Oxidative synthesis of aromatics from propane on mixed VMgO-zeolite catalysts

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Abstract

The transformation of propane into aromatics has been carried out in the presence of oxygen, on a combined catalyst formed by an oxydehydrogenation (ODH) function (MgO-supported vanadium oxide catalyst) and a cyclo-aromatization (H-ZSM-5 or Ga/ZSM-5) function. When the two functions are in close proximity, the yield to aromatics and the selectivity to alkylbenzenes increases with respect to the zeolitic catalysts in absence of the ODH function. The influence of reaction temperature, partial pressure of oxygen and the relative amount of the two catalytic functions on propane conversion and selectivity has been studied.

Keywords: Vanadium magnesium oxides; Ga-containing MFI; Oxidative dehydrogenation; Cycloaromatization; Propane

1. Introduction

The transformation of propane into aromatics on Ga/MFI zeolite catalysts is generally carried out at temperatures higher than 500°C in order to favor the endothermic steps of the reaction which involve the dehydrogenations of propane to propylene, and cycloalkanes to aromatics [1–8]. However, at those relatively high reaction temperatures other undesired reactions such as cracking, demethylation, and coke formation also occur, decreasing both the selectivity to alkylaromatics and the life of the catalyst [3]. In this way, the presence of intermetallic hydrogen

acceptor increases the aromatic yield as a result of allowing hydrogen elimination [9].

An alternative to this would be to carry out the dehydrogenation at lower temperatures by using an oxidative dehydrogenation catalyst combined with the zeolitic function in the presence of oxygen. Thus propylene could be obtained at lower temperatures, at which the zeolite could be highly efficient to carry out the olefin oligomerization and cyclization, shifting the distribution of aromatics towards a lower production of benzene and a larger of alkylaromatics [10]. In this way, Xu and Suib [11] observed by pulse experiments that the transformation of butane into aromatics in absence of oxygen is favored by using a dual (oxydehydrogenation and aromatization) cata-

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lyst. In this case the rate-limiting step (butane to butene) is increased by adding an oxydehydrogenation catalyst.

Following these hypothesis, we have studied here the transformation of propane into aromatics by combining a vanadium magnesium mixed oxide, VMgO (oxydehydrogenation function), which was optimized for the transformation of propane to propylene [12,13], with an acid zeolite (H-ZSM-5) with or without gallium. It was intended in this way to shift the aromatic composition towards toluene and xylenes, decreasing the formation of the, in some cases, less desired benzene.

2. Experimental

2.1. Catalyst preparation

ZSM-5 zeolite (with a Si/Al ratio of 20) was synthesized, in the presence of TPA Br as structure directing agent, in an autoclave at 180°C for 72 h following the procedure described in the literature [14]. The acid form, H-ZSM-5 (H-Z), was obtained by exchanging the Na form with NH_4Cl followed by calcination at 550°C for 3 h. The Ga-containing ZSM-5 (Ga-Z) sample was prepared by filling the pore volume of the H-ZSM-5 zeolite with an aqueous solution of $Ga(NO_3)_3 9H_2O$ followed by drying at 100°C and calcination at 550°C for 3 h [9]. The final amount of gallium in the catalyst was 2.0 wt%.

The VMgO catalyst was prepared by impregnation of magnesium oxalate with an aqueous solution of vanadyl oxalate, according to the procedure described previously [6,7]. The magnesium oxalate was prepared by precipitation, at pH = 5–6, of a magnesium acetate solution with an oxalic acid solution. The solid obtained was filtered, washed, and dried at 80°C for 16 h. After the impregnation step, the solid was filtered and dried at 100°C for 16 h, and calcined at 600°C for 4 h. The catalyst has a vanadium content of 19.7 wt% of V_2O_5 and a surface area,

S_{BET}, of 136 m^2 g^{-1}. XRD patterns showed the presence of crystalline MgO and $Mg_3V_2O_8$ [6].

2.2. Catalytic experiments

The catalytic results were obtained in a stainless steel, fixed bed, continuous reactor (2 cm internal diameter and 52 cm length), at atmospheric pressure, in the 400–550°C temperature interval.

The yields have been calculated on the bases of the carbon atoms of the reactant. In addition to pure catalysts, two type of catalyst arrangements have been used:

(i) In one of them, the feed finds first a VMgO bed and then a zeolitic bed with a catalyst particle size of 0.59–0.84 mm diameter. In this system the VMgO catalyst particles (0.25–0.42 mm) were diluted (1:2) with SiC particles (0.59 mm). The systems formed by these two consecutive catalytic beds have been nominated as TB[H-Z] and TB[Ga/Z], depending on the zeolite in the second catalytic bed being H-ZSM-5 or Ga-ZSM-5, respectively.

(ii) The other catalyst arrangement involves only one catalytic bed in which the VMgO and the zeolitic (H-ZSM-5 or Ga/H-ZSM-5) catalysts were physically mixed. These systems have been nominated as PM[H-Z] or PM[Ga-Z], respectively.

