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Hydroconversion of n-hexadecane with Pt-promoted monoclinic and/or tetragonal sulfated zirconia catalysts

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A series of mixed Pt-promoted monoclinic and tetragonal sulfated zirconia catalysts were prepared and characterized. The catalysts contained 27–86% of the monoclinic phase. The zirconia samples were prepared by varying the speed of precipitation of the hydrous zirconia and the pH of the final solution. The hydrous zirconia was then calcined prior to promotion with Pt and sulfate. The catalysts were activated just prior to activity studies with n-hexadecane. This synthesis route and pretreatment produced mixed-phase catalysts which yielded comparable conversion and selectivity data to that of a purely tetragonal catalyst using optimum conditions. The data show that an active catalyst can be obtained with the monoclinic phase present and that addition of sulfate after development of the crystalline phases can yield an active catalyst.

Keywords: monoclinic/tetragonal Pt–SO_4^{2-}–ZrO_2 catalysts, hydrocracking, hydroisomerization

1. Introduction

Sulfated zirconia catalysts have attracted a significant amount of interest due to their ability to effect hydroconversion of hydrocarbons at low temperatures ([1] and references therein). However, there still exists much debate on many of the properties of these catalysts which contribute to their activity.

One of the controversial topics is the crystalline phase of zirconia in the active catalyst. It has been generally accepted that the active phase was tetragonal since the addition of sulfate to amorphous zirconia stabilizes this phase [2]. A number of authors have stated that the monoclinic phase has little or no activity for hydrocarbon conversion [3,4]. While the majority of the catalytic studies used n-butane as the feedstock, a number of different precursors, calcination temperatures and/or synthesis conditions were used to prepare the monoclinic and/or tetragonal phases. For example, Comelli et al. [3] studied the influence of the crystalline structure and sulfate ion concentration on butane conversions. These authors used a number of different precursors and calcination temperatures to produce catalysts with mixed tetragonal/monoclinic phases. The authors reported little or no activity for the conversion of n-butane for the monoclinic phase catalysts. Another example is the work of Ward and Ko [4]. These authors used a number of sol–gel syntheses for the preparation of sulfated zirconia catalysts and examined two different sulfation promotion points in their synthesis. By varying these parameters, the authors were able to obtain the mixed-phase catalysts for their catalytic studies with n-butane. They reported little or no activity with their monoclinic/tetragonal phase catalyst.

Recently Stichert and Schüth [5] synthesized a catalytically active monoclinic sulfated zirconia catalyst for the isomerization of n-butane. The authors aged the precipitated hydrous zirconia as a synthetic route to produce a purely monoclinic as well as mixed-phase catalysts. The authors report that the catalytic activity of their monoclinic sulfated zirconia catalyst is lower by a factor of 5 and 7 than the highest activities reported for tetragonal catalysts. They conclude that their monoclinic catalyst is catalytically active.

2. Experimental

In this study, a series of mixed-phase catalyst were prepared by varying the rate of precipitation and the pH of the end point of the precipitation of the hydrous zirconia. Zirconia tetrachloride was used as the precursor and ammonium hydroxide as the precipitation agent. The rate of precipitation varied from a few seconds up to 8 h. The amount of NH_4OH was varied to produce a pH of 9–11 at completion of the precipitation. After precipitation, the hydrous zirconia was dried overnight. Prior to promotion with sulfate and Pt, the hydrous zirconia was calcined at 400 °C for 4 h in air. The calcined samples were then promoted using H_2SO_4 (15 ml, 1 N H_2SO_4/g) and Pt (as H_2PtCl_6) to give a Pt concentration of 0.6 wt%. Prior to activity testing, the promoted catalysts were activated at 650 °C for 1 h in air. These synthesis routes produced catalysts with monoclinic concentrations ranging from 27 to 86%. The catalysts were identified by an alphanumeric name indicating the percentage of monoclinic phase after activation, e.g., M86 indicates a catalyst with a 86% monoclinic phase concentration. A duplicate synthesis of the 86% monoclinic catalyst was done and these catalysts were designated M86A and M86B, respectively. The activity of the catalysts synthesized using the methods described above was compared to a tetragonal catalyst prepared by the authors' "standard" procedure [6]. Briefly, the hydrous zirconia was prepared by rapid precipitation of the $ZrCl_4$ solution with NH_4OH to an end pH of 10.5. The hydrous zirconia was promoted with sulfate (15 ml, 1 N H_2SO_4/g) and Pt (0.6) prior to activation. Activation was done at 650 °C for 2 h in air just prior to activity testing. The catalyst was designated M00.

The X-ray diffraction data were obtained using a Philips X-ray diffractometer with a graphite crystal monochromator as the diffracted beam path. The radiation used was a Cu K_α at 40 kV and 20 mA. The data were collected at a step width of 0.02°, counting 2 s at each step. Each sample was scanned from 26 to 32.5° (2θ). The fraction of tetragonal phase was calculated from the ratio peak intermediates [6].

Surface areas were determined using the standard BET method. Total sulfur analyses were obtained using standard instrumental combustion (Leco) methods.

