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Hybrid catalysts containing zeolite ZSM-5 and supported gallium oxide in the aromatization of *n*-butane

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Abstract

It is shown that in the aromatization of *n*-butane, hybrid catalysts containing irreducible oxides (silica and alumina) as co-catalysts provide aromatic yields which are almost twice that obtained with "pure" zeolite ZSM-5 zeolite. The interpretation of these results is based on the hydrogen back spillover concept. The addition of Ga_2O_3 to these co-catalysts enhances further the aromatizing performance of the hybrid catalysts. It is believed that such an additional improvement is due to the gallium species located in the interface between the two types of particles, and the Ga containing regions of the zeolite crystallites near the pore openings. This contamination results from the transfer of some partially reduced gallium oxide from the co-catalyst surface to the zeolite pores. In such a case, it is probable that the reaction is governed by the conventional bifunctional catalysis mechanism. These gallium oxide sites appear more active than the normal ones because of their location near the zeolite pore openings which enables them to react with both inward- and outward-diffusing molecules.

Keywords: Hybrid catalysts; Low alkane aromatization; ZSM-5 zeolite; Supported gallium oxide as co-catalyst; Hydrogen back spillover; Bifunctional catalysis; Joint HBS/bifunctional hypothesis

1. Introduction

Production of aromatics from light alkanes and alkenes is one of the most studied reactions of the last two decades, particularly since the development of the commercial Cyclar process [1]. Many patents and papers have been published and the many recent review articles [2–4] are an indication of the importance of this reaction.

As has been extensively discussed, it is unquestionable that gallium species are capable of significantly enhancing the production of aromatics, although substantial amounts can be formed on the acid form of the "pure" zeolite ZSM-5 [4,5]. Controversy has however arisen with reports supporting the hydrogen spillover phenomena over gallium and other metal sites [6–13], particularly with the hybrid catalyst configuration [8–11,14–19]. In this case, the explanation of long-distance effects is seen as a serious deviation from the classical scheme of

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bifunctional catalysis [3,4,9,14–16]. Massive migration of the gallium species during the catalyst preparation/activation or testing under reducing atmosphere, is the principal argument of several researchers against the data interpretation based on hydrogen spillover. In fact, high temperatures are used for the reaction which may force in some occasions the partially reduced gallium component of various non-(or non-fully) incorporated catalyst systems, to migrate onto the internal surface of the zeolite particles. These include: hybrid catalysts or synthetic gallo-aluminosilicates as opposed to gallium impregnated zeolite catalysts.

The aim of this paper is to show that the hybrid catalyst configuration results in a catalytic behavior in the conversion of *n*-butane which can be explained both by the back-hydrogen spillover (HBS) and the conventional bifunctional catalysis concepts.

2. Experimental

2.1. Preparation and characterization of the zeolite ZSM-5

The zeolite ZSM-5 with a Si/Al atom ratio of 36 was synthesized, converted to the acid form (called hereafter HZ) and characterized as reported in [10].

2.2. Preparation of Ga_2O_3 and the irreducible oxides

Ga_2O_3 was obtained by calcining gallium nitrate (13 H_2O from Strem Chemicals) overnight at 550°C.

The irreducible oxides used in this work were: LuSi = solid powder obtained by evaporation of the Ludox colloidal silica (AS-40, from Dupont); Qu = crushed quartz (from Fisher) obtained by first heating the solid under reflux conditions in the presence of a HCl 2 N solution for 30 min, washing thoroughly with distilled water, drying and finally activating in air at 750°C for several hours; Al = activated alumina, acid, powder form purchased from Strem Chemicals.

2.3. Preparation of the supported gallium oxide co-catalysts

(Ga/LuSi) = 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 h and activated in air at 550°C for 10 h.

(Ga/Qu and Ga/Al) = Gallium nitrate hydrate in aqueous solution was first impregnated onto the solid support and then decomposed into gallium oxide at 550°C in air overnight (gallium oxide content = 18.8 wt%).

