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Bimetallic Zn and Hf on Silica Catalysts for the Conversion of Ethanol to 1,3-Butadiene

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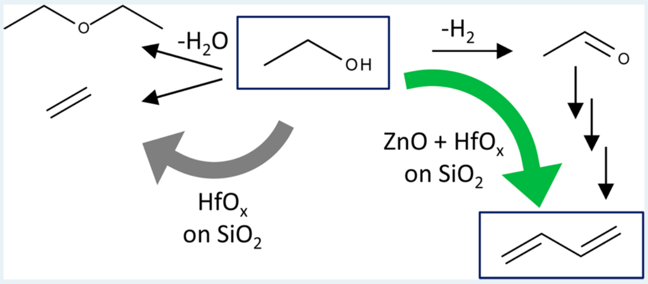
Supporting Information

ABSTRACT: Silica-supported catalysts for the conversion of ethanol to 1,3-butadiene were investigated. The combination of Hf(IV) and Zn(II) resulted in a stable, active, and selective catalyst in which the Zn(II) effectively suppressed the dehydration activity of Hf(IV); the catalyst preparation method plays a crucial role. Using the crystalline Zn-silicate hemimorphite as an alternative Zn(II) source proved to be even more successful in suppressing ethanol dehydration.



KEYWORDS: *1,3-butadiene, ethanol, zinc silicate, hemimorphite, heterogeneous catalysis, silica impregnation*

1,3-Butadiene (BD) is a frequently used building block in polymer chemistry. It is typically obtained as a byproduct from steam cracking where ethene and propene are the main products. However, the recent changes to the use of a lighter feedstock for steam cracking and the increased usage of shale gas as an alternative source for ethene have resulted in a price increase for BD.[1] To meet the global demand for BD, alternative synthesis routes that preferentially do not rely on fossil fuels are being investigated. One of these routes that has received an increasing amount of attention over the past years is the conversion of ethanol to BD.[2−12] This reaction, which is also known as the Lebedev process, has already been described in the early twentieth century using mixed metal oxides as catalysts, typically MgO/SiO_2 or ZnO/Al_2O_3.[13−16]

The mechanism of the multistep reaction of ethanol to butadiene is complex and has not yet been fully elucidated, in spite of large research efforts (e.g., in a recent publication by Chieregato et al.[17]) Nevertheless, there is a consensus on a number of key steps (Scheme 1): (1) the dehydrogenation of ethanol to acetaldehyde catalyzed by basic or redox sites, (2) the aldol condensation of acetaldehyde, (3) dehydration and a Meerwein−Ponndorf−Verley type reduction on basic or Lewis acid sites resulting in crotyl alcohol, and (4) a final dehydration step to 1,3-BD, possibly on weak acid sites.[4,9,18−22] The acetaldol and crotonaldehyde products are not always observed, presumably due to their short lifetime under reaction conditions.[8] On the other hand, ethene and diethyl ether are frequently detected as side products, resulting from reactions promoted by Brønsted acid sites.[8,23] The different types of catalysts used for this reaction have recently been reviewed by Makshina et al.[16] For instance, MgO/SiO_2 systems, as studied by Ohnishi et al.,[24] or by Kvisle et al.,[18] are a well-studied class of catalysts, which, for a long time, had the highest reported butadiene selectivities (up to 87%).[24] However, the compositional optimum seems narrow, and catalyst stability is uncertain.

Scheme 1. Generally Accepted Overall Scheme for the Formation of BD from Ethanol

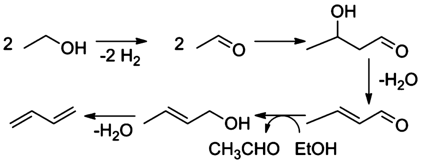


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Table 1. Catalytic Performance of Trimetallic Silica-Supported Catalysts[a]

