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Catalysts for the aromatization of *n*-butane prepared by surface-contact transfer of gallium onto ZSM-5 zeolite particles

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ZSM-5 zeolite particles into which 0.6 weight per cent or less of gallium oxide has been incorporated by surface-contact transfer, may exhibit very high activity in the aromatization of *n*-butane. In some cases, the yield in aromatics is as high as that obtained with the hybrid catalyst wherein the cocatalyst is prepared by evaporation of a solution of gallium nitrate in Ludox colloidal silica.

Keywords: Butane aromatization; hybrid catalysts; transfer of gallium by surface contact; ZSM-5 zeolite particles

1. Introduction

The commercial Cyclar process uses a gallium ZSM-5 zeolite to convert low cost liquefied petroleum gas (LPG) into valuable aromatics [1]. Such a catalyst is prepared according to the classical concept of bifunctional catalysis [2,3]. However, it was observed that the metal oxide species (ZnO or gallium oxide) did not require to be adjacent to the ZSM-5 zeolite acid sites to be efficient for aromatization. Indeed, highly active hybrid and selective catalysts can be prepared by mechanical mixing of the two components (zeolite and metal oxide containing cocatalyst) followed by embedding in an inert clay matrix [4–9]. The hydrogen transfer concept, also called hydrogen back (or reverse) spillover (HBS), has been formulated [5,7]. The highest performance for the aromatization of *n*-butane was obtained with a hybrid catalyst wherein the cocatalyst was

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prepared by evaporation of a solution of gallium nitrate in a colloidal silica (Ludox silica) [8]. Recently, Le Van Mao et al. [10] showed that the higher aromatization performance and the higher "on-stream" stability of such a hybrid catalyst were mainly due to the physical presence of the gallium bearing cocatalyst. Upon reduction in a hydrogen atmosphere, some gallium species were transferred from the cocatalyst's surface to the zeolite particles. Such a transfer involved only a small fraction of Ga contained in the cocatalyst. This suggests a coating of the zeolite particles with the gallium species transferred from the cocatalyst. In any event, the "gallium-contaminated" zeolite exhibited an aromatic yield considerably lower than that obtained with the corresponding hybrid catalyst [10].

The main objectives of this work are: (i) to determine the concentration of the gallium species in the (Ga/Ludox silica) cocatalyst, which provides the maximum aromatizing performance and (ii) to produce a "gallium contaminated" ZSM-5 zeolite which has a comparable aromatization activity. In the latter case, the technique used involves a gallium transfer by surface contact, under reducing conditions, between the cocatalyst and the zeolite particles.

2. Experimental

2.1. PREPARATION AND CHARACTERIZATION OF THE HYBRID CATALYSTS WITH VARIOUS GALLIUM CONCENTRATIONS

The parent ZSM-5 zeolite was synthesized according to the well-known technique of Argauer and Landolt [11]. The acid (powder) form was obtained by ion-exchange with ammonium ions and subsequent activation in air at an elevated temperature [5,6]. Its structure and degree of crystallinity were determined according to the procedures described in previous papers [5,6]. The Si/Al atomic ratio of the resulting zeolite, also called HZ, as determined by atomic absorption spectroscopy was 36 and its Na_2O content was lower than 0.2 wt%.

Hybrid catalysts which comprised a ZSM-5 component (HZ, powder form, size lower than 106×10^{-6} m, 80 wt%) and a cocatalyst (size = $(500-250) \times 10^{-6}$ m, 16 wt%), were obtained by mixing mechanically these two powders and then extruding with bentonite clay (Anachemia, USP grade, 4 wt%) in the presence of water as described in refs. [5,6], which also reported the drying and activation procedure of the catalyst extrudates.

Five hybrid catalysts were thus prepared by varying the cocatalyst composition.

