

The results of the present investigation demonstrate that a photoelectrochemical technique of using a membrane-type semiconductor can provide valuable information concerning photoinduced charge separation processes occurring on a semiconductor particle suspended in a dye solution.

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Catalytic Conversion of Alcohols. 15. Alkene Selectivity from the Conversion of 2-Octanol over Hafnium-Zirconium Mixed Oxide Catalysts

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The substitution of Zr ions for Hf does not alter the 1-octene selectivity from that of pure HfO₂ until 0.70–0.85 mole fraction Zr, whereupon the selectivity abruptly changes to that of pure ZrO₂.

The catalytic activities and selectivities for hydrocarbons conversions vary among the group VIII B metals.¹ In many cases, the catalytic parameters change uniformly with position within the group. They may be altered by alloying two or more of the metals^{2,3} even though the surface compositions may vary significantly from the bulk composition for some of the alloys.⁴ The purpose of this study was to look for catalytic activity and selectivity changes for oxide systems as a different metal ion is substituted for the metal atoms in a pure oxide.

Hafnium and zirconium mixed oxides should be an ideal system to carry out a study with mixed oxides that would parallel the studies with metal alloy catalysts. Our earlier study shows that zirconia⁵ forms greater than 90% 1-octene from the dehydration of 2-octanol while hafnia produces only 30–33% of the 1-octene isomer.⁶ The precipitation of the mixed hydroxide should not lead to surface enrichment since the solubilities are so similar that separation of the two elements is not possible by fractional precipitation of the hydroxide.⁷ The free energies of the oxides are so similar that surface enrichment should not occur after calcination.⁸ This, together with the same crystal structure and ionic size, should permit uniform solid so-

lutions over the entire composition; this has been verified for mixtures after high temperature calcination.⁹ Furthermore, the same valence of the metal ions and the difficulty of reducing the oxides⁸ should eliminate the necessity of introducing a third ion to maintain electrical neutrality as is the case in some mixed oxides such as silica-alumina where the hydrogen ion imparts protonic acidity.

The pure and mixed metal hydroxides were prepared by precipitation from a rapidly stirred aqueous solution by the rapid addition of about a fivefold excess of concentrated ammonium hydroxide. The hafnium(IV) solution was prepared by dissolving the metal in hydrofluoric acid, precipitating the hydroxide, and then redissolving in the minimum amount of an approximately equal mixture of hydrofluoric and hydrochloric acids. The zirconium(IV) solution was prepared by dissolving zirconyl nitrate in water. Appropriate volumes of these solutions were mixed to give the desired Hf-Zr composition with a concentration of about 20 g of metal oxides per liter. The mixed hydroxide, after drying at 120 °C, was calcined at 600 °C in air for 18 h. The surface area for all oxides was in the range 18–35 m²/g; it increased uniformly from the

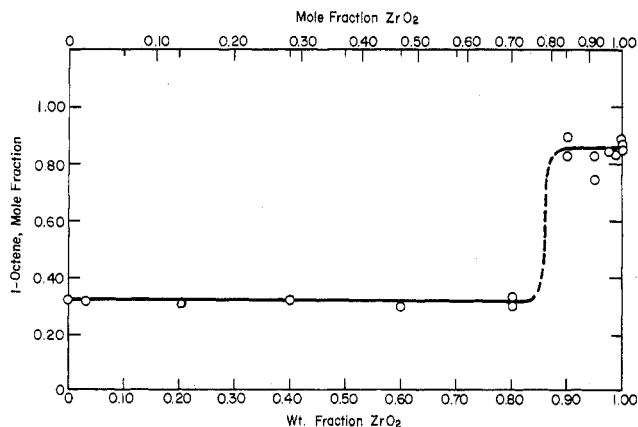


Figure 1. 1-Octene formation from 2-octanol conversion over various Hf-Zr mixed oxide catalysts.

low area of the pure oxide (HfO₂, 18; ZrO₂, 22) to a maximum of 35 m²/g at 60 wt % ZrO₂. Prior to use as a catalyst, the material was heated in situ at 500 °C in 5 mL/min air flow. After this activation, the catalyst was cooled to the reaction temperature in a flow of air. The experimental procedure is outlined in ref 5. The reaction temperature was 250 °C.

As the mole fraction of Zr increases from zero, the 1-octene selectivity from 2-octanol dehydration remains the same as hafnia over much of the composition range (Figure 1). In the composition range of 0.70–0.85 mole fraction Zr, there is an abrupt change in the 1-octene selectivity to that of pure zirconia. The selectivity of the catalysts from 0.70 to 1.0 mole fraction Zr represents repeat preparations of the mixed oxide catalyst and/or repeat runs over the same mixed oxide preparation. The difference in selectivities for the repeat runs is much smaller than that obtained as the composition is varied. Thus, the selectivity changes in an abrupt manner rather than paralleling the uniform change in oxide composition. The 2-octanol conversion, converted to the same flow rate, was in the range 4–20 mol % and, in general, the higher surface area material gave the higher conversion.

The addition of an alkene that is similar to the octenes formed from 2-octanol dehydration shows that pure ZrO₂ and HfO₂ does not catalyze alkene isomerization as long as the 2-octanol pressure is nearly 1 atm.^{5,6} Extrapolating the thermodynamic data for the four, five, and six carbon straight chain 1- and 2-alkene isomers indicates that at equilibrium 1-octene would be less than 10% of the 1- and 2-octenes and the *cis*-2-octene/*trans*-2-octene ratio would be about 0.5. The experimental *cis*-2-octene/*trans*-2-octene ratio for all of the runs was in the range of 1.2–1.6. Thus, the octene isomers from 2-octanol dehydration was not near the equilibrium value for any of the oxide catalysts used in this study.

It appears that the catalytic selectivity is determined by a feature that is not characteristic of the commonly measured bulk properties nor of the surface area. If selectivity is determined by electronic effects then it would appear that they are restricted to surface sites.

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