Catalyst decomposition during temperature programmed desorption of bases from promoted sulfated zirconias

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Results from temperature programmed desorption of ammonia, pyridine, and benzene from sulfated zirconia catalysts promoted with Fe, Mn, and Ni are compared. Without adsorbates, catalysts are thermally stable below 900 K. With adsorbates, catalysts decompose partially or completely between 700 and 900 K. It is shown that previously reported conclusions regarding acid strength distributions for promoted sulfated zirconia catalysts that were based on the results of ammonia and benzene thermal desorption studies are likely incorrect because the decomposition of adsorbates and the catalyst were not considered.

Keywords: sulfated zirconia; temperature programmed desorption; solid acids; catalyst decomposition

1. Introduction

Temperature programmed desorption (TPD) of adsorbed bases is a commonly employed method for characterizing acid strength distributions for solid acid catalysts [1–6]. Implicit in this method are the assumptions that adsorption processes are reversible and that the temperature at which a base desorbs from a catalyst surface reflects the acidity of the site to which the base was adsorbed. Ammonia and pyridine TPD studies have been used effectively to characterize acid sites on a variety of catalyst surfaces. Whereas ammonia and pyridine TPD can provide information regarding nearly all catalyst acid sites, TPD studies with weaker bases such as CO or benzene can selectively probe only the most acidic sites [7].

Recent studies have clearly shown that the catalytic activity of sulfated zirconia catalysts can be enhanced by introducing Fe, Mn, or Ni into the oxide [8–13]. One

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theory devised to explain the observed increased catalytic activity for *n*-butane isomerization by promoted sulfated zirconia catalysts suggests that the presence of the promoters increases the catalyst acidity [14], whereas other theories explain enhanced catalytic activity without assuming increased acidity [12,13]. In order to validate these theories, TPD methods have been used to measure acid strength distributions for promoted sulfated zirconias [12–14]. Lin and Hsu reported that a large benzene TPD peak at 835 K was detected for sulfated zirconia catalysts promoted with Fe and Mn and that a much smaller peak was detected at 800 K for the unpromoted catalyst [14]. The peak area of this benzene TPD peak could be correlated with catalyst activity. Corma et al. detected three peaks in NH_3 TPD studies of unpromoted sulfated zirconias and assigned a peak at 815 K to the desorption of ammonia from the strongest acid sites of the catalyst [15,16]. Volatile products were detected in these TPD studies by using a non-selective thermal conductivity detector. Therefore, it was not possible to identify the species evolved during TPD experiments.

In TPD studies employing a mass spectrometer for detection of evolved species, Lee and Park found that adsorbed ammonia and pyridine caused sulfated iron oxide catalysts to decompose at lower temperatures [17]. Their pyridine TPD studies indicated that significant quantities of CO_2 were produced at about the same temperature where catalyst decomposition began. Also using mass spectrometric detection, Jatia et al. found that benzene decomposed to CO_2 at 800 K on the Fe- and Mn-promoted sulfated zirconia and that the catalyst decomposed to yield SO_2 in the presence of benzene at about 850 K [10]. Because these decomposition temperatures are close to those previously attributed to ammonia and benzene desorption from promoted sulfated zirconia catalysts, it is possible that volatile decomposition products were mistaken for ammonia and benzene desorption in those studies. In this paper, we present the results of ammonia, pyridine, and benzene TPD studies of sulfated zirconia catalysts promoted with Fe, Mn, and Ni. TGA-MS was employed for TPD experiments so that volatile products evolved when the catalyst samples were heated could be identified.

2. Experimental

Catalysts were prepared by a previously published procedure [10]. Zirconium hydroxide (BET area 180 m^2/g) was precipitated from a 0.5 M zirconium tetrachloride solution by dropwise addition of NH_4OH. The Fe, Mn, and Ni promoters were added to the zirconium hydroxide by incipient wetness impregnation with aqueous nitrate solutions. After heating in air at 473 K, sulfate was added by incipient wetness impregnation with a NH_4SO_4 solution, yielding a nominal sulfate loading of 8 wt%. After drying, catalysts were calcined in air at 873 K for 4 h. The surface areas of calcined samples were 100–120 m^2/g. The Fe-promoted catalyst contained 0.5% Fe, the Fe- and Mn-promoted catalyst contained 1.5% Fe and 0.5% Mn, and the Ni-promoted catalyst contained 1.0% Ni by weight.