(a) Ga_2O_3 was obtained by calcining gallium nitrate (13 H_2O from Strem Chem.) overnight at 550°C. The resulting aggregates were gently crushed and sieved in order to obtain the size as mentioned earlier. The hybrid catalyst

Table 1
Gallium contents of the hybrid catalysts and the corresponding cocatalysts

Catalyst	Preparation of the initial solution for the cocatalyst (g)		Composition of the cocatalyst (wt%)		Content of the hybrid catalyst in Ga_2O_3 (wt%)
	Ga nitrate	Ludox silica	Ga_2O_3	SiO_2	
HZ//LUSI	none	7.0	none	100	none
HZ//(2, 8)	1.15	6.0	8.4	91.6	1.3
HZ//(4, 6)	2.34	4.5	19.9	80.1	3.2
HZ//(6, 4)	3.45	3.0	35.4	64.6	5.7
HZ//(8, 2)	4.60	1.5	59.4	40.6	9.5
HZ//(Ga ox)	6.0	0	100	0	16.0

prepared according to the recipe described in the previous section, was called HZ//(Ga ox).

(b) An appropriate weight of gallium nitrate were dissolved in 5 ml of distilled water. The required weight of Ludox colloidal silica (Dupont, AS-40, 40 wt% in silica) were added to the previous solution. The mixture was stirred thoroughly for a few minutes and evaporated to dryness on a hot plate. The resulting solid was dried overnight at 120°C, activated in air at 550°C overnight and finally gently crushed and sieved to the desired size. The final hybrid catalysts which were prepared using these solids as cocatalysts, were referred to as HZ//(n, m) wherein n and m indicate the approximate concentrations of the preparation solution for the cocatalyst in (dehydrated) Ga nitrate and in silica, respectively. The contents in Ga_2O_3 of the hybrid catalysts used in this work are reported in table 1. In particular, the reference sample, HZ//LUSI, was prepared by using as cocatalyst the powder which was obtained by evaporation of the Ludox colloidal silica.

Studies of the textural properties of the cocatalyst aggregates were carried out by using a nitrogen adsorption apparatus, the Micromeretics ASAP 2,000, as described in ref. [8].

2.2. PREPARATION AND CHARACTERIZATION OF THE Ga CONTAMINATED ZEOLITE CATALYSTS

In order to assess the influence of the gallium species which are transferred to the zeolite particles upon reduction of the hybrid catalysts, gallium contaminated zeolite samples were prepared according to the following procedure. The previously obtained cocatalyst aggregates (1 g) having a well-defined size (250–500) $\times 10^{-6}$ m) were intimately mixed with the zeolite powder (size less than 106×10^{-6} m, weight = 4.8 g). The solid mixture was heated in a quartz reactor in the presence of hydrogen (flow rate: 17.5 m/min) at 540°C for 3 h. The contaminated zeolite particles were recovered by sieving and the content of Ga_2O_3 was determined by atomic absorption spectroscopy. The final catalysts, obtained by extrusion of these zeolite particles (90 wt%) with bentonite (10 wt%), were called HZ*(*n*, *m*) or HZ*(Ga ox) wherein *n*, *m* and (Ga ox) have the same meanings as mentioned earlier. The reference sample used, the HZ, was prepared by extrusion of the parent zeolite (HZ, powder, 90 wt%) with bentonite (10 wt%).

2.3. PREPARATION AND CHARACTERIZATION OF THE CYCLAR-TYPE CATALYSTS

These catalysts, also called HZ/Ga(R, E), were prepared by ion-exchange/impregnation according to the recipe reported in ref. [6]. The reference sample was prepared by extrusion of the parent zeolite (HZ, powder, 80 wt%) with bentonite (20 wt%).

2.4. CATALYTIC TESTING

The experimental set-up for the catalytic testing was identical to that described in refs. [5,6]. The reaction parameters were as follows: temperature = 540°C, WHSV (weight hourly space velocity or grams of injected *n*-butane per hour and per gram 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 (diameter of the catalyst extrudates = 0.1 cm). The procedures for catalyst testing and analysis of products were very similar to those described in refs. [5–8].

