

THERMAL STUDIES OF METAL PROMOTED SULFATED ZIRCONIA

Melody Bi, Hanxu Li, Wei-Ping Pan, William G. Lloyd, and Burtron H. Davis*
Department of Chemistry and Materials Characterization Center, Western Kentucky University,
Bowling Green, KY 42101, *Center for Applied Energy Research, University of Kentucky,
Lexington, KY 40506

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ABSTRACT

$\text{SO}_4^{2-}\text{-ZrO}_2$ is considered to be a superacid catalyst. The metal promotion on sulfated zirconia has been shown to enhance the stabilities of the catalysts. The activation of these catalysts involves complex chemical changes. In the present investigation, a simultaneous TG/MS technique was utilized to investigate the weight loss and to monitor the chemical compounds that evolve under controlled heating in different environments. Some insight of the activation mechanism of the catalysts was thus obtained. The evolution of HCl and Cl_2 were well identified according to the mass ratio of Cl isotopes. The evolution of SO_2 and SO showed a continuum beyond 900°C which corresponds to the TG results. This indicated SO_4^{2-} is present in the solid in a variety of structures. The samples were also analyzed in STD (TGA-DTA). The results show so far sulfate ion is the most efficient species to retard the phase transformation process of zirconia.

INTRODUCTION

Solid oxide catalysts have been widely used in petroleum refineries for skeletal isomerization of n-paraffins and to isomeric alkanes to produce oxygenates, which are important components of automobile fuels. Among the solid oxide catalysts, zirconium oxide (ZrO_2) is claimed to be the only oxide catalyst that has acidic, oxidizing and reducing properties. The discovery by Tanabe and Hattori of the superacidic properties of sulfuric acid treated zirconium oxide ($\text{ZrO}_2/\text{SO}_4^{2-}$), the acidity of which was estimated to be as high as $H_0 < -14.5$ by the adsorbed Hammett base technique, has given a new impulse to solid catalysis.¹ Sulfated zirconia was obtained by immersing hydrous ZrO_2 catalyst powders in a sulfuric acid solution. Such sulfated zirconia catalysts have exhibited superacidic properties and show high activity for isomerization of hydrocarbons.²⁻⁴ It was suggested that the superacid sites are generated by the interaction between the oxide and sulfate ions, and the presence of sulfate ion somehow inhibits the recrystallization of ZrO_2 , therefore the sulfated zirconia retained a much greater fraction of the initial surface area than the unsulfated catalysts.⁵ The addition of platinum to a sulfated zirconia catalyst has been shown to enhance the stability of the catalyst for the isomerization of butane and pentane at low temperatures, though the state of platinum in this type of platinum impregnated zirconia catalysts is still a matter of controversy.⁶ Recently, another class of solid superacid catalysts--sulfated zirconia oxide, containing Fe and Mn, have been shown to be active for the skeletal isomerization of n-butane at room temperature.⁷⁻⁹ Kinetic results indicated that this class of catalysts was about three orders of magnitude more active than a sulfated ZrO_2 . Though extensive characterization studies have been carried out on the sulfate modified zirconia, less has been reported for the metal promoted sulfated zirconia. Commonly, these catalysts are activated at temperatures in the region of $600\text{-}725^\circ\text{C}$ in air prior to use as catalysts for various reactions. The activation of these catalysts involves complex chemical changes. In the present investigation, simultaneous TG/MS and TG/DTA techniques were utilized to investigate the weight loss and the phase transformation of the solid and to monitor the chemical compounds that evolve under controlled heating in different environments.

EXPERIMENTAL

Zirconia was prepared by rapidly precipitating from a 0.3M solution prepared from anhydrous ZrCl_4 with an excess amount of NH_4OH to a final pH of 10.5. The resulting precipitate was washed thoroughly with deionized water until a negative test was obtained for the presence of chloride ions in the wash. The dried hydroxide gel was sulfated by immersing the powder in 0.5M H_2SO_4 and stirring for 2 hours. The precipitate was collected by filtration without further washing, and dried. $\text{Pt-SO}_4^{2-}\text{-ZrO}_2$ was obtained by impregnating sulfated zirconia powders with an aqueous solution of H_2PtCl_6 . The Fe/Mn promoted sulfated zirconia were prepared by dissolving appropriate amounts of Fe(III) and Mn(II) nitrate/sulfate salts in the amount of water needed to prepare a catalyst containing the desired amount of Fe and Mn using an incipient wetness impregnation technique. All catalysts, after impregnation, were dried at 120°C overnight and stored in a desiccator until used for thermal analysis. The samples thus prepared used in the present analysis include 1%(5%)Pt- $\text{SO}_4^{2-}\text{-ZrO}_2$ and 2%Fe/0.5%Mn (sulfate salt/nitrate salt)- $\text{SO}_4^{2-}\text{-ZrO}_2$.