TGA-MS measurements were made by connecting the gas outlet of a Du Pont (Wilmington, DE) model 951 TGA analyzer to a Hewlett Packard (Palo Alto, CA) 5985 quadrupole mass spectrometer by using a Scientific Glass Engineering Inc. (Austin, TX) MCVT-1-50 variable splitting valve. The TGA-MS interface was maintained at 473 K during measurements. Mass spectra were acquired by using 70 eV electron bombardment ionization and scanning from m/z 10 to m/z 250 at a rate sufficient to record at least one signal-averaged spectrum for each 10 K temperature increment. Sample masses ranged from 10 to 20 mg. Prior to addition of adsorbates, samples were heated to 873 K in the TGA and allowed to cool under vacuum. After samples had cooled, enough ammonia, pyridine, or benzene was added to the sample chamber to attain a pressure of at least 25 Torr. Helium was then added to the sample chamber until the total pressure exceeded atmospheric pressure. At this point a valve was opened to permit He flowing into the sample chamber to exit. Helium flow through the TGA during measurements was at a rate of 50 cm^3/min. Ion signal temperature profiles shown in figs. 1, 3, and 4 were generated by plotting the molecular ion intensities for SO_2 (m/z 64), NH_3 (m/z 17), pyridine (m/z 79), and benzene (m/z 78) as a function of catalyst temperature.

3. Results and discussion

In the absence of adsorbed bases, TGA-MS analysis revealed that the primary volatile product generated by the thermal decomposition of sulfated zirconia and sulfated zirconia promoted with Fe, Fe and Mn, and Ni was SO_2 (m/z 64). It is well known that sulfated zirconia decomposes at high temperatures to yield SO_2 [10,11,17,18]. As shown in fig. 1a, the rate of maximum SO_2 evolution for the sulfated zirconia sample promoted with Fe and Mn occurred at about 1100 K. The ion signal temperature profiles in figs. 1b–1d show that the thermal stability of the Fe- and Mn-promoted sulfated zirconia sample was affected by the presence of adsorbed bases. Whereas SO_2 evolution was first detected near 900 K for the sample without adsorbed bases, SO_2 evolution began near 775 K when ammonia was present, near 675 K when pyridine was present, and near 725 K when benzene was present.

Fig. 1b shows that the rate of ammonia desorption reached a maximum near 525 K and decreased at higher temperatures. This behavior is consistent with our previous ammonia desorption studies of the same catalyst sample in which infrared spectroscopy was employed to selectively monitor desorption from Lewis and Brønsted acid sites [13]. However, the NH_3 ion signal temperature profile shown in fig. 1b is inconsistent with results reported by Corma et al. Based on our findings, the increase in the rate of volatile product evolution at 815 K reported by Corma et al. [15,16] was more likely due to SO_2 formed as a result of catalyst decomposition

