Isomerization of *n*-butane over Fe,Mn-promoted sulfated zirconia: catalytic activity and surface features of the catalyst

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The catalytic properties of Fe,Mn-promoted sulfated zirconia catalysts have been tested as a function of: (i) the temperature of the preliminary calcination step; (ii) the conditions of the catalyst activation step; (iii) the temperature of the catalytic reaction. It was observed that the promotion effect is mainly ascribable to the Fe component, and requires: (i) a preliminary calcination at $T_{\mathrm{calc}} > 850$ K, most likely to liberate from sulfates as much as possible of the surface Fe component; (ii) an activation cycle (at $T_{\mathrm{act}} \approx 700$ K) in strictly oxidizing conditions, in order to have as much as possible of the surface $\mathrm{Fe^{III}}$ component in a reducible form; (iii) reaction temperatures close to ambient temperature, in order to prevent the predominance of poisoning reactions and to avoid an extensive reduction of the Fe component. When the Fe component becomes reduced, the catalytic promotion effect is lost, and the reduced Fe^{n+} component ($n < 3$) can be easily revealed by the ambient temperature adsorption of CO, which yields a typical IR band centered at $\sim$2170 cm^{-1}.

Keywords: sulfated zirconia, Fe,Mn-promoted catalysts, *n*-butane isomerization

1. Introduction

Over ten years after the first works by Hino et al. [1] and by Tanabe et al. [2], the catalytic and surface chemical properties of sulfated zirconia (SZ) are still attracting much attention, as demonstrated by the number of papers and reviews still published on the subject (e.g., see refs. [3–5]). This persisting interest derives, among other reasons, from the fact that some catalytic and surface chemical properties of SZ systems are not yet fully understood.

In order to improve the still largely unsatisfactory catalytic performances of SZ catalysts, in recent years several researchers have suggested the promotion of SZ systems by the addition of small amounts of either noble metals (e.g., see ref. [6], and references therein) or transition metal oxides (e.g., see refs. [7–9]); Fe,Mn-promoted SZ catalysts (FMSZ), the importance of which was first proposed by Hollstein et al. [7], belong to the latter category of promoted SZ systems.

Aim of the present contribution is the description of some catalytic and surface chemical features of a FMSZ system in relation to some important preparative steps (namely, the calcination and the activation step), and to the temperature of the catalytic process. In order to do so, the main features of plain SZ catalysts in relation to the same variables are herewith briefly recalled.

The *calcination* step is a thermal treatment to be carried out after the sulfation process (normally in air) at a temperature of at least 773–823 K. When the precursor of the SZ catalyst is amorphous, the calcination step favours the migration of sulfates from the bulk to the surface, and brings about the crystallization of ZrO_2 in the tetragonal form [10]. But a calcination step has been shown to be strictly necessary also in the case of SZ catalysts deriving from crystalline precursors because, in any case the thermal treatment at $T_{\mathrm{calc}} > 773$ K must bring about the selective elimination of some sulfates. The fraction of sulfates that is eliminated during the calcination step is thermally weaker and is mainly localized in the crystallographic defects of the ZrO_2 network [11]. After the calcination step, abundant sulfates will remain on crystal terraces, i.e., the regular crystal terminations of the ZrO_2 particles [11,12], while the defective terminations liberated from sulfates will become covered by hydroxyls, if the SZ system is rehydrated, or will present Lewis acid sites of medium-high strength (coordinatively unsaturated (CUS) $\mathrm{Zr^{4+}}$ sites) if the SZ system is dehydrated [12]. This family of strong Lewis acid sites can be revealed and "titrated" by the adsorption of CO at ambient temperature, as only these strong Lewis acid sites can interact with CO at ambient temperature, and the relevant $\mathrm{CO/Zr^{4+}_{CUS}}$ interaction yields a typical IR band centered at $\sim$2200 cm^{-1}.

The *activation* step is a thermal treatment carried out, before catalytic tests, at a temperature in the range

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500–723 K. In the case of plain SZ systems, this treatment can be carried out indifferently in a dry air stream, in inert gas, or in vacuo, for its only role is to clean up the surface and bring it to the desired degree of dehydration. The degree of dehydration determines the ratio between Lewis acid sites (Zr^{4+}_{CUS}) and Brønsted acid sites (proton-releasing OH groups).

As for the *temperature of* the *n*-butane isomerization catalytic process, temperatures of the order of ~423 K are normally preferred when using plain SZ catalysts, as lower reaction temperatures yield very low conversions and higher temperatures lead to the occurrence of undesired concurrent reactions and to a faster deactivation of the catalyst.

2. Experimental

2.1. Materials

$Zr(OH)_4$ was prepared by the sol–gel method. A mixture of isopropyl alcohol (300 ml) and water (43 ml) was added to a solution of Zr *i*-propoxide (184 ml) in anhydrous *i*-propyl alcohol (600 ml), containing HNO_3 (65%, 6 ml) as a catalyst. This solution was aged for 20 h at 313 K in order to complete the polycondensation reaction, and the gel so obtained was dried overnight at 423 K. The sulfation was performed by incipient wetness, using an appropriate amount of 1 M aqueous solution of $(NH_4)_2SO_4$ to produce on the sample a final theoretical 8% weight amount of SO_4^{2-}.

Promotion of sulfated zirconia with Fe and Mn (FMSZ samples) was achieved by sequential incipient wetness impregnation by using appropriate amounts of aqueous solutions of $Fe(NO_3)_3 \cdot 9H_2O$ and $Mn(NO_3)_2 \cdot 6H_2O$, so as to obtain ~1.5% weight of Fe and ~0.5% weight of Mn. For reference, also catalysts containing only Fe (~2 % weight; FSZ samples) and only Mn (~0.5 % weight; MSZ samples) were used, and their preparation procedure was at all similar to that just described for FMSZ catalysts. After each sequential impregnation, the samples were dried overnight at 383 K. Finally, on all samples the calcination step was carried out in dry air flow (or, in alternative, in a muffle open to the atmosphere, as specified in the text) at different temperatures (673, 823, 923 and 998 K) for 3 h. After calcination, the catalysts were cooled to ambient temperature and were then allowed to rehydrate by exposure to the atmosphere.

BET surface areas were determined with N_2 at −196°C (on a Micromeritics Asap 2000 apparatus), and are reported in table 1. Fe and Mn analysis was performed by AA spectroscopy. Quantitative determination of sulfates was performed on all samples by ion chromatography (see table 1); details of the experimental procedure have been reported elsewere [13].

