Silica-Supported Zirconia. 2. Effect of Sulfation on the Surface Acidity and Its Potential as a Catalyst for Methane−Olefin Coupling

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A 10 wt % silica-supported zirconia catalyst has been sulfated by oxidation of SO_2 or by impregnation with H_2SO_4, and its surface properties and acidity have been characterized by infrared spectroscopy. The supported catalyst shows IR bands due to the sulfate species which are present when either oxide alone has been sulfated (1390 cm^{-1} for ZrO_2 and 1440 cm^{-1} for SiO_2); these sulfates are at least as thermally stable as that on ZrO_2 and more stable than that on pure SiO_2. Uniquely, SiO_2 in the mixed oxide catalyst can be sulfated by oxidation of SO_2 whereas this could only be effected via impregnation with H_2SO_4 for the pure oxide. The acidity, which has been characterized by IR spectroscopy of adsorbed ammonia or pyridine and temperature-programmed desorption (TPD) of adsorbed NH_3, is much greater than that of the unsulfated mixed oxide or of pure ZrO_2, particularly with respect to the presence of strong Bronsted acid sites. The latter are absent on pure ZrO_2 or are very weak and not numerous on the unsulfated SiO_2/ZrO_2 catalyst. Finally, the potential for sulfated SiO_2/ZrO_2 to catalyze the coupling reaction between methane and ethylene or propylene to give propane or butane, respectively, has been assessed at temperatures between 225 and 275 °C where either reaction is thermodynamically favorable. In common with many other strongly acidic catalysts, rapid deactivation of the catalyst occurred, presumably due to the deposition of carbonaceous products on the discolored catalyst, and no significant coupling products were detected.

Introduction

There have been many recent studies of the surface and catalytic properties of the supposed superacid catalyst sulfated zirconia.[1−19] However, zirconia is expensive relative to other acid oxides, and its surface area is generally not large, in the range from about 30 to 50 m^2/g.[20] To circumvent these problems, we have prepared a series of SiO_2/ZrO_2 catalysts containing 5, 10, and 20 wt % ZrO_2 by a wet impregnation method. These materials have a surface area which is nearly the same as that of the parent silica (200 m^2/g), and their properties have been characterized previously.[21]

In this work we have studied the surface characteristics of one of these materials, the 10% ZrO_2 on SiO_2 catalyst, after sulfation using varying quantities of sulfate. Sulfation was carried out by direct oxidation of gaseous SO_2 or via impregnation with H_2SO_4, and infrared spectroscopy and temperature-programmed desorption have been used. Where appropriate, the properties have been compared with those of the nonsulfated catalyst.[21] Although there have been several studies of SiO_2/ZrO_2 systems,[15,22−30] to our knowledge there has been only one study of sulfated SiO_2/ZrO_2.[15] However, this catalyst was prepared by coprecipitation, and its surface acidity was not characterized using IR spectroscopy.

Finally, we have examined the potential of this catalyst after incorporation of 1000 μmol/g of sulfate to catalyze the direct coupling reaction between methane and ethylene or propylene, the reaction being represented as $CH_4 + RCH{=}CH_2 \rightarrow RCH_2CH_2CH_3$ (R = H or CH_3). This reaction is thermodynamically favorable at temperatures at or below 300 °C.[31] It is known[32−35] that a strongly acidic catalyst is necessary in order to protonate the olefine to give the necessary carbenium ion intermediate, $RCH_2CH_2^+$.

Experimental Section

The silica support was Cab-O-Sil grade M-5 (BET surface area 205 m^2/g) and was provided by the Cabot Corp. The 10 wt % zirconia-impregnated sample was prepared by mixing 2 g of silica with 6 mL of an aqueous solution of zirconyl nitrate, followed by drying in air overnight at 110 °C and then calcining in air for 24 h at 450 °C. The calcined sample was ground into a fine powder using a mortar and pestle and was stored for further use. Its BET surface area was 190 m^2/g. Although designated SiO_2/ZrO_2-10% in our previous publication[21] (to distinguish it from 5% and 20% loading), this will be designated SiO_2/ZrO_2 here because only the 10% loaded catalyst was studied.

