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Enhancement of the n-butane aromatization activity of ZSM-5 zeolite by incorporation of alpha-quartz *

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It is shown that pure alpha-quartz used as co-catalyst can enhance the aromatization activity of ZSM-5 zeolite.

Higher conversion of n-butane and higher production of aromatics and molecular hydrogen are obtained when higher amounts of quartz are embedded within the hybrid catalyst and when the particle size of quartz is smaller.

Keywords: Butane aromatization; hybrid catalyst; ZSM-5 zeolite; alpha-quartz as co-catalyst; hydrogen spillover concept

1. Introduction

Aromatics and particularly BTX aromatics (benzene, toluene, xylenes, ethylbenzene) can be produced from olefinic or paraffinic feedstocks [1–3]. The Cyclar process developed jointly by BP (catalyst) and UOP (regeneration technology) is now commercially available for the conversion of propane and butanes to aromatics [2]. The catalyst used is a gallium ZSM-5 zeolite and is prepared according to the classical bifunctional catalysis [4–9].

In our laboratory, it was observed that metal oxide species (ZnO or gallium oxide) did not require to be adjacent to the zeolite acid sites to be efficient as aromatization co-catalysts. Indeed, highly active and selective hybrid catalysts can be prepared by mechanical mixing of the two catalyst components and embedding in an inert clay matrix [10–13]. As a result, a hydrogen transfer mechanism called hydrogen back spillover (HBS) mechanism has been formu-

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lated [10–12]. With this concept, the hydrogen species which are released by the aromatization alkene or alkane molecules, diffuse through the zeolite pores and on rather large distances from the zeolite reaction loci to the co-catalyst surface [12]. The role of the co-catalyst may be to lower the barriers of potential energy which exist at the zeolite pore openings [14]. The resulting effect may be to ease the outward-diffusion of product molecules, particularly hydrogen. Recently, mobile Ga species with a degree of oxidation lower than 3, have been identified [15–17]. This raises the concern that the enhanced activity of our hybrid catalysts may be due to some kind of solid state ion exchange [18] or on-stream reduction (by the hydrogen evolved by the reaction itself) [15]. The latter effect which can also be obtained with pre-reduced Ga containing materials, may lead to a serious contamination of the zeolite internal surface by the volatile Ga species, therefore to higher aromatization activity as normally expected according to the bifunctional catalysis concept. However, the already high activity of the Ga oxide bearing hybrid catalyst when compared to the parent zeolite, observed at the very beginning of the reaction [18] and the enhancement of the aromatic production observed with pure silicas or aluminas used as co-catalysts [14], are indications that beside the improvement obtained by (in situ or as pretreatment) reduction of the Ga oxide, a more important improvement in the aromatization activity may be obtained by the use of the co-catalyst as proposed by the HBS concept [18]. This paper aims at providing additional experimental evidence of such a positive effect by using pure alpha-quartz as co-catalyst. Two parameters related to the quartz co-catalyst are investigated: its content in the hybrid catalyst and its granulometry (particle size).

2. Experimental

The ZSM-5 zeolite used in this work was synthesized according to the known method of Argauer and Landolt [19]. The zeolite acid form was prepared and characterized as described in ref. [10]. Its chemico-physical properties are reported in table 1. The final catalyst of the parent zeolite was obtained by

Table 1
Some physico-chemical characteristics of the zeolite and quartz particles used.

ZSM-5	Degree of crystallinity = 100%; Si/Al = 30, Na_2O = 0.2 wt%, APS (a) = 3 microns, BET = 436 m^2/g
Quartz A	APS (a) = 90 microns, BET = 0.7 m^2/g
Quartz B	APS (a) = 165 microns
Quartz C	APS (a) = 375 microns
Quartz D	APS (a) = 675 microns

(a) APS: average particle size.

extrusion with bentonite and subsequent drying and activation at 550°C as described elsewhere [10,11].