				selectivity (%)[c]											
	catalyst[b]	TOS (h)	X_{EtOH} (%)	$C_2^=$	$C_3^=$	Ac.	BD	$C_4^=$	DEE	BuOH	BuO	other	yield$_{BD}$ (%)	$g_{BD}\ g_{cat}^{-1}h^{-1}$	BD (ppm)
1	$Cu_{1.0}Zr_{1.0}Zn_{0.5}$	0.5	98	16	2.8	5.8	61	6.6	2.3	0.49	<0.01	4.8	59.5	0.074	16 500
		10	79	15	2.2	8.4	61	5.3	2.7	0.50	<0.01	5.3	48.0	0.060	13 400
2	$Cu_{1.0}Hf_{1.5}Zn_{0.5}$	0.5	96	7.3	2.8	9.8	65	6.0	1.3	0.50	<0.01	7.9	61.8	0.077	17 200
		10	95	6.5	2.8	11	65	4.0	1.1	0.62	<0.01	8.7	61.9	0.077	17 300
3[d]	$Cu_{1.0}Zr_{1.5}Zn_{0.5}$	0.5	96	9.5	2.4	7.9	66	5.3	2.1	0.41	<0.01	6.3	63.3	0.079	17 600
		10	91	9.0	2.3	10	64	4.8	2.1	0.44	<0.01	7.3	58.4	0.073	16 300
4	$Cu_{1.0}Hf_{0.75}Zn_{0.5}$	0.5	99	6.2	3.7	22	52	2.6	0.5	0.62	<0.01	12	51.8	0.065	14 400
		10	96	5.1	3.4	29	46	2.2	0.4	0.36	<0.01	14	44.6	0.056	12 400
5	$Cu_{1.0}Hf_{3.0}Zn_{0.5}$	0.5	99	7.9	3.4	2.6	72	6.4	1.0	0.28	0.27	6.4	71.6	0.090	19 900
		10	99	7.2	3.1	4.2	71	5.5	1.1	0.30	0.16	7.2	71.1	0.089	19 800

[a] Catalytic results are shown after 0.5 and 10 h reaction at 360°C preceded by a 3 h reaction period at 300°C using a feed rate of 0.21 $g_{EtOH}\ g_{cat}^{-1}\ h^{-1}$. Catalysts were prepared using $Cu(OAc)_2$, $Zn(NO_3)_2{\cdot}6H_2O$, $ZrO(NO_3)_2{\cdot}H_2O$ and $HfCl_4$ as metal precursors. [b] Subscript refers to the metal content (wt %). [c] Selectivity to ethene, propene, acetaldehyde, BD, butenes, diethyl ether, butanol, butanal and other condensation products, respectively. [d] Prepared with $ZrCl_4$.

Table 2. Catalytic Performance of Mono- And Bimetallic Silica-Supported Catalysts[a]

				selectivity[c]											
	catalyst[b]	TOS (h)	X_{EtOH} (%)	$C_2^=$	$C_3^=$	Ac.	BD	$C_4^=$	DEE	BuOH	BuO	other	yield$_{BD}$ (%)	$g_{BD}\ g_{cat}^{-1}h^{-1}$	BD (ppm)
1	$Hf_{3.0}$	0.5	48	82	0.1	1.0	0.4	0.1	17	<0.01	<0.01	0.0	0.2	0.001	48
		10	43	82	0.0	0.6	0.1	0.1	17	<0.01	<0.01	0.0	0.0	<0.001	10
2[d]	$Cu_{1.0}Hf_{3.0}$	0.5	99	29	2.2	3.2	49	7.7	5.3	0.27	<0.01	2.8	48.9	0.061	13 600
		10	75	52	1.0	5.1	25	3.0	12	0.17	<0.01	2.0	18.8	0.023	5200
3	$Zn_{0.5}$	0.5	66	10	1.2	57	14	0.4	0.7	2.5	1.3	12	9.5	0.036	2640
		10	67	7.5	1.0	62	12	0.2	0.6	2.6	1.2	13	7.6	0.029	2100
4	$Hf_{3.0}Zn_{0.5}$	0.5	72	7.7	2.0	13	63	4.1	2.0	2.6	0.37	6.0	45.3	0.179	12 600
		10	68	7.0	1.9	15	60	4.0	1.9	3.0	0.50	6.5	41.0	0.154	11 400
5[e]	$Hf_{3.0}Zn_{0.5}$	0.5	60	26	1.5	21	36	5.1	5.4	0.32	1.5	2.9	21.6	0.081	6000
		10	34	21	1.1	34	29	2.9	6.6	0.46	2.5	3.0	9.8	0.037	2700

