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Thermal studies of $(NH_4)_2 Cr_2O_7$, $(NH_4)_2 WO_4$, and $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ deposited on ZrO_2[1]

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Abstract

Ammonium molybdate, ammonium dichromate or ammonium tungstate modified zirconia are considered to be catalysts with superacid properties. The activation of these catalysts involves complex chemical changes. In the present study, combined TGA–DTA, TG–MS and TG–FTIR techniques were used to investigate the weight loss and the phase transformations of the solids and to monitor the chemical compounds that evolved under controlled heating in different environments. Through online analysis of the evolved species, some insight into the activation mechanism can be obtained. The phase transformation temperature of zirconia was shifted to a higher temperature when the sample was treated with any of these anions, which indicates that the thermal stability of the catalysts was enhanced.

Keywords: Activation; Catalyst; Phase transformation; Thermal analysis

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1. Introduction

In recent years, solid superacid catalysts have attracted great attention in the refining industries. There are many advantages in using solid superacid catalysts. Firstly, they are easy to separate from the reaction mixture. Secondly, they may decrease or eliminate corrosion of the reactor or remove corrosive products from the reactor, thus satisfying environmental regulations. Thirdly, they have high activity at low tempera-

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tures; this permits operations where thermodynamic equilibrium compositions contain a high fraction of the desired isoalkane/isoalkene components that have high octane ratings. They are of great importance with respect to obtaining high octane ratings in the absence of other toxic octane boosters, such as lead or aromatic compounds. Zirconium oxide, ZrO_2, is a very interesting material because of its thermal stability, its mechanical properties, and its chemical properties including acidic, basic, oxidizing and reducing abilities. It has been widely used for the synthesis of isobutene or methanol from carbon monoxide and hydrogen. Tanabe and Hattori [1] first reported the superacidic properties of sulfuric-acid-treated zirconia, which has an estimated acidity, H_0, greater than -14.5 as measured by the Hammett technique. However, it was found that the catalytic activity of sulfated zirconia for *n*-butane isomerization is higher in the region where the Lewis acidity is high [2].

Although the study of sulfate adsorption on zirconia has received attention recently, reports on zirconia modified by other anions are scarce. The addition of ammonium molybdate, ammonium dichromate or ammonium tungstate to the zirconia surface is also considered to greatly promote its acidity, resulting in superacid catalysts. Moreover, these salts may also increase the surface area of zirconia because of their presence. The activation of these catalysts involves complex chemical changes. Thermal studies by SDT (DTA/TGA) can provide physical measurements, while MS and FTIR can provide chemical information about the evolved species during dynamic heating which covers the activation temperature range. Thus, some insight into the activation mechanism of the catalysts can be obtained. In this study, combined TGA–DTA, TG–MS and TG–FTIR techniques were used to investigate the weight loss and thermal transformations of the solid and to monitor the chemical compounds that evolve under controlled heating in different environments.

2. Experimental methods

Zirconium oxide was prepared from anhydrous $ZrCl_4$ with an excess amount of ammonium hydroxide to produce a final pH of 10.5. After washing the precipitate thoroughly with water, ethanol was used to remove most of the remaining water. Ammonium tungstate, ammonium molybdate and ammonium dichromate adsorption on a zirconia sample was carried out by immersing the hydrous zirconia in the salt solution and stirring the mixture for hours. Water was removed using a Rotovap, the sample was then dried at 110°C for 2h. Finally, the catalyst was ground to a fine powder.

The samples were 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. Platinum crucibles were used as sample holders, and Al_2O_3 was used as a reference material. The samples were also analyzed using a DuPont TG 951 instrument which was coupled to a Perkin-Elmer 1650 FTIR spectrometer or a VG Mass Spectrometer. Both FTIR and mass spectrometry were used to identify the evolved gas species during dynamic heating which covers the activation temperature range of the catalyst samples. They provide information complementing one another. Mass spectrometry has a lower detection limit for HCl; it can also identify gas speecies such as oxygen, nitrogen etc., which cannot be identified by FTIR. However, FTIR can help to identify different species which have the same molecular weight. In the present case, ammonium cannot be identified by mass spectrometry because of its similar mass with water isotope; however, it was clearly identified by the FTIR system. The TG–MS and TG–FTIR systems have an operating range from room temperature to 1000°C. The runs were conducted separately in a purge gas of helium or air at a flow rate of 100 ml min^{-1}. Heating rates were 20°C min^{-1}.

