



Overcoming the deleterious effect of hafnium in tungsten–zirconia catalysts: The use of doping and thermal treatments

David Simon^a, Bradley Taylor^{b,*}

^a Analytical Services, ConocoPhillips, Bartlesville Technology Center, 234 Petroleum Laboratory, Bartlesville, OK 74004, USA

^b Advanced Hydrocarbon Fuels, ConocoPhillips, Bartlesville Technology Center, 333-1 Petroleum Laboratory, Bartlesville, OK 74004, USA

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ABSTRACT

The effect of hafnium and aluminum addition to Ni/WO₃/ZrO₂ was examined as a function of calcination temperature for the isomerization of a 5 wt% cyclohexane in *n*-hexane feed. Hafnium, a common and difficult to separate impurity in zirconia, was found to decrease catalytic activity, primarily through the generation of monoclinic and cubic phases that are considered inactive for acid-catalyzed reactions. A hafnium induced monoclinic phase is formed at relatively low calcination temperatures and is fundamentally different from the thermodynamically stable monoclinic phase generated at higher temperatures. The addition of aluminum as well as higher calcination temperatures limited the formation of this monoclinic phase resulting in very active catalysts without the use of more expensive, hafnium-free catalyst precursors. Catalysts with tetragonal zirconia contents less than 40 wt% had initial isomerization activities that scaled linearly with tetragonal zirconia content. Catalysts with a tetragonal zirconia contents greater than 40% had initial *n*-hexane isomerization activities that were unrelated to zirconia morphology; a limitation that was a result of the hydrogenation function. The lack of correlation between zirconia crystal phases and catalytic activity for high tetragonal zirconia content catalysts implies that the measured isomerization activity may better represent the hydrogen spillover rate of nickel and not necessarily the intrinsic acid-catalyzed rate. Improved control over hydrogenation activity would allow for the preparation of more active catalysts.

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1. Introduction

As part of a continuing effort to regulate the production of cleaner automotive fuels, the U.S. Environmental Protection Agency (EPA) has adopted new rules concerning the composition of gasoline that would further reduce the maximum benzene content to 0.62 vol% by 2011 [1]. This reduction effectively halves the content of benzene within gasoline sold in the United States and results in a significant loss of octane within the gasoline blending pool. The isomerization of *n*-hexane represents one method of providing high octane, paraffinic compounds for blending into gasoline.

Hexane isomerization over Pt/chlorided alumina is a mature and widely commercialized technology. However, these materials require replenishment of corrosive chlorine as well as the use of an expensive hydrogenation metal. Tungsten–zirconia represents one class of materials that could find use in future industrial applications.

Despite research into the catalytic properties of tungsten oxides dating back to the early 1900's [2], interest in these materials

was rekindled in 1987 with the discovery of Hammett acidity in excess of that of sulfuric acid for tungsten oxides supported on zirconia [3]. Though Hammett acidity is considered an inaccurate measure of acidity in solid materials, tungsten oxides supported on zirconia were subsequently shown to be active in a number of acid catalyzed reactions such as xylene isomerization [4–6], 2-butanol dehydration [7,8], paraffin isomerization [9–11] and paraffin cracking [12]; often at reaction temperatures lower than for acidic zeolites. Additionally, in contrast to zeolites, which provide acidity within the confines of a pore system, tungsten–zirconia materials provide the high acidity of H-mordenite [13] without any mass transfer limitations or shape selectivity introduced by microporosity.

Hafnium is a common impurity in some zirconia precursors that is difficult and expensive to separate because of its chemical similarity to zirconium. This work focuses on the effect of hafnium on the catalyst morphology and ultimately the isomerization activity of Ni/WO₃/ZrO₂. Thermal treatments and aluminum doping are presented as an efficient means of mitigating the adverse effects of hafnium. Special care has been taken to track catalyst morphology as a function of metals content and calcination temperature. While the materials presented in this work do not possess all of the prop-

* Corresponding author. Fax: +1 918 662 1097.

E-mail address: brad.m.taylor@conocophillips.com (B. Taylor).

Table 1
Calcination temperature and elemental composition of prepared catalysts.

Catalyst	Nickel loading (wt%)	Tungsten surface loading (W/nm ²)	Tungsten loading (wt%)	Aluminum doping (wt%)	Hafnium impurity (wt%)	Calcination temperature (°C)	Surface area (m ² /g)
Ni/WO ₃ /ZrO ₂ -600 °C	3.32	5.85	18.2	–	–	600	102
Ni/WO ₃ /ZrO ₂ -650 °C	2.78	10.6	16.2	–	–	650	50.2
Ni/WO ₃ /ZrO ₂ -700 °C	2.54	9.83	16.4	–	–	700	54.7
Ni/WO ₃ /ZrO ₂ -800 °C	2.78	10.9	16.2	–	–	800	48.9
Ni/WO ₃ /ZrO ₂ -900 °C	2.33	17.1	16.9	–	–	900	32.4
Ni/WO ₃ /ZrO ₂ (Hf)-500 °C	2.74	4.46	17.0	–	1.41	500	125
Ni/WO ₃ /ZrO ₂ (Hf)-600 °C	3.18	6.52	16.4	–	1.38	600	82.5
Ni/WO ₃ /ZrO ₂ (Hf)-700 °C	3.04	7.98	16.2	–	1.41	700	66.6
Ni/WO ₃ /ZrO ₂ (Hf)-800 °C	2.26	13.2	16.7	–	1.41	800	41.6
Ni/WO ₃ /ZrO ₂ (1Al,Hf)-600 °C	2.86	4.77	15.7	1.03	1.43	600	108
Ni/WO ₃ /ZrO ₂ (1Al,Hf)-750 °C	2.93	7.30	16.5	1.13	1.41	750	74.1
Ni/WO ₃ /ZrO ₂ (1Al,Hf)-825 °C	3.14	10.8	17.4	1.08	1.40	825	52.9
Ni/WO ₃ /ZrO ₂ (1Al,Hf)-900 °C	2.59	17.8	16.6	1.07	1.35	900	30.6
Ni/WO ₃ /ZrO ₂ -750 °C-3h	2.85	17.9	26.8	–	–	750	49.0
Ni/WO ₃ /ZrO ₂ -750 °C-24h	2.37	18.6	27.1	–	–	750	47.8

