



Effect of Mn Promoter on Sulfated ZrO₂ Studied by IR Spectroscopy

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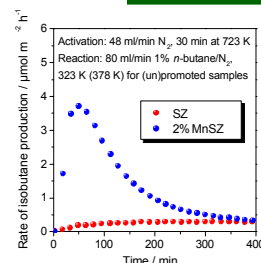
Introduction

Addition of Mn to sulfated zirconia ("SZ") increases the activity for *n*-butane isomerization [1] by 2-3 orders of magnitude [2]. To clarify the role of the promoter, SZ and Mn-promoted SZ ("MnSZ") and their interaction with hydrogen and *n*-butane were investigated by IR spectroscopy in diffuse reflection mode.

Experimental

Precursor (NH₄)₂SO₄ doped hydrous zirconia (XZO 682/01, MEL Chemicals)
Preparation drying (21 h, 383 K) – [incipient wetness (Mn(II)nitrate aq.)] - calcination flowing air for 3 hours at 823 (SZ) or 923 K (MnSZ) [3]
Pressing 10 MPa for 2 seconds, then sieving to 1.0-0.5 mm
Evacuation 10⁻³-10⁻⁴ mbar: room temp. –15 min→ 383 K (1 h) –1 h→ 723 K (1 h) ca. 67 mbar oxygen: 723 K (20 min), evacuation (20 min)
DRIFTS Nicolet "Impact 410" (home-made diffuse reflection attachment [4]), resolution 4 cm⁻¹, background CaF₂
Data analysis conversion to Kubelka-Munk units (OMNIC 2.1 / Nicolet), reflectivity of the samples at 5000 cm⁻¹ was taken as equal to 0.9

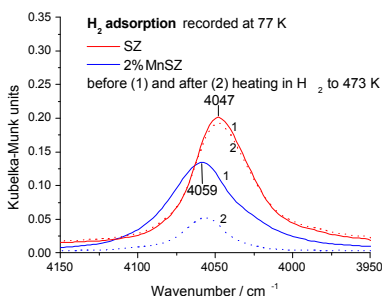
Characterization



Maximum *n*-butane isomerization rate of MnSZ (BET surface area: 108 m²/g) at 323 K is 10 times higher than the rate of SZ (119 m²/g) at 378 K.

Both samples are tetragonal according to XRD analysis. After pressing the monoclinic moiety was about 10 wt% (Powdercell 2.4 [5]).

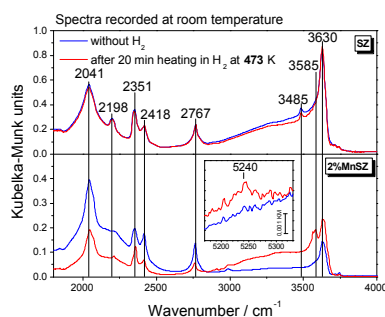
Hydrogen as probe molecule



Adsorption of 67 mbar hydrogen (gas phase vibration 4160 cm⁻¹ [6]) at 77 K results in a single band centered at 4047 cm⁻¹ (SZ) and 4059 cm⁻¹ (MnSZ).

There is no significant difference in Lewis acid strength ($\Delta\nu = 12$ cm⁻¹).

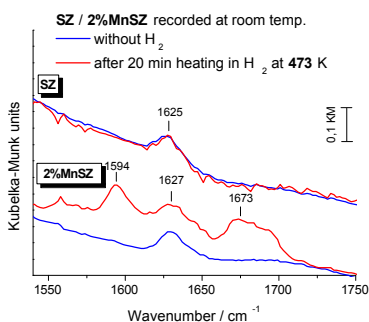
Decrease in band intensity of MnSZ after heating in hydrogen at 473 K means loss of adsorption sites due to hydride or water formation (see below).



SZ shows no changes after adsorption of and heating in hydrogen at 473 K.

Changes in the spectrum of MnSZ:

- Decrease of the bands of sulfate vibrations (2044 cm⁻¹, 2417 cm⁻¹, 2764 cm⁻¹)
- Formation of water on the surface (5244 cm⁻¹)
- Formation of H-bridges (3585 cm⁻¹, increase in OH stretching region)



The spectrum of SZ shows no changes in the OH deformation region after adsorption of and heating in hydrogen at 473 K.

In the spectrum of MnSZ two additional bands appear at 1594 cm⁻¹ and 1673 cm⁻¹. The band at 1594 cm⁻¹ is the OH deformation of water (see *n*-butane adsorption). The species at 1673 cm⁻¹ is as yet unidentified. Hydride formation has been considered, but hydrides of zirconium are found in the range 1520-1660 cm⁻¹ [7-8].

