JOURNAL OF CATALYSIS **174,** 242–245 (1998)
ARTICLE NO. CA971962

RESEARCH NOTE

Synthesis of Catalytically Active High Surface Area Monoclinic Sulfated Zirconia

Wolfram Stichert and Ferdi Schüth[1]

Institut für Anorganische Chemie, Johann Wolfgang Goethe-Universität, Marie Curie Strasse 11, 60439 Frankfurt/Main

Received January 13, 1997; revised October 11, 1997; accepted November 10, 1997

Sulfated zirconia has found great interest in heterogeneous catalysis because of its capability to isomerize *n*-butane (1). Up to now, only tetragonal sulfated zirconia has been reported to be reasonably active as a catalyst for this reaction.

Zirconia may be amorphous, tetragonal, cubic, or monoclinic. Amorphous precipitates transform irreversibly upon thermal treatment first to the metastable tetragonal phase and then to the monoclinic phase. The first transformation occurs at about 723 K. Calcination at higher temperatures results in a mixture of tetragonal and monoclinic zirconia. The higher the temperature the higher is the monoclinic fraction. At about 1073 K pure monoclinic zirconia can be obtained. If sulfate groups are adsorbed to the surface of the amorphous precipitate before calcination, the tetragonal structure of the calcined zirconia is stabilized up to a temperature of 923 K, where the sulfate groups begin to leave the zirconia surface. Sulfated zirconia needs activation temperatures in the same range to be active in *n*-butane isomerization. This fact led some authors to the conclusion that monoclinic sulfated zirconia may not be stable (2) or that the tetragonal phase is the active phase and necessary to obtain activity of sulfated zirconia in *n*-alkane isomerization (3). However, Ward and Ko report a weak activity of monoclinic sulfated zirconia samples (4). The same authors consider the crystal phase of sulfated zirconia as less important with respect to its activity in *n*-butane isomerization. They report the hydroxyl content of the sample being a basic requirement for the activity.

If this is correct, sulfating a monoclinic hydrous zirconia sample and subsequent calcination should lead to purely monoclinic zirconia active in *n*-butane isomerization, taking advantage of the irreversibility of the phase transformation from the tetragonal to the monoclinic phase of zirconia. Clearfield described the formation of hydrous monoclinic zirconia in 1964 (5). In the following we show the synthesis of monoclinic sulfated zirconia which is active in *n*-butane isomerization.

$ZrOCl_2 * 8H_2O$ (ABCR, 95%) was dissolved in water within 5 min to obtain a zirconium concentration of 0.34 M. Subsequently hydrous zirconia was precipitated by adding an aqueous solution of NH_4OH (Roth, $\geq$25%) to reach a final pH of 5 ± 0.4. The precipitation was carried out within a few seconds. The resulting solution was aged under different conditions. Sample 1 was aged in a closed polypropylene flask at 363 K for 63 days, sample 2 was aged in an autoclave at 423 K for 1 day, and sample 3 was aged in an autoclave at 423 K for 3 days. Sample 4 was not aged. The aging conditions are given in Table 1. In a following step the precipitate was filtered off, washed with distilled water, and dried at 363 K for 24 h. The subsequent sulfatation was carried out by stirring a slurry containing the hydrous zirconia and 0.5 M $(NH_4)_2SO_4$ (Fluka, 99%) for 2 h. After filtering and washing, the samples were dried again at 363 K for 24 h. The products were calcined at 823 K for 5 h with a heating rate of 1 K/min.

Clearfield had refluxed the precipitated hydrous zirconia over extended periods of time to get monoclinic hydrous zirconia (5). However, ageing at 363 K leads to the same result.

The X-ray diffraction (XRD) patterns were recorded using a Stoe STADI P diffractometer equipped with a Germanium monochromator. The scans were taken within the range of 27 to 34.5° (2Θ) using Cu$K\alpha$ radiation.

The nitrogen adsorption–desorption isotherms were measured at 77 K with a Micromeritics ASAP 2010 system. Prior to the measurements the samples were outgassed for 4 h at 393 K. The specific surface areas of all samples were calculated according to the BET method.