The total conversion of *n*-butane, C_t, is calculated as follows:

$$C_t(\text{C atom\%}) = 100 \times [(\text{NC})_f - (\text{NC})_p]/(\text{NC})_f,$$

where $(\text{NC})_f$ and $(\text{NC})_p$ are the numbers of carbon atoms of *n*-butane in the feed and in the reactor outstream, respectively.

The yield in product hydrocarbons is defined as follows:

$$Y_i(\text{C atom\%}) = [(\text{NC})_i/(\text{NC})_f] \times 100,$$

where $(\text{NC})_i$ is the number of carbon atoms of hydrocarbon (i) in the reactor outstream.

The production of molecular hydrogen is determined as moles of product hydrogen per C atoms of *n*-butane converted (yield, Y_H).

3. Results and discussion

Fig. 1 shows the aromatic yield, Y_{Ar}, as a function of the chemical composition of the cocatalysts. The maximum aromatic yield was observed with the hybrid

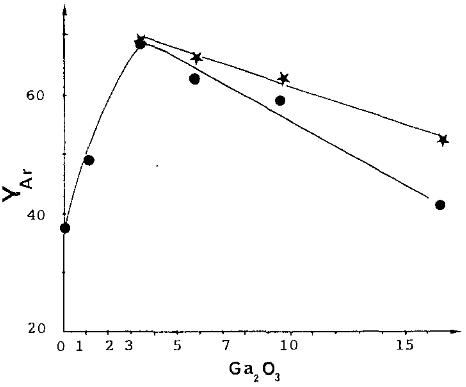

Fig. 1. Aromatic yield (Y_{Ar}) of the hybrid catalysts (●) and their reduced forms (∗) versus Ga_2O_3 content (wt%).

catalyst HZ//(4, 6). The superiority of the HZ//(4, 6) was previously assumed to derive from its optimum content in gallium species (table 1) and to its textural properties (surface area and volume of pores, table 2), which would likely favor the highest gallium dispersion on the cocatalyst surface [10]. However, this explanation did not seem to be entirely satisfactory. Thus, it was decided to use X-ray photoelectron spectroscopy (XPS) and energy dispersive X-ray (EDAX) techniques to study the phenomenon of transfer of Ga species from the cocatalyst to the zeolite particles [10]. It was shown that upon drastic reduction with hydrogen, significant Ga transfer occurred within the HZ//(Ga ox) sample whereas only a small amount of Ga species underwent such a redistribution within the HZ//(4, 6) hybrid catalyst. For the latter, Ga species were transferred, upon reduction, from the cocatalyst surface to the external surface of the zeolite particles. In fact, EDAX data indicated a decrease of the surface Ga/Si ratio (by 40%) of the cocatalyst aggregates while XPS data showed an invariable surface Ga/Si ratio for the overall hybrid catalyst [10]. In any event, the fresh HZ//(4, 6) catalyst was as active and selective as the reduced form (fig. 1). This shows that the gallium species, regardless of their position, whether on the external surface of the cocatalyst aggregates or on that of the zeolite particles,

Table 2
Textural properties of the cocatalysts used in this work

Cocatalyst	BET surface area (m^2/g)	Volume of nitrogen adsorbed (ml/g)		Average pore diameter (nm)
		total	micropores	
LUSI	120	0.247	0	6.8
(2, 8)	116	0.380	0.001	12.2
(4, 6)	105	0.348	0.001	12.5
(6, 4)	104	0.303	0.001	11.5
(Ga ox)	61	0.191	0	12.1

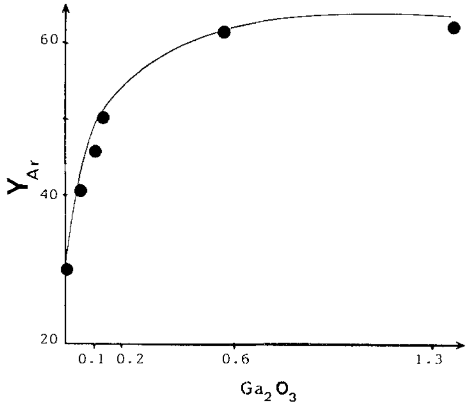

Fig. 2. Aromatic yield (Y_{Ar}) of the "gallium contaminated" zeolite catalysts versus Ga_2O_3 content (wt%).

can promote the aromatization in the same way [10]. The high dispersion of the gallium species at the interface of "zeolite particles//cocatalyst aggregates" seems to play a key role in such an enhancement.

