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AROMATIZATION OF n-BUTANE OVER NEW LD-HBS CATALYSTS. EFFECT OF THE GALLIUM OXIDE SUPPORT.

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It is shown that even "pure" quartz, other silicas or aluminas can enhance the aromatization activity of a ZSM-5 zeolite. Incorporation of gallium oxide onto these supports increases further the production of aromatics. The use of supported gallium oxide co-catalyst obtained by co-evaporation of a colloidal silica and a Ga salt has led to extremely high aromatization performance for the hybrid catalyst.

1. Introduction

Aromatics and particularly BTX aromatics (benzene, toluene, xylenes, ethylbenzene) can be produced from olefinic or paraffinic feedstock [1,3]. The so-called Cyclar process developed jointly by BP (catalyst) and UOP (regeneration technology) is about to be commercialized for the conversion of propane and butanes to aromatics [2]. The catalyst used is a gallium ZSM-5 zeolite. Such catalysts, which have been thoroughly investigated [4-9], the operating principles of which are closely related to the classical bifunctional catalysis, are usually prepared by wet impregnation of a gallium salt onto the acidic surface of the zeolite, or sometimes by ion-exchange.

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, by simply setting the zinc or galllium-bearing co-catalyst in physical contact with the zeolite particles, hybrid catalysts could be prepared which exhibited very high performance in the aromatization of light alkenes [10] and alkanes [11,12]. Therefore, a hydrogen transfer mechanism called hydrogen back spillover (HBS) mechanism has been formulated [10-12]. With this concept, the hydrogen species which are released by the aromatizing 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]. Several techniques of incorporation of Ga species at the external surface of the zeolite particles have been developed [13]. These include one which consists of mixing mechanically the two catalyst components and embedding them in an inert clay matrix. The co-catalyst can be supported Ga oxide or Ga/Al oxide coprecipitate [13]. Ga species can also be directly incorporated to the external surface of the zeolite particles by means of the dry impregnation technique also developed in our laboratory. Results from our previous work [13] implies that it is possible to vary heavily the co-catalyst formulation without losing any acquired advantages related to this component. This flexibility arises from the fact that the co-catalyst surface is located at a fairly large distance from the zeolite acid sites.

In the present paper, we offer further support for the demonstration of the Long-Distance Hydrogen Back Spillover (LD-HBS) concept by investigating the role played by the gallium oxide support in the co-catalyst component. Three aspects of the co-catalyst support will be particularly taken into consideration: texture (surface area and pore size distribution), surface acidity and nature of the surface.

2. Experimental

PREPARATION OF THE CATALYSTS

ZSM-5 zeolites with Si/Al atomic ratios ranging from 71 to 19, were synthesized according to the well-known method of Argauer and Landolt [14]. The acid forms of the zeolites (also called HZ (x), where x is the Si/Al atomic ratio) were prepared and characterized as described in ref. [13] (particularly, high degree of crystallinity and Na content around 0.2 wt%). Final catalysts of the parent zeolites were obtained by extrusion with bentonite and subsequent drying and activation at 550 °C as described elsewhere [10,13].

Hybrid catalysts which comprise a zeolite component (having the ZSM-5 structure, powder form, 80 wt%) and a co-catalyst component (silica, alumina or gallium oxide supported on one of these oxides, powder form, 13 wt%), were obtained by mixing mechanically these two powders and then extruding with bentonite clay (7 wt%) in the presence of water as described in ref. [10–13], which also reported the drying and activation procedure of the catalyst extrudates.

The silicas used in this work were: silica gel from Grace, silicalite from Linde, microporous silica (n-C7 aerogel) [15], solid powder obtained by evaporation of the Ludox colloidal silica (AS-40, from Dupont) and crushed quartz (quartz beads from Fisher). The aluminas tested were: activated aluminas (acid and basic, powders, from Strem Chem.) and activated alumina (neutral, 70–230 mesh, from Merck). Table 1 reports the textural properties of the various silicas and aluminas used as co-catalysts or co-catalyst supports. In particular, the pore size distribu-

Table 1
Texture properties of the silicas and aluminas used in this work

Silica	BET surface area (m^2/g)	Average pore size (Å)[1]	Pore size distribution (% based on adsorbed nitrogen volume)	
			Larger pores[2]	Smaller pores[3]
Silicalite (Linde)	404	28	<10	>90
Silica Aerogel (n-C7)	651	167	>99	<1
Silica gel (Grace)	580	28	>90	<10
From Ludox colloidal silica	99	124	>99	<1
Quartz	0.4	519	100	0
Acidic alumina	146	53	100	0
Basic alumina	171	52	100	0
Neutral alumina	133	65	100	0

[1] Pore diameter (in angstrom, Å or 10^{-10} m) by the BJH adsorption technique for larger pores only;
[2] between 17 Å and 3,000 Å;
[3] lower than 17 Å.

tion and the average pore diameter were determined by means of the BJH nitrogen adsorption technique [16] and using a Micromeretics ASAP Model nitrogen adsorption apparatus.