For infrared investigation, about 30 mg of the sample was compacted at about 10^7 Pa in a 25 mm diameter stainless steel die, and the resulting disk was mounted in a previously described 300 mL volume quartz cell.[36] IR spectra were recorded using a Bomem Michelson MB100 instrument (DTGS detector) at a resolution of 4 cm^{-1}.

Sulfation was carried out either by oxidizing a known quantity of SO_2 in excess O_2 for about 4 h at 450 °C in the IR cell after disk preparation or via impregnation of the catalyst with an aqueous solution (3 mL/g of catalyst) of H_2SO_4 of known molarity so as to give between 100 and 1500 μmol of sulfate per gram of catalyst after drying at 110 °C. Disks of the H_2SO_4 impregnated samples for IR or TPD studies were prepared directly from the dried oxide.

For temperature-programmed desorption (TPD) studies and catalytic reactivity studies, sample disks of the type which were used for the IR studies were broken up and sieved; granules ranging from 16 to 32 mesh (0.5−1.0 mm) were used. The sample holder consisted of a $^3/_8$ in. diameter stainless steel tube into which 100 mg of the sieved particles was placed on top of a Pyrex wool support. The resulting bed was 1 cm deep. For TPD, samples were typically activated under vacuum at 450

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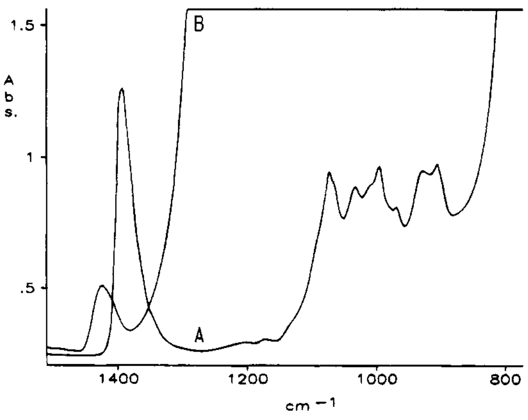

Figure 1. (A) Infrared spectra of Degussa ZrO_2 after sulfation with 500 μmol/g of SO_2 in excess O_2 at 450 °C. (B) IR spectra of SiO_2 after impregnation with 800 μmol/g of H_2SO_4 followed by heating under vacuum at 450 °C.

°C for 1 h prior to cooling to room temperature under vacuum. (See preceding publication[21] for further details of the TPD apparatus.)

Catalytic reactivity studies were conducted at atmospheric pressure using the TPD apparatus which was modified so as to be a single-pass flow system. An on-line gas chromatograph was used to monitor the course of the reaction with time. Methane (99.7% minimum), ethylene (99.5% minimum), and propylene (99.0% minimum) were used as received. Helium (<1 ppm O_2 and H_2O) was further deoxygenated by passing through an oxygen trap. All catalysts (1000 μmol/g of sulfated SiO_2/ZrO_2, 1000 μmol/g of sulfated ZrO_2, and unsulfated SiO_2/ZrO_2, about 200 mg in each case) were activated in flowing helium (10 mL/min) at 500 °C for at least 16 h. These conditions are similar to those used by Scurrell.[34] Following activation the catalysts were isolated in helium, and the temperature was reduced to that used during the experiment, 225 or 275 °C. During this time gaseous reactant mixtures were flowed through a bypass at room temperature. A fresh catalyst was used for each run.

Following catalyst activation, reactant gas mixtures were diverted through the reactor. Reactant mixtures included $C_3H_6/CH_4/He$ or $C_2H_4/CH_4/He$ (olefin/methane mole ratio 0.1 or 0.5), C_2H_4/He, and CH_4/He. In each case the hydrocarbon/helium volume ratio was about 1:10, and the flow rate was 5 mL/min.

Results and Discussion

Infrared Characterization of Sulfated SiO_2/ZrO_2. *Background Spectra.* Infrared spectra of sulfated SiO_2[37] and of sulfated ZrO_2[19] have been published by one of us previously. Figure 1A shows the IR spectrum of zirconia after sulfation. Figure 1B shows a corresponding spectra for sulfated silica. The steeply rising background near 800 cm^{-1} for ZrO_2 represents its low wavenumber limit of transmission, and the corresponding cutoff for SiO_2 is near 1300 cm^{-1}.

