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In Situ Spectroscopic Study of Isomerization of Light Alkanes over Sulfated Zirconia Catalysts

Abstract

In situ DRIFT and DR-UV/Vis spectroscopies were performed during *n*-butane (1 or 5 kPa partial pressure, 358 – 453 K) and *n*-pentane (1 kPa, 298 – 323 K) isomerization in the presence of two different sulfated zirconia catalysts: a sulfate containing ordered mesoporous zirconia of the MCM-41 structure and a conventional sulfated zirconia catalyst with a tetragonal zirconia bulk structure. After a 100 min induction period, the mesoporous zirconia deactivates slowly during *n*-butane isomerization at 453 K while an absorption band at 285 nm grows, indicating the formation of unsaturated surface species. The conventional catalyst which is more active and produces the same maximum rate already at 378 K deactivates rapidly and a band grows at 310 nm, indicating the formation of allylic carbocations on the surface. During *n*-pentane isomerization, both catalysts deactivate rapidly while bands at 285 and 310-320 nm (mesoporous) and 335 nm (conventional) are formed. The spectra clearly show that the surface species on the two catalysts differ, although in principle the same gas phase products are observed, indicating an influence of the underlying wall or tetragonal bulk structure, respectively.

Keywords: low temperature alkane isomerization, sulfated zirconia, in situ, DRIFTS, UV/Vis spectroscopy, *n*-butane, *n*-pentane, coke

Introduction

Sulfated zirconia (SZ) is a potentially interesting catalyst for isomerization of light alkanes because it is already active, e.g., for *n*-butane isomerization, at temperatures below 373 K [1]. However, the catalyst suffers from rapid deactivation. It is believed that the tetragonal crystalline ZrO₂ bulk of an SZ catalyst plays an important role in the isomerization activity [1]. Sulfate-containing ordered mesoporous zirconia of MCM-41 structure [2] can be considered as an SZ catalyst without the typical tetragonal ZrO₂ bulk of conventional SZ catalysts. Earlier we reported that the catalytic performance for *n*-butane isomerization of such a sulfated mesoporous zirconia differs significantly from that of a conventional SZ with a tetragonal bulk [3]. At 378 K and 1 kPa *n*-butane, the conventional SZ reached its maximum conversion

after an induction period of ca. 60 min and then deactivated until a "steady state" was reached after ca. 600 min. Sulfated mesoporous zirconia of the MCM-41 structure that was tested under the same reaction conditions did not display a conversion maximum at short time-on-stream; instead, the conversion rose very slowly and within 1000 min reached the same steady state level as conventional SZ. Comparing the structural difference and the different catalytic performance of these two types of sulfated zirconia catalysts prompted us to hypothesize that there are two groups of active sites, one is associated with the presence of the tetragonal zirconia phase and generates a short-lived high activity, the other, present on the surface of both catalysts, generates the long-term steady state activity. An alternative explanation for the different time-on-stream profiles arises from the higher maximum conversion that is achieved with conventional vs. mesoporous SZ under identical reaction conditions; a significant concentration of product on the surface, or a sufficient density of active sites may allow for secondary reactions which lead to deactivation by carbonaceous deposits. Further comparison of the two materials and particularly of their deactivation behavior under different reaction conditions should answer these questions and ultimately clarify the role of the tetragonal phase.

In situ IR and in situ electronic spectroscopy provide the possibility to monitor changes of the catalyst surface as well as the evolution of adsorbed species. These methods are thus suitable to detect not only reaction intermediates but also side products and thus species responsible for deactivation. In the present work, in situ DRIFT and DR-UV/Vis spectroscopies were performed during *n*-butane and *n*-pentane isomerization at various temperatures. The results obtained for ordered mesoporous SZ are compared to those obtained for a conventional SZ catalyst with a tetragonal crystalline zirconia bulk.

Experimental

Sulfate containing ordered mesoporous zirconia was synthesized according to a procedure from the literature [2,3]. A hydrogel prepared by mixing zirconium *n*-propoxide (70 wt% in 1-propanol, Fluka), hexadecyl-tri-methyl-ammonium chloride (CTAB, Aldrich), ammonium sulfate (Aldrich), 37 wt% HCl (Fluka), and water (Zr:S:CTAB = 2:2:1) was heated to 373 K under autogeneous pressure for three days. Solid products were then recovered by filtration, washed, dried, and calcined at

813 K for 960 min in air. For comparison, a conventional SZ catalyst with a typical tetragonal bulk was prepared by calcining sulfated zirconium hydroxide (MEL XZO 682/01) at 823 K in air for 180 min.

