Characterization of FeMCM-41 and FeZSM-5 Catalysts to Styrene Production

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FeMCM-41 and FeZSM-5 catalysts have been prepared and tested in the dehydrogenation of ethylbenzene to produce styrene. These new catalytic systems have high specific areas and can stabilize the trivalent state of iron. It was found that the FeZSM-5 catalysts are more active and selective than the FeMCM-41 ones and this behavior is explained in terms of the higher amount of the active oxidation state (Fe^{3+}) on the catalyst surface. These catalysts also result more active and selective than α-Fe_2O_3 (hematite) and are less toxic than the chromium-containing commercial catalysts used for this purpose.

1. INTRODUCTION

Styrene monomer is one of the most important high value chemical used extensively for the manufacture of plastics, including crystalline polystyrene and styrene-butadiene rubber (SBR) [1]. Direct catalytic dehydrogenation of ethylbenzene has been the dominant technology for styrene production since its first commercial application [2-4]. In this process ethylbenzene is dehydrogenated to styrene and hydrogen over a catalyst in the presence of steam; toluene and benzene are formed as by-products. The overall reaction is highly endothermic and thermodynamically limited and thus the conversion is increased when increasing the temperature. The feed is much diluted with steam for limiting the coking rate of the catalyst, decreasing the temperature fall due to the reaction and improving the conversion at the equilibrium [5].

The most widely used industrial catalysts comprise iron oxide and promoters such as K_2CO_3, Cr_2O_3, CeO_2, MoO_3, V_2O_5 and so on [2]. Other promoters like aluminum, cadmium, magnesium, manganese, nickel and uranium oxides as well as rare-earths

have been used [6]. However, potassium-promoted iron oxide is better than any other catalyst known for ethylbenzene dehydrogenation in the presence of steam [2,3]. It is generally believed that potassium acts as a chemical promoter in the catalyst, whereas chromium oxide is a textural promoter stabilizing the high surface area of the active phase [2, 3, 7].

Despite its high activity and selectivity, the commercial catalyst still has some disadvantages which need to be improved in order to minimize the manufacturing costs of styrene. On the one hand, the active oxidation state is unstable; hematite (α-Fe_2O_3) is preferred for styrene production, but it tends to go into oxides with lower oxidation states and even to elemental iron, and they catalyze carbon formation and dealkylation [3]. On the other hand, the iron-based catalysts have low specific areas and deactivate with reaction time being susceptible to poisoning by halides and residual organic chlorine impurities [2]. The most serious deactivation is caused by the loss of potassium promoter, which migrates in two directions as the catalyst ages. Potassium chloride is found downstream in the water layer of the condensed product as well as in the center of the catalyst pellets [2,3]. Besides, the large amounts of steam used in commercial operations increase the operational costs. The catalyst has the additional disadvantage of being toxic causing damage to the humans and to the environment. Therefore, the investigation for new systems which have high specific area, can stabilize the trivalent state of iron and are potassium and chromium free is much needed. With this goal in mind, this work deals with the evaluation of FeMCM-41 and FeZSM-5 as catalysts to the styrene production.

2. EXPERIMENTAL

The FeZSM-5 sample was prepared by mixing an aqueous solution of ferric sulfate (0.09 mol.L^{-1}) with an aqueous solution of sodium metasilicate (2.5 mol.L^{-1}) and a tetrapropylammonium bromide (template) solution (0.2 mol.L^{-1}) under stirring. The resulting solution was kept in an autoclave at 170 °C for 72 h. Then, the sample was rinsed with water, centrifuged and dried at 120 °C for 2h. After this, the solid was calcined at 500 °C under nitrogen flow (3 h) and under air flow (5 h). The FeMCM-41 sample was prepared from a gel with sodium metasilicate (2.5 mol.L^{-1}), tetramethylcethylammonium bromide (0.02 mol.L^{-1}), ferric sulfate (0.1 mol.L^{-1}) and tetramethylammonium hydroxide, which was aged for 4 h under stirring and then kept under hydrothermal treatment in autoclave. The pH was adjusted to 12 with ammonium hydroxide, aged for 4 h under stirring and kept in an autoclave under hydrostatic pressure in an oven at 140 °C, for 16 h. The sample was rinsed with water, centrifuged and dried at 90 °C, for 12 h. The material was calcined at 500 °C under nitrogen flow (1h) and under air flow (6 h). An iron oxide sample (hematite) was also prepared to be used as a reference catalyst. This solid was prepared by adding, under stirring, an aqueous solution of iron nitrate (1.0 mol.L^{-1}) and a concentrated (25% w/w) solution of ammonium hydroxide to a beaker with water. The sol produced was centrifuged, rinsed with water, dried in an oven at 120 °C and calcined at 500 °C under nitrogen flow (2 h).

