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Catalysis Today 100 (2005) 397–401

CATALYSIS TODAY

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Iron and manganese promoted sulfated zirconia: acidic properties and *n*-butane isomerization activity

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Abstract

Sulfated zirconia catalysts promoted with Fe and Mn have been synthesized and the acidity characterized by IR spectroscopy of adsorbed pyridine. The catalytic isomerization of *n*-butane was investigated in a fixed bed reactor operated at low conversion at atmospheric pressure and 250 °C. The main effect of the promoters was to change the ratio Brönsted:Lewis acidity of the samples. The catalytic activity was found to be correlated with the number of strong Brønsted acid sites.

Keywords: Sulfated zirconia; Iron; Manganese; Acidity; *n*-Butane isomerization

1. Introduction

Sulfated zirconia (SZ) is an interesting material for acid catalysis, with the potential to replace strongly corrosive mineral acid catalysts used for processes like isomerization, alkylation, etherification and oligomerization [1]. The present interest in sulfated zirconia (SZ) as a solid acid catalyst is attributed to the seminal work by Arata and co-workers [2]. The activity and stability of sulfated zirconia can be improved by adding various metals to the catalyst. Hsu and co-workers [3,4] found that by promoting sulfated zirconia with iron and manganese (FMSZ) the activity for *n*-butane isomerization at room temperature was increased by about three orders of magnitude, and they ascribed the increased activity to an increase in the acid strength of the catalysts [5]. Later other theories for the role of iron and manganese as promoters have been proposed. Adeeva et al. [6] reported that there was no difference in the acid strength of neither the Lewis or Brønsted sites of FMSZ and SZ. Yori and Parera [7] claimed that the metals promoted the production of olefinic intermediates. Tabora and Davis [8] and Lange et al. [9] supported that iron and manganese participate in the formation of olefins on the catalyst surface. But they suggested that olefins are formed in a non-catalytic redox reaction rather than in a catalytic cycle. In addition to the role of iron and manganese in the formation of hydrogen deficient intermediates, it has been emphasized that the metal promoters also enhance the stability of these intermediates [10,11]. The mechanisms are, however, still disputed. In this work we report a study of Fe and Mn-promotion of SZ and the influence of the promoters on the acidity and activity in *n*-butane isomerization.

2. Experimental

The zirconia used was prepared by precipitation of the hydroxide from an aqueous solution of $ZrOCl_2 \cdot 8H_2O$ at pH 10. The precipitated gel was aged for 20 h, filtrated, washed and dried before addition of the metal promoters (Fe and Mn as nitrates, total loading 2 wt.% metal). The solid was dried, and the sulfur was added (0.5 M H_2SO_4, 2.1 cm^3/g solid) before the final drying and calcination (600 °C, 3 h in flowing air). The catalyst material was pressed to disks, then crushed and sieved to the size of 160–400 μm. The catalysts

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doi:10.1016/j.cattod.2004.09.071

are termed according to composition, where (1.0)F(1.0)MSZ describes a material with 1 wt.% Fe and 1 wt.% Mn, and SZ is the unpromoted sulfated zirconia.

The catalytic isomerization of *n*-butane was performed in a fixed bed reactor operated at low conversion. Prior to the reaction the catalysts were pretreated in situ with air at 450 °C for 3 h. The reaction was performed at atmospheric pressure and 250 °C, $N_2/n\text{-}C_4 = 9:1$ and WHSV = 4.7 h^{-1}. The product was analyzed on line by a Varian 3400 GC equipped with a Valco multiposition valve (10 positions) and a flame ionization detector. FT-IR measurements of adsorbed pyridine were carried out with a Nicolet Magna IR 550. The samples were activated in situ in the IR cell in flowing dry air at 450 °C for 3 h. Pyridine was adsorbed on the sample at 150 °C. The IR spectra were carried out at room temperature after (i) the activation period and (ii) pyridine thermodesorption in vacuum at increasing temperatures: 150, 250, 350 and 450 °C. The area of the bands corresponding to the Brønsted- and the Lewis-acid sites (1544 and 1447 cm^{-1}, respectively) were measured by integration. Further details of the acidity characterization are given by Tran et al. [12]. The crystallinity of the samples was characterized by XRD. The XRD spectra were obtained by a Siemens D5005 X-ray diffractometer with Cu Kα radiation, scanned at a rate of 2° min^{-1}. The surface areas of the samples were determined by adsorption of N_2 at 77 K with the BET method using a Micromeritics ASAP2010. The sulfur content of the samples was analyzed by the LECO method by NGU (The Geological Survey of Norway).