Unless specified, all the experiments were carried out using a propane/oxygen/ helium molar ratio of 40/30/30, and a contact time, W/F, of 26 or 32.6 g_{cat} h (mol $C_3H_6)^{-1}$, referred to the VMgO (W_{ODH}/F) or zeolite (W_{Zeo}/F) catalyst, respectively.

The analysis of vaporized products emerging from the reaction was carried out 'on line' in two gas chromatographs equipped with an injection valve. The products were separated using three columns: (i) in the DB-1 (methyl silicone) capillary column C_1–C_{11} hydrocarbons were separated and analyzed using a FID detector; (ii) in a 5A molecular sieves column (1.5 m length and 1/8″ e.d.) O_2, N_2 and CO were separated; (iii) in a Porapak Q column (3 m

length and $1/8''$ e.d.) light hydrocarbons and CO_2 were separated.

Blank runs with a reactant molar composition propane/oxygen/helium of 40/30/30 and a total flow of 133 ml min^{-1}, in the 375–500°C temperature range, were carried out. At 500°C reaction temperature, a total conversion of 4.25 and selectivities to ethane and propene and carbon oxides of 2.8, 66.5 and 30.7, respectively, were obtained. At lower reaction temperatures the propane conversion was negligible.

3. Results and discussion

A series of experiments was carried out in order to investigate the effect of the oxygen on the catalytic behavior of the two zeolitic catalysts, i.e. H-ZSM-5 and Ga/H-ZSM-5 (Table 1). These results were taken as reference values to discuss the effect of the ODH component when combined with the zeolite catalyst.

Results of Table 1 show that, at low reaction temperatures, the presence of O_2, instead of N_2, increases the propane conversion on either of the two zeolite catalysts. However, these differences in the propane conversion are reduced when the reaction temperature increases in a way parallel to the O_2-consumption.

During the transformation of propane on H-ZSM-5 catalyst, the presence of oxygen produces carbon oxides (CO and CO_2), decreases the selectivity to aliphatic C_1–C_6 alkanes and alkenes, but increases the selectivity to aromatics. Thus higher yields of aromatics are obtained using O_2 (Fig. 1). A similar effect of oxygen on cyclodimerization of propane has been previously reported, and has been explained assuming that the oxygen reacts with an adsorbed hydrogen coming from the dehydrogenation of propylene [15,16].

When oxygen is used together with a Ga-containing zeolite catalyst (Table 1), not only a high amount of carbon oxides is formed, but the selectivities to aromatics and C_1–C_3 hydrocarbons strongly decrease at low reaction temperature. In this case, lower yield of aromatics are obtained with O_2 (Fig. 1). However, at high

Table 1
Transformation of propane on H-ZSM-5 and G-ZSM-5 under anaerobic and aerobic conditions

Sample	Oxygen	T (°C)	X_T (%) [a]	Selectivity (%)									
--------	--------	---------	--------------	CH_4	C_2H_4	C_2H_6	C_3H_6	C_4–C_6	B	T	X	C_9^+	CO_x
H-Z	No [b]	400	2.17	14.9	14.7	11.7	6.1	52.6	0	0	0	0	0
		450	9.95	17.6	12.2	14.4	11.0	30.0	1.8	6.5	5.0	1.5	0
		500	32.3	22.7	11.1	16.7	10.2	10.2	5.9	12.9	7.6	2.9	0
		530	50.1	26.8	9.0	16.4	7.7	3.5	10.3	16.5	7.4	2.6	0
	Yes [c]	403	5.94	1.6	6.0	0.9	4.2	0	15.8	15.7	5.9	6.8	43.1
		441	12.9	3.2	5.9	1.5	4.9	0	17.6	13.7	4.4	4.1	44.8
		487	25.8	6.2	6.5	2.5	4.4	0	15.8	13.6	3.5	3.3	44.1
		514	35.1	9.3	8.0	3.5	4.8	0	15.3	14.4	3.7	3.8	37.2
Ga/Z	No [b]	400	5.59	8.7	3.2	15.4	2.9	0	19.6	28.8	17.8	3.7	0
		450	21.3	9.9	3.1	11.1	3.8	0	22.7	28.3	14.0	7.0	0
		500	44.3	12.0	2.9	8.2	2.9	0	25.1	27.9	12.1	9.0	0
		530	53.4	12.5	2.8	8.5	2.5	0	25.8	26.8	10.6	10.5	0
	Yes [c]	400	8.34	1.0	3.6	0.8	2.0	0	10.2	7.7	0	1.4	73.5
		437	14.0	2.8	4.8	1.7	3.4	0	15.5	8.3	0.9	1.0	61.7
		475	26.3	5.7	5.3	2.9	3.6	0	21.8	9.3	1.0	1.5	52.4
		505	40.1	9.3	6.3	3.8	3.6	0	22.2	16.7	2.9	3.0	32.1

[a] Propane conversion in %.

[b] Propane/helium molar ratio of 40/60 and a contact time, W_{Zeo}/F of 32.6 g_{cat} h (mol C_3)$^{-1}$.

