

Isomerization of *meta*-Xylene over Offretite Catalysts

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The conversion of *meta*-xylene has been investigated over offretites with different levels of ion exchange. The ratio isomerization/disproportionation increases with the degree of exchange, most probably due to an increased accessibility of the reactant to the internal surface and to a higher number and strength of acid sites. The addition of a hydrogenation function, in H₂ atmosphere, slightly increases the activity and decreases the deactivation as a function of time. The conversion of 1-3-dimethylcyclohexene-1 yields experimental evidence that a bifunctional path exists for the reaction in these conditions. The supposed intermediate olefin isomerizes and disproportionates faster than *meta*-xylene, but the *ortho/para* selectivity remains unchanged. © 1990 Academic Press, Inc.

INTRODUCTION

Synthetic tetramethylammonium (TMA)-offretite is the end member of the offretite-erionite family, prepared from aluminosilicate gels containing tetramethylammonium and K⁺ and Na⁺ ions (1-3). Offretite has a hexagonal structure and the channels, formed of 12-membered rings of aperture 0.67 nm, run parallel to the *c* axis. These channels are circumscribed by gmelinite cages with 8-membered oxygen openings in the *a* direction. These windows are large enough to admit molecules smaller than 0.5 nm (4, 5). The bulky organic cations which block the channels can be removed by oxidation at 773 K in air, without decreasing appreciably the crystallinity of the zeolite (4). The inorganic cations are located in part in the inaccessible cancrinite cages and in part in the gmelinite cages which restrict the access to the channels (6).

Protonic offretite prepared by NH₄⁺ exchange of K⁺ ions and calcination has a stronger acidity than protonic Y zeolite (3, 7-9), and is highly active for cracking of *n*-hexane and isomerization of xylenes. Offretite was six times more active than Y in *n*-hexane cracking, as expected from its

higher acidity, but one-half as active as Y in *ortho*-xylene isomerization, probably because of configurational limitations caused by stacking faults present in the crystal (10). Pyridine poisoning of *n*-hexane cracking revealed a residual activity attributed to the presence of very strong acid sites located in the gmelinite cages not accessible to aromatics. In the conversion of xylenes (9), it was concluded that only isomerization was catalyzed by the internal surface of the zeolite, disproportionation being catalyzed by the acid sites at the external surface of the crystals. Coke formation is slower on offretite than on Y, but the toxicity of coke is 18 times higher on offretite due to the unidimensional network of the zeolite (11).

The influence of the degree of K⁺ exchange has been reported briefly (12) but with contradictory results since a higher degree of ion exchange led to a decrease of the rate of isomerization of *meta*-xylene, an increase of the conversion of *ortho*-xylene, and a constancy of the conversion of *para*-xylene. In the conversion of *meta*-xylene, the selectivity to *para* was high and disproportionation was very low.

All this previous work was performed using pure acid catalysis. It has been known

for years (13) that the addition of a hydrogenation function to silica-alumina catalysts stabilizes activity. This effect has also been reported in the case of mordenites by introduction of nickel (14). Operating the catalyst in hydrogen at atmospheric pressure reduces coke formation and disproportionation. Nickel exchanged into the mordenite, or added as Ni/SiO₂ in a mechanical mixture, shows the same effect. A spillover of hydrogen onto the support was proposed to account for this effect (15). This H species would then be able to react with the benzylic cations considered as the intermediates of disproportionation and coke formation, thus decreasing these side reactions. This effect should be favored when increasing the H₂ pressure; however, under industrial conditions, disproportionation remains at a noticeable level (16), which explains the success of pure acidic processes for isomerization in the liquid phase.

This mechanism of H₂ inhibition of disproportionation therefore needs further clarification. The present article is devoted to the influence of the degree of ion exchange on the catalytic properties of offretite for the isomerization of *meta*-xylene, and to the influence of hydrogen and of a hydrogenation function in this reaction. As Ni exhibits high hydrogenolysis activity, Pt was selected as the hydrogenating metal.