Crushed quartz (from Fisher) was first heated under reflux conditions in the presence of a HCl 2N solution for half an hour, washed thoroughly with distilled water, dried and finally activated in air at 750 ° C for several hours. The resulting material was sieved into different portions having average particles sizes ranging from 90 to 675 microns (1 micron $= 10^{-6}$ m). Hybrid catalysts which comprise the parent zeolite (acid, powder form, 80 wt%) and the quartz co-catalyst (13 wt% for the study on the granulometry and "*x*" wt% for the study on the content of the quartz particles with an average size of 90 microns), were obtained by mixing mechanically these two components and then extruding with bentonite clay (wt% = balance) in the presence of water as described in refs. [10,11]. The latter references also reported the drying and activation procedure of the catalyst extrudates. The experimental set-up for the catalytic testing was identical to that described in refs. [10,11,13]. The reaction parameters were as follows: temperature = 540°C, W.H.S.V. (weight hourly space velocity or g of injected n-butane per hour and per g of catalyst) $= 0.5\ \mathrm{h}^{-1}$, flow-rate of nitrogen (used as carrier gas) = 10 ml/mn, weight of catalyst = 4 g and duration of a run = 4 hours.

The testing procedure and product analysis techniques used were identical to those described in refs. [11,13].

In the following section, the total conversion of n-butane is defined as follows:

$$C_\mathrm{t}\ (\mathrm{C\ atom\%}) = \frac{(NC)_\mathrm{f} - (NC)_\mathrm{P}}{(NC)_\mathrm{f}} \times 100$$

where $(NC)_\mathrm{f}$ and $(NC)_\mathrm{P}$ are the numbers of C atoms of n-butane in the feed and in the reactor outstream, respectively.

The yield for product *i* is defined as follows:

$$Y_1\ (\mathrm{C\ atom\%}) = 100 \times (NC)_1/(NC)_\mathrm{f}$$

where $(NC)_1$ is the number of C atoms of product *i*.

The yield of molecular hydrogen, Y_{H_2}, is defined as the ratio of the number of moles of hydrogen produced to the number of C atoms of n-butane in the feed.

R_AH is the ratio of the aromatic yield (Y_Ar) to the hydrogen yield (Y_{H_2}), both expressed in %.

3. Results and discussion

Fig. 1 reports the total conversion of n-butane (C_t), the aromatic yield (Y_Ar) and the hydrogen yield (Y_{H_2}), as functions of the amount of the 90 micron-sized quartz (A) particles used as co-catalyst ("*x*") in the hybrid catalyst. As the result, the higher content of quartz, the higher the conversion of n-butane, and