2.4. Preparation of the Ga "contaminated" zeolites

In order to study the phenomena of surface-contact transfer of gallium from the Ga/LuSi co-catalyst into the zeolite ZSM-5 (HZ) particles, two "contaminated" zeolites were prepared according to the following procedure [20,21]. The previously obtained (Ga/LuSi) co-catalyst aggregates were intimately mixed with the micron-sized zeolite crystallites as follows:

CONTA 1 = 20 wt% of co-catalyst + 80 wt% of zeolite, almost the same proportion as in the HZ//(Ga/LuSi) hybrid catalyst.

CONTA 2 = 80 wt% of co-catalyst + 20 wt% of zeolite.

The solid mixture was heated in a quartz reactor in the presence of hydrogen (flow rate: 17.5 ml/min) at 540°C for 3 h. The contaminated zeolite particles were recovered by sieving. The content of Ga_2O_3 determined by atomic absorption, was as follows:

CONTA 1 = 0.12 wt% and CONTA 2 = 0.60 wt%

2.5. Preparation of the Ga bearing zeolite ZSM-5 by conventional impregnation method

Ga was incorporated in zeolite ZSM-5 (HZ) by the "Cyclar-like" impregnation/evaporation procedure described in [10]. Two samples were prepared with the following Ga_2O_3 loadings:

CONV 1 = 1.0 wt% and CONV 2 = 2.5 wt%

2.6. Characterization of the Ga_2O_3, the irreducible oxides, the supported gallium co-catalysts and the Ga "contaminated" zeolite

The solids were characterized by various techniques [8–11,14–20] including the following: atomic absorption spectroscopy, X-ray diffraction, nitrogen and argon adsorption, scanning electron microscopy equipped with an energy dispersive X-ray analysis microprobe (EDAX), X-ray photoelectron spectroscopy (XPS) and differential thermal and gravimetric analysis (DTA-TGA).

2.7. Preparation of the final catalysts

HZ, Ga/LuSi, CONV 1, CONV 2, CONTA 1 and CONTA 2 = the corresponding powder (80 wt%) and bentonite clay (Anachemia, laboratory grade, 20 wt%) were mechanically and intimately mixed. Water was added dropwise until a malleable paste was obtained. This paste was extruded into 1 mm o.d. "spaghetti". The final extrudates were dried at 120°C for several hours and activated in air at 550°C for about 10 h.

HZ//Ga_2O_3 = extrusion of the mechanical mixture of HZ (80 wt%) and Ga_2O_3 (13 wt%) powders with bentonite (7 wt%), and then activation as previously described. The final hybrid catalyst contained 13 wt% of Ga_2O_3.

HZ//Qu, HZ//LuSi, HZ//Al, HZ//(Ga/Qu), HZ//(Ga/LuSi) and HZ//(Ga/Al) = extrusion of the mechanical mixture of HZ (80 wt%) and oxide or supported Ga oxide co-catalyst (16 wt%), and then activation as previously described. The last three final hybrid catalysts contained 3 wt% of Ga_2O_3.

2.8. Catalytic testing

The experimental set-up for the catalytic testing with *n*-butane was identical to that described in [8] and [16]. The reaction parameters were as follows: temperature = 540°C, WHSV (weight hourly space velocity or g of injected *n*-butane per hour and per g of catalyst) = 0.5 h^{-1}, flow-rate of nitrogen (used as carrier gas) = 10 ml/min, weight of catalyst = 4 g and duration of a run = 3.5 h. The quartz reactor had the following dimensions: i.d. = 2.0 cm, o.d. = 2.4 cm, length of the catalyst bed = 2.5 cm.

The procedures for catalyst testing and analysis of products were very similar to those described in [10] and [16].

The total conversion of *n*-butane, C_t, is calculated as follows: C_t(C atom%) = 100. $[(NC)_f - (NC)_p]/(NC)_f$, where $(NC)_f$ and $(NC)_p$ are the numbers of carbon atoms of *n*-butane in the feed and in the reactor outstream, respectively.

The selectivity (S_i) and yield (Y_i) in product hydrocarbon (i) are defined as follows: S_i(C atom%) = 100. $(NC)_i/[(NC)_f - (NC)_p]$, and Y_i(C atom%) = $S_i \times C_t \times 1/100$, where $(NC)_i$ is the number of carbon atoms of hydrocarbon (i) in the reactor outstream.