The MS spectrometer allows the determination of multiple gas components in the mass range of 1–300 amu. It has a specially designed flexible capillary tube with a fused silica liner, which is heated to 170°C to avoid condensation of evolved gases. It requires 60 ms 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). 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 TG systems are coupled with an FTIR using an insulated teflon tube heated to a temperature of 150°C by a Powerstat Variable Autotransformer. The gas cell (25cm × 10cm) with KBr windows used with the FTIR is heated using a Barnant Thermocouple Controller to prevent condensation. FTIR scans were obtained 9 times for 53.0 s so that the change in the concentration of a species in the gas stream can be followed and displayed using either the time or temperature scale. In this manner, MS and FTIR data can be related to SDT events.

3. Results and discussion

TG results show a distinctive weight loss of about 14% (Table 1) when the samples were heated up to around 500°C, Fig 1. This corresponds to the loss of water, ammonia and carbon dioxide as evidenced by the endothermic peak on the DTA, and by MS and FTIR data (Figs. 2–4). The variation in the weight loss in this region depends upon the drying conditions and the amount of ammonium salt adsorbed on zirconia. The evolution of NH_3 commences at around 140°C and reaches a maximum at 300°C. The evolution of NH_3 was not captured by mass spectroscopy bacause it has a same mass as water isotope. Zirconia samples also undergo dehydroxylation in this temperature range. There are two water peak maxima in this temperature range, which indicate two types of interaction between water and zirconia. Water adsorbed on the surface of the sample which is loosely attached on the sample comes out first, while the second water peak indicates a tighter bonding between water, which is a Lewis base, and zirconia, which is a Lewis acid. Thus, the chemical changes during this temperature range can be described as the ammonium salts on the surface of zirconia being decomposed to give

Table 1
TGA and DTA results for zirconia samples treated with $(NH_4)_2Cr_2O_7$, $(NH_4)_2WO_4$ and $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ heated in helium and air atmosphere

Sample name	Purge gas	TGA results						DTA results
		T_i/°C	T_f/°C	$-W$%	T_i/°C	T_f/°C	$-W$%	T_{exotherm}/°C
$(NH_4)_6Mo_7O_{24}$	Air	25	502	13	891	1198	8	533
$\cdot 4H_2O$ on ZrO_2	Helium	25	500	14	879	1168	8	533
$(NH_4)_2WO_4$	Air	25	500	14	1214	> 1940	> 11	465
on ZrO_2	Helium	25	506	14	1175	> 1490	> 12	456
$(NH_4)_2Cr_2O_7$	Air	25	521	14	–	–	–	521
on ZrO_2	Helium	25	509	14	–	–	–	520

Key: T_i, initial temperature of the weight loss region; T_f, final temperature for the weight loss region; $-W$%, percentage of weight loss; T_{exotherm}, temperature at the exotherm peak maxima.

