EXPERIMENTAL PROCEDURES

Catalyst Preparation. The WZ catalyst was prepared according to the procedure described elsewhere for a refluxed, impregnated (R/IM) catalyst [9]. Hydrous zirconia was first prepared, which was thereafter calcined to form ZrO_2. This preparation was carried out by added aqueous 10 M NH_4OH dropwise to a stirred $ZrOCl_2$ aqueous solution to precipitate the hydrous zirconia (final pH ≈9). After filtering, the solid was washed with distilled water and dried overnight at 95°C. The solid was reslurried in excess water, the pH adjusted to ≈9.0 with 10 M NH_4OH, and refluxed overnight. After cooling, the solid was filtered, washed with water, and dried overnight at 95°C. The $Zr(OH)_4$ was then impregnated with an ammonium metatungstate $[(NH_4)_6H_2W_{12}O_{40}\cdot xH_2O]$ solution, air-dried at 95°C, and calcined at 825°C for 3 hr. This gave a solid containing nominal 15 wt% W loading and a surface area of 69 m^2/g after calcination, of similar properties as the Mobil Technology Co. preparation with 16.9 wt% tungsten and area of 62 m^2/g [9].

Catalyst Testing. The alcohol coupling reaction was carried out in a downflow stainless steel tubular reactor operated in the differential regime, as described in our earlier study [6]. Typically, 1 g of catalyst diluted with approximately 5 ml of 0.8 mm Pyrex beads was placed in the middle of the reactor between plugs of Pyrex wool. The reactor void volume below and above the catalyst bed was filled with 5 mm Pyrex beads. A J-type thermocouple was inserted into the top of the catalyst bed using an axial stainless steel thermowell.

The reaction rates were typically measured at temperatures between 127°C and 150°C. A mixture of 17.8 vol% N_2 in He (Airgas Northeast, Inc.) was used as a carrier gas. The gas flow rate was controlled using a calibrated mass flow meter (Union Carbide, Model FM-4550). The reactants, methanol and isobutanol (99.9+%, Alfa), were fed separately as liquids to heated lines leading to the inlet port at the top of the reactor using two metering pumps (ISCO, Model 314). The reactants were vaporized in a preheated section of the reactor as they were mixed with the carrier gas before reaching the catalyst bed. The furnace had three heating zones, which provided for very good temperature control. The reactor pressure was controlled by a MightyMite back pressure regulator.

The exit gas stream from the reactor was analyzed by using an on-line Hewlett-Packard gas chromatograph (Model 5890, Series II), which was equipped with automated heated sampling valves. Product analyses were achieved with a Cpsil-5CB capillary column (Chrompack) using a thermal conductivity detector. No dehydration of alcohols was observed over a bed containing only Pyrex beads nor on the reactor walls at temperatures up to 150°C. Steady state activities over the catalysts were achieved within 2 hr of initiating alcohol injection and after changing the reactor temperature and alcohol feed rate. The catalyst performance was steady over a few hundred hours of testing. For kinetic studies, the total conversion was kept at less than 5% at 127°C and approximately 10% at 150°C. In this range, the system performs as a differential reactor.

Catalyst Characterization by Optical Spectroscopy. All measurements were made with a computer-controlled, scanning, double-beam Cary 5E spectrophotometer (Varian Instruments, Inc.) with diffuse reflectance accessory and extended sample chamber. The integrating sphere was coated with polytetrafluoroethylene (PTFE).

Spectral data were stored on a PC disk and transformed using the Kubelka-Munk relation before being plotted. The diffuse reflectance theory yields quantitative results [10-12] for low absorbing, semi-infinite samples based on the Kubelka-Munk relation, i.e.

$$K/S = (1 - R_\infty)^2 / 2 R_\infty, \qquad (1)$$

where K = the absorption coefficient of the sample, S = the scattering coefficient of the sample, and R_∞ = the reflectance of the sample. Where needed, corrections at high absorbances are made [12]. The reflectances of the samples were measured between 4,500 and 50,000 cm^{-1}. The two spectral regions of principal interest are the NIR region between 4,500 and 8,000 cm^{-1} and the UV region between 10,000 and 50,000 cm^{-1}. The NIR region contains vibrational combination bands and overtones of hydrogen-containing species, e.g. hydroxyl groups, which is useful for quantitative analysis of materials with low electronic spectral background. The UV region includes electronic spectra and was used to characterize the optical band edges of the samples.