erties necessary for a commercialized isomerization catalyst, the results show that relatively inexpensive and impure catalyst precursors, in combination with base metals, can be engineered to produce considerable hydroisomerization activity.

2. Experimental

Three variations of Ni/WO₃/ZrO₂ catalysts were prepared using zirconia precursors with and without a hafnium impurity. One of the hafnium-containing series was doped with aluminum. Nickel and tungsten content were kept essentially constant on a per weight basis.

2.1. Catalyst preparation

Catalyst preparation began with the precipitation of amorphous Zr(OH)₄. Sufficient concentrated aqueous ammonium hydroxide was added drop-wise to a 0.25 molar aqueous solution of zirconyl chloride (Aldrich, Reagent Grade, 98%, ~0.5% Hf or Aldrich, 99.99%) under vigorous stirring to obtain a final pH of 10.5–11. The resulting slurry was allowed to age for 1 h under vigorous stirring before being filtered and washed with approximately 3 times its volume in distilled water. The filter cake was dried in a vacuum oven for 2 days at 120 °C and approximately 0.5 bar. Once dry, the Zr(OH)₄ was washed a second time in approximately 3 times its volume of distilled water to ensure all of the residual chloride ions were rinsed from the solid. The Zr(OH)₄ was dried overnight in a vacuum oven at 120 °C and approximately 0.5 bar. Tungsten was deposited on the zirconium hydroxide via incipient wetness impregnation using an aqueous solution of ammonium metatungstate ((NH₄)₆H₂W₁₂O₄₀·xH₂O, Aldrich, ≥66.5% W) added drop-wise to Zr(OH)₄ taken directly from the vacuum oven. The ammonium metatungstate solution concentration was adjusted so as to produce a final material containing approximately 15 wt% W. The wetted support was dried overnight in a vacuum oven at 120 °C and approximately 0.5 bar. The dried material was calcined in air for three hours at temperatures ranging from 500 to 900 °C resulting in materials with different crystal phase compositions and surface tungsten loadings (W/nm²). Nickel was subsequently added by incipient wetness impregnation to calcined tungsten–zirconia materials that had been dried overnight in a vacuum oven (120 °C, ~0.5 bar) using aqueous solutions of nickel(II) nitrate (Aldrich, Reagent Grade) at a concentration sufficient to produce a 3 wt% Ni material. The catalyst was again dried overnight in a vacuum oven (120 °C, ~0.5 bar) before being calcined at 500 °C for 3 h in air.

Aluminum was incorporated into the zirconia phase through the addition of aluminum nitrate (Aldrich, Reagent Grade) to the

zirconyl chloride solution prior to precipitation with ammonium hydroxide. In this work, aluminum content ranged from 0–3 wt% aluminum in the final catalyst. The results of the 1 wt% aluminum catalysts are presented for brevity.

A summary of the prepared catalysts can be found in Table 1, where the catalyst names are derived from the approximate aluminum content, hafnium content and calcination temperature such that Ni/WO₃/ZrO₂(1Al,Hf)-600 °C denotes a Ni/WO₃/ZrO₂ catalyst containing approximately 1 wt% aluminum, a hafnium impurity and calcined at 600 °C. Nickel and tungsten loading is not incorporated into the naming scheme as they were kept roughly constant for all of the materials. Hafnium content was either 0 or 1.4 wt%.

2.2. Catalytic measurements

Catalytic measurements were taken using a typical ¾-inch outer diameter down flow packed bed reactor. Liquid feed was metered to the system using an ISCO Model 500 D syringe pump while gases were supplied by Brooks 5850E mass flow controllers. The temperature at the center of the catalyst bed was measured using a type K thermocouple. Pressure was maintained using a Moore regulator. Analysis of the reactor effluent was completed using a slipstream line to an online gas chromatograph. The online effluent sampling allowed for the quantification of light cracking products, however, the conditions in this study were sufficiently mild that cracking is not a significant reaction path. The online analysis was performed using an HP 6890 gas chromatograph outfitted with a 60 m × 0.25 mm CP-Sil 5 Low Bleed/MS column (1 μm film) plumbed to the split/splitless inlet and a flame ionization detector.

The *n*-hexane isomerization activity was determined using a 5 wt% mixture of cyclohexane (Aldrich, CHROMASOLV[®], ≥99.7%) in *n*-hexane (Aldrich, CHROMASOLV[®] Plus, ≥95%). Reactor pressure was 15 bar with a liquid weight hourly space velocity (LWHSV) of 17 h⁻¹ and hydrogen to hydrocarbon ratio (H₂/HC) of 0.7. The typical charge of catalyst in the reactor was 1 g, sieved to 40–100 mesh and mixed with sufficient alundum to produce a 13 mL catalyst bed. The catalyst was pretreated *in situ* using a 120 sccm stream of hydrogen at 370 °C and 15 bar for one hour to fully reduce the hydrogenation metal and eliminate any water intercalated in the catalyst pores. All gases were industrial grade and supplied by Best Welders Supply, Tulsa, Oklahoma.