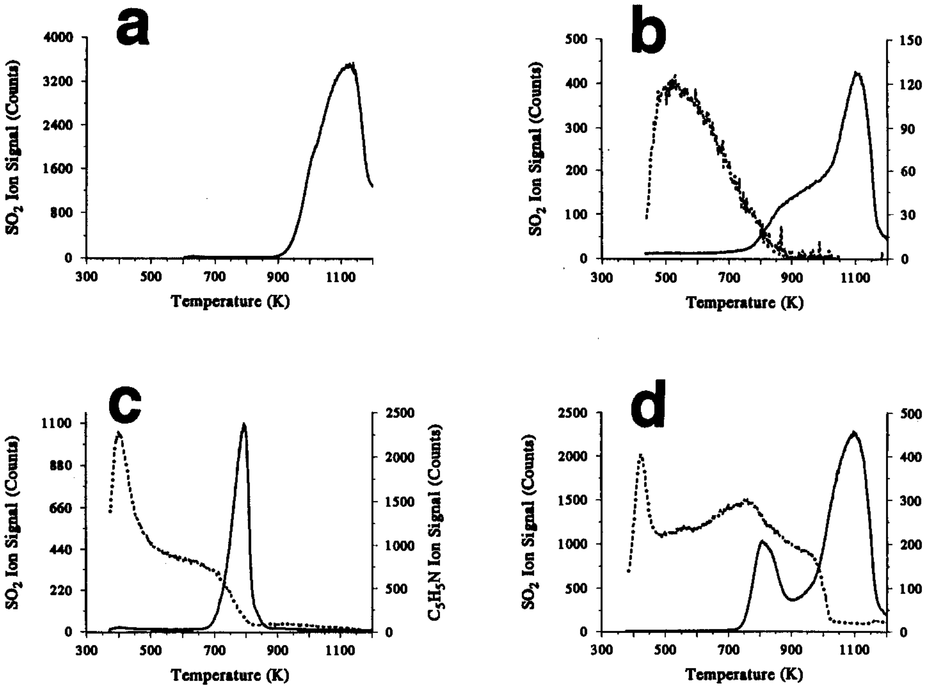

Fig. 1. Ion signal temperature profiles obtained by TGA-MS analysis of an Fe- and Mn-promoted sulfated zirconia catalyst (a) without adsorbates, (b) with adsorbed ammonia, (c) with adsorbed pyridine, (d) with adsorbed benzene. Solid curves denote SO_2 evolution and dashed curves denote base evolution.

than from ammonia desorption. Because Corma et al. used thermal conductivity to detect species evolved during TPD, they could not distinguish SO_2 from ammonia. The fact that we observed no catalyst decomposition below 900 K in the absence of adsorbates (fig. 1a) is consistent with the fact that Corma et al. found no TPD peak at 815 K during their blank measurement (e.g. TPD of the catalyst without adsorbed ammonia).

The ion signal temperature profiles for desorbed bases and SO_2 shown in figs. 1b–1d indicate that each of the bases had a different effect on the thermal stability of the catalyst. Pyridine had the most dramatic effect on catalyst stability. As shown in fig. 1c, the TPD ion signal temperature profile for SO_2 obtained for the sample with adsorbed pyridine exhibited a maximum near 800 K. Catalyst decomposition for this sample was complete by 875 K and no pyridine was evolved above 815 K. The SO_2 ion signal temperature profile obtained by benzene TPD exhibited two distinct maxima. The first TPD maximum occurred near 800 K and the second maximum was found at 1100 K. The fact that the second maximum in fig. 1d occurred near the SO_2 TPD peak maximum measured for the sample without adsorbates (fig. 1a) suggests that this peak represented catalyst thermal decomposition without assistance from adsorbed benzene. The presence of an SO_2 maximum near 800 K in fig. 1d suggests that the large benzene TPD peak reported by Lin and Hsu at 835 K for their Fe- and Mn-promoted sulfated zirconia sample may have been caused by catalyst decomposition. This is consistent with the claim made by Jatia et al. that this TPD peak was due to a combination of CO_2 from benzene decomposition and catalyst decomposition, which resulted in the evolution of SO_2 and O_2 [10].