EXPERIMENTAL

Catalysts. A sample of K—TMA—offretite, of chemical composition (0.86 K + 0.03 Na + 0.11 TMA)₂O; Al₂O₃; 6SiO₂ was synthesized using the method previously described (17). This sample was obtained in the form of spheroids of small size (0.3 μm in diameter) of pure offretite, with 100% crystallinity. The characterization of similar samples has been described previously (18). The organic template was eliminated by calcination in air at 823 K for 5 h. The K⁺ ions were exchanged for NH₄⁺ using contact with a saturated solution of NH₄Cl, at 353 K, for half an hour. After filtration and drying at 393 K, the sample was deammoniated by

TABLE I
Characteristics of the Catalyst Samples

Sample	Percentage exchange	Wt% Pt	H/Pt
C ₁	32	0	—
C ₂	56	0	—
C ₃	68	0	—
C ₄	74	0	—
C ₅		0.37	0.9
C ₆	32	1	
C ₇	74	1	0.30
C ₈	74	0.5	0.34

calcination at 823 K and then reexchanged with NH₄Cl. After each exchange, the amount of K⁺ was analyzed in the solution. Catalyst C₁ corresponded to one exchange, C₂, C₃, and C₄ to 2, 3, and 4 successive exchanges, respectively. XRD powder diffraction performed after calcination showed more than 90% retention of the crystallinity of the original TMA—OFF sample. Catalyst C₄ sorbed 7 wt% of cyclohexane at room temperature and a relative pressure of 0.2, indicating the absence of faulting. Catalyst C₅ was a Pt/Al₂O₃ catalyst, loaded with 0.37 wt% Pt, the dispersion of which was 90% as determined by hydrogen chemisorption.

Catalyst C₆ was prepared from C₁ by impregnation with chloroplatinic acid using the incipient wetness technique. C₇ and C₈ were obtained from C₄ by the same method. After impregnation, the samples were dried at 393 K overnight, calcined at 823 K in air for 5 h, then reduced in flowing H₂ at 673 K for 3 h.

The characteristics of these samples are summarized in Table 1.

Catalytic measurements. These were performed at atmospheric pressure in a conventional flow microreactor at low conversion. The reaction temperature was 623 K, and a fresh sample was used for each determination.

Two procedures were used for the test: for pure zeolites (without Pt), a stream of N₂ was established over the catalyst, then

the temperature was raised to 623 K at 10 K/min. The temperature of 623 K was maintained for 30 min, then raised to 723 K for 30 min, and finally decreased to 623 K, being maintained 30 min at this temperature before the introduction of the reactant mixture $N_2/\text{hydrocarbon} = 4/1$.

With Pt-containing catalysts, the reaction mixture $H_2/\text{meta-xylene} = 4/1$ was used. The general procedure was similar, but the temperature of 723 K was maintained for 3 h, before reaching the reaction temperature of 623 K. *Meta*-xylene (Scharlau, purity > 99%) was introduced using a Braun Mel-sungen syringe. The effluents were collected at short times on stream in order to follow catalyst deactivation. These effluents were analyzed by GLC on a Varian 3700 gas chromatograph equipped with a column (4 m) filled with silicon phases DC 200 Me (16%) and Bentone 34 (3%) on chromosorb W (80–100 mesh).

In the course of the reaction, the catalysts suffered deactivation. Activity decay followed a first-order rate law:

$$x_t/(x_t)_0 = \exp(-k_d t),$$

where x_t is the average conversion at time t , $(x_t)_0$ the conversion on the fresh catalyst, and k_d the deactivation rate constant. This equation enables one to calculate $(x_t)_0$ and k_d . The possible influence of diffusional limitations was estimated by using the equation $\Phi = R(\lambda/D)^{1/2}$, proposed by Weisz for first-order kinetics (19), where R is the radius of the particles (1.5×10^{-4} cm), λ the reaction rate constant (taken here equal to the reaction rate 10^{-4} mole/sec/cm³), and D the diffusion coefficient reported by Chutoransky and Dwyer (20) ($D = 10^{-7}$ cm²/sec). The value found ($\Phi = 10^{-2}$) ruled out a limitation of the kinetics by diffusional resistance.