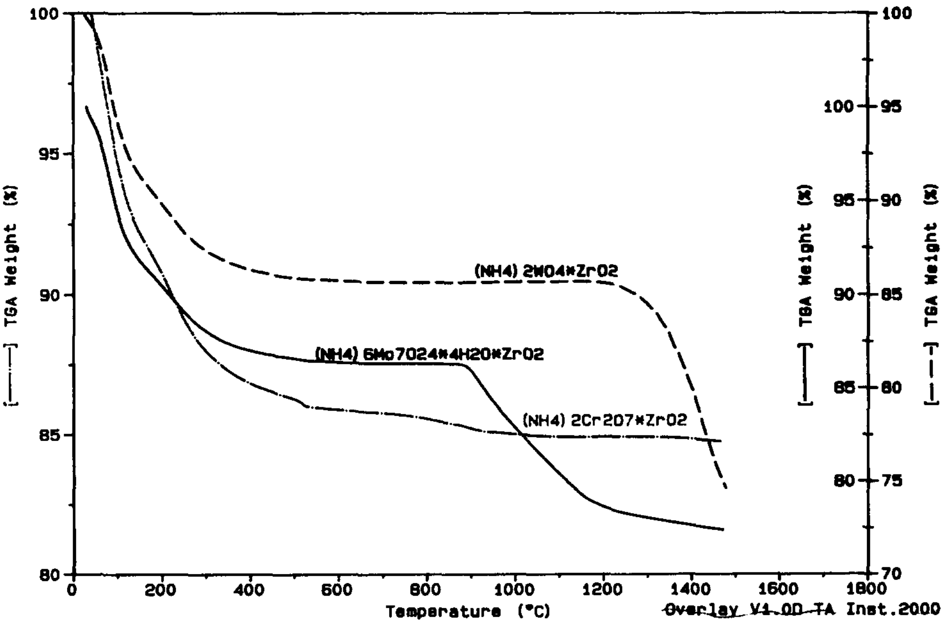

Fig. 1. TG curves for the three samples in an air atmosphere.

off ammonia and leaving metal oxides on the surface of the zirconia. These metal oxides on zirconia can be indicated as $Cr_2O_3\cdot ZrO_2$, $WO_3\cdot ZrO_2$ and $Mo_nO_m\cdot ZrO_2$.

For molybdena-zirconia, a second weight loss occurs from 900°C till 1300°C, and could be due to the loss of MoO_3 which has a vapor pressure of 40 mmHg at 892°C, For tungsten oxide-zirconia, a second weight loss takes place at 1200°C which is beyond the

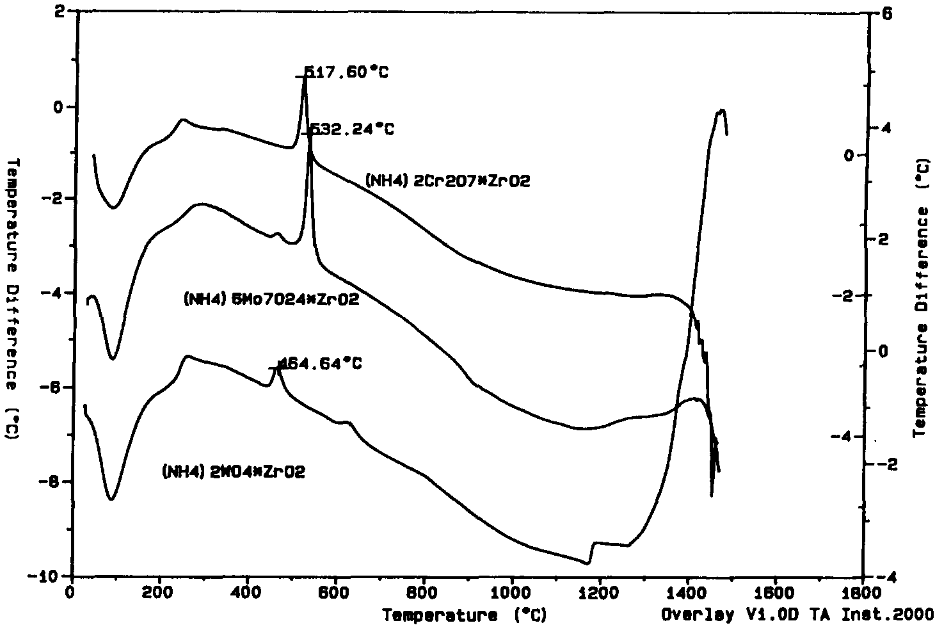

Fig. 2. Differential thermal analysis (DTA) curves for the three samples in an air atmosphere.