Fig. 2 shows mass spectra obtained by TGA-MS analysis during TPD studies of the Fe- and Mn-promoted sulfated zirconia sample. The mass spectrum in fig. 2a was obtained during ammonia TPD at 850 K. Ion intensity at m/z 64 and m/z 48 represented SO_2 and denotes SO_2^+ and SO^+, respectively. The ion detected at m/z 44 most likely represented CO_2. Because CO_2 cannot be produced by reactions between the pristine catalyst and NH_3, the carbon dioxide formed during catalyst decomposition likely resulted from oxidation of organic impurities on the catalyst

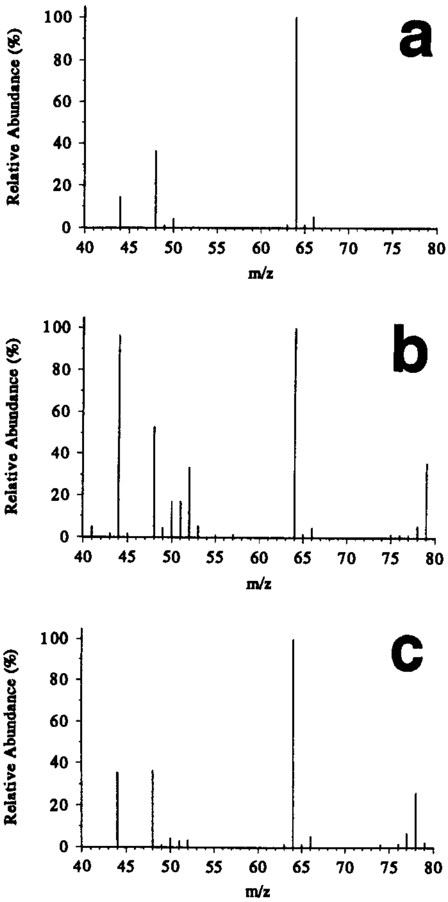

Fig. 2. Mass spectra obtained by TGA-MS analysis of an Fe- and Mn-promoted sulfated zirconia catalyst (a) at 850 K with adsorbed ammonia, (b) at 790 K with adsorbed pyridine, (c) at 800 K with adsorbed benzene.

surface [10], which were apparently present despite heating samples at 873 K in vacuum prior to ammonia adsorption. The mass spectrum shown in fig. 2b was obtained during pyridine TPD of the Fe- and Mn-promoted sulfated zirconia sample at 790 K, the temperature at which the SO_2 evolution rate was greatest. Ions at m/z 50, 51, 52, 53, 78, and 79 are representative of pyridine. The CO_2 ion intensity at m/z 44 in this mass spectrum is nearly as large as the SO_2 ion intensity, suggesting that significant oxidation of adsorbates on the catalyst surface occurred at this temperature. Fig. 2c is a mass spectrum obtained at the temperature corresponding to the first SO_2 evolution maximum (800 K) during benzene TPD. Ions at m/z 50, 51, 52, 77, 78, and 79 are representative of benzene. Again, this mass spectrum shows that CO_2 was detected in significant quantities when the catalyst decomposed.

Fig. 3 contains ion signal temperature profiles obtained from TPD measurements for the sulfated zirconia sample promoted with Ni. In general, the same features exhibited by the temperature profiles in fig. 1 are evident in the profiles shown in fig. 3. However, unlike the Fe- and Mn-promoted catalyst, the ammonia TPD temperature profile for SO_2 obtained for the Ni-promoted catalyst contained two distinct maxima. The low temperature maximum occurred at 850 K, which is