The catalytic properties of sulfated zirconia (as powder on quartz wool) were studied for *n*-butane isomerization

---

[1] To whom correspondence should be addressed. Fax: 069/798 29260. E-mail: ferdi@schueth.chemie.uni-frankfurt.de.

0021-9517/98 $25.00

TABLE 1

Sample	Preparation	BET surface area (m^2/g)
1	63 days at 363 K	121
2	1 day at 423 K	104
3	3 days at 423 K	99
4	No aging	19

in a fixed bed flow reactor (inner diameter, 8 mm) with external heating at 573 K. A total of 0.5 g of the zirconia was exposed to a 50 : 50 Vol% mixture of *n*-butane and nitrogen with a constant feed of 10 ml/min. The reaction products were analyzed with a Carlo Erba GC6000 equipped with a DB-5 column and a flame ionization detector. Prior to the measurement the samples were activated at 723 K for 2 h under a constant nitrogen flow of 20 ml/min.

Figure 1 shows the X-ray diffraction patterns of the sulfated and calcined samples synthesized according to the methods given above. The monoclinic fraction of these samples depends on the crystallinity of the hydrous zirconia precursor. If the precursor is amorphous, the resulting sulfated zirconia will be tetragonal, if the precursor is partly or completely monoclinic, the sulfated zirconia will be partly or completely monoclinic as well. The phase composition after a certain pretreatment is reproducible within ±20% of the phases present. The phase composition of a sample containing the tetragonal and the monoclinic is very sensible to slight temperature differences. It is not necessary to age a sample for 63 days at 363 K to obtain a completely monoclinic phase. Under the conditions applied here aging for about 8 days was sufficient. On the other hand, 1 and 3 days at 423 K, respectively, were not sufficient to reach a completely monoclinic product. Under these conditions, completely monoclinic samples could be obtained after 5 days.

Table 1 shows the BET surface area of the prepared samples. The BET surface area of the monoclinic samples is one order of magnitude higher than for the tetragonal sample. It is certainly possible to produce tetragonal sulfated zirconia with higher BET surface areas by modifying the precipitation conditions. However, since samples with comparable history (except the aging time and thus the phase) should be investigated, a tetragonal sulfated zirconia with relatively low surface area was used here.

Figure 2 shows the catalytic activity of these samples in *n*-butane isomerization, normalized to the surface area. Catalytic properties of different samples prepared by identical procedures are reproducible within ±10%. The initial activity of the tetragonal sample is higher than the activity of the monoclinic samples. However, the activity per gram of catalyst of the monoclinic sample is higher than the corresponding activity of the tetragonal sample.