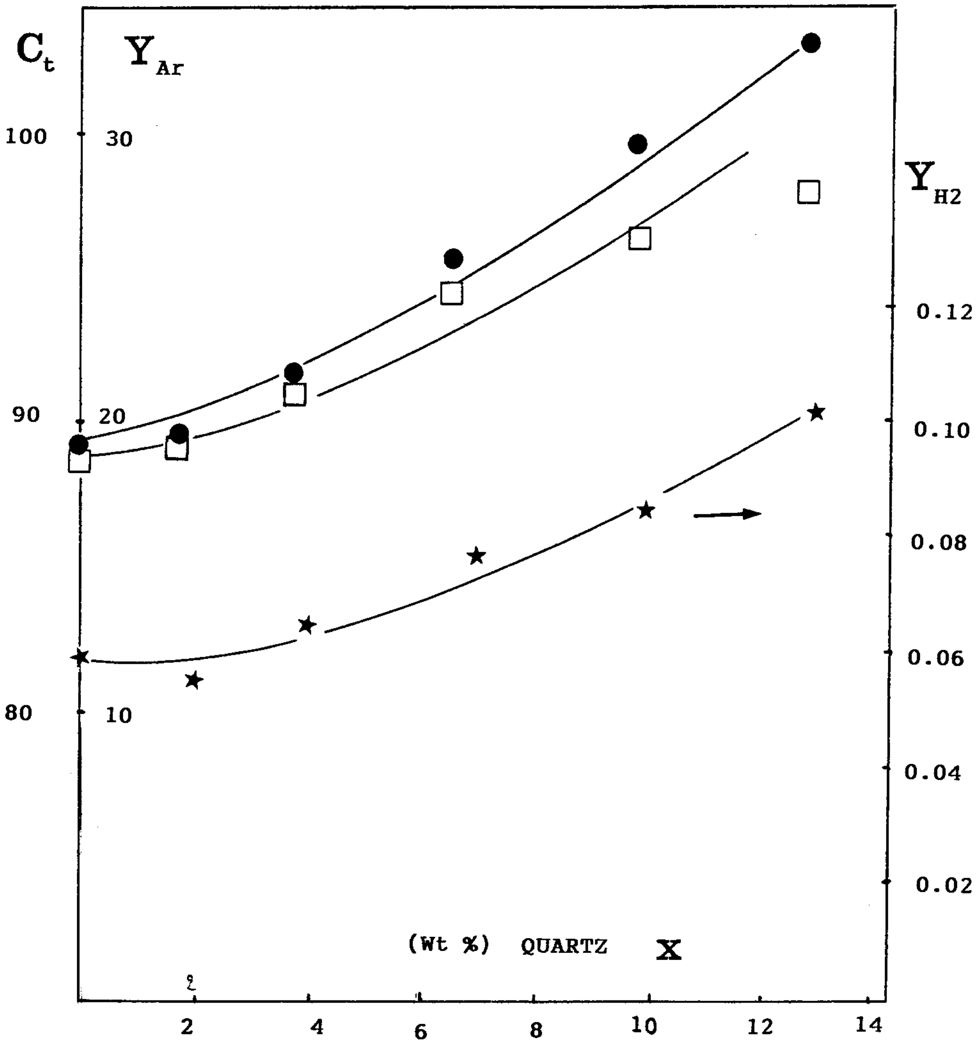

Fig. 1. Variations of C_t (– □ –), Y_{Ar} (– ● –) and Y_{H_2} (– * –) with "x", the quartz (A) content in the hybrid catalyst.

also the higher production of aromatics and hydrogen. The use of the same yield scale for C_t and Y_{Ar} allows us to see that all the increase in n-butane conversion goes to the production of aromatics (and hydrogen). On the other hand, fig. 2 shows that the ratio R_{AH} is practically constant when the quartz content in the hybrid catalyst increases. This means that hydrogen and aromatics are the only reaction products which are directly and simultaneously affected by the enhancement of activity due to the presence of quartz in the hybrid catalysts. Fig. 2 also shows the variations of the yield of C_1–C_3 products (Y_{1-3}) with the increasing quartz content in the hybrid catalysts. Let us assume that Y_{1-3} is a measure of the extent of the cracking reactions. Since it is said that n-butane