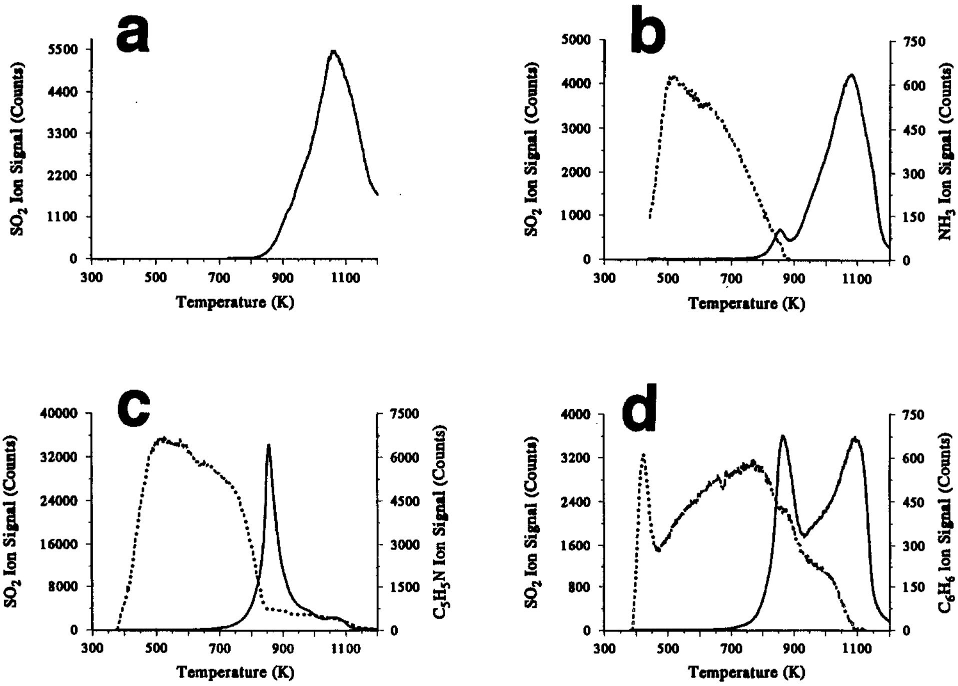

Fig. 3. Ion signal temperature profiles obtained by TGA-MS analysis of a Ni-promoted sulfated zirconia catalyst (a) without adsorbates, (b) with adsorbed ammonia, (c) with adsorbed pyridine, (d) with adsorbed benzene. Solid curves denote SO_2 evolution and dashed curves denote base evolution.

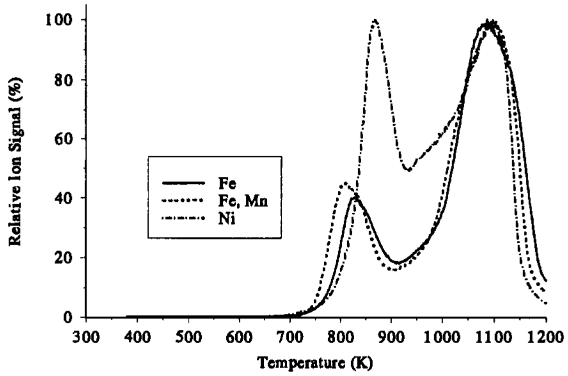

Fig. 4. SO_2 ion signal temperature profiles obtained by TGA-MS analysis of benzene TPD from promoted sulfated zirconia catalysts. Metal promoters are indicated in the figure legend.

close to the temperature at which Corma et al. previously reported ammonia TPD peaks [15,16]. Another difference between the Ni-promoted catalyst and the Fe- and Mn-promoted catalyst can be found in the SO_2 temperature profiles obtained from benzene TPD measurements. Comparing fig. 1d with fig. 3d reveals that the fraction of catalytic sites that had decomposed by 850 K was much greater for the Ni-promoted catalyst than for the Fe- and Mn-promoted catalyst. Interestingly, as shown in fig. 4, the low temperature SO_2 evolution occurred at different temperatures for the different catalysts. This evolution maximized at 800 K for the Fe-, Mn-promoted catalyst, at 825 K for the Fe-promoted catalyst, and at 860 K for the Ni-promoted catalyst. However, the high temperature SO_2 evolution maximized at about the same temperature (ca. 1100 K) in all three TPD curves.

4. Conclusions

Because the thermal stability of promoted sulfated zirconia catalysts is affected by adsorbates, the adsorption of bases on at least some of the catalyst sites cannot be considered to be reversible. Therefore, TPD profiles for desorbed bases may not provide an accurate measure of the acid strength distributions for these catalysts. Indeed, the ion signal temperature profiles for the ammonia, pyridine, and benzene molecular ions derived from TPD measurements for the same catalyst sample were all different. The fact that CO_2 was detected in significant quantities when catalysts decomposed indicates that oxidation reactions occurred concurrently with molecular desorption during TPD studies.

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