[c] Propane/oxygen helium molar ratio of 40/30/30 and a contact time, W_{Zeo}/F of 32.6 g_{cat} h (mol C_3)$^{-1}$.

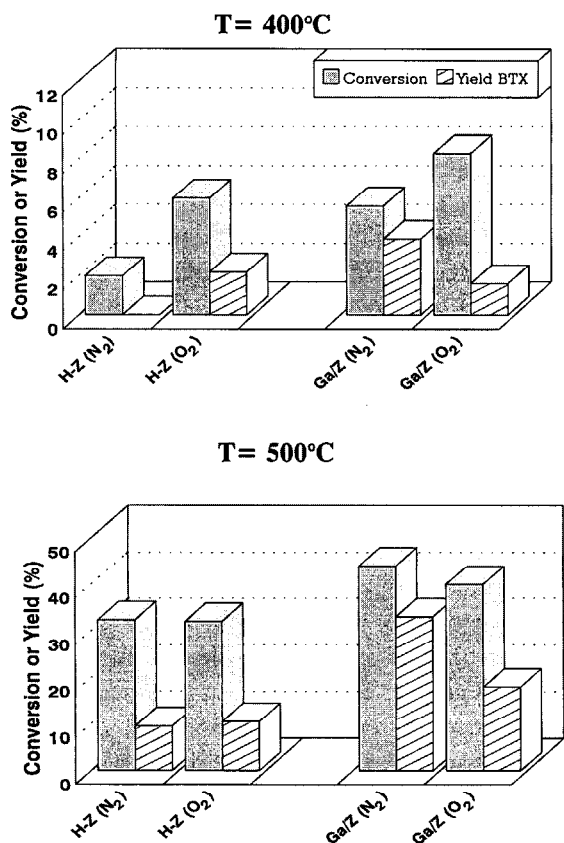## T= 400°C

T= 500°C

Fig. 1. Conversion of propane and yield of aromatics (BTX: benzene + toluene + xylene) on H-ZSM-5 (H-Z) and on Ga/H-ZSM-5 (Ga/Z), at 400 and 500°C, in the presence of N_2 or O_2 in the reactant mixture. $W_{Zeo} / F = 32.6$ g_{cat} h (mol C_3H_6)$^{-1}$.

temperature, similar selectivities to benzene are achieved on both aerobic and anaerobic conditions, although the selectivity to alkylaromatics

(toluene, xylenes and C_9^+) were lower on aerobic conditions.

It has been observed that reduced Ga/H-ZSM-5 shows an activity in propane transformation that is lower than that in the oxidized form [7]. This has been explained on the basis that oxidized Ga/H-ZSM-5 contains almost exclusively Ga_2O_3 clusters and probably few Ga^{3+} in cationic positions, while an opposite trend is expected in reduced ones where the incorporation of Ga^{3+} in the zeolitic framework reduces its acid character. The results shown in Table 1 indicate that, in the presence of O_2 and at low reaction temperatures, the incorporation of gallium oxide is responsible for the lower selectivity to aromatics observed on Ga/H-ZSM-5 with respect to H-ZSM-5.

3.1. Combination of VMgO and H-ZSM-5 catalysts

Table 2 shows the catalytic results obtained during the oxidation of propane on VMgO and zeolite when they are located in two separated catalytic beds (TB[H-Z]) or physically mixed forming a single uniform catalytic bed (PM[H-Z]). From a comparative purpose, the results obtained on the pure VMgO catalyst are presented in Table 3.

Fig. 2 shows the variation of the propane conversion with the reaction temperature on the pure and mixed catalysts. At lower reaction

Table 2
Oxidation of propane on mixed VMgO and H-ZSM-5 catalysts [a]

Sample [b]	T (°C)	X_T (%)	Selectivity (%)										
			CH_4	C_2H_4	C_2H_6	C_3H_6	C_4–C_6	B	T	X	C_9^+	CO	CO_2
TB[H-Z]	400	7.67	1.5	6.7	0.9	3.5	0	8.7	11.7	6.7	1.9	14.5	43.9
	437	14.8	2.4	7.4	1.4	6.0	4.1	4.5	7.6	4.7	1.0	13.5	47.3
	477	19.8	4.2	10.0	2.3	8.5	5.4	3.6	6.0	3.2	0.7	12.0	44.3
	492	23.4	5.7	12.2	3.0	10.3	6.2	2.9	4.3	2.1	0.4	12.5	40.4
PM[H-Z]	400	16.7	0.5	3.3	0.2	3.0	0	6.9	3.7	1.2	0.6	24.3	56.3
	437	20.2	1.7	5.5	0.7	5.0	1.1	6.9	4.5	2.0	0.9	19.6	52.2
	462	22.6	2.6	6.9	1.4	6.3	4.2	6.3	5.3	2.6	0.9	16.8	46.7
	477	28.5	6.1	7.4	4.0	6.9	9.6	5.8	5.6	2.9	1.1	13.3	37.3

[a] Propane/oxygen helium molar ratio of 40/30/30 and contact times, W_{ODH}/F and/or W_{Zeo}/F, of 26 and 32.6 g_{cat} h (mol C_3)$^{-1}$, respectively.
[b] VMgO and H-ZSM-5 were placed in a two-catalytic bed TB[H-Z] sample or were physically mixed in a PM[H-Z] sample.

