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Hydrogen sorption sites in the gallium containing hybrid catalysts used for the aromatization of light alkanes

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Gallium species which were incorporated initially in the oxide form, were all in the (+3) oxidation state in the hybrid catalyst and exhibited two types of hydrogen chemisorption sites, S_{Hw} and S_{Hs}. The stronger sorption sites S_{Hs} which predominated at higher gallium dispersion, corresponded probably to the most effective surface configuration for gallium in the aromatization of *n*-butane.

Keywords: *n*-butane aromatization; gallium hybrid catalysts; hydrogen chemisorption sites

1. Introduction

Aromatization of light alkanes (propane, butanes, liquefied petroleum gas) is an important industrial process and an exciting topic of research in the field of catalysis. The catalyst used in the commercial Cyclar process [1–3] is a gallium ZSM-5 zeolite which is prepared according to classical bifunctional catalysis. A fairly large number of scientific papers and patents are related to such reactions. The catalysts investigated contain as dehydrogenating component Zn [4–6], Pt [7–10] or Ga [11–25]. New hybrid catalysts were prepared by intimately mixing the ZSM-5 zeolite particles with the cocatalyst aggregates and embedding the resulting solid mixture into a clay matrix. The cocatalyst might contain Zn [25–27] or gallium [25,28–31]. Even cocatalysts which did not contain any Zn, Pt or Ga were capable of enhancing the aromatizing properties of the ZSM-5 zeolite [28,32]. The hydrogen back spillover (HBS) concept was then devised as an explanation for such an activity enhancement [31,33].

It was recently found that the amount of gallium species transferred, upon a drastic reduction under hydrogen atmosphere, from the Ga/Ludox silica cocatalyst to the zeolite particles was extremely low [34]. These small amounts of gallium which were probably deposited on the external surface of the ZSM-5 zeolite particles, resulted in high performances for the aromatization of *n*-butane [35].

This work was aimed at (i) determining unambiguously the oxidation state of the gallium species present in the hybrid catalysts, (ii) identifying the nature of the hydrogen sorption sites of the gallium species and (iii) relating such sites to the catalyst's activity in the aromatization of *n*-butane.

2. Experimental

2.1. PREPARATION OF THE CATALYSTS

The gallium containing cocatalysts and the resulting hybrid catalysts were prepared according to the procedures described in previous work [32,34]. The ZSM-5 (acid form, HZ) had a Si/Al atomic ratio of 36. The cocatalysts were called (CO *n m*) wherein *n* and *m* indicate the concentrations in the preparation solution of gallium nitrate and Ludox colloidal silica, respectively [35]. The (GaOx) cocatalyst was obtained by calcining gallium nitrate at high temperature [34,35].

The "gallium-contaminated" ZSM-5 zeolites, also called HZ*, were obtained by using the surface-transfer technique as described in ref. [35].

The final catalysts were obtained by extrusion with bentonite clay as already reported in previous publications [34,35]. In particular, hybrid catalysts are hereafter called HZ-(CO *n m*) or HZ-(GaOx) according to the cocatalyst used.

2.2. CHARACTERIZATION

The main techniques used to characterize our samples were as follows: X-ray diffraction of powders (XRD), X-ray photoelectron spectroscopy (XPS) and hydrogen chemisorption/temperature programmed desorption (hydrogen-TPD). XRD analyses were performed using a Rigaku D/Max-II diffractometer, while the XPS spectra were recorded with a Fisons M-Probe ESCA spectrometer. Details of the XPS technique used were reported elsewhere [36].

Hydrogen-TPD analyses were performed in a high vacuum stainless steel apparatus provided with a special system for gas introduction and equipped with a Carlo Erba QTMD quadrupole mass spectrometer (fig. 1). The following procedure was used. 0.32 g of the sample was outgassed at 423 K ($<10^{-2}$ mm Hg) for 1 h, then heated up to 823 K (heating rate: 10 K/min) and maintained at such a temperature under $<10^{-5}$ mm Hg vacuum for a further 2 h. The sample was then cooled down to 673 K and an accurately measured amount of hydrogen was introduced into the system. The solid was allowed to chemisorb hydrogen at 673 K for