2.2. Methods

n-butane isomerization experiments were performed in a quartz tubular reactor (200 mm long, 8 mm i.d.) externally heated by an oven. The temperature was controlled with a thermocouple immersed in the catalytic bed. The reaction was carried out at atmospheric pressure at either 323 or 423 K. Prior to reaction, all catalysts (0.5 g) underwent the activation step, either in dry air or He flow (50 ml/min), as specified in the text, at different temperatures (473, 573 and 723 K) for 1.5 h. The feed mixture (total flow 25 ml/min) consisted of *n*-butane and He in the ratio 1 : 4. *i*-butane was analyzed on line by gas chromatography. Reaction rates were defined as mol of *n*-butane converted per gram of catalyst per unit time. Reaction rates were measured in a conversion range between 0.5 and 10%. All catalysts exhibited high selectivity: after reaction times of 150–200 min, reaction mixtures consisted of $> 90\%$ *i*-butane, and minor amounts of propane ($< 6\%$) and pentanes ($< 4\%$). Under the analysis conditions adopted for the separation of products, traces ($< 1\%$) of methane could be detected, but not quantified.

IR spectra were obtained at 2 cm^{-1} resolution in a strictly in situ configuration using a Bruker FTIR spectrometer (IFS 113v) equipped with MCT cryodetector. The samples for in situ IR experiments were in the form of thin-layer powder depositions (ca. 5 mg cm^{-2}) obtained on pure Si platelets by air drying of water sus-

Table 1
Some physical and chemical characteristics of SZ catalysts

Sample	Calcination temperature	BET s.a. ($m^2 g^{-1}$)	Sulfate content (SO_4^{2-}/nm^2)	wt% Fe	wt% Mn
SZ	823	188	2.60	–	–
SZ	923	128.6	1.52	–	–
FMSZ	673	225	1.81	n.d.	n.d.
FMSZ	823	150	2.11	n.d.	n.d.
FMSZ	923	131	1.55	1.64	0.53
FMSZ	998 (oven)	86	1.03	n.d.	n.d.
FMSZ	998	71	0.46	n.d.	n.d.
FSZ	923	108.2	1.27	1.94	–
MSZ	923	133.2	1.57	–	0.51

pensions of the starting powdery materials deriving from the calcination step. The design of the in situ quartz-KBr IR cell did not allow thermal treatments to be carried out in flux, and all activation steps were carried out in a conventional high vacuum (residual pressure $< 10^{-5}$ Torr).

3. Results and discussion

The interest in FMSZ catalysts resides in the fact that, with FMSZ systems, *n*-butane isomerization rate vs. time-on-stream plots of the type shown in figure 1 are often observed. The figure shows that: (i) At reaction temperatures close to ambient temperature, the isomerization rate over FMSZ systems (curve 1) is definitely higher than over SZ catalysts in the same conditions (curve 2); (ii) On FMSZ catalysts the reaction rate profile presents a characteristic shape. There is a steep initial burst (the break-in period), in which the conversion can reach relatively high percent figures. The break-in period is then followed by a first steep deactivation period, and eventually by a much more gradual deactivation. The last two reaction phases correspond to the gradual conclusion of the promotion effect.

It is important to stress that isomerization rate vs. time profiles of the type illustrated in figure 1 are not obtained with FMSZ catalysts *in all* conditions. In fact, the preparative steps and the catalytic reaction parameters mentioned in the introduction have been observed to play a determining role on the actual catalytic activity of promoted SZ catalysts. For the sake of clarity, these points will be dealt with separately as far as possible.

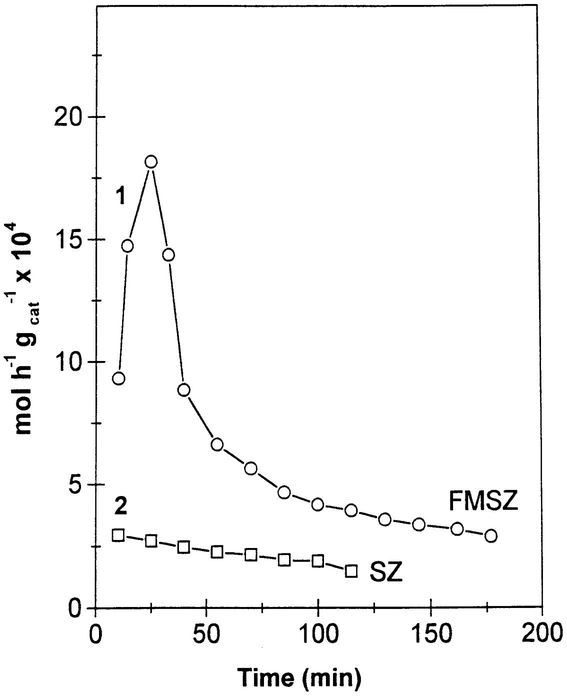

Figure 1. *n*-butane isomerization rate vs. time-on-stream plots measured at 323 K over FMSZ (curve 1) and over SZ catalysts (curve 2). The catalysts were calcined in a dry air stream at 923 K, rehydrated, and activated in a dry air stream at 723 K.

3.1. The calcination step

The spectra in figure 2 refer to FMSZ systems that were calcined at different temperatures, and that after the calcination step were rehydrated by exposure to the atmosphere and were then vacuum activated in the same conditions. Different samples present different spectra, both in the surface OH stretching region (ν_{OH}; section a) and in the spectral region of surface sulfates (ν_{SO} modes; section b). This is due to the fact that: (i) At the various calcination temperatures, different degrees of crystallinity and different surface areas were attained, as typical of catalysts deriving from an amorphous precursor (as in the present case); (ii) Different amounts of sulfates were eliminated during the calcination step (see data in table 1). But both ν_{OH} and ν_{SO} spectral patterns do not present peculiar features to be specifically ascribed to the presence, on FMSZ systems, of the promoting metals. In fact, there are no appreciable differences with respect to the corresponding patterns of plain SZ systems, as shown by comparison with the dotted-line traces in figure 2. In particular, the drastic spectral changes observed in the sulfates stretching region on passing from $T_{calc} = 823$ K to $T_{calc} = 923$ K are not due to the presence of Fe,Mn additives, but are mainly due to the different population and distribution of sulfates on the ZrO_2 support [11]. Other authors have also reported that the IR spectral features of FMSZ systems do not differ appreciably from those of non-promoted SZ systems treated in similar conditions [14,15], although their observations did not concern specifically the effect of the calcination step.