RESULTS AND DISCUSSION

1. Influence of the degree of exchange.

The degree of exchange of the different samples is reported in Table 1. The first exchange substituted 30–35% of the initial K^+ cations, which corresponded roughly to 1

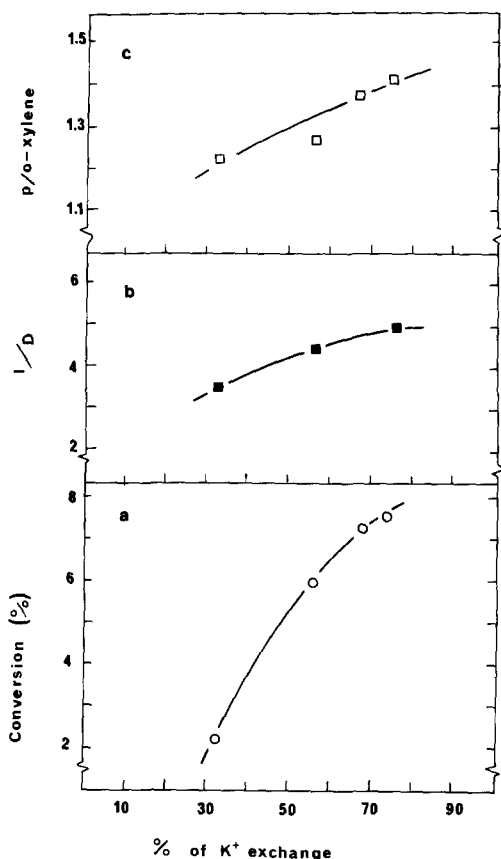


FIG. 1. Influence of the percentage of exchange of the potassium cations on the activity and selectivity of offretite in the conversion of *meta*-xylene at 623 K (a) total conversion; (b) isomerization/disproportionation ratio; (c) *para*-xylene/*ortho*-xylene ratio.

K^+ per unit cell as the original solid contains $3.8 K^+/\text{u.c.}$ The successive exchanges increased the degree of decationization and the final solid contained one $K^+/\text{u.c.}$

The influence of cation exchange on the catalytic properties of offretite for the conversion of xylenes is reported in Fig. 1. Both the activity and the selectivity were affected by cation exchange. The activity was low at 32% exchange and increased with decationization. This behavior reflects the increase of acidity (7) and the higher accessibility to the internal surface of the crystals after removal of K^+ ions. Aiello *et al.* (6) described the changes of adsorption capacity

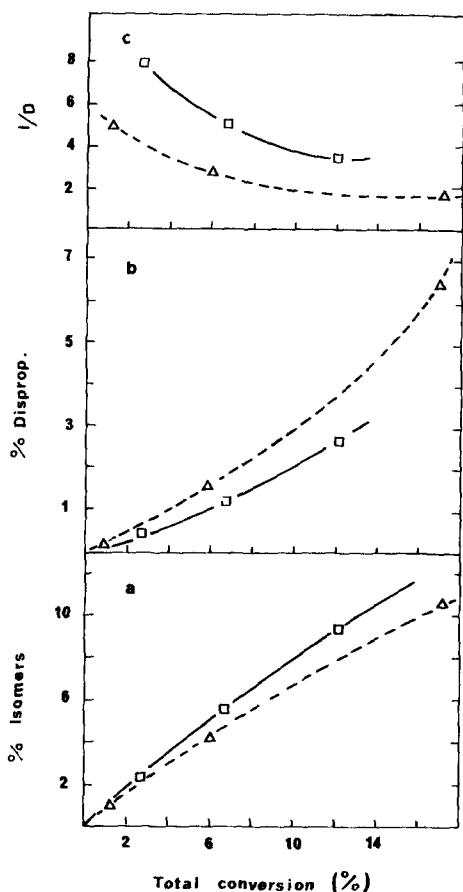


FIG. 2. Yields of isomers (a) and disproportionation products (b) and selectivity (c) of catalysts C_1 (Δ , 32% exchange) and C_4 (\square , 74% exchange) as a function of the total conversion.

for *meta*-xylene of offretite as a function of the degree of K^+ exchange. Intracrystalline adsorption of *m*-xylene requires an offretite containing less than 2 K^+ per unit cell, as obtained after two successive exchanges.

Decationization increased the yield in disproportionation from 0.46 at 30% exchange to 1.1 at 55% exchange and 1.3 at 70% exchange, but promoted more isomerization which increased from 1.6 to 4.9 then 6.3%. Therefore the increase of the ratio isomerization/disproportionation (I/D) (Fig. 1b) is mainly due to the increase of the rate of isomerization. Simultaneously the selectivity for *para*-xylene increased (Fig. 1c).

However, these comparisons are made at different conversions. The evolution of the yields and selectivities with conversion are reported in Fig. 2 for catalysts C_1 and C_4 : at the same conversion, the yield of isomerization was increased (Fig. 2a) but the yield of disproportionation was decreased (Fig. 2b) by cation exchange and this explains the changes of selectivity reported in Fig. 2c.

