

Investigation of influence of Fe content in Fe-promoted zirconia: UV/Vis/near-IR spectroscopy and conversion of *n*-butane

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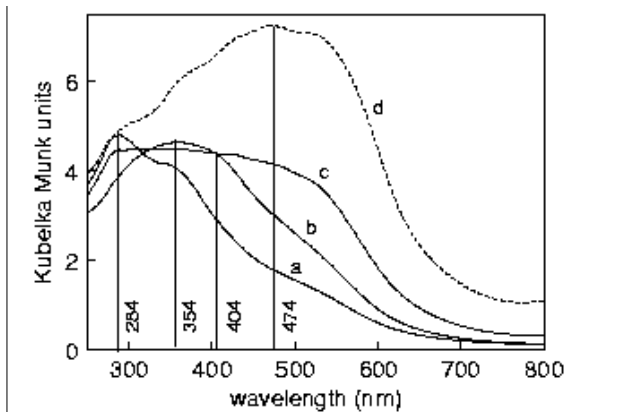
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The activity of sulfated zirconia (SZ) for *n*-butane isomerization can be promoted through the addition of Fe [1]. The nature of the promotional effect is unknown. It has been reported that the isomerization activity of SZ is enhanced in the presence of butenes in the feed [2]; and Fe-promoted zirconia (FeZ) is a catalyst for dehydrogenation, though at high temperatures, e.g. 1-butene is converted to butadiene at 873 K [3]. Our work focusses on the nature of the Fe species in FeZ and on the question whether butenes are produced by FeZ at low temperatures. FeZ was prepared from zirconium hydroxide (MEL Chemicals) and $\text{Fe}(\text{NO}_3)_3$ through the incipient wetness method and subsequent calcination at 923 K for 3 hrs. The samples (~ 1g) were transferred into a microreactor cell suitable for in situ UV/Vis/near-IR spectroscopy and activated in 30 ml/min O_2 for 1.5 h at 723 K. The feed for the reaction was a 50 ml/min flow of 5 vol-% *n*-butane in helium at $p = 1$ atm; analysis was performed by on-line GC (FID).

FeZ samples with Fe contents of 1, 2, and 5 wt% were all active for *n*-butane conversion. Products included small amounts of butenes at 523 K, suggesting that the formation of butenes may even be possible at temperatures below 523 K although the butenes may not desorb or be too few to detect.

UV/Vis-spectra taken after activation show a band at 290 nm that is attributed to ZrO_2 (figure). The ligand to metal charge transfer (LMCT) bands of the Fe species of the various FeZ catalysts differ considerably in shape and position. Evidently, the lower the Fe content, the more blue shifted the LMCT band. With increasing Fe content, the spectral features resemble more and more those of Fe_2O_3 .

Conclusions: Fe-promoted zirconia converts traces of *n*-butane into butenes at 423 K. This dehydrogenation function may also be active on Fe-promoted SZ and may contribute to the activation of *n*-butane for its conversion into isobutane.



UV/Vis spectra of ZrO_2 promoted with 1 (a), 2(b), 5(c) wt% Fe, and of pure Fe_2O_3 (d).

References

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3. L.A. Boot, PhD Thesis, Utrecht University, 1994.