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Conversion of Synthesis Gas to Isobutylene over Zirconium Dioxide Based Catalysts

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Recent amendments to the Clean Air Act have renewed interest in synthesizing isobutylene from coal derived synthesis gas for use in producing methyl-tertiary-butyl ether. Previous work in isosynthesis was performed at extreme conditions or at very low conversions. This paper reports on both the process conditions and the catalyst that give the highest yield of isobutylene. The catalysts were zirconia based and were synthesized by both a precipitation and a hydrothermal method. The effects of sodium, titanium, manganese, cerium, and thorium additives were investigated. Catalysts prepared by the precipitation method were most active while those prepared hydrothermally were more selective to the i-C_4's. Results for the most active catalyst for each preparation method are as follows. A CO conversion of 35% (34% CH_4, 20% i-C_4's, 26% C_5+, wt basis) was achieved at 673 K, 50 atm, 1/1 CO/H_2 ratio, and 150 sec space time over a precipitated 7% (wt) Ce–ZrO_2. A 1.6% Na, 10.3% Ti, ZrO_2 prepared hydrothermally gave a CO conversion of 16.7% (37% CH_4, 30% i-C_4's, 22% C_5+) under the same conditions.

INTRODUCTION

Recent amendments to the Clean Air Act will, once again, require reformulation of gasoline. The Environmental Protection Agency has set new standards for fuel vapor pressure, aromatic content, and oxygen content (1). The purpose of these stricter guidelines is to limit both exhaust and evaporative emissions.

Methyl-tertiary-butyl ether (MTBE) is an octane-enhancing additive that has received increased attention because of its potential to solve some of the problems associated with current gasoline blends. The demand for MTBE is currently the fastest growing of any petrochemical and is likely to continue increasing at a high rate (2). The supply of MTBE is directly linked to the supply of isobutylene, a key reactant. The demand for reformulated gasoline could result in a shortage of isobutylene on a worldwide basis (3). Isomerization of 1-butene and dehydrogenation of isobutane are two current processes that could supplement the isobutylene pool. These two processes are expensive and are limited by the supply of C_4 feedstocks (2–5). Catalytic cracking can also be utilized to produce a stream with 10–15% isobutylene, but this process is very energy intensive. A process that could take advantage of an ample supply of feed gas is the direct conversion of coal derived synthesis gas into isobutylene. Such a process could be combined with a methanol synthesis unit and a MTBE synthesis unit since the technology already exists for these two operations.

Pichler and Ziesecke (6) were the first to study the isosynthesis reaction. Isosynthesis refers to the synthesis of i-C_4 hydrocarbons from carbon monoxide and hydrogen. In their study, several single component and multicomponent oxide catalysts were tested for activity toward isosynthesis. Thorium dioxide (ThO_2) and zirconium dioxide (ZrO_2) were found to be the most active single-component catalysts. Most of their work was performed over thoria-based catalysts. Overall, a 20% Al_2O_3/ThO_2 catalyst was found to be most active. Pichler and Ziesecke (6) performed experiments at high temperatures (648–773 K) and high pressures (150–1000 atm) (1 atm = 1.01325 × 10^5 N/m^2). Although high conversions were obtained, in most cases the isobutylene yield was low. Additionally, operation at lower pressures would be desirable because of the cost associated with high pressure equipment.

More recent investigations on the activity and selectivity of zirconium dioxide have been performed (7–12). Maehashi *et al.* (7) reported very high selectivities to isobutylene (~80%) among all hydrocarbons in experiments conducted at 623 K and 0.68 atm. Conversion, however, was only 0–5%.

Maruya *et al.* (8, 9) investigated the effects of various metal promoters. They found that sodium increased the selectivity to C_4's while decreasing overall activity. Ce-

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rium was found to increase activity while maintaining high C_4 selectivity (~75%). The electronegativity of the dopant oxide was thought to play an important role in selectivity toward C_4's, especially isobutylene. This work was also performed at very low conversions.