2.3. Catalyst characterization

Catalyst composition was determined by X-ray fluorescence (Philips 1480 or 2440 Wavelength Spectrometer), surface area by nitrogen adsorption (QuantaChrome AS-3 or AS-6) and crystal

phase composition by refinement of powder X-ray diffraction patterns (Pan Analytical Xpert Pro, $\text{CuK}\alpha$). Tungsten surface loading, expressed in atoms per square nanometer, was calculated using X-ray fluorescence data and BET surface area. X-ray refinements were performed on all materials following calcination at 500 °C for three hours and prior to activity testing.

The primary features of the X-ray diffraction patterns were modeled using tetragonal zirconia and tungsten oxide. Monoclinic zirconia, cubic zirconia and nickel tungstate were added to improve the fit to the major features and account for peaks unassociated with tetragonal zirconia. There was some difficulty in determining the location of a predominance of the deposited nickel. Since the nickel loading was known from X-ray fluorescence data, an attempt was made to begin the refining of the complete pattern containing nickel tungstate.

A significant amount of tungsten was not accounted for in the tungsten oxide phase or the nickel tungstate phase. The examination of tungsten–zirconia materials (results not shown) showed that in the absence of nickel, a zirconium tungstate phase was present. The inclusion of this phase allowed for the accounting of the deposited metal. In essence, the zirconium tungstate phase modeled the interface between tungsten-containing phases and the zirconia support. Similarly to the modeling of nickel phase, X-ray fluorescence data provided starting compositions for the structural refinements of the tungsten phases.

Despite a good overall fit to the experimental data, the three-zirconia-phase model (tetragonal, monoclinic and cubic) did not perfectly reproduce some of the small peaks ($35\text{--}50^\circ 2\theta$) and shoulders ($\sim 60^\circ 2\theta$) in the X-ray diffraction data. These minor discrepancies led to the inclusion of an orthorhombic zirconia phase and, in the case of amorphous materials, an additional monoclinic phase. The data presented in this report utilizes X-ray fluorescence data coupled with X-ray diffraction data to assign nickel tungstate (Space Group $P12_1/c1$) and zirconium tungstate ($P2_13$) contents and includes up to five zirconia phases to fit the features of the diffraction pattern (monoclinic = $P12_1/c1$, tetragonal = $P4_2/nm$, orthorhombic = $Pbc2_1$ and cubic = $P2_13$). In an effort to prevent over specification of the system, only the tetragonal phase was modeled with Williamson–Hall strain.

3. Results and discussion

A number of $\text{Ni}/\text{WO}_3/\text{ZrO}_2$ catalysts, some containing hafnium and/or aluminum and calcined at temperatures ranging from 500 to 900 °C were prepared and are presented in Table 1. These catalysts were prepared at essentially a constant weight of tungsten with the surface tungsten concentration being set by the sintering of the support at various calcination temperatures.

3.1. The effect of hafnium

Catalysts $\text{Ni}/\text{WO}_3/\text{ZrO}_2(\text{Hf})\text{-}500^\circ\text{C}$ through 800°C were prepared from the comparatively inexpensive, hafnium-containing zirconia precursor. Shown graphically in Fig. 1, increasing calcination temperature results in an increase in tetragonal zirconia content at the expense of the monoclinic. $\text{Ni}/\text{WO}_3/\text{ZrO}_2(\text{Hf})\text{-}500^\circ\text{C}$ was best fit using a short-range-ordered and a long-range-ordered monoclinic phase. If viewed as two separate monoclinic phases, the long-range-ordered phase comprised 19.5% and the short-range-ordered phase comprised 45.8% of the sample by weight. The short-range-ordered monoclinic phase can be considered an amorphous phase given the low crystal domain size and its identification only at the lowest calcination temperature. The elimination of the monoclinic phase with thermal treatments is somewhat contrary to literature accounts which show high temperatures pro-

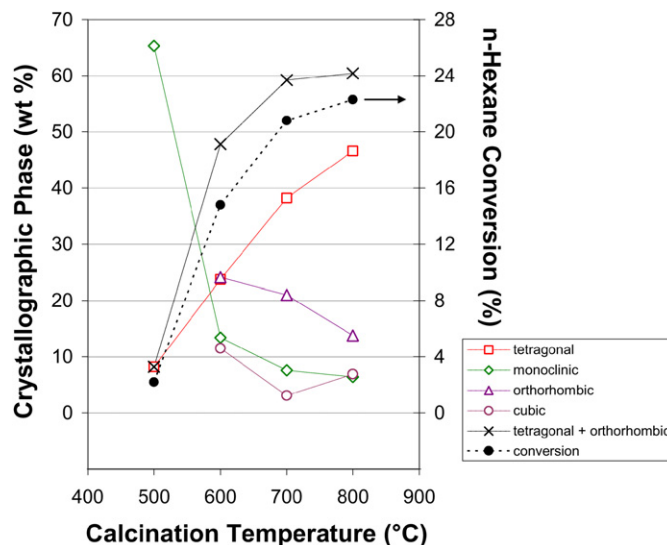


Fig. 1. Crystallographic phase content and initial *n*-hexane isomerization activity versus calcination temperature for catalysts $\text{Ni}/\text{WO}_3/\text{ZrO}_2(\text{Hf})\text{-}500^\circ\text{C}$ through 800°C (288°C , 15 bar, $\text{LWHSV} = 17 \text{ h}^{-1}$, $\text{H}_2/\text{HC} = 0.7$).