The samples were analyzed in a TA TGA 2950 instrument which was coupled to a VG Mass Spectrometer (from ThermoLab), Figure 1. The MS spectrometer allows the determination of multiple gas components in the mass range of 1-300amu. It has a specially designed flexible capillary tube with a fused silica liner, which is heated to 170°C to avoid condensation of evolved gasses. It requires 60 milliseconds for gas transfer from the TGA to the MS. The mass spectrometer has a Nier type enclosed ion source, a triple mass filter, and two detectors (a Faraday cup and a secondary emission multiplier). The TG-MS system has an operating temperature range to 900°C. Data from the mass spectrometer was acquired using a log histogram mode scan (LHG) in which the intensities of all peaks in a specified mass range were monitored and stored repeatedly during the temperature program. A data conversion program was used to display the intensities of the desired ions as a function of temperature. The runs were conducted separately in a purge gas of helium or air at a flow rate of 50 ml/min. Heating rates were 20°C/min. The samples were also analyzed in a TA SDT 2960 instrument, which is an analysis module that is capable of performing both thermogravimetric analysis (TGA) and differential thermal analysis (DTA) at the same time in a temperature range from room temperature to 1500°C in a controlled atmosphere. While the physical measurement of weight loss is obtained by TGA, in the meantime, the thermal events occurring to the samples are recorded by DTA. An upward peak represents for an exothermic event while a downward peak represent for an endothermic event on a DTA curve. Platinum crucibles were used as sample holders, and Al₂O₃ was used as the reference material.

RESULT AND DISCUSSION

When 1%(5%)Pt-SO₄²⁻-ZrO₂ samples were heated in helium, two major weight loss regions are seen on TG curve, see Figure 2, curve (a), (b). According to the MS data, Figure 3, the first weight loss region is between room temperature to 620°C, which corresponds to the loss of water, carbon dioxide, hydrogen chloride and chlorine. The identification of HCl and Cl₂ is based upon the molar mass of the compounds as well as the mass ratio of the Cl isotopes. In the case of HCl evolved from 5%Pt-SO₄²⁻-ZrO₂ sample, the ratio of peak area integration of HCl(38)/HCl(36) is around 1:3, which meet very well with the theoretical data. The integration of Cl₂ peak area didn't give a good agreement with theoretical isotope ratio. This is because when only trace amount of chlorine is released from the sample, the magnitude of noise is comparable to the Cl₂ profile. In that case, the integration can not be precise to give the real isotope mass ratios. However, the trend does agree with that isotope peaks Cl(70)>Cl(72)>Cl(74). Water is lost during this temperature range. The long tail of water peak profile indicated most of water is present as adsorbate on the surface area, whereas some water exists in the deeper pores within the solid. The evolution of carbon dioxide at different temperature ranges is due to the coordination between carbon dioxide, which is a Lewis acid, and zirconia, which is a Lewis base, during sample preparation. The variation of weight loss at this temperature region depend upon the drying condition of the catalyst sample as well as the amount of sulfuric acid adsorbed on the sample. The second weight loss region is from 620°C to a temperature beyond 900°C, which corresponds to the decomposition of sulfate ion to give off sulfur oxides as well as a continuous evolution of HCl (MS data). The peak profiles of sulfur oxides show a continuum beyond 900°C since the profiles of SO₂ and SO didn't go back to the base line level. This can be evidenced by TG data which shows that the TG curve doesn't level off at this point. The results indicated that there could be different types of sulfate in zirconia. The evolution profile of HCl also shows 3 peak maxima which indicated several forms of bonding between Cl and zirconia. Thus, in the inert gas the heating events can be described as occurring in two temperature regions:

Region I (<620°C)



Region II (>620°C)

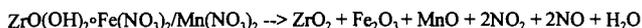


The evolution of oxygen coincides with the evolution of sulfur oxides as shown on the MS data and suggests that SO₃ might form prior to the evolution of SO₂ and SO. However, SO₃ was not identified by mass spectrometry. The results obtained when pretreating gas was air are similar to those of the runs in helium; however, when air is used it is not possible to measure the evolution of oxygen.