In situ DRIFT spectroscopy was carried out on a Bruker ifs 66 spectrometer with a spectroscopic resolution of 1 cm^{-1} . Powder samples (0.10 g of mesoporous SZ or 0.16 g of calcined XZO 682) were packed in the in situ cell (Graseby Specac), activated at 773 K in a flow of $50\text{ cm}^3/\text{min}$ N_2 , cooled down to reaction temperature (358 or 378 K), and fed with $30\text{ cm}^3/\text{min}$ of 1 vol% *n*-butane in N_2 . Spectra were taken using KBr under N_2 purging as a reference. Reaction products were analyzed by on-line gas chromatography using flame ionization detection [4].

The instrumentation of in situ DR-UV/Vis spectroscopy is described in detail in reference [5]. A modified Perkin-Elmer Lambda 9 spectrometer equipped with an integrating sphere and a microreactor cell (in-house design) has been used. The horizontally mounted micro-reactor consists of an inner tube with a circular frit near an end to accommodate the powder bed. The inner tube is enclosed by an outer tube, whose circular optical quartz window (Suprasil[®], Heraeus) holds the powder bed in place. The reactor is placed in a tubular oven with its window 12 mm from the integrating sphere; this distance is bridged by a ceramic tube of high reflectivity and low thermal conductivity (Macor[®], Kager). The temperature is measured with a thermocouple at the backside of the frit, i.e., upstream from the bed and towards the center of the oven. Powder samples (0.6 g of mesoporous SZ or 1.2 g of calcined XZO 682) were charged in the microreactor, activated for 90 min in He or O_2 flow at 723 K, cooled down to the reaction temperature (378 or 453 K for *n*-butane, 298, 323, or 378 K for *n*-pentane reaction), and fed with a $50\text{ cm}^3/\text{min}$ flow of 5 vol% *n*-butane or 1 vol% *n*-pentane in He at atmospheric pressure. Spectroscopic measurements were carried out sequentially in the range of 250-860 nm with a scan speed of $240\text{ nm}/\text{min}$, a slit width of 5.0 nm and a response time of 0.5 s. Spectralon[®] (SBS-99-010, Labsphere) was used as the white standard. The spectra are shown as difference spectra, i.e., $(R_{\text{SZ}}/R_{\text{Spectralon}}) - (R_{\text{SZ+alkane}}/R_{\text{Spectralon}})$. $R_{\text{SZ}}/R_{\text{Spectralon}}$ corresponds to the spectra of the activated catalysts in He atmosphere at the respective reaction temperature, and $R_{\text{SZ+alkane}}/R_{\text{Spectralon}}$ corresponds to the spectra under reaction conditions. Reaction products were analyzed by on-line gas chromatography using flame ionization detection.

Results and discussion

n-Butane isomerization

Figure 1 shows the evolution of DRIFT spectra under a feed flow of 30 cm³/min of a 1 vol% *n*-butane/N₂ mixture, the reaction temperature for the ordered mesoporous SZ was 378 K and for the conventional SZ was 358 K.

Under the specified conditions no *iso*-butane formation was measurable in the presence of the

ordered mesoporous SZ, while the conventional SZ has a stable production of 5 μmol h⁻¹ g_{cat}⁻¹ *iso*-butane after a 100 min induction period [4]. In spectra of the mesoporous SZ, the absorption band at around 1382 cm⁻¹, corresponding to stretching vibration of a sulfur oxygen bond with a bond order close to 2, shifts slowly to 1364 cm⁻¹ upon contact with the feed. The corresponding band in the spectra of the conventional SZ is narrower and located at slightly higher wavenumbers, i.e. 1403 cm⁻¹, and is subject to a shift to 1391 cm⁻¹ under reaction conditions [4]. The spectra indicate differences between the two materials in the surface sulfate structure after activation; the position of the band at higher wavenumbers indicates a somewhat higher bond order for the sulfur-oxygen bond for the conventional SZ. The behavior in the feed stream is similar, in both cases the sulfate structure is altered through an unknown adsorbate and the band shift can be interpreted as a decrease of the bond order of the discussed sulfur oxygen bond.

