Catalysis Letters 47 (1997) 71–72

Skeletal isomerisation of 1-butene on 10-member ring zeolites or on 10-member ring silico–alumino-phosphate microporous materials

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Received 26 February 1997; accepted 23 May 1997

The study of the skeletal isomerization of 1-butene on 10-member ring zeolites or on 10-member ring silico–alumino-phosphate microporous materials has shown that the isobutene selectivity is correlated to the pore diameters, the solid exhibiting the highest pore constraint having the highest selectivity.

Keywords: butene isomerization, medium-pore zeolites

It is generally accepted that the location of active sites within the micropores is at the origin of high shape selectivity for zeolites or silico–alumino-phosphate catalysts.

Medium-pore materials such as zeolites or SAPOs have received a renewed interest because of their high selectivity for skeletal isomerisation of linear butenes [1,2] or of their use in hydroisomerisation of linear alkanes [3,4]. Recently, it has been shown that MTT and FER zeolites are much more selective for skeletal isomerisation of linear butenes than MFI catalysts, this being attributed to their narrow pore dimensions [5–7]; it was pointed out that MTT was less selective than FER despite the fact that the free diameter of the FER intersection is 0.4 Å larger than that of MTT [6], or that SAPO-11 was less selective than FER [7]. In order to clarify this apparent contradiction, we have reinvestigated the catalytic properties of FER and MTT zeolites and of medium pore SAPOs such as SAPO-11, SAPO-31, SAPO-41, for 1-butene isomerisation.

FER was obtained from TOSOH.USA, Inc.; MTT was prepared, as described in the literature [8]. SAPO-11, SAPO-31 and SAPO-41 were synthesised as described earlier [9]. All samples were used in their acid form, the zeolites being ion exchanged with ammonium chloride (1 M solution) three times and then calcined under a flow of oxygen up to 600°C. SAPOs were calcined first in a flow of N_2 and then in a flow of O_2 up to 600°C for 24 h. All samples exhibited high crystallinity as reported earlier [9]. The solids under study are 10-member ring zeolites or SAPOs having tubular non-intersecting pores except FER zeolite which exhibits cavities due to the intersection of 10-rings (5.4×4.2 Å) and 8-rings (4.8×3.5 Å). The pore sizes of the other solids are increasing from SAPO-11 (3.9×6.3 Å), MTT (4.5×5.2 Å), SAPO-41 (4.3×7 Å) and SAPO-31 (5.4×5.4 Å).

It is known from the literature [6] that the catalytic properties of the FER catalyst change with time on stream and that the formation of carbonaceous deposits on the catalyst is at the origin of an increase in the isobutene selectivity. To avoid the secondary effect of carbonaceous deposition within the pores on the selectivity in the skeletal isomerisation of linear butenes, only the initial catalytic properties measured on the "fresh samples" were considered. Initial catalytic properties were determined by using the bracketing technique:

The catalytic measurements were performed by using a dynamic flow microreactor: the reaction was performed for 2 min, reactants and products being analyzed by gas chromatography; after 2 min on stream, the reactor was flushed with nitrogen for 5 min and then oxygen (30 min) and again nitrogen (10 min) before the next experiment. Conversions were kept low by adjusting the contact time. Within these experimental conditions (low conversion, short time on stream, bracketing technique) the deactivation was minimized and results can be considered to be obtained on non-deactivated samples (see figure 1, open and black symbols).

In figure 1, the isobutene selectivity has been plotted as a function of the butene conversion. The first experimental point was obtained by using the highest WHSV and corresponds to the lowest conversion; then the other experimental points were obtained at increasing conversions. A final experimental point (open symbol) was obtained under experimental conditions identical to those used for having the first experimental point. The quite good reproducibility (first and last experimental points) indicates that due to the method used here (bracketing technique, low conversions) the catalytic properties of the different solids are not modified by the catalytic tests.