Still, the *n*-butane isomerization rate plots obtained at 323 K on FMSZ systems calcined at various temperatures, and reported in figure 3, show that the calcination temperature is a critical parameter for the catalytic properties of Fe,Mn-promoted SZ systems. In particular it is observed that calcination temperatures of the order of some 823 K (see curve 2), which are largely sufficient to induce catalytic activity in plain SZ catalysts [11], are still insufficient to induce in FMSZ catalysts the desired promoting properties. Only for $T_{calc} > 873$ K the promoting properties are present, as monitored in the rate vs. time plots by the initial break-in period. If the reaction rate is referred to the unit mass, as in figure 3, the maximum height of the induction period is observed for $T_{calc} = 923$ K (curve 3), whereas for $T_{calc} = 998$ K the height of the induction period decreases and the catalyst tends to deactivate faster (curves 4 and 5). If the reaction rate is referred to the unit area, the break-in period turns out to be maximum for $T_{calc} = 998$ K (oven), and declines for $T_{calc} = 998$ K (dry air stream). Other authors, using different test reactions, have observed

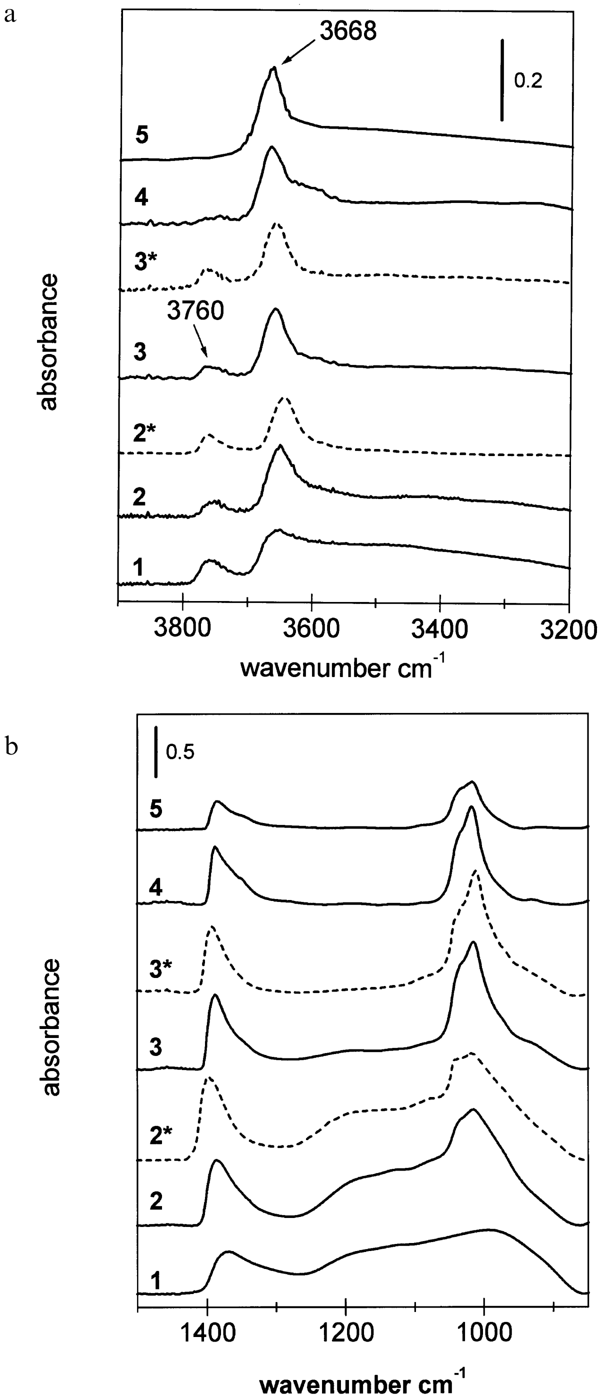

Figure 2. Absorbance IR spectra in the OH stretching region (section a) and in the sulfate stretchings region (section b) of FMSZ catalysts calcined at various temperatures in a dry air stream (unless otherwise specified), rehydrated, and then activated in vacuo at 673 K. (1) $T_{\mathrm{calc}} = 673$ K. (2) $T_{\mathrm{calc}} = 823$ K; (2*) reference SZ sample, $T_{\mathrm{calc}} = 823$ K. (3) $T_{\mathrm{calc}} = 923$ K; (3*) reference SZ sample, $T_{\mathrm{calc}} = 923$ K. (4) $T_{\mathrm{calc}} = 998$ K, in oven. (5) $T_{\mathrm{calc}} = 998$ K.

that the promotion effect of FMSZ caytalysts is maximum for T_{calc} close to 1000 K [16], even if for $T_{\mathrm{calc}} \geqslant 1000$ K the overall amount of surface sulfates is reduced to very low levels.

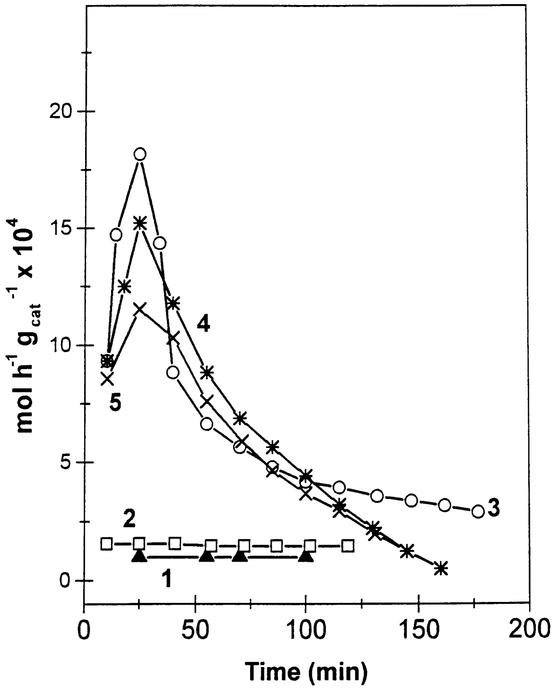

Figure 3. n-butane isomerization rate vs. time-on-stream plots measured at 323 K over FMSZ catalysts calcined at various temperatures in a dry air stream (unless otherwise specified), rehydrated, and then activated in a dry air stream at 723 K. (1) $T_{\mathrm{calc}} = 673$ K. (2) $T_{\mathrm{calc}} = 823$ K. (3) $T_{\mathrm{calc}} = 923$ K. (4) $T_{\mathrm{calc}} = 998$ K, in oven. (5) $T_{\mathrm{calc}} = 998$ K.