[a] Catalytic results are shown after 0.5 and 10 h reaction at 360°C preceded by a 3 h reaction period at 300°C using a feed rate of 0.64 $g_{EtOH}\ g_{cat}^{-1}\ h^{-1}$. Catalysts were prepared using $Cu(OAc)_2$, $Zn(NO_3)_2{\cdot}6H_2O$, and $HfCl_4$ as metal precursors. [b] Subscript refers to the metal content (wt %). [c] Selectivity to ethene, propene, acetaldehyde, BD, butenes, diethyl ether, butanol, butanal and other condensation products, respectively. [d] Feed rate 0.21 $g_{EtOH}\ g_{cat}^{-1}\ h^{-1}$. [e] As a 1:1 mixture of silica containing 6.0 wt % Hf and silica containing 1.0 wt % Zn.

Considerable improvements were realized by adding Ni or Ag to the catalyst to facilitate the dehydrogenation.[5,12,25] Such recent work shows that correct tuning of the transition metal composition allows significant progress in comparison with the binary MgO/SiO_2 systems. A related type of catalyst comprises a combination of transition metal oxides deposited on a silica support without the use of MgO. This approach has for instance been investigated by Jones et al.,[4] where the highest selectivity to BD (67% at 45% ethanol conversion) was obtained using a trimetallic combination of Cu(II), Zr(IV) and Zn(II) (1 wt % each). In the present work, a fumed silica support was doped with different transition metal combinations; the catalytic function of each compound in the conversion of ethanol to butadiene was investigated, and the influence of the deposition method on catalyst performance was studied. Special attention was devoted to maximizing the butadiene effluent concentration and to minimizing the loss of ethanol to byproducts from acid-catalyzed reactions like ethene and diethyl ether.

As a starting point, the trimetallic Cu(II)−Zn(II)−Zr(IV) system of Jones et al.[4] was taken (Table 1, entry 1, Figure S1, S2). With this catalyst, a high selectivity of 61% to BD at nearly full conversion was obtained, which remained stable after 10 h of reaction in spite of a small decrease in conversion. Unfortunately, this system still produces a significant amount of ethene (>10%) and related acid-catalyzed byproducts. Therefore, Hf(IV) was chosen as a softer metal to replace Zr. This resulted in a much lower ethene production and an even higher selectivity to BD (Table 1, entry 2, Figure S3, S4, Table S1). By replacing $ZrO(NO_3)_2{\cdot}H_2O$ in the synthesis by $HfCl_4$, the counteranion of the metal precursor salt was simultaneously changed to chloride. To investigate the influence of the presence of chloride anions in the impregnation slurry, the Zr(IV)-containing system was prepared using $ZrCl_4$. This catalyst (Table 1, entry 3) shows a higher stability and BD selectivity and a lower selectivity to ethene compared to the Cl-free system (Table 1, entry 1), indicating a beneficial effect of changing the metal source. However, the ethene production is still higher than in the case of $HfCl_4$, demonstrating the beneficial effect of the latter metal on decreasing acid catalyzed byproduct formation. With increasing Hf(IV)-content of the catalysts (Table 1, entries 2, 4, 5) the BD selectivity increases further at the expense of the acetaldehyde production. Clearly, increasing the Hf(IV) content enhances the capacity of the catalyst for the aldol condensation step and increases the BD-productivity.