note the formation of the more thermodynamically stable monoclinic phase [4,5,7–12,14,15]. These literature accounts, however, generally refer to calcination temperatures above 800 °C. The generation of tetragonal zirconia with increased calcination temperature may also be an effect of tungsten surface loading. Surface tungsten has been shown to stabilize the tetragonal zirconia phase [14] and studies of hafnia/zirconia mixtures in the absence of tungsten implied no regeneration of tetragonal zirconia following formation of the monoclinic phase [16]. The elimination of zirconia surface area due to sintering at high temperature may result in a tungsten surface loading that ultimately stabilizes, in this case, the tetragonal and cubic zirconia phases. The stabilizing effect of tungsten is manifested in two respects. First, these materials required higher calcination temperatures to produce crystalline materials as compared to the tungsten-free case presented in reference [16]. Second, tungsten addition generated tetragonal zirconia at the expense of monoclinic, but only with the aid of thermal treatments.

The orthorhombic phase appears as an intermediate phase during the transition from monoclinic to tetragonal phase. Increases in calcination temperature reduce the orthorhombic content in favor of the catalytically active tetragonal phase. It is not clear there is any real trend with calcination temperature in the cubic phase content. Given the similar tungsten and nickel loadings for each catalyst, the nickel tungstate and zirconium tungstate concentrations were constant. The appearance of tungsten oxide corresponded to calcination temperatures that resulted in a tungsten surface loading of approximately two monolayers.

Catalytic activity increases with increasing tetragonal zirconia content, a relationship previously asserted in the open literature [4,5,7–12]. The initial isomerization rate appears to saturate at tetragonal contents greater than approximately 40 wt%. Despite being crystallographically distinct, the tetragonal and orthorhombic phases are very similar. Their symmetry is essentially identical except for a minor lengthening in one lattice parameter. A more linear relationship between catalyst composition and activity can be reproduced when initial isomerization activity is compared to the sum of the tetragonal and orthorhombic phases. This makes a case for the over specification of the model, given that orthorhombic zirconia has not been identified as catalytically active in the literature and activity has been shown previously to scale with tetragonal content.

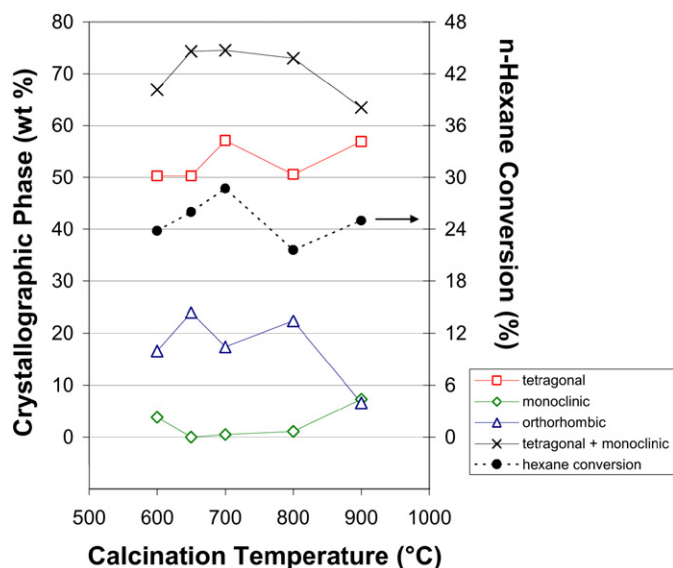


Fig. 2. Crystallographic phase content and initial *n*-hexane isomerization activity versus calcination temperature for catalysts Ni/WO₃/ZrO₂-600 °C through 900 °C (288 °C, 15 bar, LWHSV = 17 h⁻¹, H₂/HC = 0.7).

Catalysts Ni/WO₃/ZrO₂-600 °C through 900 °C were prepared using a hafnium-free zirconia precursor (Fig. 2). This group of materials has essentially no trend in crystallographic phase with calcination temperature, though the hafnium-free catalysts have lower monoclinic and higher tetragonal zirconia contents than the hafnium-containing materials. Whereas the hafnium-containing materials showed a systematic transition to the tetragonal phase at the expense of the monoclinic and orthorhombic phases, the hafnium-free materials, at best, can be viewed as having a roughly constant composition of tetragonal and orthorhombic phases. The inclusion of a cubic zirconia phase did not improve the model fit.

Catalytic activity best tracks with the tetragonal zirconia content which is consistent with the assertion in literature that tetragonal zirconia content determines the acid-character and thus catalytic activity of these materials. The trends in activity for the hafnium-free materials clearly do not track with the sum of the orthorhombic and tetragonal phases, nor does it appear to track with any of the other phases not pictured in Fig. 2. While not substantially more active than the hafnium-containing catalysts, the activity of these materials is higher in rough proportion to the increased tetragonal content.

In contrast to the hafnium-containing series of materials, monoclinic zirconia content does increase with temperature, though Ni/WO₃/ZrO₂-900 °C was calcined at a higher temperature than any other catalysts. Whereas high temperature calcination of hafnium-containing catalysts has appeared to form tetragonal zirconia at the expense of monoclinic, cubic and orthorhombic, high temperature treatment of the hafnium-free catalysts produced monoclinic zirconia at the expense of orthorhombic.