Ga was incorporated onto the surface of most solid supports by the conventional technique of impregnation of gallium nitrate (13 H_2O from Strem Chem.) in aqueous solution followed by drying at 120 °C for 12 hours and activating in air at 550 °C for 10 hours. The incorporation of Ga in ZSM-5 zeolite by the "Cyclar-like" impregnation/evaporation procedure was described elsewhere [13].

The preparation of the hybrid catalyst containing a gallium co-catalyst obtained by the technique of co-evaporation was carried out as follows. 2.34 g of gallium nitrate were dissolved in 5 ml of water. This solution was added to 4.5 g of Ludox colloidal silica and the resulting mixture was thoroughly stirred for a few minutes. Then the solution was gently evaporated to dryness on a hot plate.

The solid thus obtained was dried at 120 °C for 12 hours and activated in air at 550 °C for 10 hours.

The HZ (36) powder (80 weight %) and the gallium/silica solid (16 weight %) were intimately mixed at room temperature. Then, the solid mixture was extruded with bentonite (4 weight %) in the presence of water as described elsewhere [10–13].

CATALYTIC TESTING

The experimental set-up for the catalytic testing was identical to that described in refs. [11–13]. The reaction parameters were as follows: temperature = 540 °C, W.H.S.V. (weight hourly space velocity or g of injected paraffin per hour and per g of catalyst) = 0.5 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 was very similar to that described in refs. [11–13]. In particular, the liquid hydrocarbons formed by the catalytic reaction were collected in a flask kept at $-5\,^{\circ}\mathrm{C}$ while the gases were analyzed on-line using a Hewlett-Packard GC (Model 5790 A, FID) equipped with a 5 m long column packed with Chromosorb P coated with 20 wt% of Squalane connected in series with a 2.5 m long column packed with Carbopack C graphite modified with picric acid (0.19 wt%). The collected liquid phases were subsequently analyzed with the same GC system equipped this time with a 50 m PONA type capillary column.

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

$$C_t(\mathrm{C\ atom\%}) = \frac{(\mathrm{NC})_\mathrm{F} - (\mathrm{NC})_\mathrm{P}}{(\mathrm{NC})_\mathrm{F}} \times 100$$

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

The selectivity for product i is defined as follows:

$$\mathrm{S_i}\ (\mathrm{C\ atom\%}) = \frac{(\mathrm{NC})_\mathrm{i}}{(\mathrm{NC})_\mathrm{F} - (\mathrm{NC})_\mathrm{P}} \times 100$$

where $(\mathrm{NC})_\mathrm{i}$ is the number of C atoms of product i in the reactor outstream.

The yield of product i is defined as follows:

$$Y_\mathrm{i}(\mathrm{C\ atom\%}) = S_\mathrm{i} \times C_\mathrm{t} \times 1/100.$$

3. Results and discussion

The performance of the hybrid catalysts obtained by extruding the ZSM-5 zeolite (HZ (36)) with pure silica and alumina co-catalysts is given in table 2. It is worth mentioning that, although the ZSM-5 zeolite-type silicalite has some aluminum sites within its framework (Si/Al > 100), its aromatization activity per se is extremely low; for example, a ZSM-5 having a Si/Al atomic ratio of 71 exhibits an aromatic yield of 1.0 wt% [13]. Surprisingly, it was observed that although the texture of these silicas and aluminas is different from each other (table 1), they provided hybrid catalysts with significantly enhanced aromatizing performance. Even quartz gave an enhancement in the aromatic yield of the same order of magnitude as other silicas (or aluminas). We may tentatively explain these experimental results by assuming that the hydrogen species that diffuse out of the zeolite pores to the gaseous stream, have to face a certain potential energy barrier. Diffusional barriers on the external surface of zeolite crystallites are

Table 2
Catalytic performance of the hybrid catalysts containing (pure) silicas or aluminas as co-catalysts