In previous works [11] it was shown that, in quantitative terms, on plain SZ catalysts the main role played by the calcination step is the selective elimination of some sulfates, as pointed out in the introduction, and this datum has been confirmed also for FMSZ systems (see, for instance, the data in table 1). The reaction rate data reported in figure 3 indicate that, for $T_{\mathrm{calc}} < 873$ K, the promoting activity of the transition metal additives is not available yet. It is thus suggested that, for $T_{\mathrm{calc}} < 873$ K, the surface transition metal ions are still shielded by sulfates and, consequently, they are not yet available for their promotion role. A direct experimental evidence for the presence of sulfate groups coordinated to the transition metal promoters is virtually impossible to obtain, in view of the low concentration of promoters and of the fact that SZ, FMSZ, FSZ and MSZ systems present almost identical IR spectra in the sulfates region. In fact the spectra of sulfates at the surface of ZrO_2-based systems depend only on the calcination and/or activation conditions [12,17], as do the spectra of sulfates at the surface of Fe_2O_3 and other high area metal oxides [18].

By calcining FMSZ at $T_{\mathrm{calc}} > 873$ K, increasing amounts of the promoting metals would be freed from sulfates, and the promotion effect appears. The promotion effect will increase with increasing calcination temperature (as shown by figure 3), and the increase will last until not too many sulfates are eliminated also from the regular crystal terminations of the ZrO_2 particles, so that the acid–base catalytic properties of the sulfated zirconia system are gradually lost. The onset of the deactivation process depends on the preparative history of the catalyst and on the calcination procedure. For instance, curves 4 and 5 in figure 2b show that, at 998 K, a dry air stream treatment removes more sulfates than a static oven treatment at the same temperature, as in the two cases the effect produced on the equilibrium

$$SO_4^{2-} \rightleftharpoons SO_3 + O_{CUS}^{2-}$$

is quite different. Other spectroscopic data to be reported in the next section will indicate that the proposed interpretation is correct: there is indeed a correlation between thermal elimination of sulfates and promotion effect, and the correlation actually concerns the Fe component of the Fe,Mn-promoted systems.

3.2. The activation step

Activation is the preparative step in which we note the major differences between unpromoted SZ systems and promoted FMSZ systems. In fact, with FMSZ catalysts, it is no longer true that the activation treatment can be carried out indifferently in any kind of atmosphere [19].

Figure 4 reports *n*-butane isomerization rate vs. time plots obtained at 323 K over FMSZ catalysts that were calcined at 923 K, rehydrated, and then activated in various conditions.

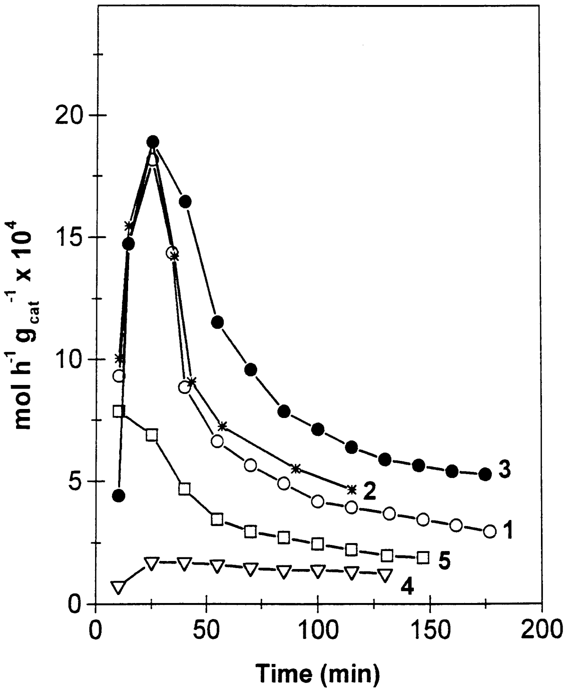

Figure 4. *n*-butane isomerization rate vs. time-on-stream plots measured at 323 K over a FMSZ catalyst calcined in a dry air stream at 923 K, rehydrated, and then activated at $T_{act} = 723$ K in various conditions. (1) First activation in a dry air stream. (2, 3) Subsequent activation cycles in a dry air stream. (4) Activation in a He stream. (5) After 4, the catalyst underwent a subsequent activation cycle in a dry air stream at 723 K.

Curve 1 of figure 4 shows that, after activation in a dry air stream at ~723 K, the isomerization rate vs. time plot presents the typical initial burst, characteristic of a system in which the promotion by the Fe,Mn additives is available. Curves 2 and 3 of figure 4 show that, after some 150–200 min reaction (i.e., when the promotion effect by the Fe,Mn additives is over), a subsequent activation cycle in dry air at ~723 K brings the catalyst to conditions very similar to the initial ones, and the break-in period is reproduced either unchanged (curve 2) or slightly increased (curve 3). This behaviour was observed, at 323 K, with all of our FMSZ catalysts as well as with other catalysts prepared with similar procedures [16], whereas other authors reported that, with somewhat different FMSZ preparations and for isomerization reactions carried out at slightly higher temperatures (373 K), the initial activity burst could be obtained only once [20].

Curve 4 of figure 4 shows that, when the activation cycle at the usual temperature (~723 K) is carried out in a He stream (i.e., in non-oxidizing conditions), no matter whether that is the first activation cycle or is a non-oxidizing activation cycle following other oxidizing ones, the catalytic isomerization rate is as low as it would be over a plain SZ catalyst in the same conditions. This means that, after a non-oxidizing activation, all the promotion effect by Fe,Mn additives is lost.

Finally, curve 5 of figure 4 shows that, whenever a non-oxidizing activation cycle has been performed and the promotion effect by Fe,Mn addidivites has been lost, the loss is almost irreversible. In fact, an oxidizing activation cycle at $T \leqslant 673$ K does not restore at all the promoting activity, and any activation cycle carried out in oxidizing conditions at $T > 673$ K restores the initial burst (i.e., the catalytic promotion effect) only to a variable and very limited extent.