Tseng *et al.* (10) examined the mechanism by the incorporation of ^{13}C-labeled oxygenated compounds into the products. These studies were performed at 623–698 K, 35 atm, and 1/1 CO/H_2 ratio. Methane and methanol were the dominant products even though conversions were low. Two chain growth steps were proposed. One involves CO insertion into a bound aldehyde or ketone, and the other involves condensation between methoxide and a surface bound enolate. Maruya *et al.* (9) also found evidence to support this mechanism.

Jackson and Ekerdt (11) doped zirconia with calcium and yttrium oxides in varying concentrations to investigate the effect of oxygen vacancies and acidity on the isosynthesis reaction carried out at conditions similar to those used by Tseng *et al.* (10). 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 sites on the surface was believed to be necessary for maximum isobutylene production.

Nearly all work in isobutylene synthesis since Pichler and Ziesecke (6) has been performed using precipitated zirconia because of its ease of preparation and lack of radioactivity. Studies done examining the crystal phase (13–17) obtained by precipitation indicate that both pH and the presence of other metal dopant ions play a role in determining the final crystal phase. However, catalytic properties have not been linked to catalyst structure. Zirconia can exist in three different crystal phases. The low-temperature stable monoclinic phase transforms to tetragonal at ~1443 K. Tetragonal then transforms into the cubic phase at ~2643 K. The higher temperature phases can be stabilized at room temperature by the addition of metal dopant ions.

The three polymorphs of zirconium dioxide mentioned above have been studied extensively. The structure of monoclinic zirconia (18) is the most complicated because it is the least symmetrical. Unit cells of tetragonal (19) and cubic (20) zirconia are simpler because of their higher degree of symmetry.

The drawback to most of the previous work on isobutylene synthesis is the extreme conditions used or the low conversions obtained. This paper reports on both the process conditions and the catalyst that give high conversions of CO while maintaining a good selectivity toward isobutylene (and isobutane) under relatively mild operating conditions. Catalysts were synthesized by both a precipitation and a hydrothermal method. Additives to the zirconia catalyst included sodium, titanium, manganese, cerium, and thorium.

METHODS

Catalyst Preparation

1. Zirconia prepared by precipitation. Zirconia was prepared by slowly adding a 5 wt% aqueous zirconyl nitrate solution to a 1.5 wt% solution of ammonium hydroxide. Before filtering, the pH of the zirconium hydroxide gel solution could be adjusted. Henceforth, acidified zirconia refers to a catalyst that had its gel pH adjusted below 7 before filtering (see Table 1). Usually after precipitation the pH of the solution with gel was between 9.5 and 10. After filtering and washing the gel was dried at 383 K. Final dehydration was accomplished by calcining at 773 K for 2.5 hr.

Sodium, titanium, thorium, manganese, and cerium were investigated as promoters. Sodium was included in the zirconia by precipitating with both NaOH and NH_4OH. In the cases of titanium, thorium, manganese, and cerium, chloride or nitrate salts containing the metal were dissolved in the same solution as the zirconyl nitrate. Table 1 gives the preparation conditions and properties of the catalysts.

2. Zirconia prepared hydrothermally. Two doped zirconias were prepared by a hydrothermal method. In one sample, the molar ratios of Zr/Ti and Na/Ti were 3 and 0.5, and in the other sample the molar ratios of Zr/Ti, Na/Ti,and Th/Ti were 18, 0.6, and 0.2. The first step in this synthesis was preparing two mixtures. In both preparations, mix A contained 25 wt% tetramethylammoniumhydroxide in methanol, 18 wt% NaOH in water, and tetrabutylammoniumbromide. In one case, mix B contained 70 wt% zirconium(IV) propoxide in 1-propanol and 97% titanium(IV) isopropoxide. In the other case mix B also contained thorium nitrate. Mix B was added to mix A while stirring. The gel formed was transferred to a 550-ml stainless-steel reactor. Water was added during the washing of the plastic containers used for the two mixtures. The reactor was then sealed and heated in an oven at 443 K. After removal from the reactor the zirconia was filtered, washed with acetone, and then calcined at 773 K for 2.5 hr. The results of these two preparations are also shown in Table 1.

Hydrothermal preparation was used, even though the procedure is much more involved than the precipitation technique, because it generally resulted in higher surface area catalysts. Also, the pore diameter of hydrothermally prepared zirconia is larger than that of precipitated zirconia. The hydrothermal preparations were not acidified because the sodium would have been removed. The surface area of each ctalyst was measured after calcination.