To further investigate the role of each compound in the Cu(II)−Zn(II)−Hf(IV) system, mono- and bimetallic catalysts were prepared (Table 2, Figure S5). If Hf(IV) is the only compound deposited on the silica support (Table 2, entry 1),

Table 3. Catalytic Performance of HM-Containing Silica-Supported Catalysts (HM = Hemimorphite)[a]

				selectivity[c]											
	catalyst[b]	TOS (h)	X_{EtOH} (%)	$C_2^=$	$C_3^=$	Ac.	BD	$C_4^=$	DEE	BuOH	BuO	other	$yield_{BD}$ (%)	$g_{BD}\ g_{cat}^{-1}h^{-1}$	BD (ppm)
1[d]	HM	0.5	76.2	4.6	2.0	60	5.5	0.1	0.2	3.1	1.1	24	4.2	0.016	1170
		10	78.3	3.9	1.6	62	4.3	0.1	0.2	3.3	0.95	24	3.4	0.013	950
2[d]	$Hf_{3.0}$ on HM	0.5	75.6	4.3	1.4	60	12	0.2	0.6	3.2	1.1	18	8.7	0.033	2400
		10	77.3	3.8	1.2	61	8.8	0.2	0.7	3.6	1.1	19	6.8	0.025	1900
3[e]	$Hf_{3.2}Zn_{5.1}$	0.5	97.6	18	11	0.8	39	27	0.2	<0.01	0.45	4.6	37.5	0.141	10 500
		10	99.4	16	14	0.3	18	32	0.1	0.23	0.83	20	17.5	0.066	4900
4[f]	$Hf_{3.2}Zn_{5.1}$	0.5	88.1	5.3	2.6	9.2	66	3.2	0.8	0.41	2.8	11	57.7	0.217	16 100
		10	90.6	4.1	2.5	11	61	3.3	0.9	0.79	3.3	13	55.3	0.208	15 400
5[f]	$Hf_{2.5}Zn_{16}$	0.5	99.2	5.8	3.6	4.0	71	3.8	0.7	0.42	2.5	8.1	70.2	0.264	19 500
		10	97.3	4.9	3.6	6.5	67	4.3	1.1	0.48	3.2	9.4	65.2	0.245	18 200
6[f]	$Hf_{3.0}Zn_{9.3}$	0.5	98.8	10	3.6	2.4	70	5.0	1.4	0.06	1.8	5.4	69.3	0.260	19 300
		10	98.6	7.5	3.3	3.3	69	5.2	1.3	0.26	2.3	7.4	68.4	0.257	19 100

[a]Catalytic results are shown after 0.5 and 10 h reaction at 360°C preceded by a 3 h reaction period at 300°C using a feed rate of 0.64 $g_{EtOH}\ g_{cat}^{-1}\ h^{-1}$. Catalysts were prepared using $HfCl_4$ as metal precursor and HM as the sole Zn source. [b]Subscript refers to the metal content (wt %). [c]Selectivity to ethene, propene, acetaldehyde, BD, butenes, diethyl ether, butanol, butanal, and other condensation products, respectively. [d]HM as support, no silica. [e]The appropriate amount of Hf was first impregnated onto the silica support and then contacted with HM in suspension under reflux conditions for 3 h. [f]The appropriate amount of Hf was first impregnated onto the silica support and then contacted with HM in suspension at room temperature for 0.5 h.

Table 4. Acid Properties of Selected Catalysts Determined via FTIR Spectroscopy Using Pyridine As Probe Molecule[a]

entry	catalyst	BAS (μmol/g)[b]	LAS (μmol/g)[b]	L/B	Y (BD,%)	S (BD,%)	S ($C_2^=$,%)
1[c]	$Hf_{3.0}$	5.0	47.3	9.4	0.2	0.4	82
2[c]	$Zn_{0.5}$	<0.1	13.9	-	7.1	9.5	6.6
3[c]	$Hf_{3.0}Zn_{0.5}$	2.0	67.9	34.4	45.3	63	7.7
4[c,d]	$Hf_{3.0}Zn_{0.5}$	1.2	21.3	18.1	21.6	36	26
5[c]	$Cu_{1.0}Hf_{3.0}Zn_{0.5}$	1.5	53.0	36.2	71.6	72	7.9
6[e]	HM	<0.1	13.0	-	4.2	5.5	4.6
7[e]	$Hf_{3.2}Zn_{5.1}$	0.7	40.6	54.5	57.7	66	5.3
8[e]	$Hf_{2.5}Zn_{16}$	<0.1	44.1	-	70.2	71	5.8
9[e]	$Hf_{3.0}Zn_{9.3}$	<0.1	25.5	-	69.3	70	10