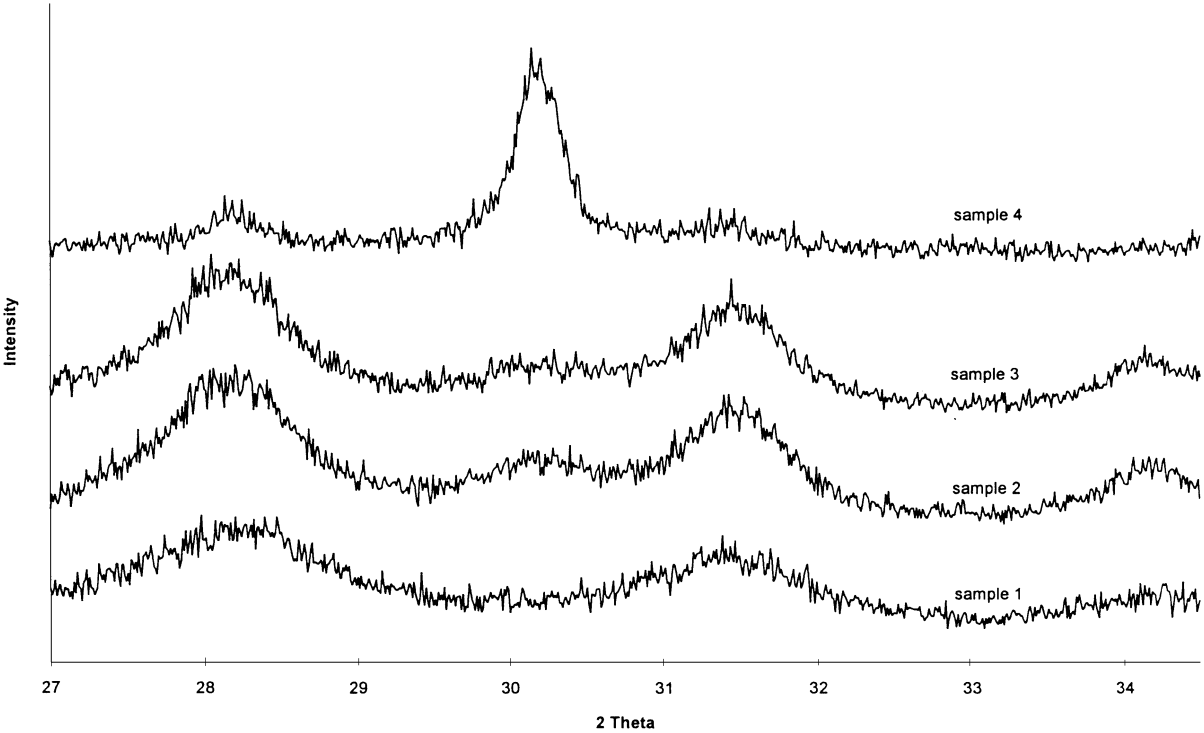

FIG. 1. XRDs of sulfated zirconia obtained from differently aged precursors: Aged 63 days at 363 K (bottom), 1 day at 423 K (second), 3 days at 423 K (third), and not aged (top).

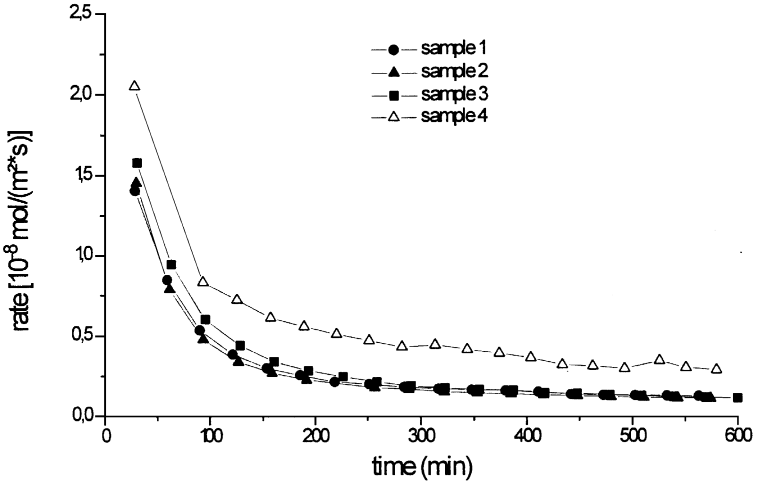

FIG. 2. Catalytic activity in *n*-butane isomerization normalized to the specific surface area of sulfated zirconia samples obtained from differently aged precursors: 63 days at 363 K (●), 1 day at 423 K (▲), 3 days at 423 K (■), and not aged (△).

Since the tetragonal zirconia reference used here is not an optimized catalyst, it was attempted to compare the activity data with literature data. This is fairly difficult, since conditions of catalytic tests vary over a wide range and the deactivation behavior of different catalysts differ as well. Therefore, the catalytic activity of all sulfated zirconia samples after 1 h on stream was estimated and converted to units given in moles per (seconds times grams) or moles per (seconds times square meter). Experiments described in the literature were all carried out at different partial pressures of *n*-butane. Thus, all data were normalized to a pressure of 1 bar, assuming a reaction order of 1.5 which is reasonable according to Liu *et al.* (6), but might lead to substantial errors, since pressures used vary by about a factor of 20. The comparability of the different values further suffers from different reaction temperatures used. However, this comparison is still sufficient to obtain an estimate of the relative catalytic performance of monoclinic zirconia. In Table 2 our data is compared with data of Morterra *et al.* (3), Ward and Ko (4), Comelli *et al.* (7), Yaluris *et al.* (8), González *et al.* (9), and Chen *et al.* (10). The rates differ by two orders of magnitude. The catalytic activity of our monoclinic sulfated zirconia samples is just by a factor of 5 and 7, respectively, lower than the highest activities after 1 h reported for tetragonal samples. Therefore, our monoclinic material could be regarded as reasonabely active in *n*-butane isomerization.