TABLE 1

Properties of Isobutylene Synthesis Catalysts

	Final pH[a]	N_2 BET surface area (m^2/g)		Time catalyst used[b] (hr)	Crystal phase[c]	Bulk density (g/cm^3)
		Before reaction	After reaction			
Precipitated catalysts						
ZrO_2	9.5	52	35	264	M	1.88
1.6% Na,[d] ZrO_2	9.5	58	45	1848	M	2.11
3.2% Ti, 2% Th, ZrO_2	4	49	14	264	T	2.62
2% Mn, ZrO_2	4	35	0.4	72	T	2.82
7% Ce, ZrO_2	6	103[e]	49	528	C	2.28
	Syn. time[f]	N_2 BET surface area (m^2/g)		Time catalyst used[b] (hr)	Crystal phase[c]	Bulk density (g/cm^3)
		Before reaction	After reaction			
Hydrothermal catalysts						
1.6% Na, 10.3% Ti, ZrO_2	116	70	68	768	C	0.94
0.6% Na, 2% Ti, 2% Th, ZrO_2	24	53	50	96	T/M	1.08

[a] Refers to the pH of the solution with precipitate.

[b] Refers to time spent at reaction conditions.

[c] M, monoclinic; T, tetragonal; C, cubic.

[d] All percentages are wt%.

[e] Cerium catalyst calcined at 723 K for 2.5 hr.

[f] Refers to the total catalyst synthesis time (hr) in reactor at 443 K.

The surface areas before and after reaction are presented in Table 1.

Materials

The majority of oxide starting materials were purchased from Aldrich. They include $ZrO(NO_3)_2 \cdot xH_2O$ (tech.), $Ce(NO_3)_3 \cdot 6H_2O$ (99%), $TiCl_3$ (99%), NaOH (97+%), tetramethyl ammoniumhydroxide (25 wt% in methanol), tetrabutylammoniumbromide (99%), titanium(IV) isopropoxide (97%), and 70 wt% zirconium(IV) propoxide in 1-propanol. $Th(NO_3)_4 \cdot 4H_2O$ was purchased from Alfa Products, while NH_4OH (A.C.S. Reagent) and HNO_3 (70.7%) were purchased from Fisher and Mallinckrodt respectively.

Carbon Monoxide, hydrogen, and nitrogen (purge) gas cylinders were acquired from Bob Smith Corporation. Hydrogen and nitrogen were passed through molecular sieve (5A) filters to remove water. The carbon monoxide was purified using both a molecular sieve and an activated charcoal bed to remove carbonyls.

Apparatus

The reactor was made from 304 stainless steel with an overall length of 29 cm and an internal diameter of 0.493 cm. The amount of catalyst loaded into the reactor varied from 5–15 g depending on bulk density and desired bed depth. All other tubing was 0.318 cm or 0.159 cm 316 stainless steel.

The purified reactant gases were fed to the reactor through Brooks 5850E mass flow meters. The reactor pressure was maintained using a Grove S-91W back pressure regulator. Temperature control was accomplished using an Omega 6100 controller. After exiting the back pressure regulator the reactor effluent could be injected into two on-line gas chromatographs (GC). An SRI model 8610-30 GC equipped with both thermal conductivity (TCD) and flame ionization (FID) detectors and a 0.318 cm × 1.83 m Porapak Q 80/100 column was used to monitor oxygenate production. Separation of CO, H_2, CO_2, and all the C_1–C_4 hydrocarbons was accomplished using a Carle series S TCD GC controlled by a Hewlett–Packard 3385A automation system. This GC used five separate columns and a palladium hydrogen transfer system. Additionally, a gas-tight syringe was used to inject a sample of the reactor effluent into a similar Carle series S TCD/FID GC. The C_5+ hydrocarbon fraction was given in the column back-flush.