3. Results and discussion

3.1. The hybrid catalyst configuration and the proposed hydrogen back spillover concept

The effects of binders or physical diluents (solids) on zeolite materials used as catalysts in number of reactions are well-known [22,23]. However, most of these studies were phenomenological descriptions of the results obtained, particularly regarding the beneficial effect of an "active matrix" (i.e. capable of converting reactant or product molecules desorbing from the zeolite active sites) [22] on the overall catalyst performance or of the binder on the catalyst stability [23]. Inui [7], Fujimoto et al. [6], and Le Van Mao et al. [8–11], showed that, specifically in the aromatization of low alkenes and alkanes, there was a more abundant transfer of product hydrogen from the zeolite particles to the co-catalyst aggregates: such a concept was named reverse hydrogen spillover [6] or back-hydrogen spillover (HBS) [8–11]. According to the conventional bifunctional catalysis mechanism, *n*-alkanes (propane, *n*-butane or LPG) are converted to aromatics on a catalytic surface which contains acid sites adjacent to the metal (gallium oxide) sites. The reactant molecules undergo first dehydrogenation over the Ga sites. The resulting olefinic molecules are adsorbed on the protonic acid site providing a carbenium ion species. Then, through a well-known sequence of reaction steps (oligomerization, cyclization/rearrangement), a cyclic carbenium ion is formed. Aromatization occurs by means of a hydrogen transfer between the aromatizing species and a new carbenium ion. The naphthenic intermediates can also be dehydrogenated to aromatics by dehydrogenating Ga sites, with thus some hydrogen produced. Guisnet and co-workers [24,25] and Meriaudeau and Naccache [26] are unconditional supporters of this mechanism, showing in many occasions that metal species participate in the reaction of alkane activation, catalyzing its dehydrogenation to the corresponding olefin [4]. It is worth mentioning that catalysts working in accordance with such a mechanism are usually obtained by incorporation of Ga species into the zeolite ZSM-5 using the ion-exchange or impregnation technique, followed by an activation in air at high temperatures. The reaction is carried out at 1 bar pressure and at a temperature in the 450–550°C range. Liquid products (commercial Cyclar process) contain about 95% BTX aromatics (benzene, toluene, xylenes) which represent up to 66 wt% or 63 wt% if the charge is *n*-butane or propane. The production of hydrogen ranges from 5.2 to 5.9 wt% [4].

Hybrid catalysts are obtained by combining two powder components: zeolite ZSM-5 (protonic acid form) and co-catalyst particles. In Table 1 are reported the chemical and physical properties of the zeolite ZSM-5 used as main component and various irreducible oxides used as co-catalysts in our investigations. It is worth noting that the hybrid catalyst configuration is quite different from that of a mere mechanical mixture of two powders, as follows:

(i) The relative positions of the two components of a hybrid catalyst must be definitely fixed by extrusion with an inert binder [8–11,14–19]. Any change in the respective positions of these component particles, mostly when the co-catalyst is a supported Ga, may result in different catalytic properties.

(ii) The pressure exerted during the extrusion (to produce the final catalyst spaghetti) allows the maximization of the surface of contact between the zeolite particles and the co-catalyst aggregates (Fig. 1).

The HBS concept was proposed after careful consideration of the catalytic results obtained

Table 1
Some physical and chemical properties of zeolite ZSM-5, Ga_2O_3 and various irreducible oxides, used as main catalyst component, co-catalyst or co-catalyst supports, respectively

	Si/Al [a]	BET surface area (m^2/g)	Average pore size (10^{-9} m)	Particle size range (10^{-6} m)
ZSM-5 (HZ)	36	408	0.56	1–3
Ga_2O_3		61	12.1	50–150
Quartz (Qu)		0.4	51.9	150–300
Ludox silica (LuSi)		105	12.5	100–350
Alumina (Al)	0	146	5.3	70–200

[a] Atom ratio.