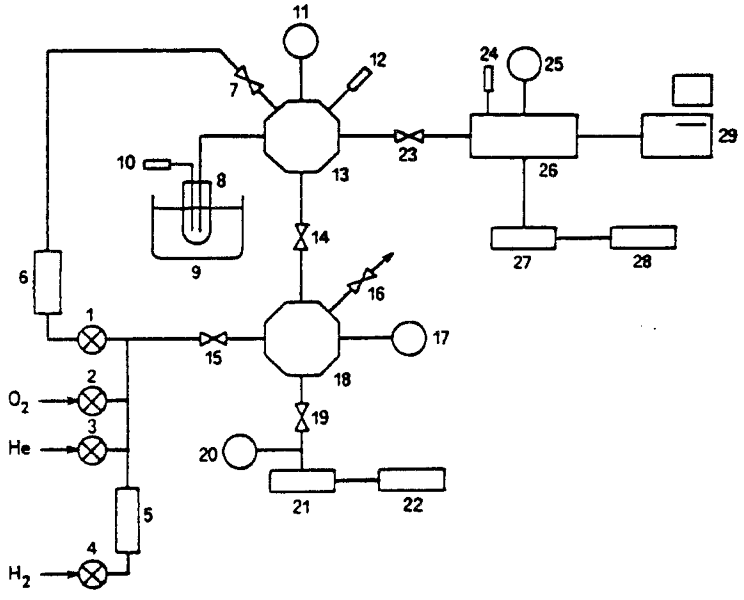

Fig. 1. Scheme of the equipment used for the hydrogen adsorption and temperature-programmed desorption (H_2-TPD). 1, 2, 3, 4: stopcocks: 5: dryer: 6: flowmeter; 7, 14, 15, 19, 23: micrometric valves; 8: sample holder; 9: thermal bath; 10, 12, 24: thermocouples; 11, 20: capacitive manometers; 13: analysis chamber; 16: outlet valve; 18: sampling chamber; 20: hot cathode gauge; 21, 27: turbomolecular pumps; 22, 28: rotary pumps; 25: Penning gauge; 26: mass spectrometer; 29: computer.

1 h. The system was then cooled down to 303 K and thoroughly outgassed for 0.5 h. The sample was now heated, always in vacuo, from 303 up to 823 K with a heating rate of 10 K/min. The desorbing molecules, analysed by means of the quadrupole mass spectrometer were water (mass: 18) and hydrogen (mass: 1 and 2). No other molecules were found in the gas effluent.

Fig. 2 shows the hydrogen-TPD curves obtained with the cocatalysts (plots of ion current intensity (ICI, expressed in arbitrary units, a.u.) versus temperature). They all exhibited a desorption peak whose maximum was located at 663 K. Although there was some shift to higher temperature of such a peak for very low gallium loading (case of the CO 28 sample), it seemed to us reasonable to assume that these hydrogen-TPD curves corresponded to one type of gallium chemisorption site. These sites were called S_{Hw}.

Fig. 3 shows the hydrogen-TPD curves obtained with the hybrid catalysts. Such plots presented significant differences with those of the cocatalysts (fig. 2), which are as follows: (i) larger amounts of desorbed hydrogen, and (ii) presence of a new desorption peak at a higher temperature, e.g. at 758 K. The chemisorption sites which corresponded to such a peak, were called S_{Hs}. In order to estimate the relative importance of these two sites, S_{Hw} and S_{Hs}, a deconvolution procedure was used which consisted basically of subtracting the TPD curves obtained with the cocatalysts from those obtained with the corresponding hybrid catalysts.

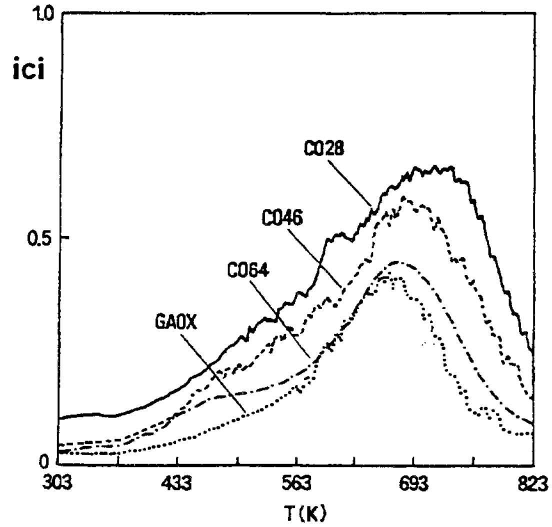

Fig. 2. H_2-TPD curves of some cocatalysts (ICI: ion current intensity in arbitrary units, a.u., versus temperature in K).