Table 3
Oxidation of propane on VMgO catalyst [a]

Sample	W_{ODH}/F	T (°C)	X_T (%)	Selectivity (%)				
				CH_4	C_2H_4	C_3H_6	CO	CO_2
VMgO	26	400	7.52		0	31.5	12.5	56.0
		430	17.2		0.1	34.5	13.6	51.9
		450	20.7		0.2	31.8	13.6	54.0
	8.2	400	3.7			34.8	9.5	55.8
		430	7.1			31.9	11.9	56.2
		450	10.5			30.0	13.5	56.5
		470	15.5		0.4	30.5	15.4	53.7
		500	19.3	0.1	0.7	30.9	16.6	51.7

temperatures, the propane conversion on the PM[H-Z] system is practically the same as the sum of conversions of the two catalyst phases when reacted separately. However, when the reaction temperature increases, the propane conversion on the mixture of the two catalysts is lower than expected from the VMgO and H-Z catalysts, but always higher than that for TB[H-Z]. We must notice that total O_2-consumption is observed, in our reaction conditions at temperatures higher than 470°C. Thus it can be concluded that the conversion of propane is limited by the concentration of oxygen in the reaction media.

With respect to product selectivities obtained on pure H-ZSM-5 catalyst (Table 1), the introduction of the ODH function produces an increase of the carbon oxides, and an increase of the olefins and the C_4–C_6 fraction (Table 2). In addition, the sum of the yields of products other than carbon oxides increases, especially in the case of the PM[H-Z] system at low reaction temperatures (Fig. 3). At higher reaction temperatures similar yields of hydrocarbons were observed on pure and mixed catalysts, although the yield of aromatics was lower on mixed catalysts. However, we must indicate that catalytic dehydrogenation reactions could also occurs at high reaction temperatures, especially in zeolite-containing catalysts.

It should however be pointed out that the introduction of the ODH function before the zeolitic bed, TB[H-Z], produces an increase in the ratio of alkylbenzenes/benzene, the increase being specially notorious for the xylene fraction (Fig. 4). Higher alkylbenzenes/benzene ratios were also achieved at high temperatures for the PM[H-Z] system.

It appears then, that in the presence of the ODH function more propylene is formed, increasing therefore the chain length of the intermediate diolefins and consequently favoring the formation of C_7^+ alkylaromatics. Unfortunately, the ODH function also catalyzes the oxidation
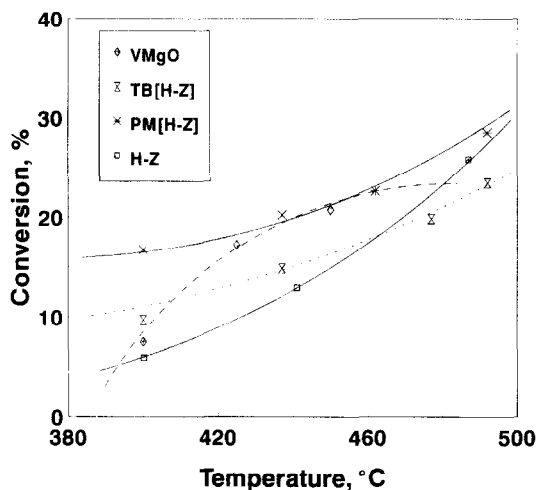

Fig. 2. Variation of the propane conversion with the reaction temperature on pure (VMgO or H-ZSM-5) or mixed catalysts: TB[H-Z] with VMgO and H-ZSM-5 in two beds, PM[H-Z] with VMgO and H-ZSM-5 physically mixed. Reaction conditions: propane/oxygen/helium molar ratio of 40/30/30; W_{ODH}/F and/or W_{zeo}/F of 26 and 32.6 g_{cat} h (mol C_3H_6)$^{-1}$, respectively.

of the intermediate olefins producing CO_2 and decreasing the global yield of aromatics.