Whereas ZrO_2 could be sulfated either by oxidation of SO_2 at 450 °C or via impregnation with H_2SO_4 followed by vacuum activation at 450 °C,[19] silica could only be sulfated via impregnation.[37] The strong asymmetric peak near 1390 cm^{-1} for ZrO_2 (which initially appeared near 1370 cm^{-1} for low sulfate coverage) has been assigned to two types of surface sulfate species, each of which was presumed to contain a single S=O oscillator corresponding to different adsorbed species having structures of the type $(ZrO)_3S{=}O$. On silica a single sulfate species was formed, having two equivalent S=O bonds, presumed to be $(SiO)_2SO_2$.

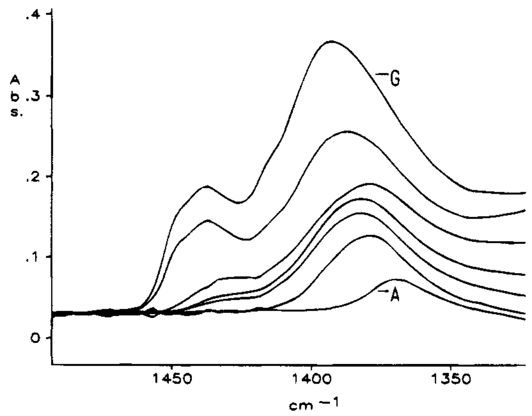

Figure 2. Infrared spectra of a sulfated 10% ZrO_2 on SiO_2 catalyst which had been preactivated under vacuum at 450 °C. Sulfation was carried by heating SO_2 in excess O_2 at 450 °C for about 4 h (see text) using the following quantities of SO_2 (μmol/g of catalyst) in the IR cells: A, 50; B, 150; C, 250; D, 700; E, 1250; F, 2000; G, 3000. All spectra are difference spectra which were obtained after subtraction of the background spectrum of the activated nonsulfated catalyst.

In view of the opacity of silica below about 1300 cm^{-1}, only the spectral region above 1300 cm^{-1} is accessible to IR investigation of the supported sulfated SiO_2/ZrO_2 catalysts. Figure 2 shows IR spectra of the SiO_2/ZrO_2 catalyst after sulfation by oxidation of increasing amounts of SO_2 in excess oxygen at 450 °C. These are difference spectra which were obtained after subtraction of the background spectrum before sulfation.

Initially, a weak band was observed near 1370 cm^{-1}, as was previously reported for pure ZrO_2.[19] At higher coverages, this peak shifted to higher wavenumber, finally appearing near 1390 cm^{-1}, a trend which also occurred for pure ZrO_2. Uniquely for SiO_2/ZrO_2, a shoulder appeared near 1425 cm^{-1} after oxidation of about 250 μmol/g of SO_2; this peak intensified with increasing sulfate loading and shifted to 1440 cm^{-1}.

The two main peaks at 1390 and 1440 cm^{-1} are close to those observed previously for sulfation of pure ZrO_2 and pure SiO_2, respectively, and are probably due to the similar species on the mixed oxide catalyst. Uniquely, silica–sulfate species can be formed on the mixed oxide catalyst via oxidation of SO_2; that did not occur with pure SiO_2.

We have shown[21] that SiO_2/ZrO_2 exhibits OH stretching bands characteristic of SiOH species (strong sharp, 3747 cm^{-1}) and ZrOH (weak broad bands at 3675 and 3775 cm^{-1}). During sulfation, there was practically no change in the intensity of the silanol peak, but those due to OH groups attached to ZrO_2 gradually diminished and finally disappeared as the sulfate loading increased (not shown).

