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Supported Organometallics. Highly Electrophilic Cationic Metallocene Hydrogenation and Polymerization Catalysts Formed via Protonolytic Chemisorption on Sulfated Zirconia

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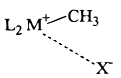
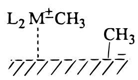
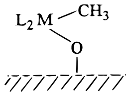
Studies of homogeneous Ziegler−Natta catalysis have shown that highly electrophilic cationic species (e.g., **A**; L = cyclopentadienyl-type ancillary ligand) can be produced using organo−Lewis acidic (alkide/hydride abstraction)[1,2] and Brønsted acidic (M-alkyl/H protonolysis) cocatalysts.[1,3] In constrast, supported Ziegler−Natta catalyst activation has been exclusively confined to intrinsically Lewis acidic surfaces (e.g., **B**)[4,5a−c] or to organo−Lewis acid activated surfaces[5a,d−f] since chemisorption of metallocenes on conventional Brønsted acid surfaces results in catalytically inert μ-oxo species (e.g., **C**) via M−CH_3 protonolysis.[4b−d] Recently, sulfated zirconia and related solid acids have received considerable attention because of their proposed "superacidity", i.e., stronger Brønsted acidity than 100% H_2SO_4 (Hammett $H_o = -12$), and high catalytic activity for various hydrocarbon transformations.[6] Two interesting questions therefore arise: First, would solid Brønsted acids such as sulfated zirconia activate Ziegler−Natta-type catalysts, and second, what type of interaction can occur between the organometallic adsorbate and such an oxide surface? We report here the formation of highly electrophilic metallocene species on "superacidic" strong Brønsted sites via metal−carbon bond protonolysis and initial observations on adsorbate α-olefin/arene hydrogenation and polymerization activities.



A



B



C

Zirconia (ZR)[7] and zirconia/tungsten-oxide (ZRW)[8] were prepared by modifications of literature procedures. Sulfated zirconia (ZRSO) was prepared by thermal decomposition of $Zr(SO_4)_2 \cdot 4H_2O$ (Aldrich, 99.99%) at 730 °C for 5 h in flowing dry O_2 (100 mL/min).[9] These ZRSO samples were then separately activated at 300, 400, and 740 °C under high vacuum (5×10^{-6} Torr), yielding supports designated ZRS300, ZRS400,[10] and ZRS740, respectively.[11] Next, $Cp_2Zr(CH_3)_2$ (**1**)[12a] and $Cp'Zr(CH_3)_3$ (**2**)[12b] [$Cp' = \eta^5$-$(CH_3)_5C_5$] were adsorbed from pentane solution onto these solid acids using the rigorously anaerobic techniques described elsewhere.[4a,c]

Catalytic hydrogenations using the supported organozirconium catalysts were studied in the rapidly mixed slurry hydrogenation apparatus described previously.[13] Turnover frequencies in molecules substrate hydrogenated per Zr atom·h^{-1} are given in Table 1.[14] The ordering of 1-hexene hydrogenation rates as a function of support and calcination temperature (entries 1−5)[15] can be approximately correlated with known strong Brønsted acid surface site populations.[6,11] Complex **2,** which is more coordinatively unsaturated/less sterically hindered than **1,** exhibits a dramatic enhancement in hydrogenation activity when supported on ZRS400; for example, it mediates rapid hydrogenation of benzene at 25 °C, 1 atm H_2.[16] Rates are zero-order in [arene] up to ∼20% conversion and critically affected by the arene substitution pattern

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(10) (a) Surface and textural properties of ZRS400: surface area = 110 m^2/g; most frequent pore radius = 3.5 nm (BET); tetragonal form: monoclinic form = 40: 60 (XRD). The "superacidic sites" are associated with the tetragonal phase. See: (b)Vera C. R.; Parera, J. M. *J. Catal.* **1997**, *165*, 254−262. (c) Corma, A.; Fornés, V.; Juan-Rajadell, M. I.; López Nieto, J. M. *Appl. Catal., A* **1994**, *116*, 151−163.