The activity testing of the catalysts have been described in detail elsewhere [6]. Briefly, the catalytic activity was determined in batch reactors using a reaction temperature of 150 °C, residence time of 15 min, feed to catalyst ratios of 2 and 10, and 500 psig (cold) of H_2 (UHP). Analyses of the gas products were done using a Carle AGC-311 gas chromatograph and liquid samples using an HP 5891 series II gas chromatograph equipped with FID detector and a 60 m × 0.33 mm (0.25 μm film thickness) DB-5 column. Quantitation for both gas chromatographs was done using HP 3396 integrators.

3. Results and discussion

Table 1 shows the analyses of the activated catalyst samples used in the catalytic studies. In general, as the amount of the monoclinic phase increases, the surface area of the catalyst increases. Also, as the surface area of the zirconia increases, the total sulfur also increases.

The conversions (disappearance of the feed) of n-hexadecane obtained using these catalysts are shown in figure 1. As can be seen in this figure, using a feed/catalyst ratio of 2, all of the catalysts have significantly high conversions: conversions of 95 wt% or greater are obtained for the catalysts containing 0.76% or less monoclinic phase. All conversion results are the average of duplicate runs (±1.0 wt%). Only the catalysts M86A, M86B and M82, which have 82–86% monoclinic phase, show slightly lower conversions. However, these catalysts still have a significant activity using these reactor conditions.

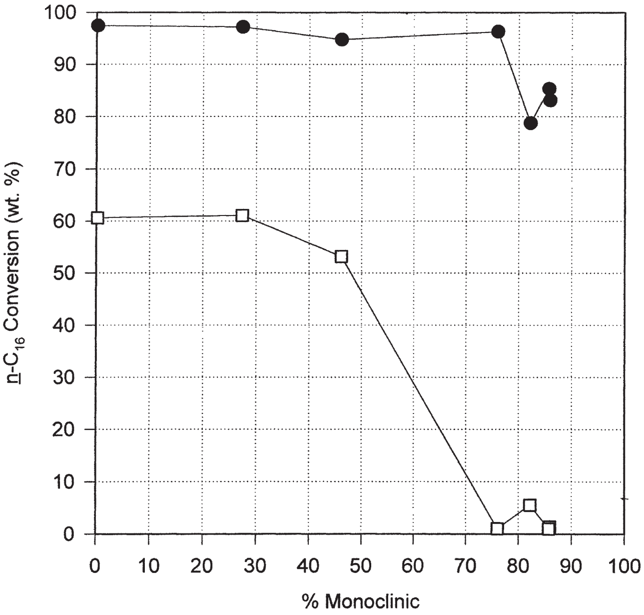

Figure 1. n-hexadecane conversion of Pt–SO_4^{2-}–ZrO_2 catalyst containing different amounts of the monoclinic phase. (●) Feed to catalyst ratio of 2; (□) feed to catalyst ratio of 10.

The selectivities for these catalysts as defined by the yield of isomerization products (isohexadecanes) and hydrocracked products (products with carbon numbers less than 16) are shown in figure 2 for the runs using a feed to catalyst ratio of 2. The data in this figure show that the isomerization and hydrocracking yields of the mixed-phase catalyst, at the same conversion levels, are identical to the yields obtained with the tetragonal catalysts. The decrease in hydrocracking yields with the conconcurrent increase in the isomerization yields for the monoclinic (76–86%) catalysts are due to the slightly lower total conversion levels obtained for these catalysts. The relationship between the total conversion and the isomerization and hydrocracking yields has been defined in our previous work [6] using tetragonal Pt–SO_4^{2-}–ZrO_2 catalysts. The mixed-phase catalysts show a similar trend in selectivity yield. Therefore, the mixed-phase catalysts show the same selectivities as the tetragonal catalysts under these conditions.

At a feed to catalyst ratio of 10, catalysts with a monoclinic content of 0–46% have significant hexadecane con-

Table 1
Catalyst characterization after activation at 650 °C in air for 1 h.

	Catalyst						
	M86A	M86B	M82	M76	M46	M27	M00
Monoclinic (%)	85.9	85.7	82.2	76.0	46.1	27.4	0.2
Sulfur (wt%)	1.53	1.55	1.56	1.27	1.25	1.26	0.65
Surface area (m^2/g)	105	106	94	93	72	83	50
Wt% S/surface area (m^2/g)	0.015	0.015	0.017	0.014	0.017	0.015	0.013