Name of the hybrid catalyst	Co-catalyst	Total of n-butane (C atom %) C_t	Product selectivities (C atom %) S_i				BTX content (%)
			C_1-C_4 paraffins [1] (methane; propane)	C_2-C_4 Olefins	C_5^+ Non-arom.	Aro-matics	
HZ (36)	–	81.4	54.62 (5.66;30.56)	21.07	3.92	20.39	91.7
HZ (36)/Q	Quartz	96.7	55.07 (11.12;25.51)	14.19	1.15	29.59	90.0
HZ (36)/SI	Silica gel	94.7	52.78 (9.26;26.89)	12.59	1.39	33.24	90.9
HZ (36) Si-C7	Silica aerogel [15]	96.9	55.08 (10.98;27.31)	11.19	1.51	32.22	90.0
HZ (36)/Silic	Silicalite	96.0	54.48 (10.29;27.11)	12.17	1.46	31.89	89.4
HZ (36)/SiL	Ludox coll. silica	90.5	44.72 (7.20;22.56)	11.44	2.16	41.67	93.1
HZ (36)/Al (A)	Acidic alumina	97.3	53.70 (11.04;24.79)	12.07	0.90	33.33	89.8
HZ (36)/Al (B)	Basic alumina	97.7	55.15 (12.27;24.10)	12.38	0.70	31.77	88.6
HZ (36)/Al (N)	Neutral alumina	97.7	53.12 (11.63;23.57)	11.98	0.76	34.15	87.8

[1] n-butane not included

Table 3
Catalytic performance of the hybrid catalysts containing Ga oxide supported on silicas or aluminas, as co-catalysts

Name of the hybrid catalyst	Co-catalyst	Total conversion of n-butane (C-atom %) C_t	Product selectivities (C atom %) S_i				BTX content (%)
			C_1-C_4 paraffins[1] (methane; propane)	C_2-C_4 Olefins	C_5^+ Non-arom.	Aro-matics	
HZ (36)/Ga-SI	3 wt% Ga Oxide/Silica gel	96.9	38.98 (10.61;16.10)	6.85	0.89	53.28	87.6
HZ (36)/Ga-silic	3 wt% Ga Oxide/Silicalite	96.8	38.83 (10.01;16.65)	6.39	0.73	54.04	89.5
HZ (36)/Ga-Q	3 wt% Ga Oxide/Quartz	96.9	39.66 (10.00;16.12)	8.13	0.53	51.68	88.7
HZ (36)/Ga-SiL	3 wt% Ga Oxide/Ludox Coll. silica	98.7	29.93 (8.31;12.53)	4.39	0.55	65.14	87.3
HZ (36)/Ga(R, E)	3 wt% Ga Oxide (convent. impregnation) [13]	82.3	34.54 (9.29;15.88)	12.28	4.01	49.17	92.9
HZ (36)/Ga-Al(A)	3 wt% Ga Oxide/acid alum.	98.3	45.19 (10.99;16.81)	7.73	0.71	46.37	86.8
HZ (36)/Ga-Al(B)	3 wt% Ga Oxide/basic alum.	98.4	47.29 (11.93;17.96)	7.73	0.57	44.41	89.1
HZ (36)/Ga-Al(N)	3 wt% Ga Oxide/neutral alumina	98.1	47.84 (12.10;18.07)	7.92	0.47	43.77	87.7

[1] n-butane not included

under intense investigations by several researchers [17]. Thus, by providing a solid surface (regardless of its surface or texture properties) onto which these hydrogen species are transferred, the desorption of these species occurs in a more efficient way.

Nevertheless, the best hybrid catalyst was obtained with evaporated Ludox colloidal silica used as co-catalyst. Two aspects of the Ludox silica texture must be considered: the presence of pores having large size and a limited surface area. These textural features may be the factors which limit the cracking of products outcoming from the zeolite particles by increasing their rate of diffusion and restricting the area of the surface capable of readsorbing these molecules. In fact, the higher yield in aromatics is accompanied by a lower production of methane and propane, two cracking products of n-butane (see table 2).

However the difference in the contribution of the co-catalyst to the aromatization performance of the hybrid catalyst was greatly enhanced when gallium oxide was incorporated onto these silicas or aluminas. First of all, results obtained with hybrid catalysts prepared by mechanically mixing the ZSM-5 zeolite (HZ (36) sample) with gallium oxide supported on aluminas with various surface acidity, are reported in table 3 (last three rows). While the role of surface acidity of the same aluminas used as co-catalysts in the aromatization performance is not very clear (table 2), there is a clear favorable effect of such a surface acidity when aluminas are used as supports for the gallium oxide.

Table 3 also reports the aromatization performance of hybrid catalysts which had been prepared by combination of the ZSM-5 zeolite with co-catalysts of gallium oxide supported on various silicas as mentioned earlier.