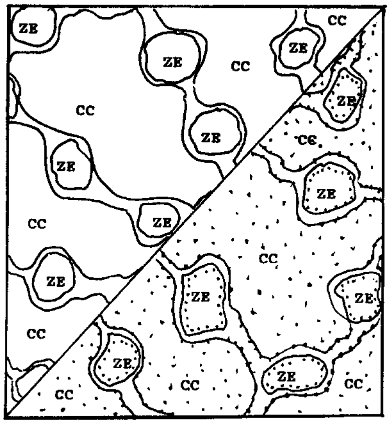

Fig. 1. Schematic representation of the "zeolite/co-catalyst" interface in the hybrid catalyst: (upper) = irreducible oxide as co-catalyst; (lower) = supported gallium oxide as co-catalyst (hybrid catalyst at equilibrium). ZE = microporous zeolite crystallites; CC = mesoporous co-catalyst particles; stippled zones = zones containing or contaminated with Ga species.

with several hybrid catalysts [8–11,14–21]. The first experimental evidence of HBS is shown in Table 2 which reports the catalytic activity of the hybrid catalysts prepared from these irreducible oxides. In fact, the incorporation of only a few wt% of these materials significantly increases the conversion and doubles the aromatic yield. Since no metal oxide with redox properties is involved, it is believed that the presence of the co-catalyst results in some positive physical action. Since the main function of this chemically "inert" co-catalyst is to adsorb and/or desorb reactant or product molecules, the hydrogen back spillover concept was primarily devised based on such a removal role of the reaction products (sink effect of the co-catalyst), particularly hydrogen [8–11,14–19]. Indeed, higher hydrogen out-diffusion from the ZSM-5 channels and a significant decrease in the production of alkenes and C_5^+ aliphatics were also observed in the aromatization of *n*-butane, propane and ethylene [15,16,19]. More recent studies of these transfer phenomena [14,15,17] resulted in a more general view that the HBS concept should be extended to all the reaction products, particularly the coke precursors [14,15,27]. In fact, the evacuation action of the co-catalyst should be also effective with respect to heavy aromatic products (C_9^+) which were trapped inside the zeolite pores when this material was used alone [15,16,27]. In a detailed study about the enhancement of the ethylene aromatization and the coking on "pure" ZSM-5 zeolite and hybrid catalysts containing ZnO or supported ZnO as co-catalyst, it was seen that ([15] pp. 190–196 and [27]):

Table 2
Catalytic activity of the reference zeolite ZSM-5 and hybrid catalysts containing irreducible oxides as co-catalysts

Catalyst	HZ	HZ//Qu	HZ//LuSi	HZ//Al
Conversion, C_t	81.5	96.7	90.5	97.7
Product selectivity, S_i				
C_1–C_4 alkanes	55.3	55.1	44.6	53.7
C_2–C_4 alkenes	20.4	14.2	11.4	12.1
(butenes)	(3.9)	(2.4)	(2.0)	(1.9)
C_5^+ aliphatics	4.5	1.2	2.2	0.9
Aromatics	19.9	29.5	41.8	33.3
Aromatic yield, Y_{ar}	16.2	28.5	37.8	32.5

(i) The conversions, aromatic selectivities and hydrogen productions were enhanced in hybrid systems.

(ii) the higher production of benzene in the BTX fraction of hybrid systems indicated a higher dealkylation activity.

(iii) The C_9^+ aromatic fractions in liquid phase obtained with the hybrid systems were much more important than with the parent zeolite. In addition, these heavy aromatics were much richer in bulky naphthalene and alkylated naphthalene molecules (2- and 1-methyl, C_{11}^+ aromatics) for hybrid systems. Similar results were obtained with the HZ//Ga/LuSi sample [16,27] (see the section "Nature of coke" of this paper). All these resulted in better catalyst stability and seemed to be in line with results from other researchers [23].

Therefore, it was suggested [11,15] that there was a modification of the surface energy barriers on the zeolite particles owing to the presence of the co-catalyst aggregates. Thus, it is important to have a maximum surface of contact between the two solid components in such hybrid systems. Other piece of evidence of such a hypothesis was provided by the study on the aromatization of *n*-butane using hybrid catalysts containing ZSM-5 zeolite and "inert" quartz [17]: smaller quartz particles used as co-catalysts resulted in better aromatization activities. It is obvious that besides the extent of the contact surface, the textural properties of the co-catalyst (large surface area and mesoporosity for easy diffusion) [15,16] are also important factors for the enhanced performance of the hybrid catalysts (Tables 1 and 2). In fact, among the irreducible oxides used as co-catalysts, the dried Ludox colloidal silica (LuSi) exhibits the best textural properties (Table 1: fairly high surface area, and decent mesoporosity). In addition, the large particle size and the malleability (during the extrusion phase) of the LuSi material allows the obtainment of the maximum contact surface with the much smaller zeolite particles (Fig. 1). Thus this explains why the hybrid catalyst containing Ga supported on Ludox silica as co-catalyst which offers such a particular hybrid catalyst configuration and an "active" co-catalyst surface (i.e. the presence of Ga species is capable of promoting some action on reactant and, more significantly, on product molecules desorbing from the zeolite particles), results in the largest increase of the aromatic yield (Table 2).