The predominance of orthorhombic and tetragonal phases in the hafnium-free catalysts implies that the hafnium impurity may catalyze, and thus be located predominantly in, the monoclinic phase. Hafnium has been shown to be extremely miscible in monoclinic zirconia phases [17,18], adding very little structural stress to the resulting solid solution [19] and has long been known to catalyze the formation of monoclinic phases [16]. The monoclinic phase found at low calcination temperatures in the hafnium-containing catalyst, however, cannot be the thermodynamically stable monoclinic phase described in the literature. A thermodynamically stable phase would not convert under heat treatments to the thermodynamically unstable tetragonal phase; particularly

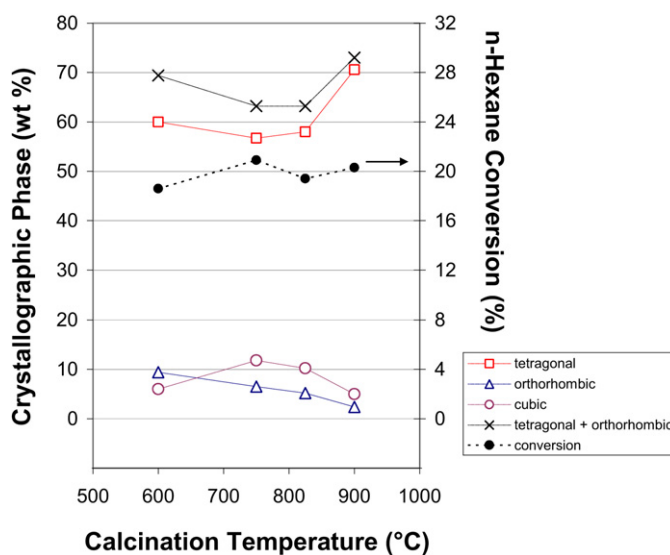


Fig. 3. Crystallographic phase content and initial *n*-hexane isomerization activity versus calcination temperature for catalysts Ni/WO₃/ZrO₂(1Al,Hf)-600 °C through 900 °C (288 °C, 15 bar, LWHSV = 17 h⁻¹, H₂/HC = 0.7).

when the monoclinic phase is again produced at high temperatures. The monoclinic phase present, especially at low calcination temperatures, in the hafnium-containing material must be a phase uniquely the result of hafnium. The increase in monoclinic zirconia in the hafnium-free materials between a calcination temperature of 800 and 900 °C is the generation of the polymorph generally discussed in the literature.

There is no discussion in the literature of the presence, let alone effect of, cubic and orthorhombic phases in these materials. Ultimately, the scattering from both phases is similar to that of the tetragonal phase making identification difficult. Monoclinic phases are easily discernable from tetragonal phases by the splitting of a strong diffraction peak.

3.2. The effect of aluminum doping

Hafnium-containing catalysts with an aluminum concentration of approximately 1 wt% and calcined at temperatures ranging from 600 °C to 900 °C were prepared. The catalytic activity of these materials as a function of calcination temperature is presented in Fig. 3.

The incorporation of roughly 1 wt% aluminum, a doping level suggested in the patent literature [9], resulted in a material with a tetragonal zirconia content commensurate with the hafnium-free materials. There was no evidence of monoclinic zirconia, while the cubic zirconia content was similar to hafnium-containing, undoped catalysts. Though appearing at lower concentrations than the aluminum-free, hafnium-containing catalysts, the orthorhombic zirconia phase shows similar behavior in that high temperature treatments promote its transition to other phases. While the orthorhombic phase appears to be a transitional phase between the monoclinic and tetragonal phase in the aluminum-free, hafnium-containing materials, this is not as clear cut in the 1 wt% aluminum samples. Given the lack of observed monoclinic phase, these materials provide no evidence that the orthorhombic structure is a transitional phase formed only upon the conversion of monoclinic phases to tetragonal. In addition, the elimination of the orthorhombic phase via heat treatments did not result solely in the generation of the tetragonal phase (as was seen in the un-doped samples); the cubic phase was also formed.

The addition of trivalent ions (Al³⁺ and Ga³⁺ [9], Ln³⁺ [20,21]) has been shown to increase isomerization activity and the addition

Table 2
Crystallographic composition of prepared catalysts.