In conclusion, our results show that the combination of the oxidative dehydrogenation of propane and the acidic function of the H-ZSM-5 zeolite does indeed produce a higher ratio of (toluene + xylene)/benzene than the H-ZSM-5 zeolite alone. However, the global yield of aromatics decreases owing to the non-selective oxidation of intermediated olefins, probably as a consequence of the inadequate coupling of the rates for olefin cyclization–dehydrogenation and the rate of olefin oxidation. Thus, it is not surprising that better results are obtained at lower temperatures owing to the higher activation energy for the oxidation of the olefins than for the cyclization–dehydrogenation reaction
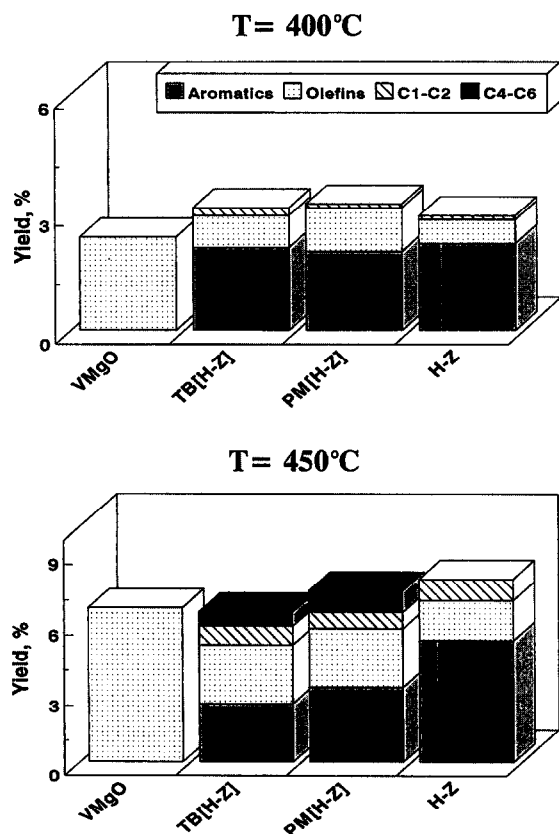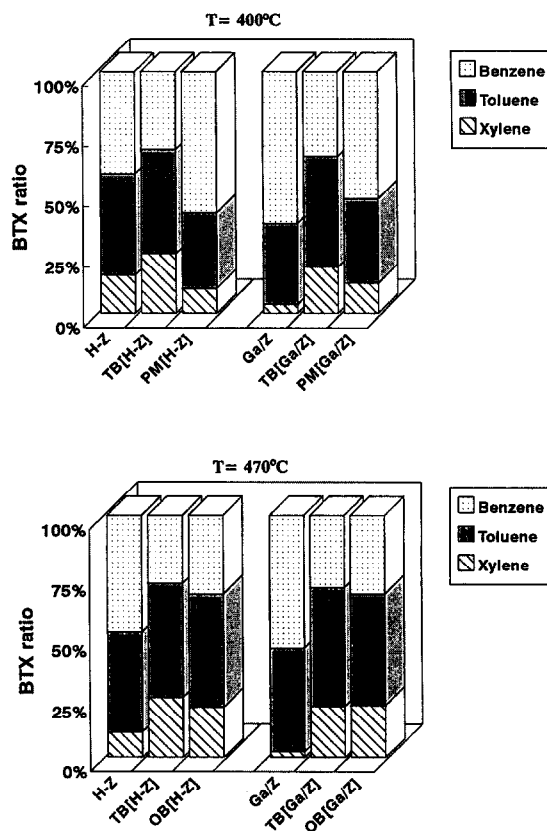

Fig. 4. Benzene/toluene/xylene (BTX) ratios obtained during the oxidation of propane on pure and mixed catalysts using H-ZSM-5 or Ga/H-ZSM-5 as zeolitic materials. Experimental conditions as in Fig. 2.

[3,17]. Furthermore, the PM[H-Z] system in which propylene formed on VMgO can encounter zeolite particles before encountering another VMgO particle to become oxidated gives better results than the TB[H-Z] catalytic system.

3.2. Combination of VMGO and Ga-ZSM-5

Table 4 shows the catalytic results obtained during the oxidative transformation of propane on VMgO and Ga/H-ZSM-5 catalysts, using different contact times with respect to the oxydehydrogenation function (W_{ODH}/F). As was studied before, both VMgO and Ga/H-ZSM-5 catalysts were placed in two catalytic beds (TB[Ga/Z]) or were physically mixed (PM[Ga/Z]).

Fig. 3. Yields of aromatics (BTX), C_2–C_3 olefins, and C_1–C_2 and C_4–C_6 hydrocarbons obtained during the oxidation of propane on pure or mixed catalysts, using H-ZSM-5 as zeolitic material, at 400 and 450°C. Catalysts and experimental conditions as in Fig. 2.

In the case of Ga-containing catalysts, when in the presence of O_2, the introduction of the ODH catalyst produces an increase in the propane conversion (Fig. 5), although they show similar selectivities to carbon oxides (Table 3). This indicates that the formation of olefins increases.