[a]Catalytic data are given for comparison. [b]Amount of pyridine adsorbed on Brønsted acid sites (BAS) and Lewis acid sites (LAS) at 150 °C as determined from the IR absorption band of chemisorbed pyridine. [c]From impregnation of the appropriate amount of $Cu(OAc)_2$, $Zn(NO_3)_2{\cdot}6H_2O$ and $HfCl_4$ on silica. [d]As a 1:1 mixture of silica containing 6.0 wt % Hf and silica containing 1.0 wt % Zn. [e]The appropriate amount of Hf was first impregnated onto the silica support and then contacted with HM in suspension at room temperature for 0.5h.

hardly any ethanol dehydrogenation takes place and ethene and diethyl ether are the main products, resulting from acid catalysis. Adding Cu(II) to the catalyst alters the selectivity entirely (Table 2, entry 2). In this case, there is sufficient dehydrogenation capacity to obtain a catalyst with all required functionalities for the synthesis of butadiene. The ethene and diethyl ether formation is correspondingly diminished but they are still produced in larger amounts than in the trimetallic system (Table 1, entry 5). Additionally, the stability of the catalyst is much lower than in the Zn(II)-containing trimetallic system. On the other hand, deposition of only Zn(II) on the silica support results in a low (<10%) selectivity to ethene and diethyl ether (Table 2, entry 3). A small amount of BD is formed, but the selectivity is low; most of the ethanol is converted to acetaldehyde without further condensation. This clearly demonstrates the contribution of Zn(II) to the dehydrogenation capacity of the catalyst; unlike Hf(IV), Zn(II) does not hydrolyze to form acid sites that give rise to large amounts of ethene or diethyl ether. The combination of Zn, which strongly increases the ethanol dehydrogenation, and Hf(IV), which catalyzes the subsequent aldol condensation, finally results in a catalyst with a good BD selectivity and a stable performance for many hours on stream (Table 2, entry 4, Table S1, entry 9). Remarkably, it is important that Hf(IV) and Zn(II) are impregnated simultaneously on the same silica support: separate impregnations of silica powders with these compounds, followed by physically mixing them together in a mortar to obtain a catalyst with the same overall metal loading, resulted in an inferior catalyst with lower BD selectivites and a low stability (Table 2, entry 5). Clearly, both metals should be present in sufficient proximity to each other in order to suppress the ethene and diethyl ether formation and to balance the different catalytic functions resulting in BD formation.

To better understand the interaction between Hf(IV) and Zn(II), the zinc silicate hemimorphite (HM) was used, both as support and as Zn(II)-source. Hemimorphite ($Zn_4Si_2O_7(OH)_2{\cdot}H_2O$) is a zinc silicate which, for instance, can be used to catalyze the addition of methanol to propyne, using Zn^{2+} ions with open coordination sites at the outer surface.[26] In the conversion of ethanol to BD, it catalyzes the dehydrogenation to acetaldehyde, but it hardly enables the subsequent reaction steps (Table 3, entry 1) resulting in a similar performance as with the Zn(II)-on-silica catalyst (Table 2, entry 3). Using it as a support for Hf(IV) barely improves the selectivity to BD but the ethene production is still strikingly low (Table 3, entry 2). Remarkably, when HM is deposited onto silica (i.e., when it is used as a Zn(II) precursor instead of the previously used $Zn(NO_3)_2{\cdot}6H_2O$), the observed selectivities change entirely. In a first experiment, the HM was contacted with a Hf(IV)-containing silica support under reflux conditions (Table 3, entry 3). This already decreased the accumulation of acetaldehyde in the product stream and resulted in an increased butadiene selectivity, but it also increased the ethene formation. Using this method of combining Hf(IV) and Zn(II) on silica, the ethanol dehydration could not be sufficiently suppressed. On the other hand, simply contacting both compounds (HM, Hf(IV) deposited on SiO_2) in suspension at room temperature largely suppresses the ethene formation (≈ 5% selectivity), and depending on the precise composition, it results in a stable BD selectivity of 70% at nearly full ethanol conversion (Table 3, entries 4−6).