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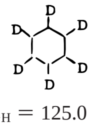
(14) Metal coverage is based on parallel ICP assays with $Cp'_2Hf(CH_3)_2$ indicating that $Cp'_2Hf(CH_3)_2$/ZRS400 contains 0.81 Hf atom/nm^2 and 3.55 S atom/nm^2.

(15) Precise activity measurements are complicated somewhat by competing substrate isomerization yielding *cis*- and *trans*-2-hexene. N_t values were obtained from initial 20% conversion during which time the isomerization is minor.

(16) (a) Product identity was confirmed by GC/MSD and ^1H and ^{13}C NMR analysis of the hydrogenation product. (b) The ^{13}C NMR spectrum of the C_6D_6 hydrogenation product confirms that $C_6D_6H_6$[4c] is formed exclusively with no evidence of C−H/C−D scrambling:



δ 26.9(C) (J_{C-D} = 18.9 Hz, J_{C-H} = 125.0 Hz).

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Table 1. Olefin/Arene Hydrogenation Catalyzed by Supported Organozirconium Complexes at 25.0 (1) °C, $P_{H_2} = 1$ atm[a]

entry	complex	solid acid	substrate	N_t,[b] h^{-1}
1	$Cp_2Zr(CH_3)_2$ (**1**)	ZR	1-hexene	~0[c]
2	**1**	ZRW	1-hexene	~0
3	**1**	ZRS300	1-hexene	32[d]
4	**1**	ZRS400	1-hexene	35[d]
5	**1**	ZRS740	1-hexene	7[d]
6	$Cp'Zr(CH_3)_3$ (**2**)	ZRS400	1-hexene	2840
7	**2**	ZRS400	benzene	970[e]
8	**2**	ZRS400	toluene	14[e]
9	**2**	ZRS400	*p*-xylene	~0

[a] In a typical experiment,[13] 50 mg of catalyst ([Zr] = 7.4×10^{-3} mmol) was agitated in 0.020 mL of 1-hexene (1.6×10^{-1} mmol) + 1.0 mL of octane solution (entries 1−5) or 0.60 mL of neat arene (entries 6−8) at a speed of 2000 rpm. [b] N_t values measured while the pressure drop in the system was <1%. All H_2 uptake results were corrected for substrate vapor pressure. [c] In NMR scale experiments, hexane was detected by ^1H NMR after 2 days at 70 °C. [d] See ref 15. [e] Turnover frequency independent of [arene] for <20% conversion.

(entries 7−9), in contrast to more conventional catalysts.[17,18b,19a,b] These substrate substituent effects suggest that the molecular surface active centers are sterically hindered. To our knowledge, the benzene hydrogenation activity of **2**/ZRS400 at 25.0(1) °C, 1 atm H_2 rivals or exceeds that of the most active arene hydrogenation catalysts known.[18,19] From poisoning experiments with degassed water, ~65% of **2**/ZRS400 sites are determined to be of catalytic importance in benzene hydrogenation, vs ~4% for $Cp'_2Th(CH_3)_2$/dehydroxylated alumina.[4d] **1**/ZRS400 and **2**/ZRS400 also catalyze ethylene homopolymerization with preliminary 25 °C activity measurements indicating 1.5×10^3 and 4.0×10^4g PE/mol Zr·h·atm C_2H_4, respectively.

Insight into the metallocene chemisorption process on sulfated zirconia is provided by ^{13}C CPMAS NMR spectroscopy with anaerobic sampling and assignment techniques described elsewhere and using $Cp'_2Th(^{13}CH_3)_2$ and $Cp_2Zr(^{13}CH_3)_2$ as model adsorbates.[4b,d,20a−c] The ^{13}C CPMAS NMR spectrum of $Cp'_2Th(^{13}CH_3)_2$/ZRS400 (Figure 1A) exhibits resonances assignable to the Cp′ ligands (δ 127.6, 9.3), to the labeled $Th-^{13}CH_3^+$ functionality (δ 72.8) and to μ-oxo species $Cp'_2Th(^{13}CH_3)-O-$ (**C**; δ 54.2). Interestingly, δ $Th-^{13}CH_3^+$ = δ 72.8 on ZRS400 is at significantly lower field than is associated with analogous “cation-like” species on other supports and is suggestive of a more electron-deficient species.[4b,20a−c] Two weak additional resonances are observed at δ 32.6 and −0.2. Although they cannot be rigorously assigned, the chemical shifts correlate with transferred methide groups i.e, $S_{surface}-^{13}CH_3$ (cf., $HOS(O)_2CH_3$, δ 39.4) and $Zr_{surface}-^{13}CH_3$, respectively.[20] However, both signals are very weak in intensity compared to the $Th-CH_3$ resonance (≤~5%).

