson and Ekerdt (4), and Deflin *et al.* (9). Pichler and Ziesecke reported that a low level of potassium (<1 wt%) promoted the formation of liquid hydrocarbons and consequently resulted in a decrease in C_4 hydrocarbons. Since an increase in C_4 hydrocarbon production was observed for K–ZrO_2 (Sol–Gel) in this work, we speculate that this difference in catalyst performance is due to different synthesis procedures. The potassium catalyst in this work was prepared by a modified sol gel method, while those in the literature were prepared by coprecipitation.

Another interesting observation for the sol–gel catalysts in this work is the change in catalytic activity after K, Mg, Ca, and Ba are loaded in the sol–gel catalysts. Under the same temperature, pressure and GHSV, CO conversions on K–ZrO_2 (Sol–Gel), Mg–ZrO_2 (Sol–Gel), Ca–ZrO_2 (Sol–Gel), and Ba–ZrO_2 (Sol–Gel) are about 77% to 95% of that on ZrO_2 (Sol–Gel), which is not a significant decline. This observation is different from the results reported in the literature. Deflin *et al.* (9) reported an increase in *iso*-C_4 production over calcium promoted precipitated zirconias; but in the meantime, CO conversion decreased from 30% to 17%. The results from this work demonstrate that the catalysts prepared from modified sol–gel procedure remain at nearly the same level of activity after potassium, magnesium, calcium, and barium were added, which may be an advantage in using the modified sol–gel method over the precipitation method reported in the literature.

CONCLUSION

Zirconium oxide prepared by a modified sol–gel method showed a higher concentration of base sites on the catalyst surface than zirconium oxide prepared by calcination of zirconyl salts, and the increased basicity results in improved selectivities of isobutane and isobutene in C_4 hydrocarbons. Sol–gel zirconias were also modified by alkali and alkaline earth metals, and the activity tests showed that potassium, magnesium, calcium, and barium promoted the production of *iso*-C_4 hydrocarbons without a significant decrease in CO conversions, which can be explained by the enhancement of basicity on the doped catalysts.

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