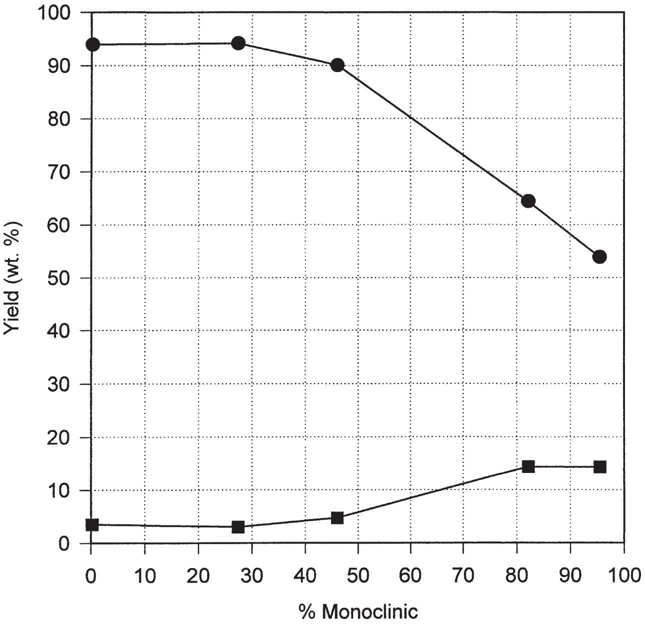

Figure 2. Selectivity yields for the monoclinic–tetragonal catalysts using the feed to catalyst ratio of 2, 150 °C, 15 min residence time and 500 psig H_2. (●) Isomerization yields; (■) hydrocracking yields.

versions. Only the catalysts containing 76–86% of the monoclinic phase have little or no activity.

These data suggest that the monoclinic phase of the Pt–SO_4^{2-}–ZrO_2 catalysts can be equally active as the tetragonal phase using the certain synthesis routes and process conditions. The reported literature results stating little or no activity for the monoclinic phase of the sulfated zirconia catalysts may be due to the fact that no attempt was made to optimize the synthesis route, calcination temperature, calcination time and/or reactor conditions.

The carbon number distributions of the hydrocracked products are shown in figure 3. As can be seen, the carbon numbers of the cracked products range from C_3 to C_{13} for the tetragonal and mixed-phase catalysts. The lower yields produced using M86A and M82 are due to the slightly lower conversions obtained with these catalysts.

The answer to the question as to whether sulfated monoclinic zirconia has catalytic activity appears to be yes. As the tetragonal phase is replaced up to 50% with the monoclinic phase, the conversion of n-hexadecane remains essentially constant. It appears impossible for half as much sulfated tetragonal zirconia in the 50/50 tetragonal/monoclinic catalyst to have the same hexadecane conversion as for the pure sulfated tetragonal catalyst. At the same time the much lower catalytic activity for the sulfated zirconia samples containing 75–85% of the monoclinic phase is consistent with the sulfated monoclinic zirconia lacking catalytic activity. Thus, the conclusion is that both phases of zirconia provide catalytic activity following sulfation but the tetragonal phase possesses higher catalytic activity.

One difference between the pseudo-stable tetragonal phase and the monoclinic phase is that the tetragonal phase has sites where oxygen can be adsorbed in a form that triggers the tetragonal to monoclinic phase [2]. Adsorbed sulfate apparently occupies these oxygen-adsorbing sites of the tetragonal or monoclinic phase precursors to inhibit the tetragonal to monoclinic phase transformation. A consistent view would be that the catalytic site residing in the complex sulfate anion–oxygen adsorbing vacancy has a significantly higher catalytic activity than sulfate adsorbed on the defect-free surface of either the monoclinic or tetragonal zirconia. Thus, adding sulfate to either the monoclinic or tetragonal precursor will lead to an active catalyst since the tetragonal phase is initially formed from either precursor and the sulfate anion stabilizes the tetragonal phase from transformation. In this view, the question of whether the monoclinic phase is active only applies for materials that have been heated at temperatures sufficient to cause crystallization and/or phase transformation to the monoclinic form.

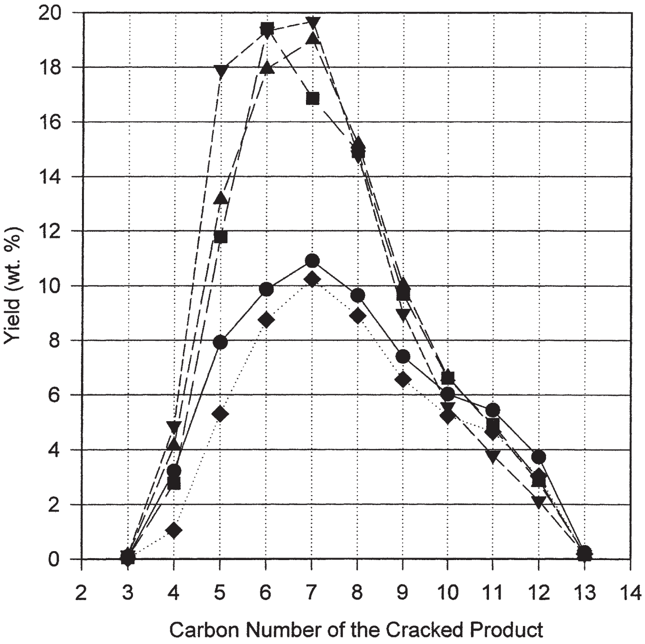

Figure 3. Carbon number distribution of the hydrocracked products (same conditions as figure 2). (●) M82; (■) M42; (▲) M00; (▼) M27; (◆) M86A.

In summary, the data presented in this work shows that the monoclinic phase can be catalytically active for the hydrocracking and hydroisomerization of n-hexadecane using optimum process and synthesis conditions.

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