Fig. 1 also shows that upon reduction, the aromatic yield for all the hybrid catalysts except for the HZ//(4, 6), improved significantly and approached to the Y_{Ar} value of the HZ//(4, 6).

Fig. 2 shows that the aromatic yield obtained with the catalyst HZ*(*n*, *m*) [or HZ*(Ga ox)] prepared from the gallium contaminated zeolite particles, increased with the gallium content. However, even at extremely low gallium loading the enhancement of the aromatization activity was very significant (fig. 2). Indeed, such gallium content actually represents small fractions of those needed by the parent hybrid catalysts for giving the same aromatic yields (table 3, for instance, case of the HZ*(8, 2) and HZ//(8, 2) (R), (R) stands for: reduced form of the hybrid catalyst). A gallium contamination of 0.6 wt% or less indicates a very high dispersion of gallium species (atomic or very small cluster form) which were deposited onto the external surface of the very fine zeolite particles as evidenced in ref. [10].

It is interesting to compare the aromatic yields of the HZ*(4, 6) and HZ*(8, 2) with those of the corresponding hybrid catalysts (HZ//(4, 6) (R) and HZ//(8, 2) (R)). As shown in figs. 1 and 2, and also in table 3, the HZ*(4, 6) gave a value of 45.4% for Y_{Ar} while that of the HZ//(4, 6) (R) was 67.4%. This indicates that the amount of Ga species transferred to the zeolite particles in the HZ*(4, 6) catalyst was not sufficient to provide the optimum aromatizing effects. Therefore, the Ga species which still remained on the cocatalyst surface, also played a role and a rather important one, in the overall enhancement of Y_{Ar} (see also ref. [10]). When the zeolite particles were coated with enough gallium (case of the HZ*(8, 2), 0.60 wt%), the presence of the cocatalyst did not seem very neces-

Table 3
Ga_2O_3 content (wt%) and aromatic yield (C atom%) of the hybrid catalysts (R = reduced forms) and the corresponding Ga contaminated zeolite catalysts

Catalyst	Ga_2O_3 (wt%)		Y_{Ar}
	total	surface [a]	
HZ*(2, 8)	0.12	0.12 [b]	41.4
HZ//(2, 8) (R)	1.1	n.a.	48.2
HZ*(4, 6)	0.14	0.14 [b]	45.4
HZ//(4, 6) (R)	3.2	0.4 [c]	67.4
HZ*(6, 4)	0.19	0.19 [b]	50.1
HZ//(6, 4) (R)	5.7	n.a.	62.6
HZ*(8, 2)	0.60	0.60 [b]	61.2
HZ//(8, 2) (R)	9.5	n.a.	63.4
HZ*(Ga ox)	1.33	n.a.	62.2
HZ//(Ga ox) (R)	16.0	n.a.	51.4

[a] n.a.: not available.
[b] Assumed to be dispersed on the external surface of the zeolite particles.
[c] At the interface of the zeolite particles and the cocatalyst aggregates, as estimated by XPS and EDAX techniques [10].

sary because no more significant increase of Y_{Ar} was observed (case of the HZ//(8, 2) (R), table 3, and figs. 1 and 2).

A direct influence of the gallium species on the mechanism of the paraffin aromatization (e.g. dehydrogenating action on the feed molecules), more or less in accord with the bifunctional catalysis concept, has been envisaged by many research groups [12–14]. However, in our cases, the small amount of gallium transferred to the (external surface of the) zeolite particles does not correspond to the conventional image of "acid–metal" site duality since the extremely low Ga_2O_3 content of the HZ* samples is far below the lower limit of "exchanged Ga^{3+} content" needed for high aromatic yields as observed by Kitagawa et al. [15].