On the other hand, the propane conversion (Fig. 5) on physically mixed catalysts, PM[Ga/Z], is higher than when they were placed in two consecutive catalytic beds, TB[Ga/Z] (Fig. 6). Similar results were observed when using H-ZSM-5, although the differences between PM- and TB-series are smaller when the Ga-zeolite component is used. What merits special attention is the fact that, independent of the reaction temperature, both the yield of aromatics and the yield of hydrocarbons are higher on PM[Ga/Z] than on TB[Ga/Z] or Ga-ZSM-5 catalysts (Fig. 6). Moreover, on either PM[Ga/Z] or TB[Ga/Z] the (toluene + xylenes)/benzene ratios are higher than on Ga-ZSM-5 alone when used either in the presence of O_2 or N_2 atmosphere. In this way, we must

indicate that the alkylbenzenes/benzene ratio decreases as follows: TB[Ga/Z] > PM[Ga/Z] > Ga/Z (Fig. 4). It appears therefore that as observed above, also in this case the presence of both the ODH and the zeolitic functions favors the obtention of olefinic intermediates with a higher number of carbon atoms, favoring a higher selectivity to alkylaromatics. In fact, it has been observed that the amount of alkylaromatics with respect to the amount of benzene in the cycloaromatization of paraffins is lower than from olefins [3].

3.3. Influence of the process variables

With the two-function catalysts (VMgO and Ga-ZSM-5) it has been found that when the contact time with respect to the VMgO catalyst (W_{ODH}) is reduced (Table 4), keeping constant the contact time for the zeolite, the propane conversion decreases in both PM[Ga/Z] and TB[Ga/Z], and the decrease in conversion corresponds exclusively to a reduction in propane combustion. On the other hand, on PM[Ga/Z] a

Table 4
Oxidation of propane on mixed VMgO and Ga-ZSM-5 catalysts [a]

Sample [b]	W_{ODH}/F [c]	T (°C)	X_T (%)	Selectivity (%)										
				CH_4	C_2H_4	C_2H_6	C_3H_6	C_4–C_6	B	T	X	C_9^+	CO	CO_2
TB[Ga/Z]	8.9	406	7.7	1.6	6.0	1.1	3.7	0	13.2	14.1	5.7	1.4	15.6	37.6
		437	16.2	2.7	5.3	1.4	3.7	0	11.9	11.5	4.4	0.7	16.1	42.1
		459	21.4	3.9	5.8	1.8	4.2	0	11.5	10.9	3.9	0.7	13.6	43.6
		500	35.0	8.4	7.2	3.2	2.9	0	14.5	12.8	4.7	1.2	12.0	31.1
	26	406	13.5	1.0	4.5	0.7	3.2	0.1	8.0	9.6	4.7	0.5	17.4	50.3
		438	19.2	1.6	5.0	0.8	4.4	2.2	5.7	7.5	3.1	0	15.7	54.1
		467	23.1	3.3	7.1	1.5	5.8	3.2	4.9	8.0	3.5	0	15.5	47.3
		494	28.5	6.0	9.3	2.3	7.1	1.4	7.4	10.5	4.8	0.2	12.8	38.2
PM[Ga/Z]	8.9	390	6.7	1.3	4.7	0.9	2.5	0	12.5	8.9	2.9	2.1	19.1	45.2
		446	18.4	6.1	4.1	2.2	2.7	1.2	12.8	6.5	2.4	0.7	19.4	42.0
		452	26.4	6.5	4.9	2.6	3.5	3.2	11.9	7.9	3.2	0.9	14.6	40.9
		476	30.6	7.5	5.6	3.2	4.0	2.4	12.1	9.6	4.0	0.9	13.1	37.6
	26	400	21.1	2.7	2.3	1.2	1.3	4.6	8.9	5.9	2.1	1.0	15.8	54.4
		439	25.6	3.7	3.2	1.7	1.9	3.6	7.4	9.8	5.1	1.1	12.7	49.8
		459	32.9	5.8	3.3	2.3	2.0	t	10.9	12.2	4.9	1.7	10.7	46.3
		476	34.0	7.0	4.8	3.2	3.2	0	10.0	14.1	6.7	2.2	7.6	41.2