Figure 2a shows the rates of formation of various hydrocarbons in the presence of mesoporous SZ at 453 K in a 50 cm³/min flow of 5 vol% *n*-butane in He during the first 1000 min time-on-stream. A maximum conversion of *n*-butane was achieved at ca. 120 min time-on-stream, followed by gradual deactivation. The main product of *n*-butane conversion was the expected product of isomerization, viz., *iso*-butane. Propane and *iso*-pentane were observed in small concentrations as by-products, and are formed through the disproportionation of C₈ intermediates. The selectivity towards *iso*-butane decreased during the induction period to a level of ca. 98.8% at

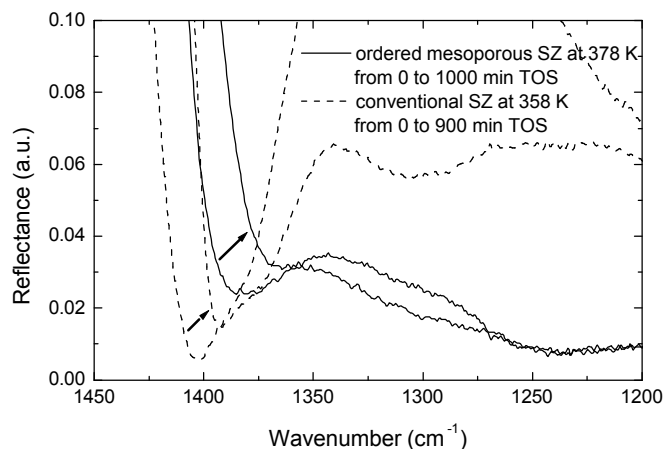


Figure 1: Evolution of DRIFT spectra of ordered mesoporous SZ at 378 K and conventional SZ at 358 K in 30 cm³/min of 1 vol% *n*-butane in N₂.

the conversion maximum, and then remained almost constant. Figure 2b shows an in-situ UV/Vis spectrum taken during the reaction corresponding to ca. 600 min time-on-stream, together with an in-situ spectrum taken from conventional SZ after the same time-on-stream though only at 378 K.

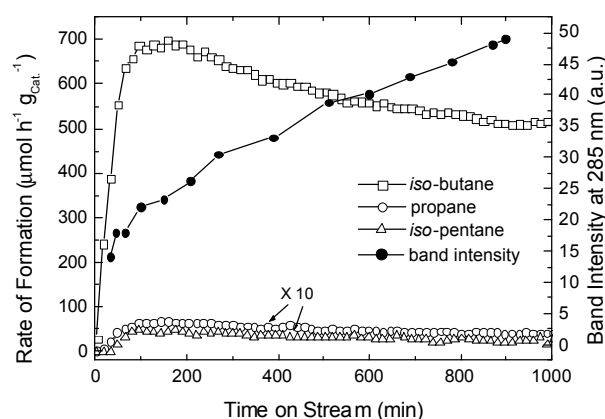


Figure 2a: Rates of product formation vs. time-on-stream during *n*-butane reaction in the presence of ordered mesoporous SZ at 453 K and $P_{n\text{-butane}} = 5$ kPa, $P_{\text{total}} = 1$ atm.

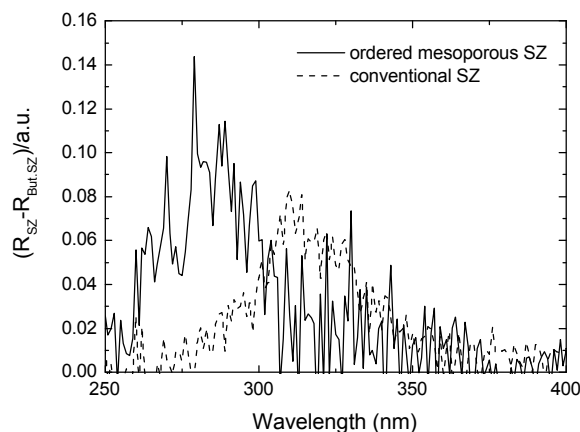


Figure 2b: In situ UV/Vis spectra recorded during *n*-butane isomerization in the presence of ordered mesoporous SZ at 453 K and conventional SZ at 378 K after ca. 600 min time-on-stream.