Catalyst	Zirconia (wt%)				Tungsten oxide (wt%)	Zirconium tungstate (wt%)	Nickel tungstate (wt%)
	Tetragonal	Monoclinic	Orthorhombic	Cubic			
Ni/WO ₃ /ZrO ₂ -600 °C	50.3	3.8	16.6	–	–	11.7	17.6
Ni/WO ₃ /ZrO ₂ -650 °C	50.3	–	24.0	–	0.2	11.5	14.1
Ni/WO ₃ /ZrO ₂ -700 °C	57.1	0.5	17.4	–	3.5	8.1	13.3
Ni/WO ₃ /ZrO ₂ -800 °C	50.6	1.1	22.4	–	0.3	11.7	14.0
Ni/WO ₃ /ZrO ₂ -900 °C	56.9	7.3	6.6	–	8.1	9.2	12.0
Ni/WO ₃ /ZrO ₂ (Hf)-500 °C	8.2	65.3	–	–	–	13.9	12.6
Ni/WO ₃ /ZrO ₂ (Hf)-600 °C	23.7	13.4	24.1	11.5	–	10.6	16.7
Ni/WO ₃ /ZrO ₂ (Hf)-700 °C	38.2	7.6	21	3.1	0.3	12.1	17.7
Ni/WO ₃ /ZrO ₂ (Hf)-800 °C	46.6	6.4	13.8	6.9	4.9	6.5	14.8
Ni/WO ₃ /ZrO ₂ (1Al,Hf)-600 °C	60.0	–	9.4	6	–	9.6	15.0
Ni/WO ₃ /ZrO ₂ (1Al,Hf)-750 °C	56.7	–	6.5	11.8	1.7	8.4	15.0
Ni/WO ₃ /ZrO ₂ (1Al,Hf)-825 °C	58.0	–	5.2	10.2	7.0	3.1	16.6
Ni/WO ₃ /ZrO ₂ (1Al,Hf)-900 °C	70.6	–	2.4	5	5.7	5.1	11.2
Ni/WO ₃ /ZrO ₂ -750 °C-3h	43.5	–	16.6	–	9.1	16.5	14.3
Ni/WO ₃ /ZrO ₂ -750 °C-24h	44.2	–	15.8	–	11.7	17.9	10.4

of aluminum was found to stabilize amorphous zirconia and delay the transition from tetragonal to monoclinic phases [22]. Supporting zirconia on an alumina support has shown similar properties [23,24]. Aluminum, in this case, serves a purpose beyond just stabilizing the tetragonal phase in that it prevents the generation of the low temperature monoclinic phase, allowing for the preparation of WO₃/ZrO₂ catalysts of high tetragonal zirconia content using more benign thermal treatments.

Despite the high tetragonal zirconia content of these catalysts, the isomerization activity was less than that of the hafnium-free materials. The relatively constant isomerization activity across a range of calcination temperatures does not track with tetragonal zirconia content. The tungsten surface loading over this range of calcination temperatures ranges from 5 to 18 W/nm² which spans the optimum loading (5–10 W/nm²) literature has shown to produce the most active catalysts [4–8,14]. The relatively constant activity across a range of surface tungsten loadings suggests a relatively unchanging number of active sites and implies a relatively small number of active sites relative to tungsten atoms. The relatively small number of active acidic sites has been noted previously [6,8]. Only the nickel tungstate phase was essentially constant with calcination temperature. While activity does not track with nickel or nickel tungstate content, an isomerization activity inconsistent with the tetragonal zirconia content and invariant with changes in tungsten surface loading reinforces the possibility that activity is determined by hydrogenation/dehydrogenation activity rather than the number of acid sites.

Though not presented for brevity, catalysts were also prepared with an aluminum content of 0.55 wt% and 2.5 wt%. The crystallographic trends mirrored those of the 1 wt% case.

3.3. The effect of tungsten loading

Catalyst Ni/WO₃/ZrO₂-750 °C-3h was prepared similarly to catalysts Ni/WO₃/ZrO₂-600 °C through 900 °C except for a near doubling of the tungsten loading. The resulting catalyst had a tungsten surface loading greater than Ni/WO₃/ZrO₂-900 °C and a surface area similar to Ni/WO₃/ZrO₂-800 °C. When adjusted for the changes in tungsten composition, the tetragonal zirconia content is consistent with the entirety of the hafnium-free series of materials. Deposited tungsten in excess of the surface capacity resulted in a tungsten oxide loading similar to Ni/WO₃/ZrO₂-900 °C. With an initial *n*-hexane conversion of 28.8%, the activity of this catalyst also fell within the range already reported and appears to show that while sufficiently high tungsten loadings to generate bulk tungsten oxide are not a detriment to activity, the high loading constitutes a waste of material. The absence of an impact on isomerization activity with the deposition of 10 wt% of material on

the external surface of zirconia reinforces the previous assertion that the density of active acidic sites appears to be small relative to the available surface area.

3.4. The effect of calcination time

Catalysts Ni/WO₃/ZrO₂-750 °C-3h and Ni/WO₃/ZrO₂-750 °C-24h were prepared from the same tungsten-zirconia starting material except that Ni/WO₃/ZrO₂-750 °C-24h was calcined for 24 h rather than the standard 3 h (Table 1). Given that the crystallographic composition for the two catalysts is nearly identical despite the difference in calcination time (Table 2), the short calcination time is sufficient at 750 °C to produce a consistent composition. The stability of the orthorhombic phase over the course of 24 h calcination period, while not eliminating it as a transitional phase between monoclinic and tetragonal zirconia, at least shows that it is a reasonably stable phase in an of itself. The similarity in phase composition between these materials and the hafnium-free series suggests that none of the trends are a result of slight variations in calcination time. With an initial *n*-hexane conversion of 22.7%, Ni/WO₃/ZrO₂-750 °C-24h has an activity that fits within the range already observed for hafnium-free materials.

3.5. Catalytic activity of orthorhombic zirconia

The apparent assignment of catalytic activity to the orthorhombic phase in the aluminum-free, hafnium-containing materials is likely either an artifact of the structural model or a coincidence. When the aluminum-free, hafnium-containing catalysts are viewed side-by-side with the hafnium-free materials (Fig. 4), the relationship between the orthorhombic content and temperature appears to be a result of drawing a trend from insufficient information. The addition of hafnium certainly retards the formation of tetragonal zirconia at a given calcination temperature as well as promotes the formation of a cubic phase. In fact, the calcination of a hafnium-free material at 600 °C produced a similar phase composition as a hafnium-containing material calcined at 800 °C. Though an artificial construct based on this observation, Fig. 4 suggests that the activity and phase composition of the hafnium-free materials are simply extensions of the trends seen in the hafnium-containing catalysts. It is in this context that assigning catalytic significance to the orthorhombic phase becomes untenable. On average, the orthorhombic content of the aluminum-free materials is 20 wt% and essentially invariant with changes in calcination temperature. As a result, the tetragonal content of the material should be more important for predicting catalytic activity.