Procedure

During heat-up of the reactor, the system was pressurized to 35 atm and nitrogen was passed over the catalyst at 100 sccm. The catalyst was pretreated at 673 K and 35 atm in flowing nitrogen for 3–18 hr. After pretreatment the pressure was adjusted to the desired reaction pressure and the CO and H_2 flows were started. Once the composition and flowrate of the feed was measured the reactor was brought on-line. Between experiments, nitrogen was passed over the catalyst at 100 sccm. A base reaction temperature of 673 K was chosen because previous work (7–11) had shown increased oxygenate production at lower temperatures and increased methane production at higher temperatures. Two hours were allowed for the reaction to come to steady state before effluent analysis began.

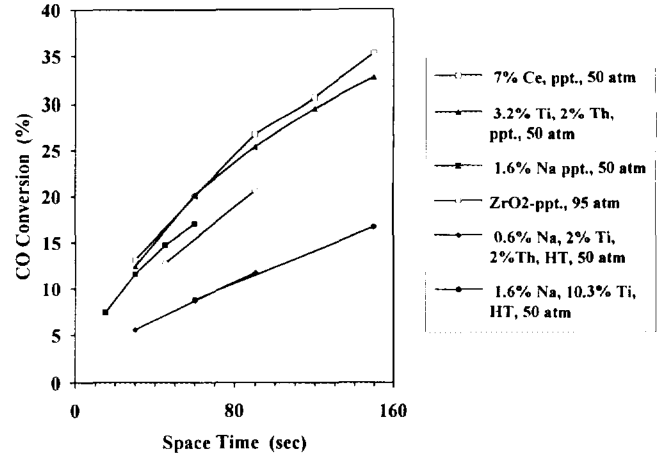

FIG. 1. Comparison of catalytic activity for precipitated (ppt.) and hydrothermally (HT) prepared zirconias at 673 K and 1/1 CO/H_2 ratio.

RESULTS AND DISCUSSION

Catalyst Characterization

Both preparation procedures resulted in catalysts with moderately high (50–100 m^2/g) surface area. The X-ray diffraction pattern of the undoped zirconia was monoclinic as expected. In most cases, addition of dopants stabilized either the tetragonal or cubic form depending on the amount of dopant added as reported elsewhere in the literature (10–17).

There are several significant differences between precipitated and hydrothermally prepared catalysts. Perhaps the most significant is the surface area stability of the hydrothermal catalysts. Table 1 shows that there is almost no change in surface area during reaction for the hydrothermal samples. All of the precipitated catalysts show some loss of surface area under the reaction conditions. Reduction in surface area of precipitated zirconia is a result of thermal sintering, which occurs at any temperature above absolute zero. The amount of sintering increases with both time and temperature. Platero and Mentruit (21) found that significant reduction in surface area of precipitated zirconia occurred at temperatures as low as 700 K. Since 700 K is only slightly above the reaction temperature in this study, some loss in surface area because of sintering is expected. Differences in pore size may be the reason the hydrothermal catalysts are more stable than the precipitated catalysts. The pore size distribution for both preparations is unimodal; however, pores are 30–40 Å in the case of precipitated samples and 150–200 Å for hydrothermal samples. Another difference between the two preparation methods is the bulk density of the catalyst obtained. Bulk densities of precipitated catalysts are generally 1–2.5 times those of hydrothermal catalysts. This also could be the result of a larger, more open pore structure.

Catalyst Activity and Selectivity

The results of all activity tests are shown in Fig. 1. The manganese-doped catalyst was almost completely inactive (cannot be shown on same scale with others). A report on the effect of manganese in reducing methane production in Fischer–Tropsch synthesis (22) motivated our investigation. Conversion was far below any of the other catalysts and the major product was methane. No further discussion on manganese is given. The precipitated catalysts are more active than the hydrothermal catalysts with 7% Ce–ZrO_2 being the most active. Most activity tests were performed at 673 K, 50 atm, and 1/1 CO/H_2. The effect of pressure on conversion at the same space time was minimal above 50 atm, but increasing pressure shifted the product distribution toward heavier hydrocarbons. Pichler and Ziesecke (6) reported a similar trend with increasing pressure. They attributed the increase in conversion at higher pressures to the pressure itself, rather than the increased contact time associated with increasing pressure (same end gas flow rate). In this work, the benefit of increased conversion at higher pressures was offset by the shift in hydrocarbon distribution toward the undesired C_5+ products. After initial experiments at higher pressures, 50 atm was chosen as the standard pressure because the product distribution was favorable and space times as long as 150 sec could be attained. As mentioned previously, Pichler and Ziesecke (6) obtained high CO conversions (50–90%), but their yield of isobutylene was low. The i-C_4 fraction obtained by Pichler and Ziesecke was predominantly isobutane, and a large percentage of the product was heavier hydrocarbons (46% at 723 K and 150 atm). These two observations can be explained by the high pressure of the reaction. Higher pressure would favor production of alkanes and C_5+ products because the number of moles of reactant gases consumed per mole of product formed is greater than for alkenes and lighter hydrocarbons. Also Pichler and Ziesecke produced oxygenates (5%), even at 723 K. This can be attributed to thoria being a more basic oxide, since