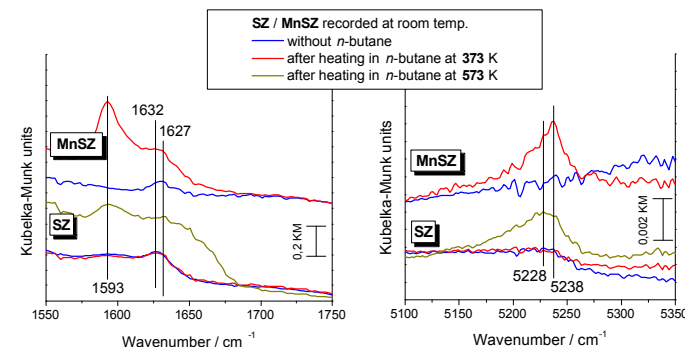
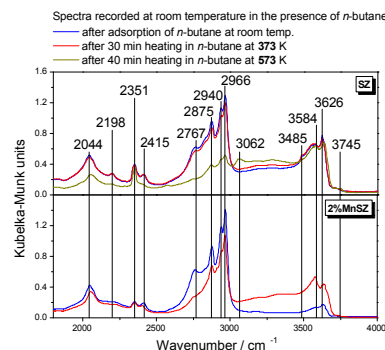
n-Butane as probe molecule

n-Butane forms H-bridges with the catalysts when adsorbed (ca. 10 mbar) at room temperature: Decrease of bridging OH groups at 3626 cm⁻¹ and new band at 3584 cm⁻¹.

SZ shows no changes after heating to 373 K.

For MnSZ already at 373 K water is formed (1593 cm⁻¹). The S=O vibration (2767 cm⁻¹) decreases.

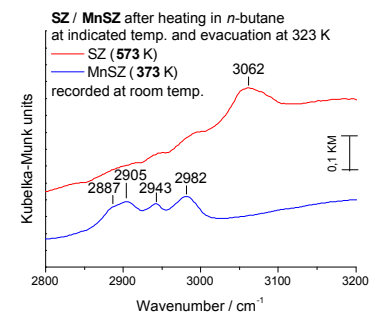
If SZ is heated to 573 K butane is decomposed: Decrease of the gasphase bands (2875 cm⁻¹, 2940 cm⁻¹, 2966 cm⁻¹), formation of CO₂ (2350 cm⁻¹) and alkene (3062 cm⁻¹). The sulfate bands decrease.



Upon evacuation at 323 K all bands of *n*-butane disappear from the spectra.

SZ shows hardly any CH stretching vibrations after evacuation.

For MnSZ bands become visible at 2887 cm⁻¹, 2905 cm⁻¹, 2943 cm⁻¹ and 2982 cm⁻¹. The bands of these surface alkyl species differ in position from the bands of *n*-butane.



Conclusions

Promotion of sulfated zirconia by Mn modifies the reactivity of the catalyst. The sulfate groups are more easily reduced on MnSZ (at 473 K by hydrogen, at 373 K by *n*-butane) than on SZ. Water is formed in the process. Alkyl groups (2887 cm⁻¹, 2905 cm⁻¹, 2943 cm⁻¹, 2982 cm⁻¹) remain on the surface of MnSZ after heating in *n*-butane at 373 K and evacuation.

The reduction seems to be different for hydrogen and *n*-butane: Using hydrogen all vibrations belonging to sulfur decrease in intensity, while this decrease is mainly constricted to the S=O group (2767 cm⁻¹) for *n*-butane.

At higher temperatures (573 K) oxidation and dehydrogenation of *n*-butane take place on SZ. CO₂ (2350 cm⁻¹) and alkenes (3062 cm⁻¹, =CH₂) are formed.

References

1. Hino, M., Kobayashi, S., Arata, K., *J. Am. Chem. Soc.* **101**, 6439 (1979).
2. Lange, F.C., Cheung, T.-K., Gates, B.C., *Catal. Lett.* **41**, 95 (1996).
3. Hahn A., Ressler T., Jentoft, R.E., Jentoft, F.C., *Chem. Comm.*, 537 (2001).
4. Kazansky, V.B., Borokov, V.Y., Serich, A., Karge, H.G., *J. Chem. Soc., Faraday Trans.*, **93**, 1843 (1997).
5. Kraus, W., Nolze, G., Federal Institute for Materials Research and Testing, Rudower Chaussee 5, 12489 Berlin, Germany.
6. Herzberg, G., Spectra of diatomic molecules, D. Van Nostrand Company, Inc., New York 1950, 2nd ed.
7. Wailes, P.C., Weigold, H., *J. Organomet. Chem.* **24**, 405 (1970).
8. Paukshtis, E.A., Kotsarenko, N.S., Shmachkova, V.P., *Catal. Lett.* **69**, 189 (2000).