TABLE 2

Recalculated Reaction Rates Observed by Other Authors after 1 h on Stream, Normalized to 1 bar Partial Pressure *n*-Butane (See Text)

	mol/(s × g)	mol/(s × m^2)
Our monoclinic SZ (573 K)	3×10^{-6}	3×10^{-8}
Morterra *et al.* (3) (423 K)	6×10^{-7}	5×10^{-9}
Ward and Ko (4) (553 K)	4.4×10^{-6}	1.7×10^{-7}
Comelli *et al.* (7) (573 K)	3×10^{-7}	—
Yaluris *et al.* (8) (423 K)	1.6×10^{-5}	1.6×10^{-7}
González *et al.* (9) (423 K)	1.3×10^{-5}	1.2×10^{-7}
Chen *et al.* (10) (523 K)	1.5×10^{-5}	2×10^{-7}

Note. The reaction temperature is given in parentheses.

There remains a difference between the surface normalized catalytic properties of monoclinic and tetragonal sulfated zirconia, which, however, is not dramatic. The existence of different kinds of acid sites on the surface of sulfated zirconia samples has already been reported (8, 11). Many recent publications concerning sulfated zirconia address the role of its hydroxylation state for the activity in *n*-butane isomerization (9, 12, 13). The geometrical arrangement of the sulfate and the hydroxyl groups could be different on a monoclinic surface compared to a tetragonal surface. The acid sites present on monoclinic sulfated zirconia can thus have different properties than those on the tetragonal phase; i.e., they may be not as active as the sites on the tetragonal sulfated zirconia. However, the observation of reasonable activity in *n*-butane isomerization of sulfated zirconia samples which are purely monoclinic contradicts earlier conclusions, where the tetragonal phase is proposed to be a necessary prerequisite for activity. The crystal phase therefore plays a role with respect to the activity of sulfated zirconia in *n*-butane isomerization, but is not as crucial as previously thought. Further investigations into the role of the crystal phase are under way.

REFERENCES

1. Hino, M., Kobayashi, S., and Arata, K., *J. Am. Chem. Soc.* **101**, 6439 (1979).

2. White, R. L., Sikabwe, E. C., Coelho, M. A., and Resasco, D. E., *J. Catal.* **157**, 755 (1995).
3. Morterra, C., Cerrato, G., Pinna, F., and Signoretto, M., *J. Catal.* **157**, 109 (1995).
4. Ward, D. A., and Ko, E. I., *J. Catal.* **157**, 321 (1995).
5. Clearfield, A., *Inorg. Chem.* **3**, 146 (1964).
6. Liu, H., Adeeva, V., Lei, G. D., and Sachtler, W. M. H., *J. Mol. Catal. A* **100**, 35 (1995).
7. Comelli, R. A., Vera, C. R., and Parera, J. M., *J. Catal.* **151**, 96 (1995).
8. Yaluris, G., Larson, R. B., Kobe, J. M., González, M. R., Fogash, K. B., and Dumesic, J. A., *J. Catal.* **158**, 336 (1996).
9. González, M. R., Kobe, J. M., Fogash, K. B., and Dumesic, J. A., *J. Catal.* **160**, 290 (1996).
10. Chen, F. R., Coudurier, G., Joly, J.-F., and Vedrine, J. C., *J. Catal.* **143**, 616 (1993).
11. Drago, R. S., and Kob, N., *J. Phys. Chem. B* **101**, 3360 (1997).
12. Kobe, J. M., González, M. R., Fogash, K. B., and Dumesic, J. A., *J. Catal.* **164**, 459 (1996).
13. Vera, C. R., and Parera, J. M., *J. Catal.* **165**, 254 (1997).