In such a context, there is no contradiction between the HBS concept and the Iglesia et al.'s theory on hydrogen desorption at "portholes" [12,13]. However, in consideration of our most recent results [15,16,27–29], the HBS concept or related hypotheses should be extended to reaction products other than hydrogen, as previously mentioned. On the other hand, the link of better catalyst performance with better surface of contact between the zeolite and the co-catalyst components in the hybrid systems (Fig. 1) was fully verified in other reactions such as the hydrocracking/hydroisomerization of long chain paraffins [28–30]. In particular, some synergistic effects attributed to the spillover of activated hydrogen species were detected within a solid mixture of H-mordenite and Pt-alumina, these components being firmly pressed to each other [30].

Table 3
Catalytic activity of the gallium containing hybrid catalysts

Catalyst	HZ// Ga_2O_3	HZ// (Ga/Qu)	HZ// (Ga/LuSi)	HZ// (Ga/Al)
Conversion, C_t	90.4	96.9	99.6	98.3
Product selectivity, S_i				
C_1–C_4 alkanes	43.9	39.7	28.8	45.2
C_2–C_4 alkenes	10.2	8.1	3.6	7.7
(butenes)	(1.1)	(1.0)	(0.6)	(1.1)
C_5^+ aliphatics	0.8	0.5	0.1	0.7
Aromatics	45.1	51.7	67.6	46.4
Aromatic yield, Y_{ar}	40.8	50.1	67.3	45.6

3.2. Role of the gallium species in the hybrid catalysts

When Ga_2O_3 is supported on the oxide co-catalysts previously described, the aromatic yield of the corresponding hybrid catalysts increases dramatically (Table 3). However, supported Ga containing co-catalysts provide better aromatic yields. The dried Ludox silica gel appears to be the best among the oxides investigated, which include also silica gels, different aluminas (acidic, neutral, basic aluminas, showing similar catalytic behaviors), ZrO_2, Cr_2O_3, TiO_2, Fe_2O_3 and MgO [16]. The dramatic increase in the aromatic yield owing to the presence of supported Ga species (Tables 2 and 3) may be, at first, ascribed to the dehydrogenating properties of the Ga_2O_3 species. However, as with ZnO and supported ZnO [9], supported (and unsupported) Ga co-catalysts when tested alone with *n*-butane under nitrogen atmosphere, do not produce large amounts of butenes or other alkenes besides the usual thermal cracking products (Table 4). Moreover, the selectivity to product butenes (and also to C_2–C_4 alkenes) displays the following sequence (Tables 2 and 3):

$$\begin{aligned}&\mathrm{HZ//(Ga/LuSi)(hybrid)}\\&\quad < \mathrm{HZ//Ga_2O_3(hybrid)} < \mathrm{HZ//LuSi(hybrid)}\\&\quad < \mathrm{HZ//Qu(hybrid)}\\&\quad < \mathrm{HZ(parent)}\end{aligned}$$