When 2%Fe/0.5%Mn(sulfate salt/nitrate salt)-SO₄²⁻-ZrO₂ samples were heated in helium to 900°C, there was also two major weight loss regions on the TG curve at the same temperature region as it for platinum sulfated zirconia. (see Figure 2, curve (c), (d). For Fe and Mn nitrate salt treated sulfated zirconia, the first major weight loss includes the decomposition of nitrate ion at around 300°C in addition to the other gas species as mentioned above for platinum sulfated zirconia sample (see Figure 4). Integration of peak area shows NO:NO₂ is 5:1, which agree with the fraction of nitrate ion that

evolves containing more NO than NO₂. Therefore, the heating events for this sample below 620°C can be described as follows:

Region I (<620°C)



The second major weight loss can be attributed to the decomposition of sulfate ion as seen in other sulfated zirconia samples in the second temperature region.

As for Fe/Mn sulfate salt treated sulfated zirconia, the result is similar to that of the platinum sulfated zirconia samples. It was shown that the existence of different metals or metal oxides does not affect the decomposition temperature of sulfate ion. Also, the results obtained when the pretreating gas was air are similar to those of the runs in helium, which indicate oxygen doesn't have any significant effect on the activation process.

When the platinum sulfated zirconia is analyzed in SDT at an air environment, we could see clearly the endothermic peak on DTA curve corresponding to the loss of gas species as water, carbon dioxide, hydrogen chloride and chlorine. There is a distinct exothermic peak on DTA curve occurring at 648°C which corresponds to the phase transformation of the solid from amorphous state to crystallite state. As a matter of fact, this exothermic event overlaps with an endothermic event which corresponds to the decomposition of the sulfate ion. Therefore, when heating the sample in air or an inert gas, the exothermic event is the result of an exothermic and an endothermic event so that the shape of the trace will depend upon the heat balance for these two events. For zirconia alone, this exotherm occurs at 450°C under the same heating condition, while in the presence of sulfate ion, the phase transformation process is retarded to a much higher temperature. It was found for sulfated zirconia samples, this exotherm occurs at 622°C under the same heating conditions. This indicates that the existence of metals on the sulfated zirconia doesn't have any significant effect on this exothermic event. When anions other than sulfate ion were used to treat sulfated zirconia, this exotherm occurs at 533°C for molybdate zirconia, 527°C for dichromate zirconia and 465°C for tungstate zirconia.¹⁰ It is found that sulfate ion is so far the most efficient species to retard phase transformation of the catalyst, thus permitting a high surface area to be maintained through a higher temperature range.

CONCLUSION

When catalyst samples of 1%(5%)Pt-SO₄²⁻-ZrO₂ and 2%Fe/0.5%Mn (sulfate salt/nitrate salt)-SO₄²⁻-ZrO₂ were heated in air or inert gas, online analysis by TG-MS shows different gas species evolved during different temperature regions. HCl and Cl₂ were identified even in trace amounts according to their isotope mass ratios. The existence of metals or metal oxides on the sulfated zirconia does not affect the decomposition of sulfate ion; neither does it affect significantly the phase transformation of the solid in air or inert gas environment. Sulfate ion was found so far to be the most efficient species to retard the phase transformation process of zirconia.