These conversion rate data suggest the following: (i) The promotion by Fe,Mn additives, that in the opinion of several researchers occurs through the formation of an olefinic intermediate (for instance, see refs. [19–22]), involves a partial reduction of the promoting transition metal(s) [23]; (ii) The reduction of the promoters caused by the isomerization reaction is *reversible* to an oxidation at temperatures of the order of ~700 K (curves 1–3 of figure 4); (iii) Reducing conditions more drastic than those obtained, during the catalytic reaction, by contact with *n*-butane + He at temperatures as low as ~323 K bring about a more severe reduction of the promoting transition metal(s); (iv) This reduction process, unlike the reduction achieved during the promoted isomerization reaction, leads to a loss of the promoting activity that is almost *irreversible* to any oxidizing treatment at temperatures from ambient temperature to T_{act} as high as ~800 K, as indicated by curves 4 and 5 of figure 4.

The latter hypothesis has been checked by IR spectroscopic methods. If a FMSZ catalyst, first calcined at $T_{calc} \geqslant 923$ K, after rehydration is activated in vacuo at 673 K, i.e., in mildly reducing conditions comparable to the activation in a He stream (these are the activation conditions of curve 4 of figure 4), and the catalyst is then exposed to carbon monoxide at ambient temperature, IR spectra like curve 1 of figure 5 are obtained. In addition to the usual CO band at ~2200 cm^{-1} (due to strong Zr^{4+}_{CUS} Lewis sites), another broad and complex CO band is observed at ~2170 cm^{-1}. Curve 2 of figure 5 shows that, if the same vacuum activation treatment is performed on a FSZ catalyst (SZ promoted with only Fe), a similar CO band is obtained at ~2170 cm^{-1}, indicating that the Fe component is mainly responsible for the new CO band. This datum is confirmed by spectrum 3 of figure 5: if the same vacuum activation treatment is performed on a MSZ catalyst (SZ promoted with only Mn), no additional CO bands form at $\nu < 2180$ cm^{-1} upon CO uptake at ambient temperature. The CO band at ~2170 cm^{-1} was not observed previously in the spectra of FMSZ catalysts (e.g., see refs. [14,15], where CO spectra at all similar to those of plain SZ systems were reported), whereas several CO bands centered at $\nu < 2180$ cm^{-1} have been reported for sulfate-free Fe/ZrO_2 systems in various stages of surface reduction [24]. The band at ~2170 cm^{-1} is assigned to CO adsorbed onto CUS surface Fe^{n+} sites, where the average oxidation number n is lower than 3 (in fact no CO adsorbs at ambient temperature on Fe^{3+} centres [24,25]), but is probably higher than 2, in view of the relatively high C–O stretching frequency.

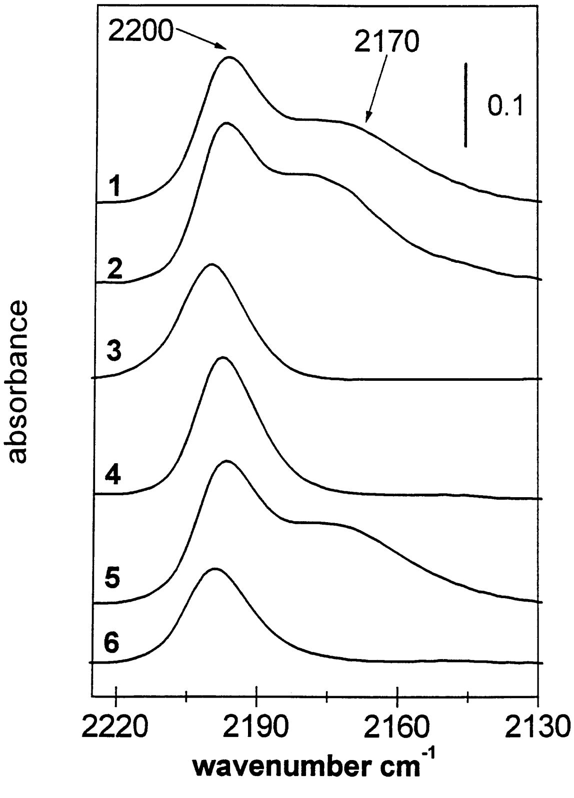

Figure 5. Absorbance IR spectra of CO (100 Torr) adsorbed at ambient temperature on catalysts calcined in a dry air stream at 923 K, rehydrated, and then treated under various conditions. (1) FMSZ activated in vacuo at 673 K. (2) FSZ activated in vacuo at 673 K. (3) MSZ activated in vacuo at 673 K. (4) After 1, FMSZ was oxidized at 298 K (40 Torr O_2 added, and excess O_2 evacuated). (5) After 4, FMSZ was activated in vacuo at 473 K. (6) After 4, FMSZ was oxidized at 723 K (40 Torr O_2), and then was activated again in vacuo at 673 K.

It may be objected that the integral absorbance of the CO band at ~2170 cm^{-1} is unexpectedly high with respect to that of the CO/Zr^{4+}_{CUS} band at ~2200 cm^{-1}, in view of the low Fe content of FMSZ and FSZ samples. Two aspects must be kept into account: (i) The extinction coefficient of the C–O stretching mode of surface carbonyl-like species may vary appreciably and, in fact, it is known to increase drastically as soon as a π back-donation contribution becomes present in the Me–C coordinative bond [26,27]. Still, in the case of the carbonyl band at ~2170 cm^{-1} the π back-donation contribution (if at all present) should be rather small, in view of the relatively high $\Delta\nu_{CO}$ blue shift ($[\nu_{CO}]_{gas} = 2143$ cm^{-1}); (ii) The intensity of the band at ~2200 cm^{-1} is expected to be particularly low, and the relevant amount of CO/Zr^{4+}_{CUS} surface complexes is known to be quite small, as on both t-ZrO_2 and sulfated t-ZrO_2 only the strongest fraction of strong Lewis acid sites (due to Zr^{4+}_{CUS} ions in crystallographic defects) can adsorb CO at ambient temperature [11,28]. The overall surface concentration of Zr^{4+}_{CUS} centres is at least one order of magnitude larger [28,29], but most of these Lewis sites are revealed by CO uptake only at low temperatures, as in the case of most d^0 metal oxides [27].