[a] Propane/oxygen helium molar ratio of 40/30/30 and a contact time, W_{Zeo}/F, of 32.6 g_{Zeo} h (mol C_3)$^{-1}$.
[b] VMgO and H-ZSM-5 were placed in a two-catalytic bed TB[H-Z] sample or were physically mixed in a PM[H-Z] sample.
[c] Contact times, W_{ODH}/F, of 8.9 and 26 g_{cat} h (mol C_3)$^{-1}$ were achieved by modifying the amount of VMgO catalyst.
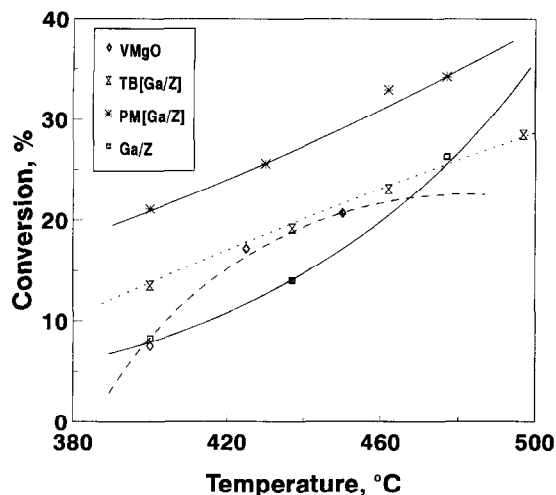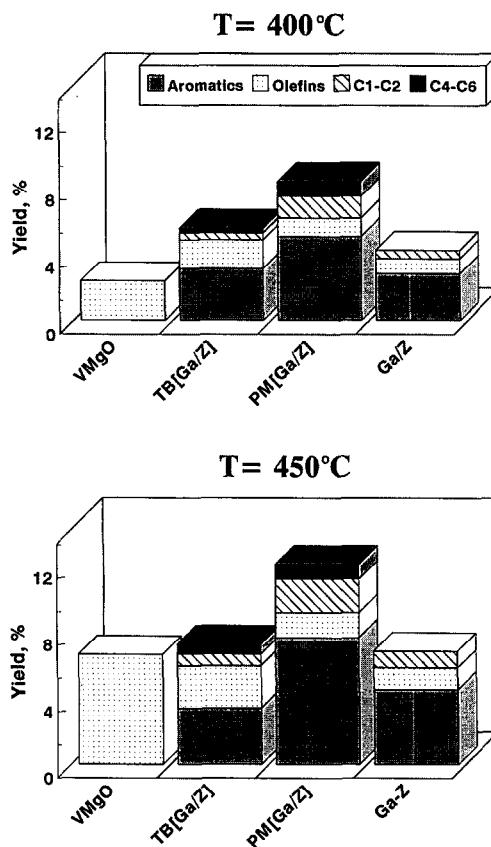
Fig. 5. Variation of the propane conversion with the reaction temperature on pure (VMgO or Ga/H-ZSM-5) or mixed catalysts: TB[Ga/Z] with VMgO and Ga/H-ZSM-5 in two beds, PM[Ga/Z] with VMgO and Ga/H-ZSM-5 physically mixed. Reaction conditions: propane/oxygen/helium molar ratio of 40/30/30; W_{ODH} /F and/or W_{Zeo} /F of 26 and 32.6 g_{cat} h (mol C_3H_6)$^{-1}$, respectively.

lower selectivity to aromatic products and a lower (toluene + xylenes)/benzene ratio than on TB[Ga/Z] is also observed (Fig. 7). This could indicate that in the case of the PM[Ga/Z] system there exists a synergetic effect between the two catalytic functions.

On the other hand, a reduction in the partial

Fig. 6. Yields of aromatics (BTX), C_2–C_3 olefins, and C_1–C_2 and C_4–C_6 hydrocarbons obtained during the oxidation of propane on pure or mixed catalysts, using Ga/H-ZSM-5 as zeolitic material, at 400 and 450°C. Catalysts and experimental conditions as in Fig. 2.
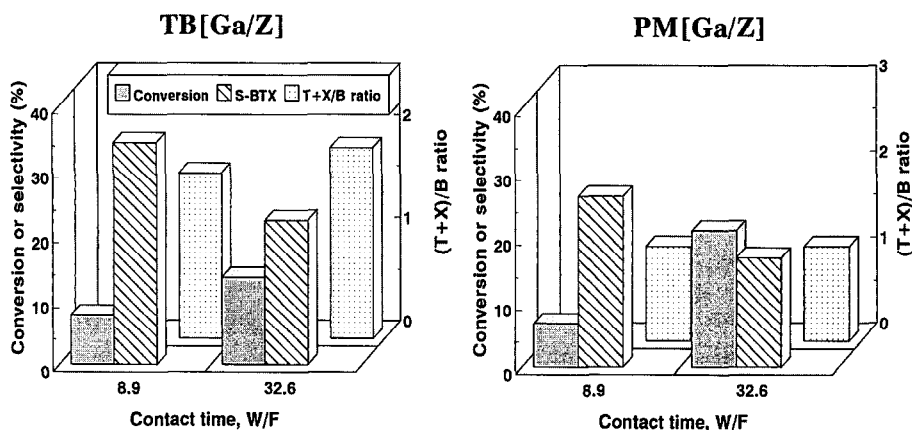