The surface-doped zirconia samples were dried at 115°C for 24 hr in a furnace, after which they were removed and allowed to cool in a positive-pressure, nitrogen-filled glove bag or box. The samples were then transferred into diffuse reflectance cells having 1 mm thick 2 cm radius circular Suprasil windows. The cells were closed using a conical rubber stopper and sealed with Mylar film.

Catalyst Characterization by XPS. X-Ray photoelectron spectroscopy (XPS) analyses of the WZ catalysts before and after adsorption of amines were carried out using the Scienta ESCA-300 high resolution photoelectron spectrometer at Lehigh University [13]. This instrument utilizes a rotating Al Kα anode to generate an unpolarized 7.6 KW X-ray flux ($h\nu = 1486.8$ eV), which is monochromatized by seven toroidally bent quartz crystals. The detector system, consisting of a 300 mm mean radius hemispherical electron energy analyzer and a multichannel plate detector, provided an overall energy resolution of 0.27 eV, as determined by the Fermi level edge from Ag at room temperature. The detector's high sensitivity and energy resolution allows for the analysis of insulated samples. To improve the quality of resolution for non-conducting materials, a Scienta hot filament flood gun with an energy range of 0-10 eV is available to supply electrons for charge compensation.

For XPS analysis, the ZrO_2 and the W/Z catalyst were each pressed into pellet form on top of a rectangular piece of tin using a hydraulic ram press. The pellet was then secured onto an ESCA analysis stub by clamping the edges of the tin piece to the stub with screws. The stub with the sample was inserted into the fast entry chamber of the Scienta instrument and evacuated to pressures $< 1 \times 10^{-6}$ Torr. The stub was then transferred into the analysis chamber where the surface of the sample was scraped *in situ* (using a SiC edge) to remove any adsorbed impurities.

Both the survey and the high-resolution scans were performed on the clean ZrO_2 and W/Z surfaces, with the pressure in the analysis chamber on the order of 5×10^{-9} Torr. Survey scans were conducted with 300 eV pass energy, an incremental step size of 1 eV, and a 0.8 mm slit width. Scans of Zr 3d, O 1s, C 1s, W 4f, and N 1s spectral regions were conducted in a high resolution mode with 150 eV pass energy, an incremental step size of 0.05 eV, and a 0.8 mm slit width. The pass energy refers to the energy to which the kinetic energy of the emitted photoelectrons is retarded by a retardation voltage for detection by the analyzer. The step size in turn refers to the energy step between each sweep of the retardation voltage. The slit width refers to the width of the slit located at the entrance of the detector. A larger slit width provides increased photoemission intensity with poorer resolution. Because the W/Z catalyst was non-conducting, a hot filament gun set at 1.3 eV was applied during the analysis to supply electrons for charge compensation and improve the resolution.

The adsorption of amines onto dehydrated W/Z (and Nafion-H microsaddles) was performed on a separate glass vacuum/adsorption system. Each dehydrated powdered sample was transferred into a glass reaction tube, which was connected *via* a Cajon ultra Torr tube connector to a port on the vacuum manifold having a Teflon/glass stopcock. The sample was evacuated to pressures on the order of 10^{-3} Torr prior to the adsorption of the amines. The amines were purified by a freeze/thaw technique using liquid nitrogen as coolant. The catalysts were exposed to the purified amines at room temperature and 15 Torr for 30 min. The catalysts were again evacuated to 10^{-3} Torr following the exposure. The adsorption system allowed for heating the catalyst before and/or after the adsorption treatment, where the latter provided for desorption of loosely adsorbed amines.

After the adsorption/evacuation treatment, the glass connecting tube between the stopcock and the vacuum system was break-opened, and the evacuated tube was moved to a nitrogen-filled glove bag or glove box. Opening the stopcock filled the tube with nitrogen, after which the tube was removed from the Cajon tubing connector, and the powdered sample was mounted on an ESCA analysis stub with the use of double sided sticking tape. The surface of the mounted sample was smoothed by using pressure applied from a smooth spatula. The prepared stub was transferred in a nitrogen-filled desiccator from the glove box or bag to a glove bag attached to the entrance port of the Scienta ESCA 300 fast entry chamber. The chamber was brought to atmospheric pressure with nitrogen and the sample was transferred from the glove bag to the fast entry chamber. After sealing the fast entry chamber, it was evacuated to approximately 1 x 10^{-6} Torr, after which the sample was moved into the analytical chamber, which maintained a vacuum of approximately 10^{-9} Torr.