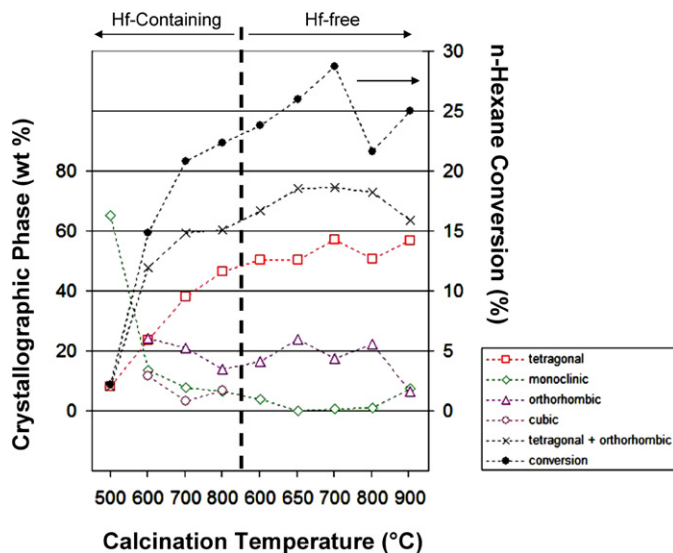


Fig. 4. Side-by-side comparison of the crystallographic composition and initial *n*-hexane conversion for catalysts Ni/WO₃/ZrO₂(Hf)-500 °C through 800 °C and Ni/WO₃/ZrO₂-600 °C through 900 °C (288 °C, 15 bar, H₂/HC = 0.7, LWHSV = 17 h⁻¹, Feed = 5 wt% cyclohexane in *n*-hexane).

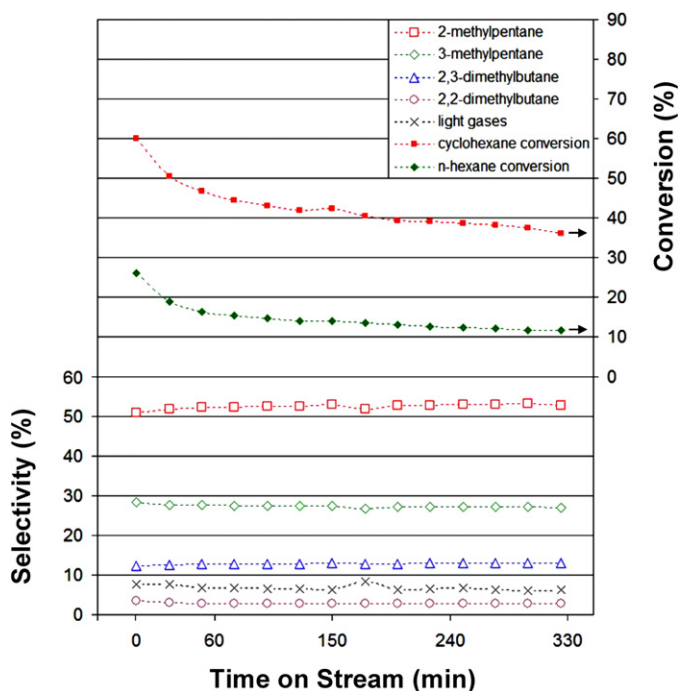


Fig. 5. Conversion and selectivity versus time on stream for catalysts Ni/WO₃/ZrO₂-650 °C (288 °C, 15 bar, LWHSV = 17 h⁻¹, H₂/HC = 0.7).

3.6. Activity and selectivity

Conversion and selectivity data for catalyst Ni/WO₃/ZrO₂-650 °C versus time on stream are presented in Fig. 5. Initial deactivation is rapid and although the deactivation rate slows after 60 min, there is no steady state isomerization rate during the 5.5 h the catalyst was examined. The higher conversion of cyclohexane relative to *n*-hexane is expected given that higher boiling compounds adsorb more strongly to the catalyst surface. The greater stability of cyclohexane/methylcyclopentane carbo-cations relative to *n*-hexane is also expected to increase the coverage of naphthenes and enhance the rate of their conversion [25]. The reaction of cyclohexane resulted almost entirely in methylcyclopentane. Despite the presence

of nearly 3 wt% nickel, there was no indication of significant hydrogenolysis activity under these conditions. The selectivity to hexane isomers was essentially constant despite the loss of 40% of the isomerization activity over the course of 5.5 h. The steady selectivity to dimethylbutanes suggests that their formation is a result of a single adsorption event of *n*-hexane. The generation of dimethylbutanes from methylpentanes would have been expected to suffer a decrease in selectivity as acid sites were eliminated with time on stream since two adsorption steps involving two different acid sites would be required. Taking into account the methylpentane impurities in the *n*-hexane feed, their conversion would have to be over 60% to account for all of the dimethylbutanes produced and would still not account for the essentially constant selectivity.