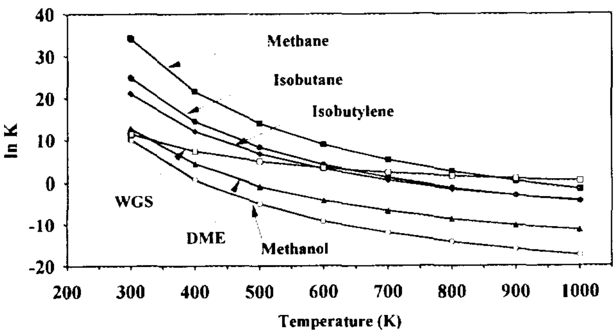

FIG. 2. Equilibrium constants for the formation of various products from CO + H_2 reactions.

this study has found that the oxygenate to hydrocarbon ratio produced over acidified zirconia is generally less than 0.05 (wt basis) at only 673 K. The most significant difference between this work and that of Pichler and Ziesecke is the decrease in undesired products (C_5+ hydrocarbons and oxygenates) while increasing isobutylene selectivity (up to 70% of C_4's) and maintaining a relatively high conversion. Increasing temperature increased conversion, but also increased methane formation. A CO conversion of 51% was achieved at 723 K, 50 atm, and 1/1 CO/H_2 over the cerium catalyst. The product, however, contained 58 wt% methane. The equilibrium constants for various reactions that can occur under isosynthesis conditions are given in Fig. 2. Methane is the thermodynamically favored product at all temperatures, while saturated hydrocarbons are slightly favored over unsaturated hydrocarbons. Conversion was also found to be a function of CO/H_2 feed ratio with 1/3 > 1/1 > 2/1. In this work, interest was focused on hydrogen lean synthesis gas and 1/1 CO/H_2 was adopted as the standard.

Sodium, thorium, and cerium increased catalyst activity over undoped zirconia. It was reported (8) that cerium increased activity while retaining the selectivity of pure zirconia, and sodium decreased activity while increasing C_4 selectivity. Addition of thorium is expected to increase activity because pure thoria was found to be the most active isosynthesis catalyst (6). The amount of titanium was decreased and thorium was added to the second hydrothermal preparation with the hope of increasing activity while retaining the same selectivity to i-C_4 hydrocarbons.

Selectivity data for all catalysts are shown in Table 2. These comparisons are made at almost equal conversions (~12%) to eliminate the effect of conversion on hydrocarbon distribution. Both pure zirconia and sodium doped zirconia produce mainly a C_5+ fraction. These two catalysts were not acidified in order to limit oxygenate production and the analysis did not account for oxygenates. Therefore, a significant portion of the C_5+ fraction could be dimethyl ether. Both dimethyl ether and methanol were injected independently and they both eluted in the column backflush (C_5+). In other cases dimethyl ether was the only oxygenate produced in detectable quantities and the dimethyl ether/hydrocarbon weight ratio was 0–4%.

Titanium was added to the precipitated zirconia with the hope of achieving the same i-C_4 selectivity as in the hydrothermal case. However, the i-C_4/total C_4 ratio remained at about 70–75% for this catalyst. There was a shift in the hydrocarbon distribution for the two catalysts that were acidified. Both showed an increase in C_1–C_4 fraction and a decrease in C_5+ fraction. The i-C_4/total C_4 ratio for the 7% Ce–ZrO_2 was slightly lower because the higher activity of this catalyst resulted in production of more linear C_4's.