Characterization of the catalysts with FTIR using pyridine as probe molecule provided further insights into the catalyst performance (Table 4, Figure S6). The impregnation of Hf(IV) onto silica clearly introduced Brønsted acidity (Table 4, entry 1), but this was significantly suppressed by the presence of Zn(II) − either introduced as $Zn(NO_3)_2 \cdot 6H_2O$, or admixed using hemimorphite as the Zn(II) source (Table 4, entries 3, 7−9). Adding Cu(II) to the catalyst only had a minor influence on the amount and type of acid sites (Table 4, entries 3, 5) . Catalysts consisting only of Zn^{2+} and silica (Table 4, entries 2, 6) show an almost negligible Brønsted acidity and correspondingly low ethene formation. Although ZnO has been described by Tanabe as being amphoteric,[27] various studies have shown that in the interaction with alcohols, ZnO primarily acts as a basic material.[28−30] For materials loaded with both Hf(IV) and Zn(II), it is therefore well conceivable that the Brønsted acidity generated by hydrolysis on Hf(IV) is neutralized by neighboring O−Zn groups, either on well-dispersed ZnO or as Si−O−Zn moieties at the hemimorphite surface. Remarkably, the mixture of Hf(IV) and Zn(II), impregnated separately onto silica (Table 4, entry 4) has a limited number of Brønsted acid sites but still produces a significant amount of ethene (26% selectivity). This again demonstrates the significance of the impregnation procedure to balance not only the amounts, but also the proximity to one another of the different catalytic functions.

Although suppression of Brønsted acidity is clearly beneficial for the BD selectivity, Lewis acid sites are needed both for the aldol condensation and for the Meerwein type reduction of the putative crotonaldehyde intermediate. For the ethanol dehydrogenation, Zn−O moieties are effective, but for the aldol reaction, the Zn(II) centers are nearly inactive. In contrast, Hf(IV) is not only effective for the aldol condensation, but it is also well-known to promote hydrogen transfer reactions in MPV reactions. In the latter, Hf(IV) is even more active than Zr(IV), which has at least partly been ascribed to the facile displacement of −OH groups on the Hf(IV) by incoming alcohol reactants, at least for MPV reactions in mild conditions.[31]

With the best HM-based catalysts of the present study, the ethene selectivity is 10% or even significantly lower. While hardly any Brønsted acidity could be detected on these materials using the pyridine probe method, it is probable that some of the water, produced during the reaction, causes a mild hydrolysis of the Hf(IV). This generates Brønsted acidity under reaction conditions, which is the likely cause for the observed, limited ethanol dehydration.

In summary, we demonstrated that bimetallic mixtures of Hf(IV)−Zn(II) and trimetallic mixtures of Cu(II)−Hf(IV)−Zn(II) and Cu(II)−Zr(IV)−Zn(II) give remarkably active, selective, and stable catalysts for the ethanol to butadiene reaction. In these trimetallic catalysts, Cu(II) acts as a dehydrogenation catalyst. However, the synthesis of bimetallic catalysts has shown that this function can also be performed by Zn(II), which, in addition, also increases the stability of the catalysts. Hf(IV) is preferred over Zr(IV), especially in order to avoid the competitive ethanol dehydration. Adding Zn(II) to the Hf(IV) containing catalyst is crucial to obtain dehydrogenation capacity and to force the Hf(IV) into catalyzing the condensation of acetaldehyde rather than the ethanol dehydration. In order to achieve this high BD selectivity, the deposition method is crucial. The use of hemimorphite as Zn(II) source was particularly successful in suppressing the ethene formation while simultaneously producing high concentrations of BD.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.5b00376.

Experimental procedures, SEM, EDX, EPR, FTIR characterization, TG analysis (PDF)

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Notes

The authors declare no competing financial interest.

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