3.7. Limitation of activity by nickel

The use of initial conversion data in Figs. 1–3 was a necessity because of the significant deactivation of these catalysts within just hours on stream. Pre-reduction in hydrogen was assumed to charge the surface with ample surface hydrogen making the initial isomerization the best measure of acid-catalyzed activity. This surface hydrogen was apparently insufficient for samples of high tetragonal zirconia content, since activity was not proportional to zirconia morphology. Catalysts Ni/WO₃/ZrO₂(1Al,Hf)-600 °C through 825 °C represent the best case for catalytic activity limitations as a result of nickel. Despite higher tetragonal zirconia contents, these three catalysts had lower initial isomerization activities than the un-doped materials. Given that the three catalysts have only minor differences in phase composition, a range of surface tungsten loadings (4.77–10.8 W/nm²) and similar nickel loadings, a difference in activity would have been expected as the tungsten surface loading reached the literature asserted maximum in activity between 5 and 10 W/nm².

Generally, as acid catalyzed isomerization activity increased, the rate of deactivation increased. Since the stability of these catalysts is dependant on the ability of the hydrogenation metal to deliver sufficient surface hydrogen to hydrogenate adsorbed isomerization intermediates [11], the deactivation of these catalysts should give some measure of the ability of nickel to supply this hydrogen. As shown in Fig. 6, the stability of the un-doped hafnium-containing materials decreases with increasing activity, a sign that the hydrogenation function of the catalyst is increasingly incapable of providing sufficient surface hydrogen to aid in the desorption of unsaturated isomerization surface intermediates. The high variability in catalyst stability for the Ni/WO₃/ZrO₂ and Ni/WO₃/ZrO₂(1Al,Hf) series of catalysts is also indicative of an accumulation of carbonaceous material on the catalysts surface. Given that there is no indication of a change in acid-site strength or concentration for these materials, this deactivation must be attributable to the hydrogenation function provided by nickel. Despite having similar nickel loadings for all of the examined catalysts, nickel is not providing spillover hydrogen to the same degree in each material. This inability to control the hydrogen spillover rate from nickel leads to the variability in catalyst stability and, in the case of the 1 wt% aluminum doped samples, the inability to achieve the high activity seen in materials with similar zirconia phase content.

4. Conclusion

These materials show that tungsten–zirconia-based catalysts are far more crystallographically complex than has previously been addressed in the open literature. The presence of a hafnium impurity is detrimental to the *n*-hexane isomerization activity of nickel–tungsten–zirconia due to the formation of catalytically inactive monoclinic and cubic zirconia. This effect can be mitigated using high temperature thermal treatments which can convert some

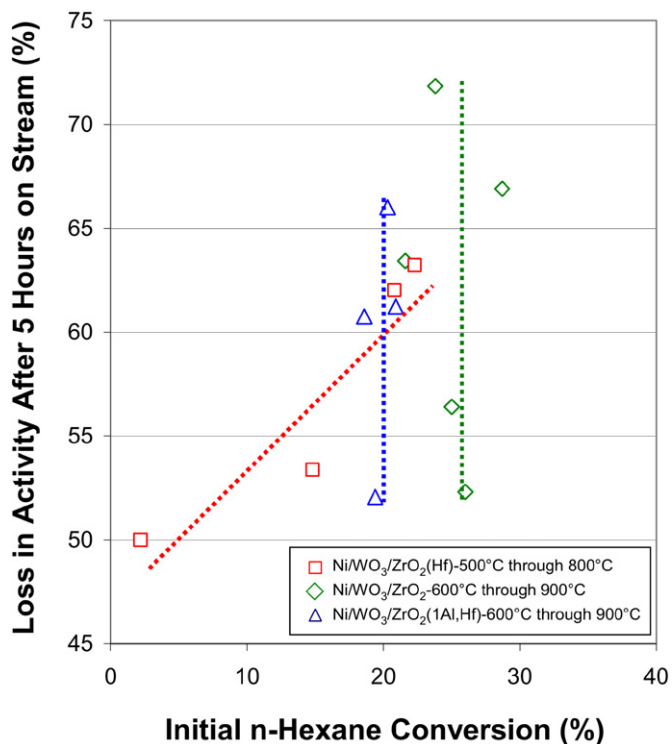


Fig. 6. Percentage loss in *n*-hexane activity after 5 h on stream versus initial *n*-hexane isomerization activity for the catalysts presented in Table 1 (288 °C, 15 bar, LWHSV = 17 h⁻¹, H₂/HC = 0.7). The lines are meant to guide the eye and represent neither a least squares fit or an average value.

of the hafnium-induced monoclinic phase into catalytically active tetragonal zirconia. Catalytic activity is determined by tetragonal zirconia content up to 40 wt%. At higher tetragonal zirconia contents, catalytic activity is limited by the hydrogenation properties of nickel. Aluminum incorporation is capable of preventing the formation of the hafnium-induced monoclinic phase and promotes the formation of tetragonal zirconia at calcination temperatures less severe than in its absence. Aluminum-doping had no effect of the formation of cubic zirconia.

This collection of catalysts shows that the use of base metals and impure catalyst precursors can produce materials of apprecia-

ble *n*-hexane isomerization activity when the acid and hydrogenation functionalities are appropriately managed. This work outlined the management of the acid functionality through the control of tetragonal zirconia content. Though intended as a means to use inexpensive catalyst precursors, an extension of this work could use the combination of hafnium and aluminum incorporation and thermal treatments as a means of controlling acid site density on tungsten zirconia materials. Unfortunately, the same level of control could not be exercised over the hydrogenation functionality.

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