Contact of the sulfated oxide with water caused the immediate disappearance of all IR bands from the 1400 cm^{-1} spectral region and the appearance of the IR band due to the HOH bending mode of water at 1620 cm^{-1} (not shown). This also occurred when H_2O was added to sulfated SiO_2[37] or ZrO_2[19] (and also for sulfated Al_2O_3,[38] TiO_2,[38] and MgO[39]). In the case of ZrO_2 (and the other oxides which are transparent in the region below 1300 cm^{-1}), new bands characteristic of ionic like sulfate species appeared between about 1250 and 1000 cm^{-1}. With SiO_2/ZrO_2 and all of the pure oxides mentioned above, prolonged evacuation at room temperature did not restore the high wavenumber IR bands, while heating at 200–450 °C did cause their reappearance, but in all cases, at slightly reduced intensity.

Sulfation could also be accomplished via impregnation with H_2SO_4. Figure 3 shows spectra as a function of sulfate loading

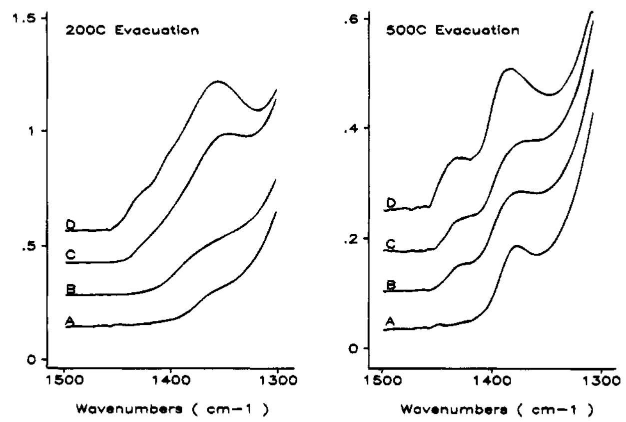

Figure 3. Infrared spectra after impregnation of SiO_2/ZrO_2 with H_2SO_4 and heating under vacuum for 1 h at either 200 or 500 °C. The quantity of sulfate used (μmol/g) was (A) 100, (B) 500, (C) 1000, and (D) 1500.

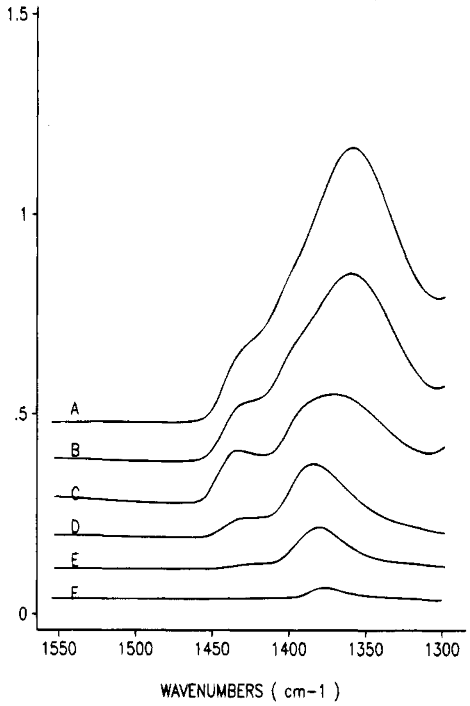

Figure 4. Infrared spectra after impregnation of SiO_2/ZrO_2 with 1500 μmol/g of H_2SO_4 followed by heating under vacuum at (A) 200, (B) 300, (C) 400, (D) 500, (E) 600, and (F) 700 °C.

after heating the catalyst under vacuum at 200 or 500 °C. The spectra observed after heating at 500 °C are qualitatively similar to those resulting from SO_2 oxidation as shown in Figure 2. (Recall that a temperature of about 450 °C is necessary when sulfating via oxidation of SO_2.)

Finally, Figure 4 shows a series of spectra following impregnation with 1500 μmol/g of H_2SO_4, but activated at increasing temperatures from 200 to 700 °C. Note that the intensity of all bands decreased with increasing temperature but that the higher wavenumber band disappeared at a faster rate and was not observed by 700 °C. All IR bands disappeared when the sample was heated under vacuum at 800 °C, and this spectrum was used as the reference spectrum to be subtracted from each of the presented difference spectra, shown in Figure 4.