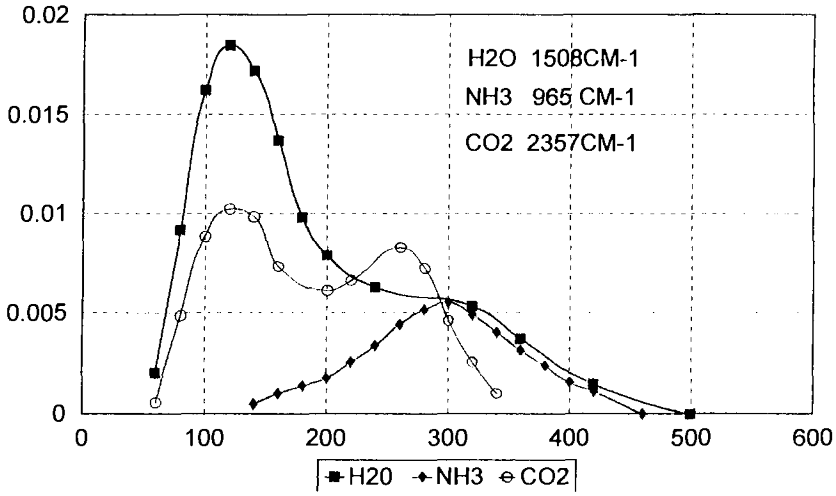

Fig. 3 The FTIR data for $(NH_4)_2WO_4$·ZrO_2 sample in an air atmosphere.

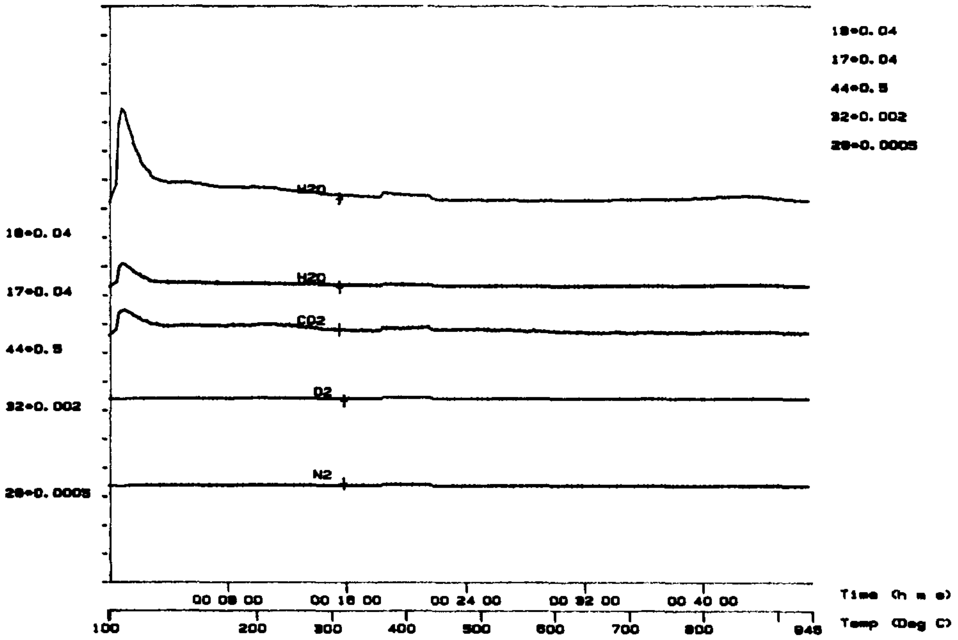

Fig. 4. The MS data for $(NH_4)_2WO_4 \cdot ZrO_2$ sample in an air atmosphere.

detection limit of the TG–FTIR or TG–MS system. This could be due to the decompositon of tungsten oxide to give off oxygen. The thermal stability of the salts adsorbed on the surface of the ZrO_2 shows the trend

$$(NH_4)_2Cr_2O_7 > (NH_4)_2WO_4 > (NH_4)_6Mo_7O_{24} \cdot 4H_2O$$

However, the decomposition of the two anions occurs at temperatures higher than 800°C, which is beyond the activation temperature range. Therefore, we can conclude that they all have very good thermal stability. Carbon dioxide also came out from the samples over different temperature ranges in trace amounts. This is because carbon dioxide can easily coordinate with zirconia during sample preparation. The amount and extent of coordination varies under different conditions.