On the other hand, the enhancement effect of such a low Ga_2O_3 content is similar to that observed with gallium enriched gallosilicates [16]. The explanation using the hydrogen back spillover concept is for the moment more plausible than that based on the dehydrogenating effects of the extraframework gallium species as envisaged by Kanai and Kawata [16] since *n*-butane does not undergo dehydrogenation in a significant way over the gallium containing cocatalysts alone (ref. [17] and table 4).

Fig. 3 shows the aromatic yields obtained with the Cyclar-type catalysts prepared by ion-exchange/impregnation [6]. In this case, to have an aromatic yield comparable to that of the HZ*(8, 2) or HZ*(Ga ox) samples, the Ga_2O_3 loading should exceed 3 wt%. Finally, table 5 reports the selectivities of product aromatics of the HZ//(4, 6), some HZ* samples and HZ/Ga(R, E). In gen-

Table 4
Conversion of *n*-butane over gallium containing cocatalysts and bentonite (used as binder in the hybrid catalysts)

	Material tested			
	none	bentonite	(4, 6)	(4, 6) (R)
C_t (C atom%)	4.5	5.9	6.3	8.3
product distribution (C atom%)				
C_1–C_4 paraffins	99.1	96.7	94.3	93.8
C_2–C_4 olefins	0.9	3.3	5.7	6.2
C_{5+} aliphatics	0.0	0.0	0.0	0.0
aromatics	0.0	0.0	0.0	0.0

Table 5
Selectivities of product aromatics (C atom%)

Catalyst	Y_{Ar}	Benzene	Toluene	Xylenes (and other C_8 aromatics)	C_9–C_{10} aromatics	BTX content (%)
HZ//(4, 6)	67.3	38.3	38.3	11.2	12.2	88
HZ//(4, 6) (R)	67.4	35.1	41.8	10.5	12.6	88
HZ//(8, 2) (R)	63.4	38.5	37.7	8.7	15.1	85
HZ*(4, 6)	45.4	34.6	40.5	17.1	7.8	92
HZ*(8, 2)	61.2	39.5	39.4	12.7	8.4	92
HZ/Ga(R, E) [a]	48.3	32.1	41.9	18.2	7.8	92

[a] $Ga_2O_3 = 3$ wt%.

eral, with the hybrid catalysts, a slightly higher production of benzene and C_9–C_{10} aromatics (and thus a lower BTX yield) is observed. The higher production of the bulky aromatics shown by such hybrid catalysts is indicative of a more efficient product removal from the zeolite pore system which leads to a higher "on-stream" stability [10].

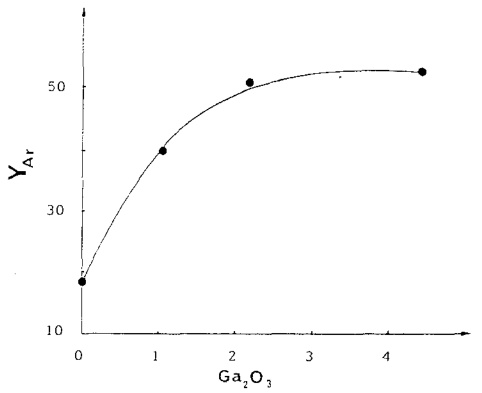

Fig. 3. Aromatic yield (Y_{Ar}) of the Cyclar-type catalysts versus Ga_2O_3 content (wt%).

4. Conclusion

By investigating the Ga transfer phenomena within the HBS hybrid catalysts, a new approach for the preparation of high performance catalysts for the aromatization of light paraffins was developed. This consists in loading gallium species in extremely small amounts (0.6 wt% or less) by using the technique of surface-contact transfer or short-distance-vapor-phase transfer. In such cases, the gallium species are probably deposited in a highly dispersed form, onto the external surface of the zeolite particles. This may explain the high aromatization performance of the hybrid catalysts wherein the amount and the dispersion state of the gallium species which are located at the interface of the zeolite particles and the cocatalyst aggregates, are similar to those of the "gallium contaminated" zeolite catalysts.

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