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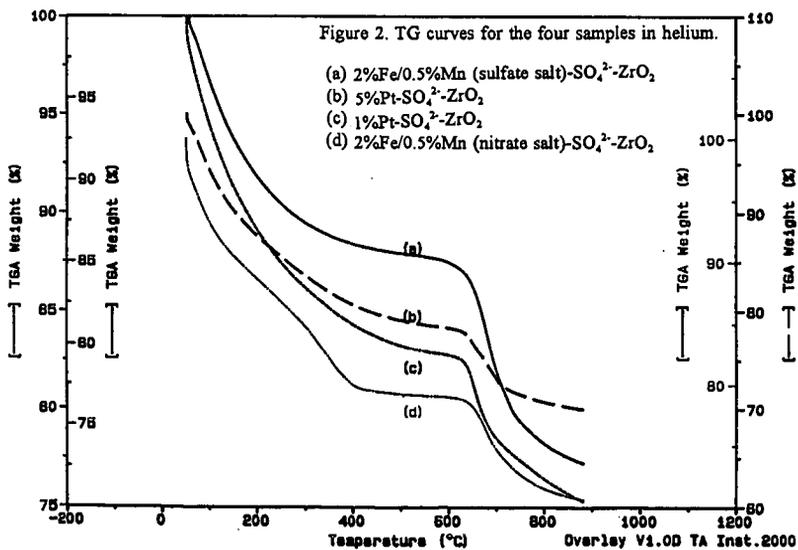
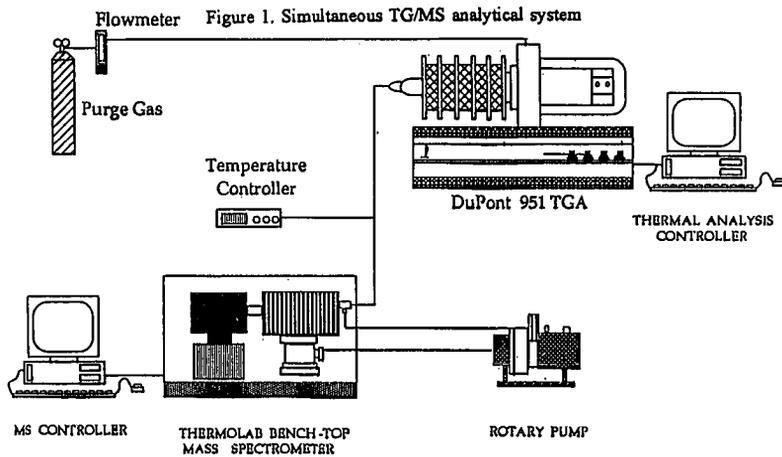


Figure 3. The MS data for 5%Pt-SO₄²⁻-ZrO₂ sample in helium.

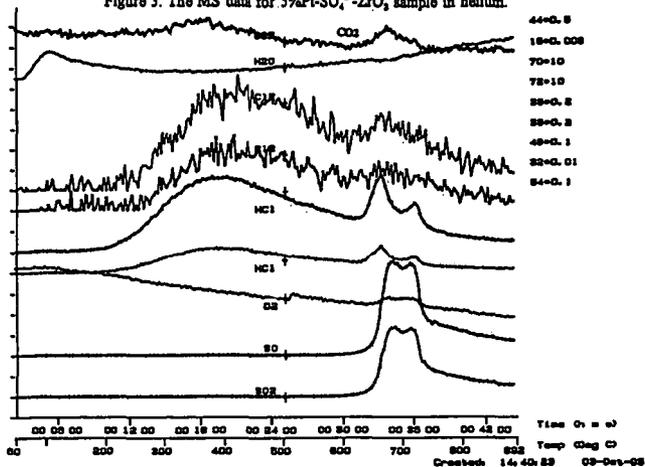


Figure 4. The MS data for 2%Fe/0.5%Mn (nitrate salt)-SO₄²⁻-ZrO₂ sample in helium.

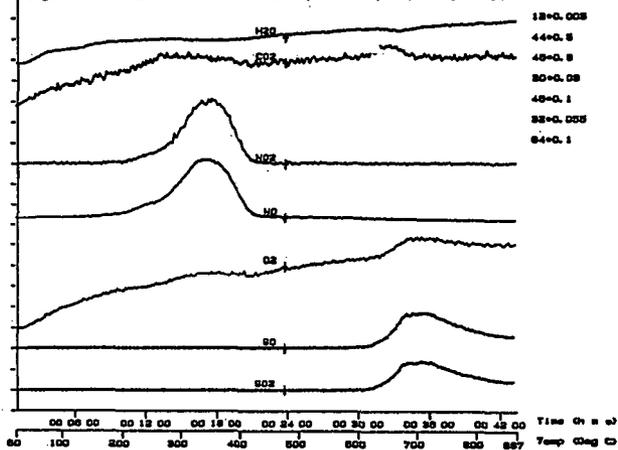


Figure 5. The SDT data for 1%Pt-SO₄²⁻-ZrO₂ sample in air.