These results exclude the possibility of having alkenes directly and massively formed by the surface of the Ga/LuSi (or Ga_2O_3). It was also observed that with the HZ//(Ga/LuSi) hybrid catalyst, the total *n*-butane conversion and the selectivity to aromatic products and hydrogen started at levels slightly lower than those determined after one hour on stream (plateau of activity). The same hybrid catalyst pretreated in-situ with hydrogen exhibited at once the catalytic performance at equilibrium [16,20]. Moreover, it was seen by using the EDAX and XPS techniques that on-stream reduction (or pre-reduction with hydrogen) of the catalyst resulted in the formation of gallium species having a lower oxidation state, leading finally to the transfer/redistribution of the metal species within the catalyst mass [16,20]. Since the decrease of Ga/Si ratio of the co-catalyst surface (EDAX) was fairly low and the number of surface Si atoms at the interface ''zeolite/co-catalyst'' (XPS) remained unchanged [16,20], it was estimated that the amount of Ga species transferred to the zeolite crystallites upon reduction, was fairly small [less than 5% of the initial 3 wt% of Ga_2O_3, e.g. less than 0.15 wt% for the whole zeolite component]. Thus, with such a low gallium loading, the ''contaminated'' zeolite catalyst, CONTA 1 sample (0.12 wt% of Ga_2O_3), which was prepared according to a procedure reproducing the on-stream ''contamination'' process of the zeolite component in the HZ//(Ga/LuSi) hybrid catalyst (see Experimental section), was not capable of showing an aromatization performance as high as that of the hybrid catalyst (Fig. 2). Thus, it is believed that the high aromatizing propensity of the hybrid HZ//(Ga/LuSi) catalyst results from the contribution of several actions involving the HZ zeolite, the LuSi co-catalyst and the Ga species located at the ''zeolite/co-catalyst'' interface (see Figs. 1 and 2).

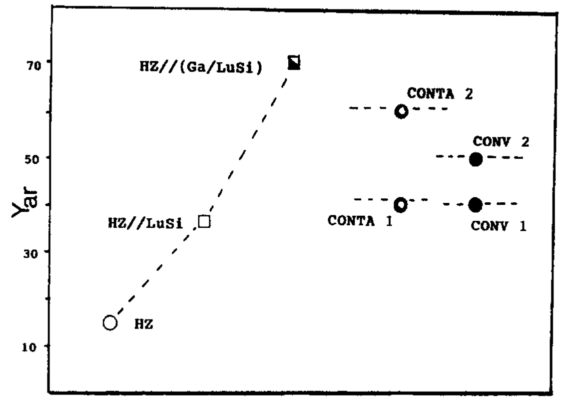

Fig. 2. Schematic representation of the aromatic yield (Y_{ar}, expressed in C atom%, all catalysts containing 80 wt% of HZ zeolite) versus the catalyst configuration and composition (see Experimental section). Circle = zeolite catalyst; square = hybrid catalyst; in black = containing or contaminated with Ga_2O_3.

Table 4
Conversion of *n*-butane over ''pure bentonite'' and Ga/LuSi co-catalyst

	Bentonite	Ga/LuSi [a]	Ga/LuSi-R [b]
Conversion	5.9	6.3	8.3
Product selectivity			
C_1–C_4 alkanes	96.7	94.3	93.8
C_2–C_4 alkenes	3.3	5.7	6.2
(butenes)	(0.5)	(4.3)	(4.4)
C_5^+ aliphatics	0.0	0.0	0.0
Aromatics	0.0	0.0	0.0

[a] Powder form, prior to extrusion: Ga/Si (bulk, chemical analysis) = 0.037; Ga/Si (surface, SEM/EDAX) = 0.031.
[b] In-situ reduction with hydrogen for 3 h.

3.3. Nature of the Ga species in the hybrid catalyst

The previous results show that the interface between the two components of the hybrid catalyst plays the key role in the enhancement of the aromatization performance (Tables 2 and 3). Regarding the nature of the Ga species, in our opinion, the formation of lower oxidation Ga species is beneficial to the catalytic activity owing only to the mobility, favoring thus the transfer/redistribution of the Ga species (for a better surface configuration) within the catalyst mass [20]. Recently, Buckles and Hutchings [31] have stated that new highly active sites for propane aromatization are formed on mechanical mixtures of gallium oxide and H-ZSM-5 zeolite. They concluded that on mechanical mixtures of gallium oxide and H-ZSM-5 zeolite, active sites are created at the interface of the two solids and that "there is no induction period during which the active sites are established". We essentially agree with the comments of Meriaudeau and Naccache [32] about the conclusions of Buckles and Hutchings, by taking into account the following results obtained with the HZ//(Ga/LuSi) hybrid catalyst:

(i) There was actually an induction period. The hybrid catalyst needed a period of at least 30 min to reach the maximum aromatization activity and this equilibrium situation was kept for a very long time (more than 10 h). There was clear evidence through EDAX and XPS analyses that some Ga was transferred to the zeolite crystallites [20]. Such an induction period was necessary to complete the transfer/redistribution of Ga species.