NH_3 Adsorption. Ammonia is a well-known probe molecule for the presence of acid sites on metal oxide catalysts.[40,41] In general, Lewis acid sites give rise to coordinated NH_3 characterized by a sharp infrared band in the range 1620−1600 cm^{-1}. The presence of Bronsted sites is characterized by a broad IR band in the 1450−1400 cm^{-1} spectral range due to protonated NH_3, i.e., the NH_4^+ ion. These bands are not affected by prolonged evacuation at room temperature and are, therefore, due to chemisorbed species. On the other hand, hydrogen-bonded NH_3, which has an IR band near 1635 cm^{-1}, can be removed by a brief evacuation at room temperature.

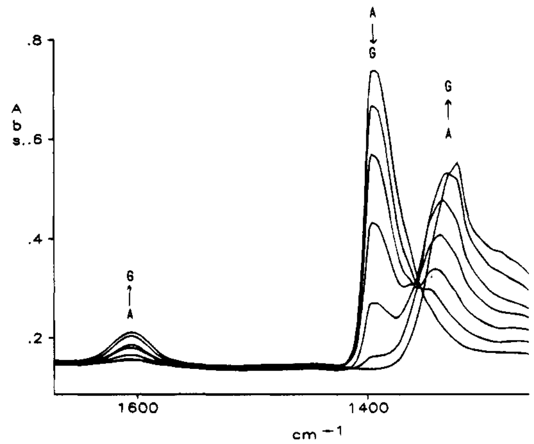

Figure 5. (A) Infrared spectrum of ZrO_2 after sulfation by oxidation of 500 μmol/g of SO_2 at 450 °C followed by evacuation at 450 °C. Curves B−F were recorded after the addition of incremental doses of about 100 μmol/g of NH_3 to the catalyst, and curve G was observe after adding excess NH_3 (more than 2000 μmol/g). In the last case the gas phase had been evacuated. (No gas phase ammonia was present in the other situations.)

Although there are no interfering IR bands in the 1700−1400 cm^{-1} spectral range due to pure SiO_2, ZrO_2, or SiO_2/ZrO_2, the sulfate bands near 1390 and 1440 cm^{-1} could potentially interfere with the strong NH_4^+ band if Bronsted acid sites were present. However, as was found in the presence of excess adsorbed water, when a large dose of ammonia was added to any of the above sulfated catalysts, the sulfate band shifted to lower wavenumber. Figure 5 shows the effect following addition of increasing doses of NH_3 to sulfated ZrO_2; the 1390 cm^{-1} band progressively shifted to about 1300 cm^{-1}. For sulfated SiO_2/ZrO_2 the shifted band cannot readily be discerned because it is superimposed on the steeply rising background spectrum of SiO_2 near 1300 cm^{-1}. For our purposes, prolonged evacuation at room temperature or at 100 °C does not alter the flat background in the region between 1450 and 1400 cm^{-1} where an anticipated IR band due to the ammonium ion might be expected if Bronsted acid sites are present. (It is necessary to heat any of the catalysts at or above 200 °C in order to appreciably restore the sulfate band near 1390 or 1440 cm^{-1}, and if heated at 400 °C, the original intensity of the sulfate band is nearly fully restored.)

We have previously established that when ZrO_2 or SiO_2/ZrO_2 was contacted for 1 h with 8 Torr of NH_3 followed by evacuation at room temperature for 30 min, all H-bonded or physically adsorbed NH_3 was removed, and only the IR spectrum of irreversibly held species (coordinated NH_3, NH_4^+, or dissociatively adsorbed NH_2) was observed. The IR spectrum of irreversibly held species on ZrO_2 and SiO_2/ZrO_2 after activation at 450 °C are shown in Figure 6, IA and IB, respectively. The spectra of NH_3 adsorbed on some H_2SO_4 impregnated SiO_2/ZrO_2 catalysts after similar activation are shown in Figure 6IC.

For all catalysts there is a band at 1607−1600 cm^{-1} due to coordinated ammonia, and with the exception of ZrO_2 (Figure 6IA) there is a band at 1552 cm^{-1} due to $SiNH_2$;[42] the latter is more prominent for the highly sulfated SiO_2/ZrO_2 catalysts.