3. Results and discussion

The physical and chemical characteristics of the catalysts are given in Table 1. The zirconia crystal structure was found to be exclusively tetragonal for all samples. The oxides of the promoters were not detected, which probably is due to the low content of these compounds. The sulfur content and surface area are of the same magnitude for all the samples, and independent of the promoter content. The samples were characterized by IR spectroscopy of adsorbed pyridine. This technique distinguishes between Lewis and Brønsted acid sites, at the same time an acid strength distribution can be obtained by desorption of pyridine at increasing temperatures, i.e. 150, 250, 350 and 450 °C [12]. A link between the promoter content and the number of strong acid sites can be found. This is presented in Fig. 1. The promoters did not change the total number of strong acid sites significantly. But, although the number of samples is limited, the trend is that addition of Fe leads to a higher B/L-ratio, whereas Mn leads to lower B/L-ratios. Similar trends were observed at weak and intermediate acid strengths.

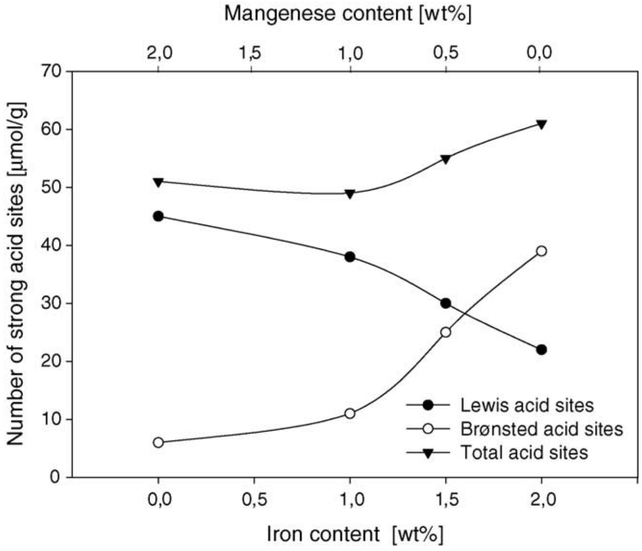

Fig. 1. The number of strong acid sites as a function of the metal content.

The activity in isomerization declined strongly over the first few minutes of reaction, and after 1 h the activity was reduced by 30–90%. The deactivation is most likely due to deposition of carbon on the active sites as discussed by Marcus et al. [13], but can also be due to loss of sulfur, as discussed by e.g. Kim et al. [14]. The selectivity to isobutane was typically 90% over most catalysts, with C_3 and C_5 as the observed by-products. This indicates a bimolecular mechanism for the cracking [15].

Fig. 2 shows correlations between acidity and activity. The absence of a correlation between the initial conversion and all Brønsted acid sites (i.e. sites after desorption at 150 °C) is shown in Fig. 2a. A good correlation between Brønsted acidity and *n*-butane conversion is only found for the strongest sites (measured after desorption at 350 °C) as shown in Fig. 2b. The unpromoted catalyst has a higher

Table 1
Characterization data for the catalysts used

Catalyst	S_{BET} (m^2/g)	Sulfur (wt%)	Total acidity[a]		Strong acidity[b]	
			Sites (µmol/g)	Ratio B/L	Sites (µmol/g)	Ratio B/L
SZ	93	2.0	210	1.6	50	1.9
(2.0)MSZ	106	1.9	260	0.9	51	0.1
(1.0)F(1.0)MSZ	101	2.6	181	0.7	49	0.3
(1.5)F(0.5)MSZ	127	2.6	265	1.0	55	0.8
(2.0)FSZ	90	2.1	210	1.9	61	1.8

[a] After evacuation at 150 °C.
[b] After evacuation at 350 °C.