For comparison purposes, the activity of the Ga bearing ZSM-5 zeolite catalyst prepared using a technique (conventional) similar to that developed for the Cyclar process is also reported. Results of table 3 also show that the presence of gallium oxide on silica supports enhances further the aromatization performance of the hybrid catalyst and consequently exalts the difference between the silicas and aluminas (silicas are better supports than aluminas) and among the silicas themselves. In particular, the hybrid catalyst obtained by combination of the ZSM-5 zeolite with the Ga oxide/Ludox colloidal silica coprecipitate exhibited the highest aromatization activity. The sample prepared according to the conventional bifunctional catalysis concept had the lowest performance. In all the cases, the cracking products (methane and propane) were produced in smaller amounts with respect to the hybrid catalysts without any gallium oxide.

Since it was hypothesized [9] that the first step in the reaction of n-butane over ZSM-5 zeolite acidic sites could be either an acidic cracking (production of methane and propylene) or a hydride transfer (our preferential reaction pathway to aromatics [12,13], it is worth reporting the ratio $RC = y_a/y_{\mathrm{Me}}$ which is the ratio of the yield in aromatics to that in methane (C atom basis). Table 4 shows at first a RC value which increases with decreasing zeolite Si/Al ratio (i.e. with increasing Bronsted acid site density which is related to the Al content of the

Table 4
RC values obtained with the hybrid catalysts tested

Hybrid catalyst Zeolite (Si/Al ratio)	 Co-catalyst	Y_a [1]	Y_{Me} [2]	*RC*
HZ (71)	–	0.97	1.66	0.58
HZ (42)	–	7.84	3.79	2.07
HZ (36)	–	16.59	4.61	3.60
HZ (19)	–	31.47	8.58	3.67
HZ (36)	3 wt% Ga oxide (conventional impregnation)	40.48	7.65	5.30
HZ (36)	Ludox colloidal silica	37.73	6.52	5.79
HZ (36)	3 wt% Ga oxide/Ludox colloidal silica	64.25	8.20	7.83

[1] Aromatic yield: Y_a.
[2] Methane yield: Y_{Me}.

zeolite framework [13]). This is in agreement with the conclusion of Ono et al. [9] who assumed that over the ZSM-5 zeolite catalyst, the hydride abstraction mechanism is favored at high conversion level. Although the nature of adsorbed (and spilt-over) hydrogen species on silica surfaces is a matter of debate [18], we believe that since hydrogen is released in rather high amount in the aromatization reaction which is carried out at relatively high temperature within our zeolite catalysts, the rate of hydrogen removal is of paramount importance and this may condition the reaction pathway followed by the reactant molecules (cracking or aromatization, see tables 2,3).

The introduction of Ga species contributes to sharply increase the *RC* value. With the conventional catalysts, the presence of gallium oxide (sample HZ(36)/Ga(R, E), ref. [13]) led readily to higher values of *RC*. This tendency was reinforced when more powerful LD-HBS action was exerted (see last rows of table 4). The presence of a significant amount of hydrogen released by the aromatization (mostly at high conversion to aromatics) could induce some hydrocracking and therefore more methane could be produced. This would decrease the *RC* ratio. However, as shown by table 4, the increasing trend of the *RC* ratio does not seem to be significantly affected by such a hydrocracking activity. This suggests that the hydrogen spillover action is much stronger than any eventual hydrocracking effect.

In order to see if Ga species present in the co-catalyst could be incorporated into the zeolite framework by a kind of solid state ion-exchange or vaporization [19], several tests were carried out. ZSM-5 particles [HZ(36)] were at first intimately mixed with Ga oxide/Ludox silica (coarse) particles and loaded into the reactor. n-butane was then fed to the system for more than 10 hours under the same conditions as for a normal catalytic run. After such a "reaction simulation" treatment the zeolite particles were carefully separated from the Ga oxide particles (such an operation was possible, owing to the difference in size of the two kinds of particles). It was observed that the resulting ZSM-5 zeolite exhibited an aromatizing activity which was not different from that of an untreated ZSM-5 zeolite sample. Therefore the notion of "contamination" of the zeolite internal surface, where the aromatization sites are thought to be located, by some Ga species from the co-catalyst may be discounted.

4. Conclusion

We report the surprising effects of the metal oxide support in the aromatization of n-butane. It was observed that the mere presence of alumina or silica (including quartz) as co-catalyst, regardless to their surface acidity, texture or nature, is sufficient to enhance the production of aromatics. Further increase in the aromatic yield, which was accompanied by an exaltation of the differences in the surface properties between the tested solid supports, was obtained when gallium oxide was incorporated onto the alumina or silica. This shows the effects of the interactions of gallium oxide with the support surface on the action of hydrogen removal by the co-catalyst. Co-catalysts prepared by evaporation of a suspension containing the Ludox colloidal silica and an aqueous solution of gallium nitrate, exhibited the highest aromatization performance.

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