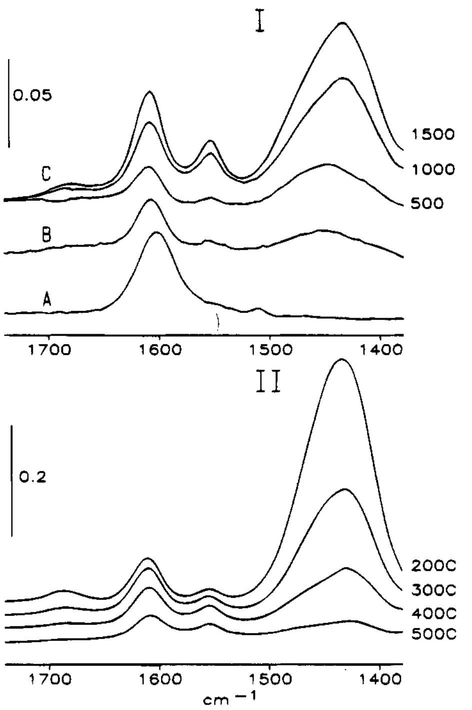

Figure 6. (I, top) Infrared spectra of chemisorbed NH_3 on the following catalysts: A, ZrO_2; B, unsulfated SiO_2/ZrO_2; C, SiO_2/ZrO_2 after sulfation with the indicated quantity of sulfate (μmol/g). (II, bottom) Infrared spectra of chemisorbed NH_3 on sulfated (1000 μmol/g) SiO_2/ZrO_2 which had been preactivated under vacuum at the indicated temperatures in °C.

However, the most noticeable feature is the increasing intensity of the band near 1430 cm^{-1} due to the NH_4^+ ion with increasing sulfation in the case of the SiO_2/ZrO_2 catalysts.

Figure 6II shows similar IR spectra of irreverisbly adsorbed NH_3 on the 1000 μmol/g sulfated catalyst as a function of the temperature of preactivation from 200 to 500 °C. The intensity of the principal peaks increased for a lower temperature of activation, particularly that due to protonated ammonia. There was also a weak new feature near 1680 cm^{-1} whose intensity paralleled that of the 1430 cm^{-1} peak; this is due to the symmetric NH stretching mode of NH_4^+ which, although forbidden in a symmetric environment, can be observed because of partial destruction of the T_d symmetry when adsorbed on a surface.

Pyridine Adsorption. Pyridine is also a suitable probe of acid sites on oxide catalysts[41,43] although its pK_b (9.3) makes it a weaker base than NH_3 ($pK_b = 4.7$). The characteristic diagnostic IR bands are between 1650 and 1450 cm^{-1} (see preceding paper[21]) as follows: H-bonded pyridine near 1595 cm^{-1}, coordinated pyridine near 1610–1600 and 1490 cm^{-1}, and protonated pyridine near 1540 cm^{-1}.

As has been discussed in the preceding paper,[21] H-bonded pyridine can only be effectively removed if evacuation is carried out at temperatures above 100 °C, and only under these circumstances can the spectra of the strongly adsorbed species be clearly distinguished from the H-bonded species. The irreversibly held species are the ones which characterize the acid sites.

Figure 7 shows spectra recorded after adsorption of excess pyridine for 1 h and evacuation for 30 min at room temperature, followed by evacuation at 200 °C for 30 min on the following catalysts: Figure 7A, sulfated SiO_2/ZrO_2 activated at 200 °C; Figure 7B, sulfated SiO_2/ZrO_2 activated at 450 °C; Figure 7C, SiO_2/ZrO_2 activated at 450 °C; Figure 7D, ZrO_2 activated at 450 °C. The most important feature to note is the presence of an IR band at 1540 cm^{-1} in the case of the sulfated catalysts (Figure 7A,B). This is the unique indication of the presence of strong Bronsted acid sites on these catalysts, there being more of these sites for the 200 °C activated sample (Figure 7A) than for the 450 °C activated sample (Figure 7B), and none on SiO_2/ZrO_2 or ZrO_2 (Figure 7C,D).