For all samples, it is observed that the isobutene selectivity is decreasing when the butene conversion is

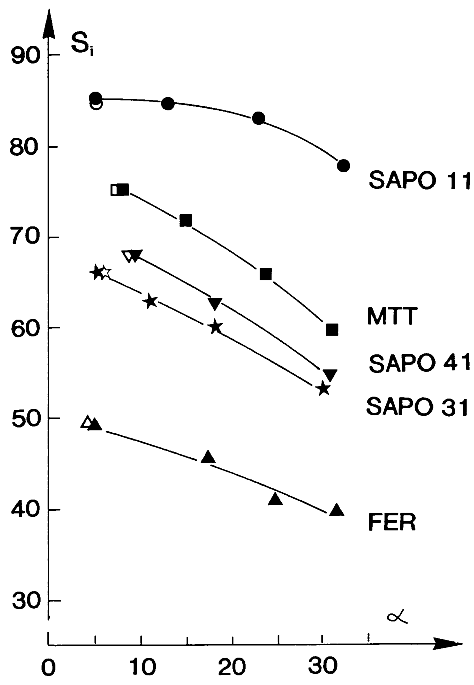

Figure 1. Transformation of 1-butene over different solids. $T = 673$ K, $P_{C_4H_8} = 26$ kPa, complement to atmospheric pressure nitrogen. Weight hour space velocity (WHSV) was varied from one sample to the other in order to have conversions in the range of 2–20%. Change in the isobutene selectivity [a] as a function of the conversion [b] for different solids. [a] Reactant is 1-butene. Selectivity (Si) on carbon basis, all linear butenes (1-butene, 2-cis- and 2-trans-butene) being considered as reactants. [b] Conversion (α) is defined as (C_{in}-C_{out}/C_{in}) $\times$ 100, with C_{in} number of mol. of 1-C_4H_8, $C_{out} = \sum$(1-C_4H_8 + 2-cis-C_4H_8 + 2-trans-C_4H_8).

increased, clearly indicating that the different solids have to be compared at the same conversion.

From figure 1, it appears that among the silico–aluminophosphate samples, SAPO-11 showed the highest isobutene selectivity and that the selectivity decreased in the order SAPO-11, SAPO-41, SAPO-31. Since it is known that the acid strengths of the three different SAPOs are almost identical [8], this classification indicates that the pore dimensions are crucial for isobutene selectivity. For SAPO-11 and SAPO-41 having elliptical pores, the smallest dimension governs the selectivity since both solids are more selective than SAPO-31, which has cylindrical pores (5.4 × 5.4 Å). As pointed out in a previous paper, the high isobutene selectivity is due to pore constraint which inhibits the transformation of *n*-butene via a bimolecular mechanism and favors its transformation via a monomolecular mechanism [10]. The results of figure 1 indicate that when the smallest pore dimension is changing from 3.9 Å (SAPO-11) to 5.4 Å (SAPO-31), the isobutene selectivity decreased from 85 to 66%, clearly indicating the very important effect of pore constraint on the selectivity towards isobutene formation. In a previous report it has been shown by using ^{13}C labelled butene that the bimolecular mechanism which involves a C_8^+ olefinic intermediate [10] followed by β-scission into either isobutene and *n*-butene or into C_3 and C_5 olefins is non-selective towards isobutene production, while the monomolecular mechanism which involves methylcyclopropyl ion is highly selective [10]. Thus our results on SAPO catalysts demonstrate clearly that, as the smallest pore diameter increases from 3.9 to 5.4 Å, the bimolecular mechanism becomes more important and, as a consequence, the selectivity towards isobutene decreases.

Comparison between SAPO-31 and zeolites having the MTT structure indicates that the solid having the lowest pore dimension is the most selective suggesting that the acid strength is not a major factor.

It can be speculated that ferrierite zeolite should be less selective than MTT zeolite due to the larger pore dimensions. The experimental results reported in figure 1 indicate that, as expected, FER zeolite is the least selective catalyst among the five different structures studied here. Thus, on non-coked materials, the isobutene selectivity is nicely correlated with the pore dimensions.

For aged solids, the order of classification is not the same, the FER sample being the most selective material, in particular for high conversions [6,7], this being attributed to the coke deposits which affect differently the different solids.

Acknowledgement

This research has been made possible by a grant obtained from Total Raffinage Distribution.

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