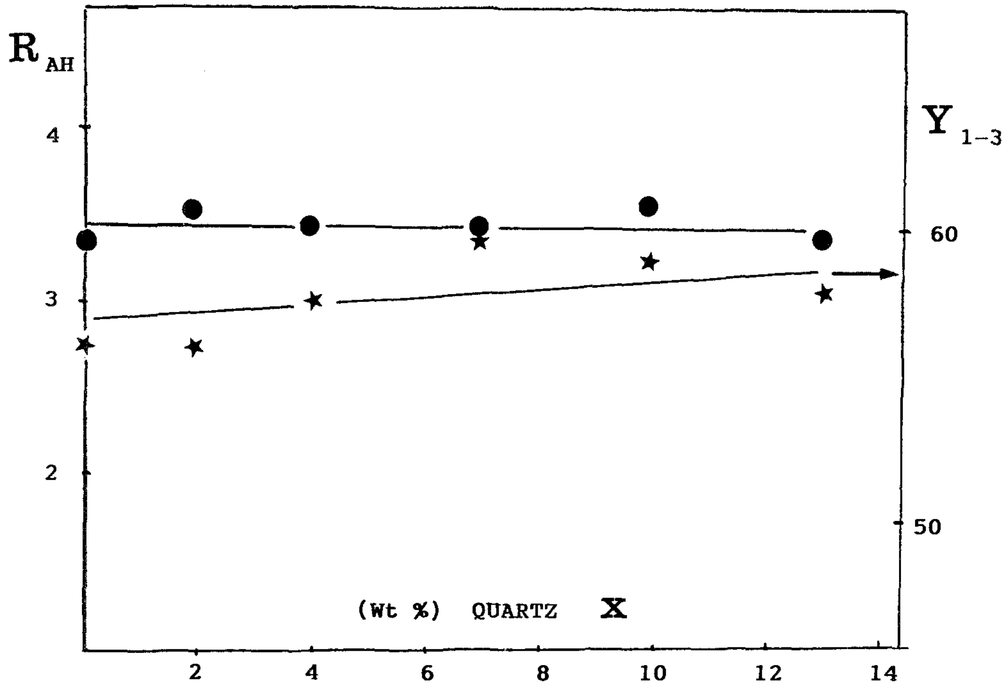

Fig. 2. Variations of R_{AH} (– ● –) and Y_{1-3} (– * –) with "x", the quartz (A) content in the hybrid catalyst.

can undergo two competing reactions onto the acid sites, i.e. cracking and hydride abstraction (the latter leading to olefinic species and then aromatics) [9], and there is practically no variation in the cracking products yield, we may state that reaction kinetics are not primarily involved in the observed phenomena.

Table 2 reports the values of C_t, Y_{Ar} and Y_{H_2} of hybrid catalysts prepared by using quartz particles with various sizes.

No large variation in catalytic properties is observed with the particle size of quartz. This is probably due to the narrow range of sizes used (from 90 to 675 microns, see table 1) which does not result in substantial variations in the area of the contact surface between such large quartz particles and the much smaller zeolite particles (3 microns). Nevertheless, the hybrid catalyst with the finest

Table 2
Influence of the size of the quartz particles on the activity of the resulting hybrid catalyst

	ZSM-5	+ quartz D	+ quartz C	+ quartz B	+ quartz A
C_t (a)	88.7	96.1	95.8	96.0	97.0
Y_{Ar} (a)	19.1	29.1	29.4	29.5	32.8
Y_{H_2} (b)	0.059	0.079	0.079	0.083	0.101

(a) C atom%.
(b) mole/C atom.

quartz particles clearly exhibits the highest n-butane conversion as well as the highest aromatic and hydrogen yields (table 2).

Possible role of quartz as heat transfer medium within the hybrid catalyst extrudates can be discarded for the following reasons:

(i) the percent weight of the ZSM-5 zeolite component is kept constant (80 wt%) either for the parent or for the hybrid catalysts. In the latter case, the amounts of quartz which is incorporated in lieu of the bentonite binder, ranging from 2 to 12 wt%, are rather small with respect to the zeolite mass.

(ii) the yields in aromatics and hydrogen are practically doubled when some Ga oxide is added to the quartz co-catalyst [13]. This is, of course, not related to any thermal phenomenon within the hybrid catalyst.

(iii) in addition, the activation energies measured with the parent and the hybrid catalyst are equal [14].

Quartz belongs to the category of materials defined by Bond as "irreducible" oxides which can exhibit some hydrogen spillover activity [20]. Our previous work on silicas and aluminas incorporated into the hybrid catalysts [13] confirmed the beneficial effects of such oxides. This work provides additional evidence to the concept of HBS: quartz particles, physically in contact with the zeolite particles, accelerate the removal of the hydrogen which is abundantly released by the zeolite acid sites during the aromatization reaction. This leads to a more rapid availability of the zeolite acid sites for adsorption of new n-butane molecules or reaction intermediate species. However, as pointed out in ref. [13], the surface area of the pure oxide used as co-catalyst, is not the only parameter involved in such HBS phenomena. The co-catalyst porosity, the nature and dispersion of the metal species eventually being incorporated on the co-catalyst surface, are elements to be considered in future works.

4. Conclusion

It is shown that pure alpha-quartz used as co-catalyst can significantly increase the aromatization activity of the ZSM-5 zeolite. At this stage of the research, it is rather difficult to give a definite explanation of this phenomenon. However, the HBS concept is getting stronger support since no contamination of the zeolite internal surface by any kind of metal species can be evoked as a possible cause of such an enhancement in the aromatization activity.

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