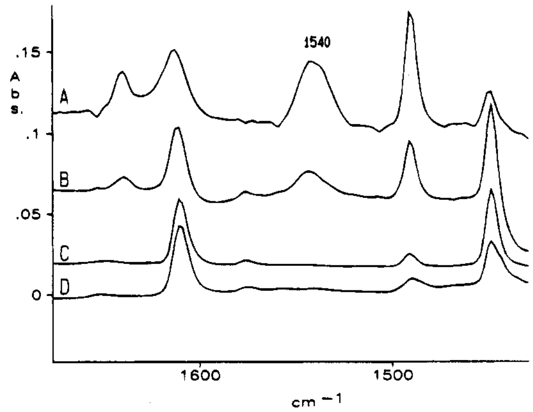

Figure 7. Infrared spectra of chemisorbed pyridine adsorbed on a 1000 μmol/g sulfated SiO_2/ZrO_2 catalyst after catalyst activation at 200 (A) or 450 °C (B). Curves C and D show chemisorbed pyridine on unsulfated SiO_2/ZrO_2 and pure ZrO_2, respectively, after catalyst activation at 450 °C. In all cases, excess pyridine had been evacuated at 200 °C for 30 min.

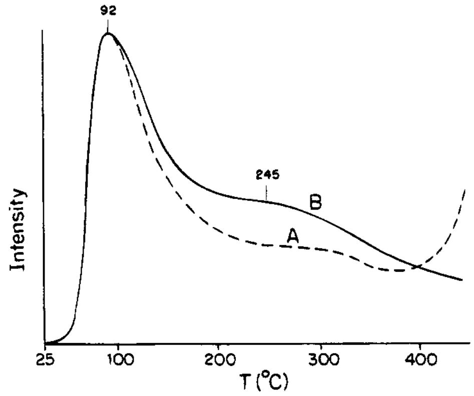

Figure 8. (A) TPD spectrum following room temperature adsorption of NH_3 on a 1500 μmol/g sulfated SiO_2/ZrO_2 catalysts after vacuum activation at 450 °C. (B) TPD spectrum from the same catalyst as used in (A) but *without* sulfate.

TPD of Adsorbed Ammonia. Figure 8A shows the TPD spectrum of NH_3 adsorbed on the 1500 μmol/g of catalyst after preactivation at 450 °C. The catalyst had been treated with 8 Torr of NH_3 for 60 min, and then the reactor was purged with He at room temperature for 30 min prior to raising the temperature. For comparison, a TDP spectrum taken under similar conditions but on the same nonsulfated SiO_2/ZrO_2 catalyst is shown in Figure 8B.

The low-temperature peak at 90 °C on the nonsulfated catalyst is due to the removal of H-bonded NH_3, and the broad peak near 245 °C is due to desorption of coordinated NH_3. The same peaks are observed on the sulfated catalyst. However, the most noticeable difference between the catalysts is the appearance of a second desorption peak at the high-temperature limit of the apparatus, its maximum being greater than 450 °C. The IR results have shown that the greatest difference between these catalysts is the quantity of protonated ammonia, this being considerably greater on the sulfated catalyst. IR spectroscopy has also demonstrated (spectra not shown) that, although the peak due to coordinated NH_3 could be removed if a sample containing chemisorbed ammonia was heated at 200 °C under vacuum, the peak due to protonated NH_3 was only slightly reduced in intensity. Therefore, it is probable that the TPD peak above 450 °C is due to the removal of protonated NH_3.

Methane–Olefin Coupling. The first report of heterogeneous alkylation of methane in a flow system was published by Olah *et al.*[33] in 1983 using solid superacids such as SbF_5 on graphite, TaF_5 on AlF_3. The coupling of methane and ethylene has also been reported to occur over sulfated-zirconia containing about 3 wt % sulfate.[25] Recently, Ng *et al.*[35] studied the reactions of methane–ethylene mixtures over zeolite-supported TaF_5 catalysts. In all cases, relatively high pressures were used, greater than 10 atm (in an effort to avoid oligomerization and cracking); nonetheless, catalyst deactivation occurred rapidly.