The coordinative unsaturation giving surface reduced Fe^{n+} centres the adsorptive capacity responsible for the CO band at ~2170 cm^{-1} is readily quenched by O_2 uptake at ambient temperature, as shown by curve 4 of figure 5. O_2 adsorption at ambient temperature is sufficient to eliminate the adsorptive activity towards CO that yields the band at ~2170 cm^{-1}, but the surface Fe component is not brought back to the original state. In fact, as reported above, a mild oxidizing treatment with O_2 at ambient temperature does not restore at all the promoting activity of the Fe component. Moreover, the oxygen species adsorbed at room temperature, that prevents the adsorption of CO, turns out to be a rather labile one, as a vacuum treatment at mild temperatures (of the order of ~473 K) is sufficient to yield back the adsorptive capacity towards CO and the band at ~2170 cm^{-1} (see curve 5 of figure 5).

If on the reduced FMSZ catalyst an oxidizing treatment is carried out at $T > 673$ K (this is the secondary activation cycle that was shown above to restore only to a minimal extent the catalytic promotion activity; see curve 5 of figure 4), the Fe component of the FMSZ catalyst is brought to a state in which Fe does not adsorb CO (i.e, no CO band forms at ~2170 cm^{-1}) and from which Fe cannot be further reduced in vacuo so as to yield the CO band at ~2170 $\mathrm{cm^{-1}}$ (see curve 6 in figure 5). This state of non-reducibility of the Fe component corresponds to the virtually irreversible loss of promoting activity of FMSZ catalysts caused by a non-oxidizing activation cycle, as presented in figure 4 and discussed above. IR spectroscopy of CO uptake at ambient temperature so gives us an indirect (and destructive) analytical tool to understand if a FMSZ catalyst possesses its promoting activity: its surface Fe component is active and available for the promotion effect if it is reducible by any mild reducing treatment at temperatures of the order of ~673 K. This reduction, that suppresses in a virtually irreversible way the promoting activity, can be easily monitored by the formation at ambient temperature of a CO IR band centered at ~2170 $\mathrm{cm^{-1}}$.

This spectroscopic tool gives also some more meaning to the dependence of the promoting activity of FMSZ catalysts on the temperature of the calcination step, dealt with in a previous section. Figure 6 shows that, when a FMSZ catalyst is calcined at $T_{\text{calc}} < 873$ K (curves 1 and 2), it does not possess reducible surface Fe. In fact, consistent with what has been proposed above, in these conditions surface Fe is likely to be still covered by sulfates, and an activation in vacuo at ~673 K followed by exposure to CO at RT does not lead to the formation at ~2170 $\mathrm{cm^{-1}}$ of a CO band of appreciable intensity. But when the calcination step is carried out at $T_{\text{calc}} > 873$ K (curves 3–5), increasing amounts of surface Fe are liberated from sulfates and become reducible, so that a subsequent activation in vacuo at ~673 K followed by exposure to CO at RT will lead to the formation of a CO band at ~2170 $\mathrm{cm^{-1}}$ of increasing relative intensity with respect to the CO band at ~2200 $\mathrm{cm^{-1}}$ (strong $\mathrm{Zr^{4+}_{CUS}}$ sites). This adsorptive behaviour towards CO, monitoring the reducibility of surface Fe on FMSZ catalysts, parallels the evolution of the promoting activity of FMSZ catalysts that was shown in figure 3.

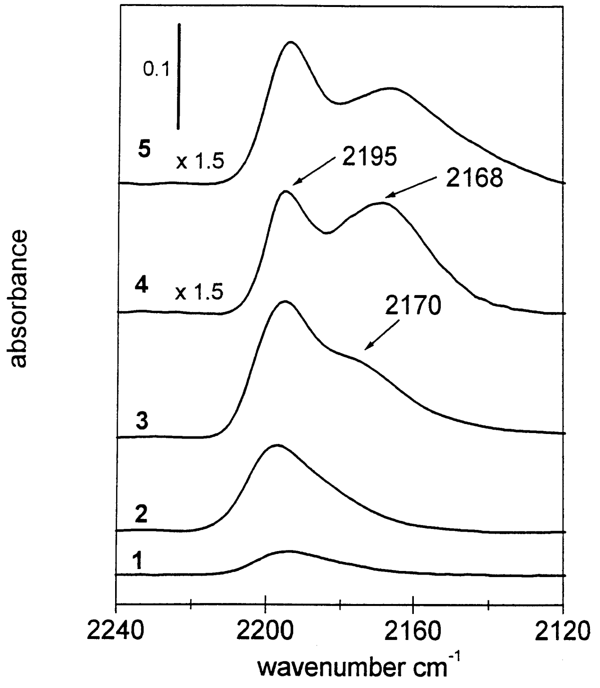

Figure 6. Absorbance IR spectra of CO (100 Torr) adsorbed at ambient temperature on FMSZ catalysts calcined at various temperatures in a dry air stream (unless otherwise specified), rehydrated, and then activated in vacuo at 673 K. (1) $T_{\text{calc}} = 673$ K. (2) $T_{\text{calc}} = 823$ K. (3) $T_{\text{calc}} = 923$ K. (4) $T_{\text{calc}} = 998$ K, in oven. (5) $T_{\text{calc}} = 998$ K. Curves 4 and 5 underwent a 1.5-fold ordinate expansion, as the high calcination temperature brought about a fair decrease of surface area.

What has been considered so far in this section concerns the effect on the catalytic performances of the atmosphere in which the activation step is performed. As for the effect produced on the promotion by Fe,Mn additives by the temperature of the (oxidizing) activation step, it has been observed to depend primarily on the temperature at which the catalytic process is carried out. This aspect is dealt with in the next section.

3.3. *The activation temperature and the reaction temperature*

3.3.1. *Reaction at low temperature*

If the catalytic isomerization reaction is carried out at temperatures close to ambient temperature (in our case a $T_{\text{react}} = 323$ K was used, but temperatures as low as some 303 K have been used with success by other authors [19]), isomerization rate vs. time plots of the type reported in figure 7a are obtained. It can be seen that, at least up to $T_{\text{act}} = 723$ K, the higher is the activation temperature, the higher is the promotion effect.