Bourdillon *et al.* (10) studied the isomerization of xylenes under comparable conditions on a sample of offretite of similar composition, formed of crystals in the size range 2–3 μm . The external surface of these crystals was then smaller than that of the sample used here (size 0.3 μm). The ratio $I/D = 20$ reported by these authors at 623 K, greater than that observed here, shows an influence of the particle size of the crystals of offretite on selectivity, which agrees with their proposal that disproportionation is mainly catalyzed by the external surface of the crystals. As reported in Fig. 2, disproportionation decreases at the higher exchange. These results have been obtained by extrapolation to zero time on stream, using fresh samples, and can hardly be due to changes in activity induced by coke deposition. Disproportionation of xylenes most probably proceeds through benzylic cations (21), which have been observed by spectroscopic methods (22). The formation of these cations is more difficult than protonation of the aromatic ring and thus requires acid sites stronger than those needed for isomerization (21). Thus the increase of acid strength induced by ion exchange should favor disproportionation in the case of a large participation of the internal surface of the zeolite to this reaction. The increased accessibility upon K^+ exchange (2) should also favor bimolecular reactions such as disproportionation at the expense of monomolecular isomerization. The observation of a lower selectivity for disproportionation at the higher degree of exchange then suggests that this reaction is indeed catalyzed mainly by the outer surface of crystals.

The increase of selectivity into *para*-xy-

TABLE 2

Influence of the Carrier Gas on the Catalytic Properties of Catalyst C₄ at 623 K (Flow of *meta*-Xylene: 28.2 g h⁻¹)

Gas	Weight of catalyst (g)	Conversion of <i>m</i> -Xylene (%) ^a	Yields (%) ^b			
			<i>p</i> -Xylene	<i>o</i> -Xylene	Tol.	TMB
H ₂	0.058	9.1	4.6	3.2	0.6	0.7
N ₂	0.052	7.1	3.6	2.6	0.4	0.5

^a Extrapolated to time zero.

^b Tol. = toluene, TMB = trimethylbenzenes.

lenes with cation exchange can be attributed to shape selectivity. The effect is weak however because of the small size of the crystals. The main conclusion of this study of the isomerization of *m*-xylene on offretite is that the catalytic activity increases monotonically upon exchange of K⁺ cations. By removal of these cations, the concentration of protons increases as the accessibility to the internal porosity of the zeolite, with the result that the selectivity for isomerization is promoted at the expense of disproportionation.

2. Influence of a hydrogenation function.

It was first checked that with pure offretite the results were comparable when using H₂ or N₂ as carrier gas. A better stability of activity was observed in H₂ (for the catalyst C₄ *k_d* values equal to 0.23 and 0.29 min⁻¹ were obtained under H₂ and N₂, respectively), but the selectivities were not noticeably altered (Table 2). Pt/Al₂O₃ alone (catalyst C₅) showed a low activity for isomerization; the conversion was lower than 0.2% with H₂ as carrier gas in the conditions of reaction.

In H₂ atmosphere, the addition of Pt/Al₂O₃ to offretite in a mechanical mixture resulted in a stabilization of catalytic activity (Fig. 3), a slight increase of activity, a decrease of disproportionation (Fig. 4), but no appreciable modification of the *para/ortho* ratio (Table 3).

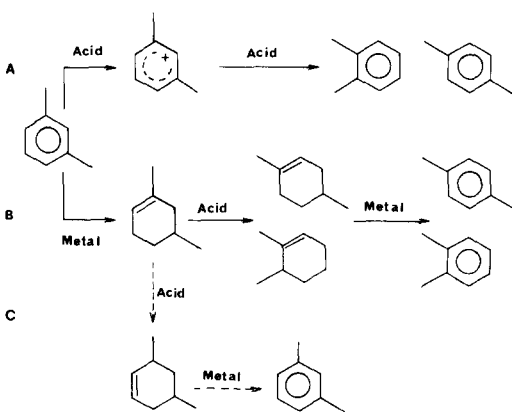
By contrast, in nitrogen the presence of Pt resulted in a faster deactivation. The same tendency was reproduced when Pt was in-

troduced onto the zeolite by impregnation: the total conversion was lower in that case, probably because Pt crystallites decreased the accessibility to the internal surface of the zeolite, as is known in the case of Pt/omega (23). Moreover, the ratio I/D increased but the *para/ortho* selectivity was unchanged.