There is a distinct exothermic peak on the DTA curves for all the samples (Fig. 4). This corresponds to the phase transformation of zirconia from an amorphous state to a crystalline state. There is no weight loss during the phase transformation process (Fig. 5). This exotherm occurs at about 450°C for zirconia [3], but is shifted to a higher temperature when another oxide is present. In the case of sulfated zirconia, this exotherm shows up at 614°C in air under the same heating conditions with a corresponding loss of surface area which indicates that a high surface area can be retained much longer than untreated zirconia [4, 5]. So far, it appears that sulfate ion is the most efficient species to retard the phase transformation process. These three oxides cause

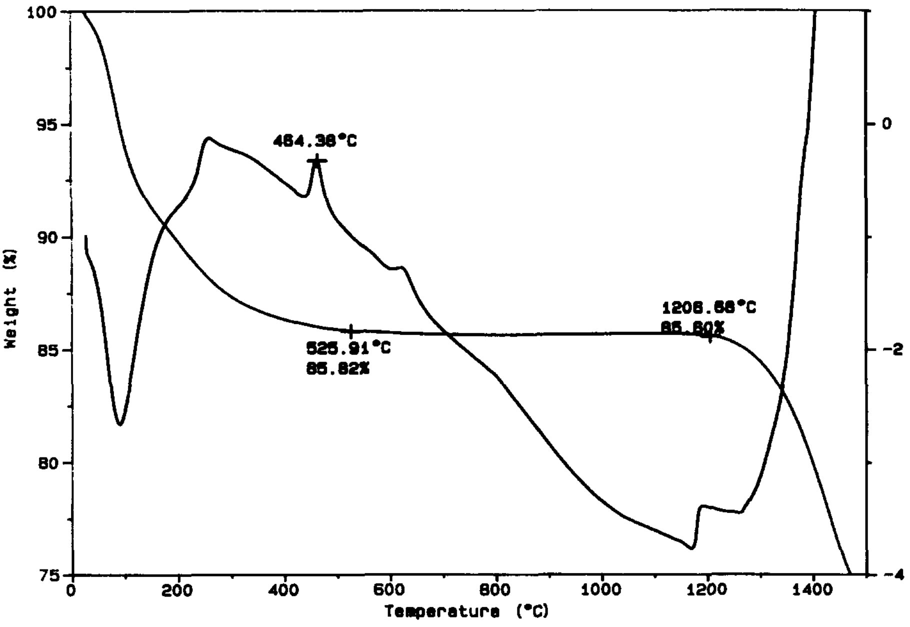

Fig. 5. TG–DTA data for $(NH_4)_2WO_4{\cdot}ZrO_2$sample heated in an air atmosphere.

the exotherm to increase in the order

$$(NH_4)_6Mo_7O_{24}{\cdot}4H_2O > (NH_4)_2Cr_2O_7 > (NH_4)_2WO_4$$

At least two factors affect the area of the exothermic peak of crystallization, i.e., the heat liberated from the samples during crystallization. One is the interaction between the anions with zirconia. Another is the packing condition of the sample: a sample spread out evenly in the sample holder can undergo crystallization during a short period of time and produce a sharp exothermic peak, whereas with a sample packed deeply in the sample holder, the phase transformation may occur gradually during a wider time range resulting in a smaller exothermic peak. In the present case, interaction is the major factor causing differences in the observed exotherms.

4. Conclusions

The three anion-treated zirconia samples have high thermal stability. The phase transformation temperature of zirconia in all cases shifted to a higher temperature. It appears that there is hardly any difference in weight loss or crystallization temperature when the samples were heated in air or helium.

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