(ii) There was no formation of new active sites, although the Ga species transferred to the zeolite crystallites were in appearance more active than the Ga sites incorporated by using a conventional technique (CONV samples, Fig. 2). In fact, when Ga species was loaded into the zeolite ZSM-5 crystallites using our surface-contact transfer method, the extremely low Ga_2O_3 loading contaminated zeolite ZSM-5 (CONTA samples, see Experimental section) exhibited very high aromatic yields when compared with the zeolite catalysts prepared by the conventional impregnation technique (Fig. 2). This is due to the unique location of the redistributed Ga species. The latter are indeed located in a zone of the zeolite particle which is near the pore openings, enabling them not only to activate the (reactant or unreacted) alkane molecule, as reported in [24–26], but also to catalyze dehydrocyclization of olefinic intermediates as assumed by Ono and co-workers [33]. Moreover, by increasing the Ga_2O_3 content of the contaminated zeolite with a more severe Ga treatment, catalysts with aromatic yields of ca. 60 wt% were obtained (CONTA 2 in Fig. 2 and others in [21]).

3.4. *Hypothesis for a joint HBS / bifunctional catalysis action*

The CONTA 1 sample may be considered as representative of the zeolite ZSM-5 component contaminated by the Ga species of the co-catalyst during the on-stream reduction of the HZ//(Ga/LuSi) catalyst. As an attempt to explain the high aromatization performance of the hybrid catalyst, we add the aromatic yield of the gallium-free (HZ//LuSi) hybrid catalyst to that of the CONTA 1 (Fig. 2). This provides an aromatic yield comparable to that of the HZ//(Ga/LuSi) hybrid catalyst. Thus, the combination of the HBS (HZ//LuSi) and the bifunctional catalysis (CONTA 1) effects, both exerting on the zeolite/co-catalyst interface, may provide a very high aromatization performance. It is worth reporting that, with the HZ//(Ga/LuSi) hybrid catalyst, the yields in aromatics and hydrogen are 67.3 wt% and 1.4 (mol/mol of converted *n*-butane) or ca 4.9 wt%, respectively, while with the reference zeolite catalyst HZ these values are 16.2 wt% and 0.2 mol/mol.

3.5. *The nature of coke in aged catalysts*

In terms of catalyst stability, one of our hybrid catalysts, which was used for several reaction/regeneration cycles (hundred of hours on stream) and then left on a shelf for months, showed almost the same catalytic performance as the fresh catalyst, after a simple in-situ regeneration operation. This interesting behavior derives from the following facts [16,27]:

(i) The amount of coke deposited in the hybrid catalyst (HZ//(Ga/LuSi) was smaller than in the parent zeolite (TGA study).

(ii) The temperature of coke combustion was much lower with the aged hybrid catalyst than with the aged HZ (TGA study). In addition, the CP/MAS ^{13}C NMR spectra showed that the coke on this aged hybrid catalyst was in a relatively early stage of formation (light coke) while the coke formed on the aged parent zeolite catalyst was in a relatively deep stage of formation (heavy coke).

(iii) The HZ//(Ga/LuSi) exhibited higher diffusion properties for heavy aromatic compounds than the parent zeolite catalyst, HZ.

Again, the joint HBS/bifunctional catalysis hypothesis can be used to link the higher catalyst stability of hybrid catalysts, when compared to the parent zeolite, with the production of a lighter coke and the easier diffusion of bulky aromatic molecules induced by the Ga containing co-catalysts.

4. Conclusion

This study shows that in the hybrid catalyst which contains Ga_2O_3 supported on dried Ludox colloidal silica, the dramatic enhancement of the aromatizing performance, when compared with the ''pure'' zeolite ZSM-5 zeolite based catalyst, results from the combination of the HBS and the bifunctional catalysis effects. The latter effect is manifested by Ga sites located near the pore openings, having been generated by the transfer (and redistribution) of the partially reduced Ga species from the co-catalyst surface to the zeolite pores.

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