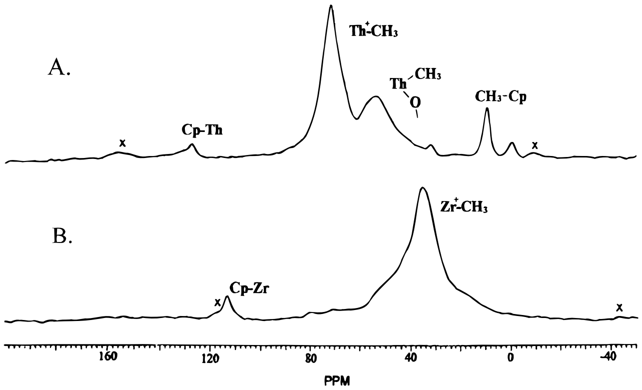
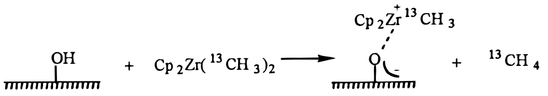


Figure 1. ^{13}C CPMAS NMR spectra (75.4 MHz) of (A) $Cp'_2Th(^{13}CH_3)_2$/ZRS400 (3430 scans, repetition time = 2.5 s, contact time = 7.1 ms, spinning speed = 6.3 kHz) and (B) $Cp_2Zr(^{13}CH_3)_2$/ZRS400 (9250 scans; repetition time = 1.2 s, contact time = 0.58 ms, spinning speed = 6.2 kHz).

Therefore, methide transfer to the surface (**B**) is not as important on sulfated zirconia as on dehydroxylated alumina, which exhibits an intense of $Al_{surface}-^{13}CH_3$ resonance (δ −12), almost equal in intensity to the $Th^+-^{13}CH_3$ signal.[20a,c] Figure 1B presents the ^{13}C CPMAS NMR spectrum of $Cp_2Zr(^{13}CH_3)_2$/ZRS400. Only two resonances are detected at δ 113.8 (Cp ligand) and δ 36 ($Zr-^{13}CH_3^+$) with a small shoulder at ca. δ 20 assignable to a μ-oxo species **C**,[4b,d] and a transferred methide group resonance is not observable. Similar observations are made for **2**/ZRS400.[21] These spectroscopic results argue that sulfated zirconia Brønsted acid sites generate cationic adsorbate species via metal−carbon bond protonolysis (eq 1). This proposed pathway is supported by the



(1)

D

following observations: (1) the correlation of **1**/ZRSx catalytic activities (entries 3−5 in Table 1) with the density of support Brønsted acid sites,[6,11] (2) after impregnation of $Cp_2Zr(CH_3)_2$ on ZRS400, the ν_{OH} transitions in the infrared (3650, 3300 cm^{-1}) disappear, accompanied by a shift of $\nu_{S=O}$ from 1395 to 1360 cm^{-1}, and (3) methane is detected in the ^1H NMR spectrum (δ 0.15) of a $Cp_2Zr(CH_3)_2$+ ZRS400 mixture in C_6D_6. Observations[20b,22] that homogeneous and heterogeneous acids with oxo counteranions such as $CF_3SO_3^-$ ($H_o = -14.1$) and ZRW ($H_o \leq -14.5$[8]), respectively, afford catalytically marginal species suggests that sulfated zirconia contains Brønsted acid sites stronger than $H_o = -14$ and/or having extensively charge-delocalized, weakly coordinating conjugate base anionic sites (e.g., **D**).

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Supporting Information Available: Details of the experimental procedures for physical, analytical, and catalytic measurements (4 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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