Initiation of Alkane Isomerization on Sulfated Zirconia Catalysts Studied by In Situ X-ray Absorption, UV-vis and IR Spectroscopy

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Introduction

Sulfated zirconia (SZ) can activate short-chain alkanes for skeletal isomerization at room temperature [1]; addition of promoters such as Fe or Mn cations improves this ability [2,3]. First it was believed that the extraordinary activity of SZ materials arises from superacidic properties [1,2], but only strongly acidic sites could be discovered by probe molecule adsorption [4]. The promoters do not increase acidity and it was suggested that they initiate the isomerization by a redox process [5]: butene is thought to be formed via oxidative dehydrogenation (ODH) and is easily protonated; the resulting “carbenium ion” serves as an isomerization reaction chain carrier. However, butane conversion is obviously initiated also on unpromoted material, and therefore, alkane activation routes must exist for SZ.

We approach the question of reaction initiation in two ways: (i) the influence of inert or oxidizing activation conditions on SZ or Mn-promoted SZ was investigated, because for ODH an oxidized surface should be favorable, and (ii) during *n*-butane isomerization, the catalyst was checked for products of ODH, i.e. for water, for a reduced catalyst component (Mn, Zr, S) and for butenes or intermediates formed from it. All pretreatment and reaction steps were monitored in situ using complementary methods, namely X-ray absorption fine structure (XAFS), UV-vis, and diffuse reflectance Fourier transform IR (DRIFTS) spectroscopy.

Materials and Methods

Sulfated zirconium hydroxide (MEL Chemicals) was dried and calcined at 823 K to obtain SZ, or impregnated with up to 2 wt% Mn via the incipient wetness method and then calcined at 923 K [6]. Mn K edge spectra were recorded in fluorescence mode at Hamburg Synchrotron Radiation Laboratory beamline E4 using a fixed-bed reactor with on-line mass spectrometric analysis. UV-vis spectra were acquired with a Harrick Praying Mantis™ diffuse reflectance attachment DRA-4-PE7, a HVC-DR3 reaction chamber and a PerkinElmer lambda 9. For DRIFTS, a Graseby-Specac "Selector" attachment with environmental chamber was placed in a Bruker IFS 66. For IR and UV-vis experiments, reaction products were analyzed by on-line gas chromatography. Activation was performed at 703–773 K in inert or oxidizing atmosphere. Reactions were conducted at 323–378 K and 1–5 kPa *n*-butane.

Results and Discussion

DRIFT spectra show that during activation, SZ and Mn-promoted SZ are being dehydrated; it is estimated that more than 90% of the adsorbed water is removed. Comparison of SO single and double bond vibrations in the activated state with results from DFT calculations [7] suggests $S_2O_7^{2-}$ as predominant surface species. Spectra of Mn-promoted SZ after activation in N_2 or O_2 reveal slight differences in the OH band intensities. XAFS and UV-vis spectra indicate significant reduction of Mn (valence before activation 2.65) in inert and slight reduction in oxidizing atmosphere. The influence of the activation atmosphere was inconclusive with respect to the ODH question. Activation in the presence of O_2 (50 or 100%) often led to a higher maximum rate than activation in inert gas, and the maximum rate increased with the Mn valence in the activated state. However, for both SZ and Mn-promoted SZ, long activation times or high O_2 partial pressures sometimes had a negative effect.

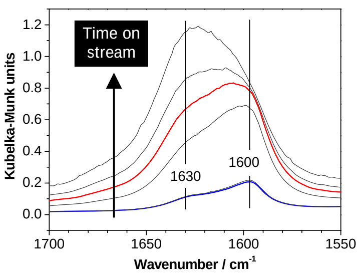

Figure 1: DRIFT spectra of 2% Mn-promoted SZ during isomerization at 323 K and 1 kPa *n*-butane.

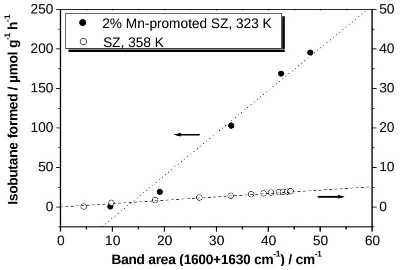

Figure 2: Rate of isomerization vs. intensity of bands in the range 1600–1630 cm^{-1}. Reaction conditions: 323 or 358 K, 1 kPa *n*-butane.

There was no evidence for reaction initiation by stoichiometric ODH via reduction of Mn, neither in the XAS nor in the UV-vis data. However, increasing intensity in the range 1600–1675 cm^{-1} in the DRIFT spectra (Fig. 1) is consistent with water formation during the initial phase of increasing activity (“induction period”) of the SZ catalysts. Especially a band at 1600 cm^{-1} grows during this period, as Fig. 1 and also the decomposition of the broad feature into individual Gauss curves demonstrate. During the induction period, the isomerization rate is proportional to the intensity of these bands (Fig. 2), supporting the idea of formation of chain carriers through ODH. It remains to be resolved whether S or Zr is reduced. Fig. 2 shows a much higher turnover per water molecule, i.e. per chain carrier for the Mn-promoted catalyst than for SZ. The main effect of Mn is thus not improved activation of the alkane but faster isomerization after reaction initiation.

Significance

For the first time, a combined catalytic and multi-method in situ spectroscopic study of sulfated zirconia catalysts during activation and *n*-butane isomerization is presented, and insight into the low temperature activation of alkanes is given.

References

1. Hino, M., Arata, K., *J. Am. Chem. Soc.* 101, 6439 (1979).
2. Hsu, C.-Y., Heimbuch, C.R., Armes, C.T., Gates, B.C., *Chem. Commun.* 1645 (1992).
3. Lange, F.C., Cheung, T.-K., Gates, B.C., *Catal. Lett.* 41, 95 (1996).
4. Adeeva, V., de Haan, J.W., Jänchen, J., Lei, G.D., Schünemann, V., van de Ven, L.J.M., Sachtler, W.M.H., van Santen, R.A., *J. Catal.* 151, 364 (1995).
5. Wan, K.T., Khouw, C.B., Davis, M.E., *J. Catal.* 158, 311 (1996).
6. Hahn, A., Ressler, T., Jentoft, R.E., Jentoft, F.C., *Chem. Commun.* 537 (2001).
7. Hofmann, A., Sauer, J., *J. Phys. Chem. B* 108, 14652 (2004).