From Figures 2a and 2b it can be seen, that an absorption band centered at 285 nm emerges upon the introduction of *n*-butane to the mesoporous SZ and becomes more intense with increasing time-on-stream. The attribution of this band to a certain species cannot yet be achieved. The band falls within the range of absorption bands of cyclic allylic carbocations, e.g., the absorption of substituted cyclopentenyl cations has been reported at around 275-310 nm [6,7]. The band intensity (Figure 2a) increases from the beginning of the reaction and continues to increase throughout the induction and deactivation process.

The band position and the temporal evolution of its intensity are different from those observed with the conventional SZ as are the activity vs. time-on-stream profiles. At 378 K, the conventional SZ reaches the same maximum rate of *iso*-butane formation [8] as the mesoporous material at 423 K, i.e., ca. $700 \mu\text{mol h}^{-1} \text{g}_{\text{cat}}^{-1}$ at 120 min time-on-stream. The isomerization rate of the conventional SZ drops within 200 min to a “steady state” at a much lower level (ca. $50 \mu\text{mol h}^{-1} \text{g}_{\text{cat}}^{-1}$ isomerization rate) while it declines very slowly in the case of the mesoporous material (Figure 2a), being about 10 times higher than that of the conventional SZ after 1000 min on stream. Furthermore, the *iso*-butane selectivity of the conventional SZ is lower than that of

the mesoporous SZ: it never reaches 95%. At the equal maximum rates, the conversions differ, i.e., the maximum conversion in the presence of the conventional SZ is about twice as high as that of the mesoporous SZ. At longer times on stream the situation is reversed, and the mesoporous SZ displays higher conversion and higher selectivity towards *iso*-butane. In situ UV/Vis spectra of the conventional SZ show an absorption band at 310 nm developing during the deactivation procedure (Figure 2b), which can be attributed to allylic carbocations [9,10]. The intensity of the band reaches its maximum at a time when the catalyst has already passed through its maximum activity, and remains unchanged during the "steady state".

Although the same reaction pathways occur the nature of the surface species formed on the two materials is different, demonstrating that indeed the nature of the surface must be influenced by the "support", i.e., the crystalline tetragonal zirconia bulk or the wall structure of the mesoporous material. The interpretation of the evolution of these bands with the reaction profiles is less straightforward. For the mesoporous material, it appears that the band grows more or less linearly from the beginning, concomitant with a slow deactivation. For the conventional zirconia, it appears that the formation of a surface species becomes only significant at high conversions, which also means higher selectivity towards the side products. The formation of the species absorbing at 310 nm may thus be a result of secondary reactions that only become significant at a certain product molecule coverage. These observations are consistent with the presence of a group of highly active sites on the conventional tetragonal SZ, which, however, lead to rapid formation of an unsaturated surface species.

n-Pentane isomerization

In situ UV/Vis spectroscopy of *n*-pentane isomerization over the mesoporous SZ has been carried out at two different temperatures, i.e., 378 K and 323 K, both with a 50 cm³/min flow of 1 vol.% *n*-pentane in He. The reactivity of *n*-pentane is much higher than that of *n*-butane; and a different product distribution and an immediate, rapid deactivation of the catalyst were observed at 378 K. At a reaction temperature of 323 K, it is possible to observe an induction period, a maximum in the activity, and the establishment of a "steady state" (Figure 3a). Both activity vs. time-on-stream profiles look very similar to those obtained with conventional SZ [8], with an immediate loss of the high activity and with *iso*-butane, not *iso*-pentane, as the main product. Small quantities of propane and hexanes are found as by-products. A corresponding in situ

UV/Vis spectrum taken during *n*-pentane reaction at 323 K after 300 min time-on-stream is presented in Figure 3b, together with a spectrum obtained from the conventional SZ during *n*-pentane isomerization at 298 K. The selectivity towards *iso*-butane is higher than that towards *iso*-pentane for both materials, so in principle enough C4 species may be present to allow the formation of the same surface species as during *n*-butane isomerization.