In figs. 2 and 3, and in other figures of this paper, the ion current intensity, ICI, was recorded as a function of the temperature. Thus, a procedure was devised in order to convert these data into the number of moles of hydrogen desorbed by the sample. For that purpose, we first carefully sampled a determined volume of hydro-

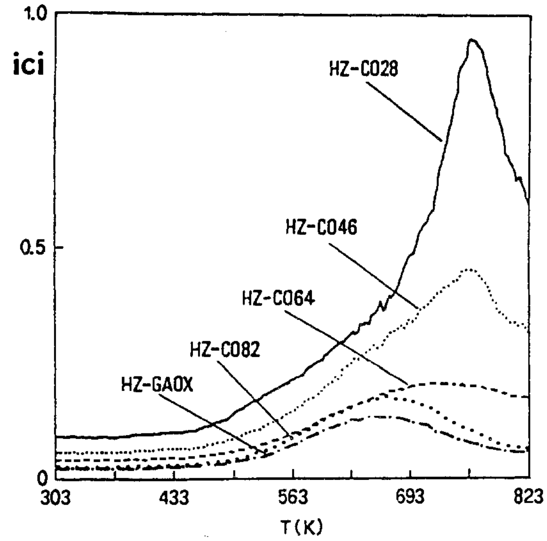

Fig. 3. H_2-TPD curves of the hybrid catalysts (see fig. 2).

gen that was then injected into the sample containing chamber (volume of the chamber = 45.9 ml; hydrogen injections with the pressure varying from 3.0 to 100 Torr, as measured with a Baratron precision pressure gauge). For each hydrogen injection, the QTMD signal was recorded as it were for a normal TPD run. A calibration curve was then established and the following function was obtained using a non-linear regression analysis method for curve fitting: $N = A + B \ln(I)$, where N and (I) were the mole of desorbed hydrogen and the integral peak area calculated from the calibration curve, respectively. The latter was obtained by plotting the ion current intensity versus the temperature as in the TPD curves. The calculated values for A and B coefficients of this equation were 2.95 E − 4 and 2.30 E − 5, respectively, with a correlation factor of 0.998.

3. Results and discussion

Table 1 reports the values of the Ga (3d) binding energies as measured by means of XPS technique with our hybrid catalysts and cocatalysts. In table 1 are also included the corresponding values resulting from the reference samples (pure gallium oxide and metallic gallium) which were close to those reported in the literature [37–39]. Combined with the results obtained by XRD, these XPS data show that all the gallium component present in our cocatalysts and hybrid catalysts was in the Ga^{3+} form. This was confirmed by XRD analysis of the cocatalyst (CO 64) for which the pattern was characterized by a low crystallinity and the presence of characteristic Ga_2O_3 lines.

Fig. 4 shows the hydrogen-TPD curves of the HZ-(GaOx) hybrid catalyst and the same after drastic reduction under hydrogen atmosphere at 540°C, the Ga-(GaOx) R sample, as described elsewhere [34,35]. Ref. [35] also reported the following inequality in terms of aromatic yield: HZ-(GaOx) R > HZ-(GaOx). Thus, the reduction of such a hybrid catalyst induced a significant rearrangement of the gallium species within the hybrid body. The enhancement of the catalytic activity should be related to the displacement of the hydrogen-TPD curve to a higher tem-

Table 1
Measured binding energies of the Ga (3d) photoelectrons of the cocatalysts and the reference samples

Sample	Ga_2O_3 content [a] (wt%)	Ga^{III}(3d) (eV)	Ga^0(3d) (eV)
Ga	[b]	20.50 [b]	18.5
Ga_2O_3	100	20.60	–
(CO 28)	5.7	20.61	–
(CO 46)	12.4	20.55	–
(CO 64)	23.3	20.63	–
(CO 82)	65.2	20.58	–

[a] As measured by atomic emission spectroscopy.
[b] Present as surface oxide.