Two explanations can be suggested, that do not necessarily exclude each other: (i) Much as in the case of *n*-butane isomerization at ~423 K over non-promoted SZ catalysts, over FMSZ catalysts the isomerization reaction at ~323 K is favoured by a high Lewis to Brønsted acid sites ratio, induced by a high activation temperature; (ii) High activation temperatures are necessary to liberate from surface water and/or surface hydroxyls the promoting metal sites that were freed from sulfates during the calcination step and were then rehydrated upon exposure to the atmosphere.

As for the latter hypothesis, it is worthwhile recalling that for activation at temperatures up to ~723 K a fair amount of hydroxyls is indeed eliminated from the surface of all zirconias, but in no dehydration stage of our FMSZ systems ν_{OH} IR bands to be specifically ascribed to the Fe,Mn promoters have been isolated. As for the first hypothesis, the importance of the Lewis acid sites in the promoted acid catalysis at 323 K over FMSZ catalysts is demonstrated, in figure 7b, by the almost complete and reversible poisoning of the catalytic isomerization process brought about by the introduction in the reagents flow of some CO. It has been shown that, at ambient temperature or above, CO interacts selectively and reversibly with strong Lewis acid sites and, in the case of SZ systems, this

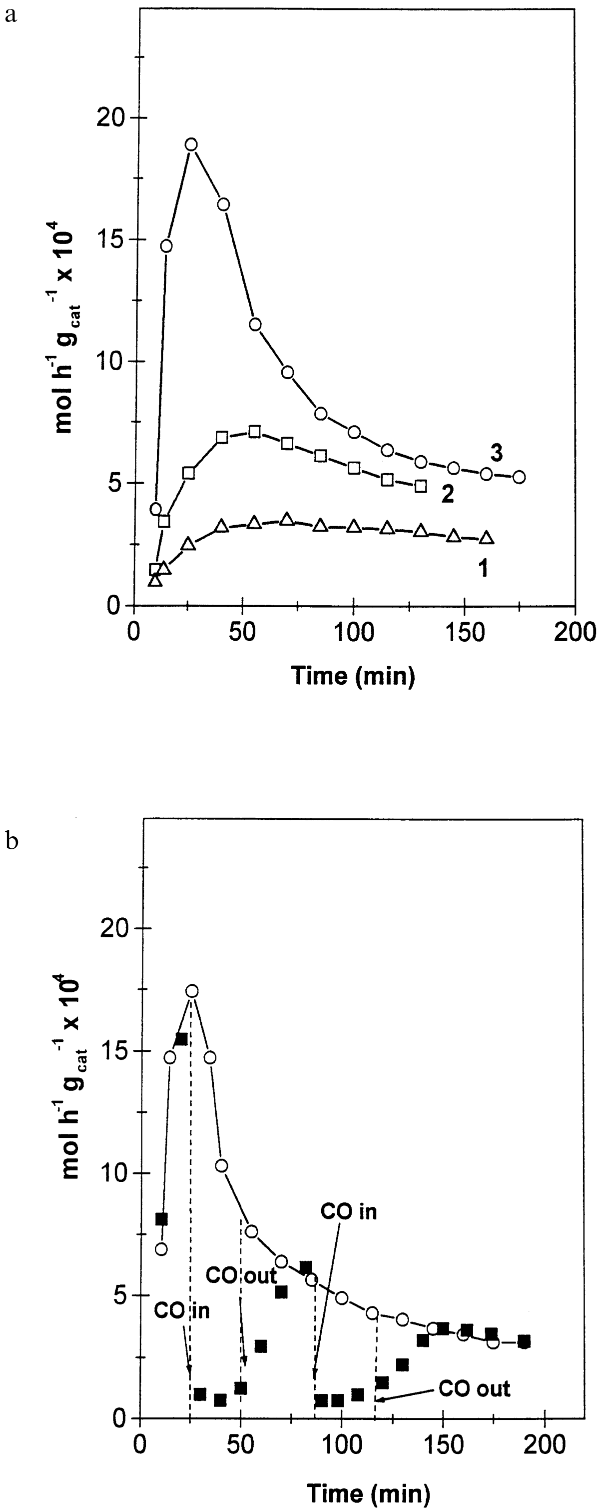

Figure 7 (a) n-butane isomerization rate vs. time-on-stream plots measured at 323 K over FMSZ catalysts calcined at 923 K in a dry air stream, rehydrated, and then activated in a dry air stream at various temperatures. (1) $T_{act} = 473$ K. (2) $T_{act} = 573$ K. (3) $T_{act} = 723$ K. (b) n-butane isomerization rate vs. time-on-stream plots measured at 323 K over a FMSZ catalyst calcined at 923 K in a dry air stream, rehydrated, and then activated in a dry air stream at 723 K. Open symbols: the carrier gas was pure He. Dark symbols: the carrier gas contained some CO (constant overall flux, constant amount of n-butane, CO to n-butane ratio = 2 : 5).

means Lewis acid sites located in crystallographic defects [12,30]. It should be noted that: (i) Unlike what has been reported by Wan et al. [19], the poisoning of our FMSZ catalysts by CO addition at 323 K is fully reversible. As soon as CO is removed from the reaction mixture, the catalytic reaction rate is recovered, both during the break-in phase and during the deactivation phase; (ii) No CO oxidation and CO_2 production was ever observed by either MS or IR (at these low temperatures, on t-ZrO_2 CO_2 would readily form surface carbonates, which should be monitored by typical bands in the 1800–1300 cm^{-1} range [31]); (iii) CO uptake does not interfere with the promotion effect, as no CO adsorbs at ambient temperature (at least to a spectroscopically detectable level) on the non-reduced Fe component.

These data seem to indicate that: (i) On FMSZ catalysts, the n-butane isomerization reaction proceeds at near ambient temperature through an acid-controlled mechanism at all similar to that typical of plain SZ catalysts at higher temperatures (see, for instance, refs. [22,32] and references therein); (ii) The promotion, mainly caused by the Fe component, consists of a limited redox process that triggers the acid-catalyzed reaction at much lower temperatures than on SZ. The reaction trigger is most likely represented by the formation, at sulfate- and OH-free oxidized Fe sites, of an olefinic intermediate. The formation of the intermediate was first postulated in the bimolecular mechanism proposed by Sachtler et al. [21], and is now accepted by most researchers (e.g., see refs. [23,32]).

3.3.2. *Reaction at higher temperature*

If the isomerization reaction is carried out at temperatures of the order of ~423 K (i.e., at the temperature corresponding to the best performances of plain SZ catalysts), parameters like the activation temperature and the activation environment turn out to be no longer of any practical importance.