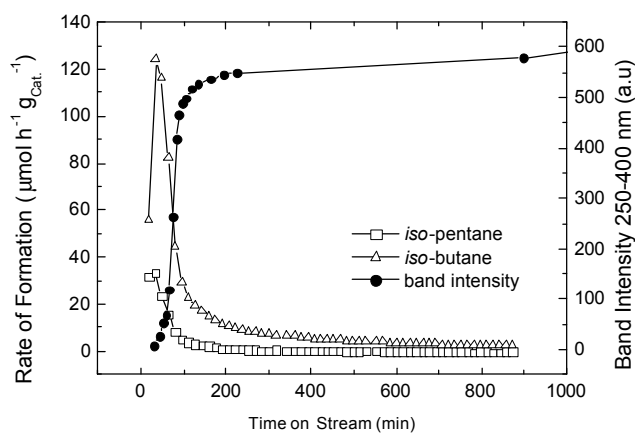


Figure 3a: Rates of product formation vs. time-on stream during *n*-pentane reaction in the presence of ordered mesoporous SZ at 323 K and $P_{n\text{-pentane}} = 10$ hPa, $P_{\text{total}} = 1$ atm.

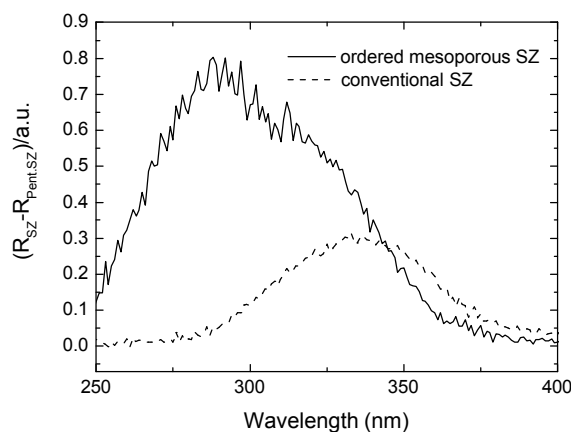


Figure 3b: In situ UV/Vis spectra recorded during *n*-pentane isomerization in the presence of ordered mesoporous SZ at 323 K and conventional SZ at 298 K after ca. 300 min time-on-stream.

Again it can be seen that the nature of the surface species on the two materials is different. On the surface of the mesoporous material, at least two different species are formed which absorb at ca. 285 and at 310-330 nm. The band observed for the conventional SZ is centered around 335 nm and the band width and shape suggest that there is also more than one species formed. A definite assignment of these bands is not possible; the species can only be classified as different types of allylic cations. The differences in the band positions that are observed for the two materials can either be explained by the formation of different structures as already discussed for the *n*-butane reaction, or, through differences in the charge of the species. The shift towards lower wavelengths (Figures 2b and 3b) of the absorption bands in the spectra of sulfated mesoporous zirconia with respect to those in the spectra of conventional SZ suggests an adsorbate with a lower positive charge, i.e., a species closer to an alkene than to an allylic cation.

The *n*-pentane reaction profile obtained with the mesoporous catalyst is not consistent with the hypothesis that there are some highly active sites only in the presence of the tetragonal bulk. A comparison of Figures 2a and 3a shows how the

band growth is correlated to the catalyst performance. Nevertheless, the nature of the surface species formed during reaction is different, demonstrating the influence of the bulk or wall structure, respectively.

Conclusions

More insight into the deactivation process of sulfated zirconia catalysts in alkane isomerization has been gained through a combined preparative and in situ spectroscopic approach. An ordered mesoporous sulfated zirconia of the MCM-41 structure was prepared and compared to conventional sulfated zirconia with a tetragonal zirconia bulk using in situ UV/Vis and DRIFT spectroscopies.

Different surface species were formed on the two different catalysts during *n*-butane reaction, they were characterized by bands at 285 (mesoporous SZ) and 310 nm (conventional SZ). The band at 310 nm is attributed to allylic cations. At low temperatures (≤ 453 K) the mesoporous SZ deactivated only slightly over 1000 min. Surface species formed during *n*-pentane reaction were characterized by bands at 285 + 320 nm (mesoporous) and 335 nm (conventional). Both catalysts deactivated rapidly (298-353 K). Under identical conditions, the conventional SZ reaches always a higher maximum conversion; the relation between conversion and rate of deactivation remains to be revealed. In situ DRIFT and UV/Vis spectra clearly show that the underlying structure – wall of the MCM-type material or tetragonal zirconia bulk – influences the sulfate configuration and the nature of carbonaceous deposits.

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