The effect of a hydrogenation function on deactivation and disproportionation has been reported by Gnep *et al.* (15) for the isomerization of *ortho*-xylene on mordenites. These authors proposed that hydrogen activated on metallic sites spills over to the acid catalyst, and reacts with the benzylic cations which are the intermediates for disproportionation and coke formation. This reaction decreases their concentration and consequently decreases the rate of these reactions.

It is interesting to note that the initial activity was slightly increased with the mechanical mixture C₄ + C₅ in hydrogen (Fig. 3). This suggests that a second mechanism, a bifunctional one, could operate in that case. Such a mechanism can be described as shown in Scheme 1, where path A is the classical monofunctional acid mechanism, and path B is the bifunctional mechanism.

A bifunctional mechanism requires only trace amounts of olefins, which may not be detected in the gas phase, as is generally the



SCHEME 1

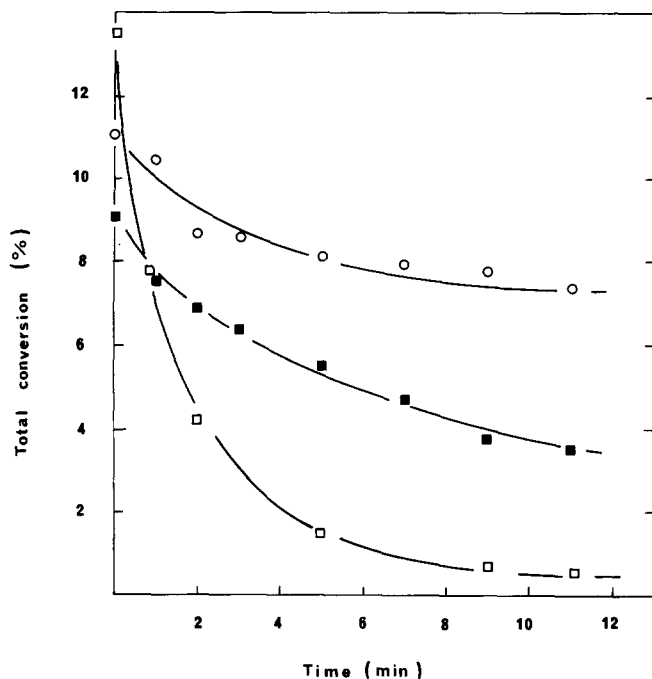


FIG. 3. Influence of the addition of a hydrogenation function to offretite and of the carrier gas on the stability of the catalytic activity. (■) Catalyst C₄, hydrogen flow, $k_d = 0.23 \text{ min}^{-1}$; (○) Catalyst C₄ + C₅, hydrogen flow, $k_d = 0.09 \text{ min}^{-1}$; (□) Catalyst C₄ + C₅, nitrogen flow, $k_d = 0.62 \text{ min}^{-1}$.

case in paraffin conversion (24). Olefins are more strongly adsorbed than aromatics and it can be postulated that the competition between olefins and aromatics would then decrease the surface concentration of aromatics. Bimolecular reactions, such as disproportionation and coke formation, would be much more sensitive to this effect than isomerization. This hypothesis then agrees

with the experimental data concerning the isomerization of xylenes. The *ortho/para* selectivity observed here shows that equilibrium (*ortho/para* = 1) is not reached in the isomerization of the intermediate carbonium ions. This may account for the absence of ethylbenzene, which is formed in small amount at equilibrium (ethylbenzene/*o*-xylene = 1/3).

TABLE 3

Activities and Selectivities of Pure Offretite and of Pt-Containing Catalysts in H₂ at 623 K (Flow of *meta*-Xylene: 28 g h⁻¹)

Catalyst	Weight (mg)		Conversion (%)	Yields (%)		Ratio I/D
	Pt/Al ₂ O ₃	OFF		<i>p</i> -Xylene	<i>o</i> -Xylene	
C ₄	—	56	9.1	4.6	3.2	6.0
C ₄ + C ₅	123	57	11.1	6.2	4.5	26.7
C ₈	—	57	7.5	3.8	2.8	7.3
C ₇	—	55	8.5	4.5	3.2	9.6

TABLE 4

Conversion of 1,3-Dimethylcyclohexene-1 at 623 K in Presence of Hydrogen (Flow of Reactant: 25.2 g h⁻¹)