Figure 8 shows that the isomerisation rate vs. time plot obtained at 423 K is virtually the same for FMSZ activated at 723 K in dry air (curve 1) and in He (curve 2), as already observed by others [19]. The reaction rate starts relatively high, but declines very steeply to almost zero. If, after the fast completion of the isomerization reaction at 423 K, a second oxidizing activation cycle is carried out at 723 K, and then an isomerization reaction cycle is performed at low temperature (323 K), the rate vs. time plot will exhibit the initial burst on the catalyst that was first activated in dry air, meaning that the promotion is active (see curve 1*), whereas almost no initial burst (i.e., no promotion) is exhibited on the catalyst that was first activated in a He stream (curve 2*). This indicates that the virtual coincidence of the fast deactivating curves 1 and 2 is not due to a similar reduction of the promoter(s) caused by the contact with the hydrocarbon at 423 K:

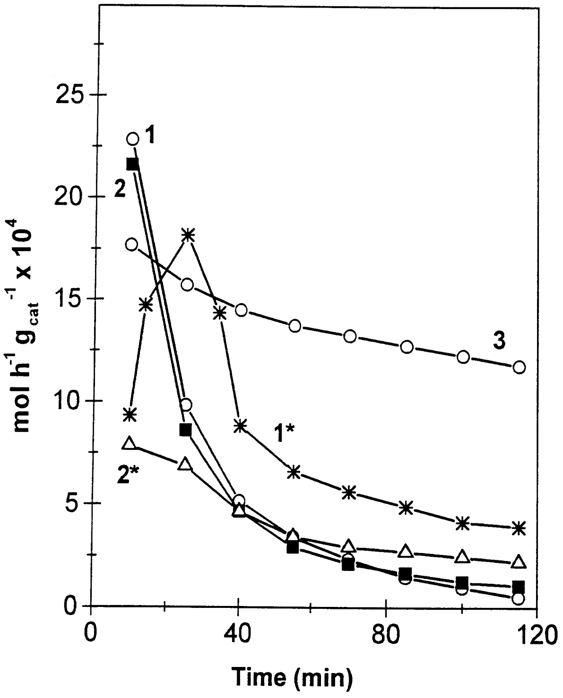

Figure 8. n-butane isomerization rate vs. time-on-stream plots measured at 423 K, unless otherwise specified. (1) FMSZ calcined at 923 K, rehydrated, and then activated in a dry air stream at 723 K. (2) FMSZ calcined at 923 K, rehydrated, and then activated in a He stream at 723 K. (1*) After 1 (120 min reaction), the FMSZ catalyst was reactivated in a dry air stream at 723 K, and then an isomerization reaction cycle was carried out at 323 K. (2*) After 2 (120 min reaction), the FMSZ catalyst was reactivated in a dry air stream at 723 K, and then an isomerization reaction cycle was carried out at 323 K. (3) Non-promoted SZ calcined at 923 K, rehydrated, and then activated in a dry air stream at 723 K.

the air-treated catalyst can be reactivated by a second activation cycle, whereas the He-treated catalyst cannot.

For comparison, curve 3 of figure 8 reports the isomerization rate vs. time plot observed at 423 K over a non-promoted SZ catalyst, calcined and activated in the same conditions as the promoted FMSZ catalyst of curve 1. It is interesting to note that at 423 K the rate plot of FMSZ (curve 1) does not decline asymptotically toward the rate level typical of a plain SZ catalyst in the same conditions, but to much lower rate values. This means that the fast loss of any promotion activity by Fe,Mn additives, brought about by a high reaction temperature, did not leave the catalyst in conditions comparable to those of the corresponding non-promoted system. It seems thus reasonable to suppose that, at 423 K, the Fe,Mn additives still play a specific catalytic role, that in this case acts against the isomerization mechanism. The fast decay can be possibly ascribed to the accumulation of olefinic reaction intermediates that, at that temperature, evolve only in part toward the isomerization product and, to a significant extent, toward the formation of oligomers capable of poisoning the active sites.

4. Conclusions

In FMSZ catalysts, the promotion effect is mainly ascribable to the Fe component, as already postulated by other authors (e.g., see ref. [20]). To the best of our knowledge, so far nobody has been able to indicate what is the possible promoting role played by the Mn component.

The promotion effect requires four conditions. (i) The calcination step must be carried out at $T_{\mathrm{calc}} \geqslant 870$ K. High calcination temperatures are needed in order to liberate, most likely from sulfates, as much as possible of the surface Fe component. The highest useful T_{calc} is determined by the thermal stability of the sulfates located on the regular crystal terminations of ZrO_2, as their presence is determinant for the acid-controlled catalytic isomerization process; (ii) The activation step must be performed in strictly oxidizing conditions, in order to leave as much as possible of the surface Fe component in an easily reducible form; (iii) The activation step must be carried out at relatively high temperatures ($\sim$673 K), in order to bring the catalyst to a high dehydration degree and to render high the Lewis to Brønsted acid sites ratio; (iv) The isomerization reaction temperature must be kept low, i.e., close to ambient temperature, otherwise reaction processes other than isomerization will prevail and poison the catalyst.

The promotion effect is a redox trigger of the acid catalyzed process. In the promotion process, sulfate-free Fe^{3+} surface species are mildly reduced to a still non-identified lower valence state, that is reversible to a further oxidizing activation step at temperatures of the order of 673 K.

Reductive treatments like, for instance, a thermal treatment at $\sim$673 K in vacuo or in a He stream are more drastic than the process leading to the promotion effect at $\sim$323 K, and bring about an extensive reduction of the surface Fe component and the loss of any promoting activity. This more drastically reduced state of the surface Fe component, monitoring the loss of the promoting activity, can be easily revealed by IR spectroscopic means, and is largely non-reversible. In fact, an oxidizing treatment at temperatures from ambient temperature up to $\sim$723 K produces an insufficient reoxidation of the Fe component, whereas treatments at temperatures above $\sim$773 K, no matter whether carried out in oxidizing or non-oxidizing conditions, lead the Fe component to a no longer reducible state. Preliminary data seem to indicate that, in these conditions, a rather stable interaction of the Fe component with the support is induced, and this strong interaction can be reversed only through a hydrothermal treatment at high temperatures. Deatils on this aspect will be reported elsewhere.

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