An active and selective alkane isomerization catalyst: iron- and platinum-promoted tungstated zirconia

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Received (in Cambridge, UK) 12th December 2000, Accepted 16th January 2001
First published as an Advance Article on the web 31st January 2001

Addition of iron sulfate to Pt-promoted tungstated zirconia increases the activity and selectivity of the catalyst for isomerization of *n*-pentane in the presence of H_2; selectivities $>98\%$ have been observed.

Environmental concerns are motivating the use of motor fuels with increased amounts of high-octane-number branched alkanes. These are made by alkylation and by isomerization of straight-chain alkanes, the latter typically carried out with bifunctional catalysts incorporating hydrogenation/dehydrogenation functions and acidic functions or by very strong acids, such as aluminium chloride supported on alumina, which has the disadvantages of being corrosive and expensive to dispose of without environmental detriment. There is a need for alkane isomerization catalysts with improved activities and selectivities. Recently investigated candidates include tungstated zirconia (WZ), which has a high activity,[1,2] especially when promoted with Pt and when H_2 is contained in the feed.[3–5] The use of group 8 metals as promotors of WZ has been claimed in recent patents.[6–8] Fe has also been incorporated in WZ catalysts,[9] but promotion was not observed in the absence of Pt in the catalyst and H_2 in the feed. We now report WZ catalysts improved by promotion with both Pt and Fe and compare their performance with that of WZ promoted by Pt only.

Catalysts were prepared by slurry impregnation of amorphous $Zr(OH)_4$ (MEL Chemicals, XZO880/01) with aqueous ammonium metatungstate, $(NH_4)_6H_2W_{12}O_{40}\cdot nH_2O$ (Aldrich). In the synthesis of Fe-promoted catalysts, the appropriate amount of either $FeSO_4$ or $Fe(NO_3)_3$ was added to the slurry. The resultant suspensions were refluxed overnight at 393 K, dried in an oven at 353 K, and then calcined at 923 K in static air for 3 h. Separate batches of these calcined materials were impregnated by the incipient wetness method with 0.6 M aqueous $Pt(NH_4)(NO_3)_2$ and calcined at 723 K in air.

Each catalyst contained W in an amount corresponding to 17 wt% as WO_3, which is close to the theoretical monolayer capacity (19 wt%).[2] The Pt content was 1 wt%. The catalysts contained either no Fe (denoted as Pt/17WZ) or Fe in amounts corresponding to 1.0 wt% as Fe_2O_3; the latter are denoted as Fe/Pt/17WZ(N) and Fe/Pt/17WZ(S), prepared from iron nitrate or sulfate, respectively. The BET surface areas of Pt/17WZ, Fe/Pt/17WZ(N) and Fe/Pt/17WZ(S) were 126, 110 and 80 $m^2\ g^{-1}$, respectively.

Catalytic conversion of *n*-pentane was carried out in a once-through packed-bed flow reactor under the following conditions: temperature, 523 K; pressure, 101 kPa; *n*-pentane partial pressure, 0.84 kPa; H_2 partial pressure, 16.8 kPa; catalyst mass, 200 mg; feed flow rate (at NTP), 10 ml min^{-1} of 1% *n*-pentane in N_2 mixed with 2 ml min^{-1} of H_2. Under these conditions, the predominant catalytic reaction product was isopentane, formed with small amounts of methane, ethane, propane, butane, isobutane and neopentane. Catalysis was also carried out in the absence of H_2 under the same conditions, except that the feed *n*-pentane partial pressure was 0.84 kPa and the total flow rate was 10 ml min^{-1}. As the Pt precursor in the catalyst was observed to be reduced in H_2 to give zero-valent Pt even at room temperature, we infer that it was also reduced in the presence of the H_2-containing reactant mixture at 523 K during the initial stages.

The dependence of *n*-pentane conversion on time-on-stream (TOS) in the flow reactor is shown for the three catalysts in Fig. 1. Fe/Pt/17WZ(S) almost immediately attained a nearly stable activity corresponding to a conversion of *ca*. 64%. In contrast, induction periods of *ca.* 15 and 60 min were observed for Pt/17WZ and Fe/Pt/17WZ(N), respectively, before a nearly stable conversion of *ca*. 48% was attained. These activities are in the reverse order of the BET surface areas of the catalysts and show that the differences are associated with the catalyst compositions and not just physical properties.