Fig. 7. Variation of the propane conversion, selectivity to aromatics (BTX) and (toluene + xylenes)/benzene ratios with the contact time (W_{ODH}/F) on mixed catalysts: TB[Ga/Z] with VMgO and Ga/H-ZSM-5 in two beds, PM[Ga/Z] with VMgO and Ga/H-ZSM-5 physically mixed. Experimental conditions: W_{Zeo}/F constant of 32.6 g_{cat} h (mol C_3H_6)$^{-1}$; propane/oxygen/helium molar ratio of 40/30/30 and reaction temperature of 400°C.
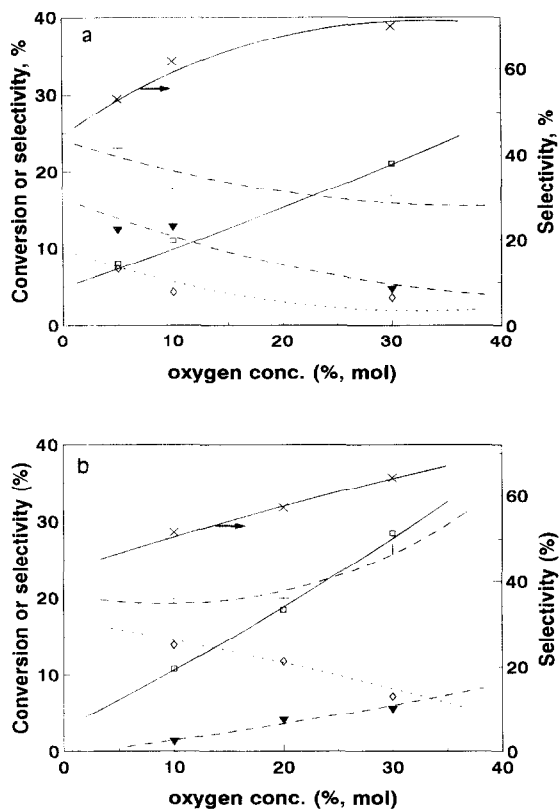
Fig. 8. Effect of the oxygen concentration in the reactant mixtures on the conversion of propane (■) and on the selectivities to BTX (+), C_2–C_3 olefins (♦), C_4–C_6 hydrocarbons (▼) and CO_x (X) on a physically mixed VMgO + Ga/H-ZSM-5 (PM[Ga/Z]) catalyst. Experimental conditions: W_{Zeo}/F constant at 32.6; propane/oxygen/helium molar ratio of $40/x/60-x$ and (a) $W_{ODH}/F = 26$ g_{cat} h (mol C_3)$^{-1}$ and $T = 400°C$. (b) $W_{ODH}/F = 8.9$ g_{cat} h (mol C_3)$^{-1}$ and $T = 430°C$.

pressure of O_2 in the reaction mixture produces similar effects as the reduction of the contact time with respect to VMgO catalyst. The decrease in the conversion of propane on PM[Ga/Z] seems to be mainly due to a reduction in the formation of carbon oxides. Moreover, when the partial pressure of O_2 was lowered, a decrease in the yield of aromatics and in the (toluene + xylenes)/benzene ratio has been observed (Fig. 8) These results can also be explained by assuming that on the mixtures VMgO and H- or Ga-ZSM-5 zeolite catalyst, the reaction can operate through a mechanism additional to the one reported previously for H-ZSM-5 or Ga-ZSM-5 catalysts [1–5]. This

mechanism involves, at the first step, the oxidative dehydrogenation of propane into propylene, which occurs at lower temperatures than the direct dehydrogenation. The olefins formed polymerize and crack in the zeolite-given intermediate diolefins (C_4–C_8) with a higher proportion of C_7 and C_8 chains with higher reaction temperature. When Ga is present, these diolefins rapidly cycle and dehydrogenate, decreasing the probabilities to become oxidated either on the zeolite or, especially, on the VMgO component.

4. Conclusions

During the reaction of propane on MFI based catalysts, the introduction of oxygen in the reaction mixture favors the formation of aromatics from propane on a H-ZSM-5 zeolite catalyst. However, the presence of gallium on the zeolite increases the combustion of hydrocarbons and reduces the selectivity to aromatics.

The introduction of an oxydehydrogenation function to the MFI catalyst strongly changes both the activity and the product distribution. The catalytic behavior of mixed catalytic systems, using at the same time an oxydehydrogenation (VMgO) and a zeolite catalyst, depends on the distribution of the two functions along the catalytic bed.

From the results obtained on mixed catalytic systems (Tables 2 and 4), it appears that if before reacting with the MFI zeolite bed the feed finds a VMgO bed (TB-series), a higher amount of alkyl-aromatics is formed than in the case where only a zeolite bed exists. This is a consequence of the higher amount of olefins reaching the H-ZSM-5 zeolite bed in the former case due to the presence of the oxydehydrogenation function (VMgO) present in the first catalytic bed.

The combination of VMgO (oxydehydrogenation function) and H-ZSM-5 zeolite, in a physically mixed catalytic bed, reduces the yield of aromatics, but produces a relative increase of the alkylaromatics. The

combination of VMgO and Ga-ZSM-5 zeolite produces an increase in the total yield of aromatics, as well as an increase in the (toluene + xylene)/benzene ratio. At this moment, the limitation of the use of these catalysts is associated, together with the undesired activity of the Ga/H-ZSM-5 zeolite for the hydrocarbon combustion, to the still too low selectivity to propylene obtained with the ODH catalyst. However, the basic idea has been proven to work. Thus if ODH catalysts are developed which can give a selectivity to propylene higher than 70% at a propane conversion of 30–40%, the oxidative transformation of propane into aromatics can produce high yields of toluene and xylenes. The use of combined catalysts, formed by an oxidative dehydrogenation function and a zeolite, could also be useful to convert ethane. In this case, the olefin, i.e. ethylene, is more stable towards oxidation than propylene, and therefore this type of catalyst association can be more suitable.

Acknowledgements

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