It is not productive to review the above background material extensively, but additional details are given by Anderson.[31] The purpose of the present study was to briefly examine the potential of the characterized sulfated SiO_2/ZrO_2 catalysts for methane–olefin coupling. The current apparatus can only operate near atmospheric pressure, and our goal was to assess the potential of these catalysts for the coupling of methane with ethylene or propylene at temperatures at or below 275 °C and at 1 atm pressure.

The initial conversion (after 5 min on stream) of ethylene or methane ranged from 18% to 90%, and traces (less than 1%) of propylene and propane were detected. However, catalyst deactivation occurred rapidly after 15 min on stream (conversion of either reactant down to a few percent) and was complete (zero conversion) after 35 min on stream. Catalyst deactivation also occurred rapidly if ethylene/He or methane/He was passed over the catalyst. In every case, the catalyst was black after 35 min on stream, presumably as a result of the deposition of carbonaceous products.

Rapid deactivation also occurred when unsupported sulfated (1000 μmol/g) zirconia was used as a catalyst. However, when using an *unsulfated* SiO_2/ZrO_2 catalyst, there was no conversion, no reaction products were detected for up to 35 min on stream, and the catalyst did not discolor. We conclude that sulfated SiO_2/ZrO_2 is not a suitable catalyst for direct coupling between methane and ethylene under the reaction conditions used. Two experiments were carried out using propylene in place of ethylene, and again, rapid catalyst deactivation over the sulfated SiO_2/ZrO_2 catalysts occurred and no gaseous reaction products were detected.

Conclusions

Sulfated ZrO_2 and sulfated SiO_2 have IR bands near 1390 and 1425 cm^{-1}, respectively, and the SiO_2/ZrO_2 catalyst after sulfation exhibits IR bands at nearly the same frequencies (1390 and 1440 cm^{-1}, respectively), leading to the conclusion that the sulfates on the mixed oxide catalysts may have structures which are similar to those which were previously identified on each oxide individually. However, the species associated with the 1440 cm^{-1} absorption on SiO_2/ZrO_2 is more thermally stable than the sulfate species on pure SiO_2, and it can be generated either by oxidation of SO_2 or by impregnation with H_2SO_4 whereas only the latter method could effect this in the case of pure SiO_2. Therefore, we presume that a type of spillover mechanism leads to the formation of the silica–sulfate species in the case of SiO_2/ZrO_2. Although the sulfate on SiO_2 had the bridging structure $(SiO)_2SO_2$, it is possible that part of the intensity associated with the 1440 cm^{-1} band might be due to a bridging structure of the type $SiO-SO_2-OZr$.

The infrared results of adsorbed ammonia and pyridine show that sulfated SiO_2/ZrO_2 has Bronsted acid sites which are capable of protonating either molecule and that the number of these sites is greater the lower the temperature of activation of the catalyst. These sites were very weak and of low concentration on the unsulfated catalyst. A greater acidity for sulfated verses unsulfated SiO_2/ZrO_2 was also reported by Sohn and Jang[15] for a coprecipitated catalyst.

The IR and TPD results indicate that protonated NH_3 adsorbed on sulfated SiO_2/ZrO_2 is more tenaciously held than coordinated NH_3 insofar as higher temperatures are required to desorb NH_4^+ than the coordinated species. However, from TPD measurements, the strength of the sites for coordinating ammonia on sulfated or unsulfated SiO_2/ZrO_2 appears to be about the same although the number of sites is slightly reduced for the sulfated catalyst.

The results of the ethylene/methane coupling reaction were not encouraging because of rapid catalyst deactivation, presumably due to oligomerization and/or cracking of the reactants. In this respect, sulfated SiO_2/ZrO_2 behaved in a similar manner to sulfated unsupported ZrO_2. However, we can conclude nothing about the relative acidity of the two catalysts (supported vs unsupported sulfated ZrO_2) because the IR results are difficult to compare even qualitatively given the greatly differing surface areas. This aspect of the problem will be pursued in future work where, for example, a milder test reaction such as the isomerization of butane might be more suitable for determining the relative acidities of these catalysts. Nonetheless, sulfated SiO_2/ZrO_2 would appear to be an attractive alternative to sulfated ZrO_2 for many catalytic applications where a catalyst of high acidity is required.

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