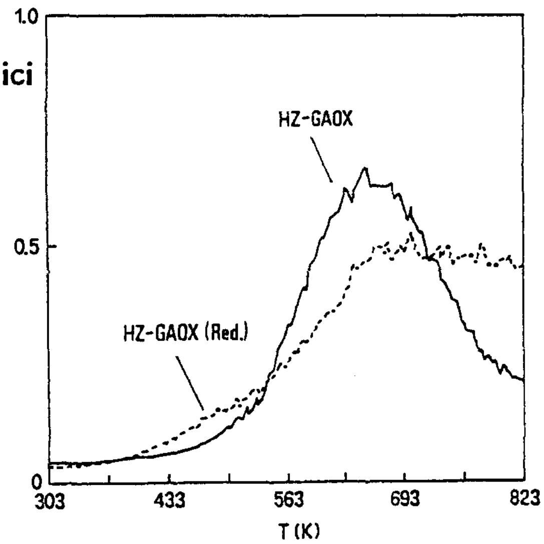

Fig. 4. H_2-TPD curves of the HZ-(GaOx) sample and its reduced form (see fig. 2).

perature region (fig. 4). This was due to the formation of more S_{Hs} sites upon reduction of the gallium component with hydrogen at high temperature (table 3).

Indeed, by using the deconvolution procedure combined with the calibration method which involved the data from the TPD curves of figs. 2 and 3, and also fig. 4, it was possible to determine for each hybrid catalyst the total amount (in mole) of hydrogen desorbed, as well as, the mole percentage of hydrogen desorbed for the S_{Hw} and S_{Hs} sites (tables 2 and 3). It was thus observed that the lower the gallium loading, the higher the (H_2/Ga_2O_3) molar ratio and the higher the percentage of the S_{Hs} sites. On the other hand, in previous work [35], on the same hybrid catalysts, we have observed the following aromatizing performance:

Table 2
(H_2/Ga_2O_3) molar ratio for the hybrid catalysts calculated as mole of hydrogen desorbed per mole of Ga_2O_3 present in the sample

Sample	Ga_2O_3 content [a]	H_2 (mole)	Ga_2O_3 (mole)	(H_2/Ga_2O_3)
HZ-(CO 28)	1.1	6.28 E−5	1.65 E−5	3.8
HZ-(CO 46)	3.2	6.59 E−5	3.39 E−5	1.9
HZ-(CO 64)	5.7	6.74 E−5	6.39 E−5	1.1
HZ-(CO 82)	9.5	6.39 E−5	1.78 E−4	0.4
HZ-(GaOx)	16.0	7.30 E−5	2.73 E−4	0.3
HZ-(GaOx) R	15.8	6.10 E−5	2.70 E−4	0.2
HZ* (from CO 82)	0.50 [b]	7.30 E−5	1.12 E−5	6.5

[a] In the final catalyst (wt%).

[b] 0.60 wt% in the contaminated zeolite particles.

Table 3
Proportion of S_{Hw} and S_{Hs} sites in the catalysts (in mol% of hydrogen desorbed) versus the aromatic yield Y_{Ar} (in C atom%) [35]

Sample	S_{Hw}	S_{Hs}	Y_{Ar}
HZ-(CO 28)	20	80	48.2
HZ-(CO 46)	25	75	67.3
HZ-(CO 64)	31	69	60.2
HZ-(CO 82)	n.a. [a]	n.a. [a]	58.8
HZ-(GaOx)	85	15	40.8
HZ-(GaOx) R	55	45	51.4
HZ* (from CO 82)	10 [b]	90 [b]	61.2

[a] Not available.
[b] Very approximate.

HZ-(CO 46) > HZ-(CO 64) > HZ-(CO 82) > HZ-(CO 28) > HZ-(GaOx).

Therefore, in a general way, a higher aromatizing activity of the hybrid catalysts corresponded to a higher number of the S_{Hs} sites. The HZ-(CO 28) sample was a separate case because although it exhibited the highest (H_2/Ga_2O_3) molar ratio and the highest percentage of S_{Hs} sites (see tables 2 and 3), its gallium content in the hybrid configuration was too low to provide a fully enhanced aromatizing activity, as in the case of the HZ-(CO 46) sample. The highest value for the (H_2/Ga_2O_3) molar ratio which was equal to 4 (table 2), was indicative of a monoatomic dispersion of Ga species and a non-dissociative adsorption of hydrogen on the S_{Hs} sites (a hydrogen molecule by atomic Ga site). This observation did not differ significantly from results of recent studies [40,41].

