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 \textit{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 tetra-chloride solution by dropwise addition of NH$_4$OH. 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$_4$SO$_4$ 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