Both hydrothermally prepared catalysts gave ~100% selectivity to the i-C_4 compounds among C_4's produced (30–70% isobutylene). The promotion of the i-C_4 com-

TABLE 2

Comparison of Hydrocarbon Distribution for Precipitated and Hydrothermal Catalysts at 673 K, 50 atm, and 1/1 CO/H_2

	Space time[a] (sec)	CO conv. (%)	Hydrocarbon distribution (wt%)					
			C_1	C_2	C_3	C_4	C_5+	i-C_4/(total C_4)
Precipitated catalysts								
ZrO_2[b]	45	12.8	10.2	2.6	2.0	21.2	64.0	70.8
1.6% Na, ZrO_2	30	11.6	6.6	3.0	1.5	18.4	70.5	76.6
3.2% Ti, 2% Th, ZrO_2	30	12.4	31.1	8.5	5.8	27.3	27.3	74.0
7% Ce, ZrO_2	30	13.1	27.8	9.6	8.0	30.7	23.9	63.2
Hydrothermal catalysts								
1.6% Na, 10.3% Ti, ZrO_2	90	11.4	35.6	3.4	6.1	29.6	25.4	99.3
0.6% Na, 2% Ti, 2% Th, ZrO_2	90	11.7	27.5	2.8	2.4	14.9	52.4	100

[a] Space time (τ) is defined as V_{bed}/v_0 (v_0 is inlet volumetric flow rate at reaction P and T).

[b] Reaction pressure is 95 atm in this case.

pounds over hydrothermally prepared catalysts could be related to the surface characteristics of the catalysts. Jackson and Ekerdt (11) suggested that branched C_4 hydrocarbons are formed by two independent paths. One involves condensation of an η^3-enolate (CH_3–$CH^{(-)}$–CH–O) with an adsorbed methoxide species and the other involves CO insertion in an η^3-enolate. Though both routes lead to the formation of branched C_4's, different surface characteristics are required. The first is catalyzed by strong Lewis acid sites, while the second is catalyzed by strong basic sites. The hydrothermal catalysts are more likely to have strong basic sites, since strong bases (sodium hydroxide and tetramethylammoniumhydroxide) were used in their preparation and they were not treated with acid. The hydrocarbon distribution was similar to that of precipitated catalysts. The C_5+ fraction increased when thorium was added in an attempt to increase activity. The overall activity of the hydrothermal catalysts was about one-third (space time three times as long to get same conversion) that of the precipitated catalysts.

Several characteristics were common to all catalysts. As space time increased the amount of methane increased and the ratio of isobutylene to isobutane decreased. The same trends were noted as temperature increased. All of these observations can be explained in terms of thermodynamics. The precipitated catalyst showed a slight shift toward production of lighter hydrocarbons with time although conversion remained constant. This shift was more pronounced when any temperature cycling occurred. This could be the result of sintering shifting the pore size distribution toward smaller pores.

CONCLUSIONS

Zirconia prepared by either precipitation or hydrothermally resulted in a catalyst with fairly high surface area (50–100 m^2/g). The surface area of the hydrothermally prepared zirconia was stable under reaction conditions while that of the precipitated zirconia decreased because of thermal sintering. The increased pore size of the hydrothermally prepared zirconia may be partly responsible for this behavior. Zirconia prepared by the precipitation method show the highest activity while zirconia prepared hydrothermally show the highest selectivity to i-C_4 compounds among C_4's. This high selectivity can be attributed to the high basicity of the hydrothermally prepared catalysts and possibly to their increased pore size. Sodium, thorium, and cerium were found to increase catalytic activity of precipitated zirconia while manganese almost completely deactivated the catalyst. None of the additives gave a marked increase in C_4 hydrocarbon production. Acidifying the catalyst seemed not only to reduce oxygenate production, but also to increase methane production. The precipitated zirconia catalyst shows promise for future investigation because of their fairly high conversions (~25–40%) and reasonable selectivities (~20% i-C_4's) under relatively mild operating conditions (673 K and 50 atm).

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