Fig. 5 shows that the "gallium-contaminated" zeolites prepared according to the procedure consisting basically of treating a mechanical mixture of "zeolite–cocatalyst particles" at 540°C in the presence of hydrogen and then separating the two components by sieving [35], contained a great number of S_{Hs} sites. This was surely the origin of the high (*n*-butane) aromatizing properties of such samples (tables 2 and 3) although these gallium species were in extremely low amounts and were probably deposited on the external surface of the zeolite particles [35]. As also reported in table 2, the (H_2/Ga_2O_3) molar ratio of the HZ* (obtained from the CO 82) sample was very high, indicating that the S_{Hs} sites should correspond to a high state of gallium dispersion on the zeolite surface. The reported value of this ratio, higher than 4 as previously mentioned, was due probably to the lack of accuracy in the determination of the Ga content of such a catalyst.

Nevertheless, such a special configuration of gallium sites which could strongly adsorb/desorb molecular hydrogen and did not require a high gallium loading as in classical bifunctional catalysis, was the origin of the high aromatizing performance of our hybrid catalysts. This, therefore, constitutes strong evidence for our hydrogen back spillover concept.

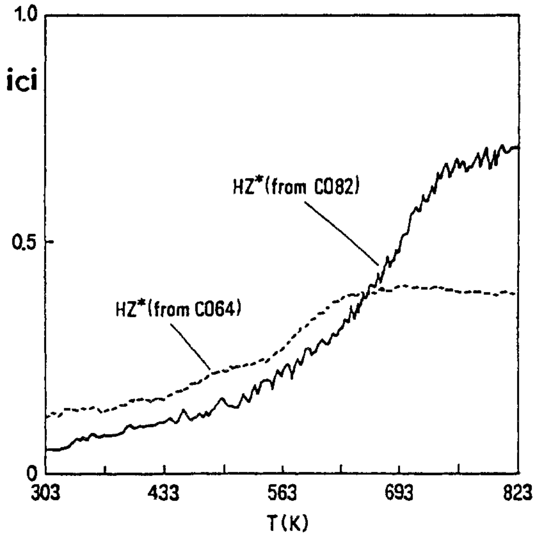

Fig. 5. H_2-TPD curves of some "gallium contaminated" zeolites (see fig. 2).

Regarding the transfer of gallium species from the cocatalyst particles to the zeolite ones, although previous work [35] pointed out that it could be induced by a prior reduction of gallium oxide (to more mobile species), two phenomena occurred which did not confirm such a need for a drastic reduction operation:

(i) The HZ-(CO 46) which exhibited the highest aromatizing performance [30,34], did not require any prior reduction or on-stream activation because it was effective (in the aromatization of *n*-butane) at the very beginning of the reaction.

(ii) The HZ-(CO 46) showed a hydrogen TPD pattern which was more important than that of the (CO 46) cocatalyst and was richer in S_{Hs} sites (see figs. 2 and 3, tables 2 and 3).

Since pure zeolite particles did not show any significant hydrogen TPD, there was one only way to explain this enhanced TPD phenomenon. Within the hybrid catalyst, there would be, during the various preparation steps and particularly during the catalyst activation at high temperature, a solid-state ion-exchange between Ga^{3+} ions (from the cocatalyst surface) and protons (from the external surface of the zeolite particles). This would increase the number of adsorption sites of the "zeolite–cocatalyst interface" by creating new gallium sites on the surface of the zeolite particles and improving the gallium dispersion on the cocatalyst surface as a direct consequence of the removal of gallium species from such a surface. In fact, solid-state ion-exchange between metal oxides and zeolite protons is known to occur easily at elevated temperatures (ref. [2] and references therein). Investigations are under way to elucidate such intriguing phenomena in our hybrid catalysts. A particular attention will also be given to the "on-stream" changes of the oxidation state of gallium, as recently pointed out by Meitzner et al. [41].

4. Conclusion

It was seen that the cocatalyst prepared by supporting gallium oxide on (Ludox colloidal) silica was capable of creating, by partial surface-transfer onto the zeolite particles, gallium sites which strongly adsorbed hydrogen. Such a transfer which might occur upon drastic reduction and/or by solid-state ion-exchange during the catalyst preparation process, dramatically increased the number of stronger hydrogen chemisorption sites, S_{Hs}, at the "zeolite–cocatalyst" interface. These sites were probably responsible for the high performance in the aromatization of light alkanes of our hybrid catalysts.

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