The selectivities of the catalysts for isopentane formation measured during these experiments are shown in Fig. 2. The selectivity of Pt/17WZ dropped from *ca*. 97% to a stable value of *ca.* 95% after 1 h, whereas that of Fe/Pt/17WZ(N) reached a stable selectivity of *ca*. 99.7% after 30 min and that of Fe/Pt17WZ(S) approached 99% after 2.5 h. This small difference in selectivies may be caused by the higher conversion on the sulfate-containing catalyst. Thus, the data show that promotion by Fe enhances the catalytic activity of WZ for *n*-pentane conversion, with the iron sulfate providing a higher activity than iron nitrate but a somewhat lower selectivity.

The importance of H_2 in the reactant feed is emphasized. It was shown[9] that Fe had no promoting effect on WZ when H_2 was absent from the feed. Only 1% conversion of *n*-pentane and 30% selectivity for isopentane were measured under our conditions for the Fe- and Pt-promoted catalyst in the absence of

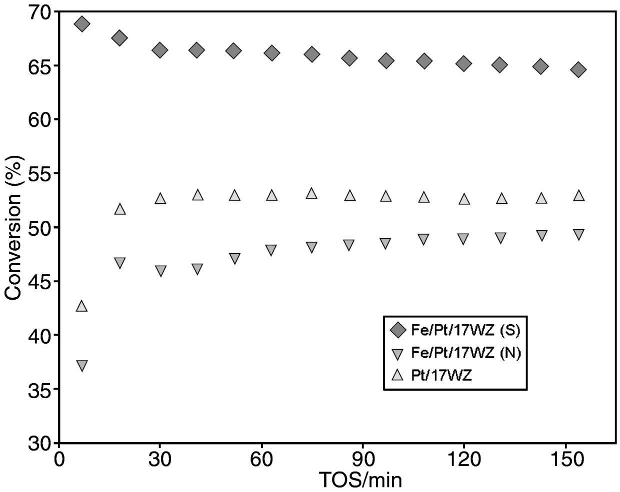

Fig. 1 Conversion of *n*-pentane catalyzed by Fe-promoted and Fe-free Pt/WZ catalysts in a flow reactor (conditions stated in text).

DOI: 10.1039/b009900g

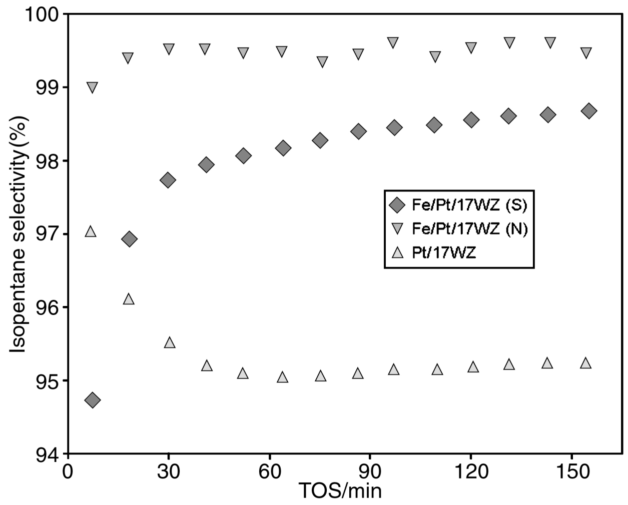

Fig. 2 Selectivity for isopentane formation of Fe-promoted and Fe-free Pt/WZ catalysts in a flow reactor (conditions as for Fig. 1).

H_2. It is therefore inferred that H_2 is essential for the optimal performance of this class of catalysts.

Sulfate is known to be strongly bonded to the zirconia surface,[10] and sulfated zirconia is itself a highly active catalyst for *n*-alkane conversions. The performance of sulfated zirconia is significantly improved by the addition of Fe and/or Pt promoters.[11] We therefore speculate that Fe/Pt17WZ(S) may incorporate surface sulfate and that Fe and sulfate may provide a cooperative promotion effect. Although the function of the Fe is at this juncture not entirely known, it is mechanistically deemed to prevent deep reduction of the tungsten by nascent hydrogen which is produced by Pt from the co-fed H_2. In this manner a redox equilibrium (steady state) is maintained on the catalyst surface which is responsible for the unusually good catalytic efficiency and stability of the Fe/Pt-WZ system.

In summary, we have shown that WZ catalysts promoted by both Fe and Pt exhibit high activity and selectivity for the conversion of *n*-pentane to isopentane. The observed performance indicates a significant improvement over known catalysts for *n*-pentane isomerization, and we suggest that the advantage may extend to other alkanes as well and be of practical value.

We thank F. Lai and A. Argo for their help. The international cooperation was made possible by financial support from the Alexander von Humboldt-Stiftung, the Max Planck-Gesellschaft and the BMBF (Max Planck-Research Award to H. K.). The work done in Munich was supported by the Deutsche Forschungsgemeinschaft (SFB338).

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