Catalyst	Weight (mg)		Aromatics	Yields			
	OFF	Pt/Al ₂ O ₃		<i>m</i> -Xyl.	<i>p</i> -Xyl.	<i>o</i> -Xyl.	Tol + TMB
C ₄	48	—	0.5	—	—	—	—
C ₅	—	97	24.9	24.6	0.2	0.1	—
C ₄ + C ₅	48	96	44.8	35.5	4.6	2.9	1.6
C ₇	49	—	0.5	0.5	—	—	—

3. *Conversion of 1,3-dimethylcyclohexene-1*. In order to check the possible contribution of bifunctional mechanisms, the conversion of 1,3-dimethylcyclohexene-1 was investigated on the same series of catalysts. The data are reported in Table 4.

On pure offretite (catalyst C₄), the activity for the production of xylenes was very low, most probably due to a fast coking of the catalyst. Pt/Al₂O₃ gave a high yield in aromatics by dehydrogenation of the reactant and showed poor activity for isomerization.

Pt/offretite (C₇) also showed poor activity, attributed to a restricted accessibility of the reactant to the zeolite pores.

With the mechanical mixture Pt/Al₂O₃ + offretite, the conversion to aromatics increased, and these aromatics included *para*- and *ortho*-xylenes, and products of disproportionation. The higher yield of formation of aromatics suggested some isomerization of the olefinic reactant. At the reaction temperature, on an acid catalyst, the double bond can shift. It is well known that the rate of hydrogenation of olefins is much lower for substituted olefins. The higher rate of production of aromatics with the mechanical mixture could then be accounted for by assuming that the double bond shifted to carbon 5 on the ring, favoring the dehydrogenation of the naphthene (path C of Scheme 1).

It is interesting also to note that *para*-xylene was formed at a higher rate here than in the monofunctional reaction: if we compare the results from Tables 3 and 4, we see

that, for nearly comparable contact times (flow of *meta*-xylene: 28.2 g h⁻¹, flow of 1,3-dimethylcyclohexene 25.2 g h⁻¹), the production of *para*-xylene was 6.2% for pure xylene, and 4.6% for a relative concentration of xylene of 35.5%. The isomerization of xylenes is a first-order reaction relative to the concentration of xylenes (25, 26), so the relative rate constant determined here for the formation of *para*-xylene would be

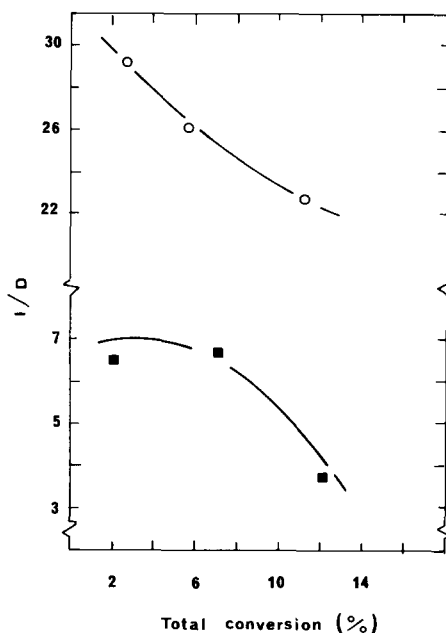


FIG. 4. Influence of the hydrogenation function on the isomerization/disproportionation ratio as a function of the total conversion. (■) catalyst C₄, (○) catalyst C₄ + C₅.

6.2 for the conversion of *meta*-xylene and $4.6/0.35 = 13$ for the conversion of 1,3-dimethylcyclohexene. The reaction was therefore faster when using the olefin as reactant. The *para/ortho* and isomerization/disproportionation selectivities (ratio I/D = 4.7) were comparable to those observed in the conversion of *meta*-xylene (I/D = 6.2) at a lower partial pressure of olefin, which agrees with the proposal of a bifunctional mechanism.

In conclusion, the addition of a hydrogenation function (mechanical mixture Pt/Al₂O₃ + OFF) reduces the decay of catalytic activity with time on stream and the selectivity for disproportionation increases the initial activity but changes only marginally the *ortho/para* selectivity. This effect can be attributed to the introduction of a bifunctional path in the reaction, as evidenced by the results of the conversion of 1,3-dimethylcyclohexene. The introduction of the metal onto the zeolite does not improve the catalytic performances because the accessibility to the channels is then restricted.

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