The iron contents were determined by inductively coupled plasma atomic emission spectroscopy (ICP/AES) by using an Arl 3410 model equipment. The absence of the templates in the catalysts was confirmed by Fourier transform infrared spectroscopy in the range of 4000-400 cm^{-1} using a model Valor II Jasco spectrometer and KBr discs. The structure of the FeZSM-5 and of the FeMCM-41 was confirmed by X-ray diffractometry experiments performed at room temperature with a Shimadzu model XD3A instrument using CuKα radiation generated at 30 kV and 20 mA. The specific area was measured (BET method) in a Micromeritics model ASAP 2000C equipment on samples previously heated under nitrogen (150 $^{\circ}$C, 2 h). The temperature programmed reduction (TPR) was performed in a Micromeritics model TPD/TPO 2900 equipment, using a 5% H$_2$/N$_2$ mixture.

The Mössbauer spectra were obtained in transmission geometry, with a 512- channel constant acceleration spectrometer at 25 $^{\circ}$C. A source of ^{57}Co in Rh matrix of nominally 50 mCi was used. Velocity calibration was performed against a 12μm thick α-Fe foil. All isomer shifts mentioned in this paper are referred to this standard at 25°C. The spectra were evaluated by using a least-squares nonlinear computer fitting program with constraints. Lorentzian lines were considered with equals widths for each spectrum component. The spectra were folded to minimize the geometric effects.

X ray photoelectron spectra were obtained with a VG ESCALAB 200R spectrometer equipped with a MgKα X-ray radiation source (hv= 1253.6 eV) and a hemispherical electron analyzer. The powder samples were pressed into small stainless steel cylinders and mounted onto a manipulator which allowed the transfer from the preparation chamber into the spectrometer. Before the analysis, they were outgassed (10^{-9} mbar) or reduced in hydrogen at 500 $^{\circ}$C (1 h). The Si2p peak was chosen as an internal reference. This reference was in all cases in good agreement with the BE of the C1s peak, arising from contamination, at 284.9 eV. This reference gave an accuracy of $\pm$ 0.1 eV.

The catalyst performance was evaluated using 0.2 g of powder within 50 and 325 mesh size, and a fixed-bed microreactor, providing there is no diffusion effect. The experiments were carried out under isothermal condition (530 $^{\circ}$C) and at atmospheric pressure, employing a steam to ethylbenzene molar ratio of 10. The reactor, containing the catalyst, was heated under nitrogen flow (60 ml.s^{-1}) up to the reaction temperature. Then the feed was interrupted and the reaction mixture was introduced. The reaction mixture was obtained by passing a nitrogen stream through a saturator with ethylbenzene and then through a chamber where it was mixed with steam. The gaseous effluent was collected in a condenser and the organic phase was analyzed by gas chromatography, using a CG-35 instrument. In order to save the energy related to the steam consumption, the catalysts were also evaluated in the absence of steam.

3. RESULTS AND DISCUSSION

Table 1 compiles the amount of iron in the catalysts, their specific area and their rates of ethylbenzene conversion and selectivity towards styrene in the steady state. It can be seen that the FeZSM-5 sample is active only in the presence of steam. This can

Table1.
Amount of iron (%Fe) and specific area of the catalysts (Sg) and their activity (a), activity per weight of iron (a/g) and selectivity (S) to styrene of the catalysts in the dehydrogenation of ethylbenzene

Sample	% Fe	Sg $(m^2.g^{-1})$	$a.10^3$ $(mol.h^{-1}.g^{-1})$		a/g $(mol.h^{-1}.g.\ Fe^{-1})$	S (%)	
			With steam	Without steam		With steam	Without steam
FeZSM-5	1.32	425	3.5	0.0	4.7	100	0
FeMCM-41	1.04	1112	1.8	0.9	3.1	52	33
α-Fe$_2$O$_3$	71.32	17	2.4	0.0	$4.4.\ 10^{-3}$	92	0

be related to the role of steam in reacting with the carbonaceous deposits according to the Boudart reaction. On the other hand, the FeMCM-41 sample was active both in the presence and in the absence of steam, although the activity and selectivity strongly decreased without it As FeMCM-41 has larger pores than FeZSM-5, one can suppose that it can afford a large amount of coke and then it can work even without steam. The other role of steam is to keep the trivalent state of iron highly selective to styrene [2,3]. As MCM-41 and ZSM-5 did not show any activity towards the reaction, the performance of the catalysts may be directly related to iron oxides. The FeZSM-5 catalyst was more active than the hematite-based sample. As hematite has larger amount of iron, and then larger number of active sites than the zeolite, one can conclude that iron is much more active in the zeolite structure, as confirmed by the values of activity per gram of iron. The FeZSM-5 catalyst was the most selective whereas the FeMCM-41 sample was the least one.

Figure 1 shows the activity and the selectivity to styrene as a function of time. In all cases, the activity varied in the first hours of reaction and reached stables values after 4h. Concerning the selectivity, FeZSM-5 and hematite show stable values since the beginning of the reaction, while FeMCM-41 showed stable values only after 6h.
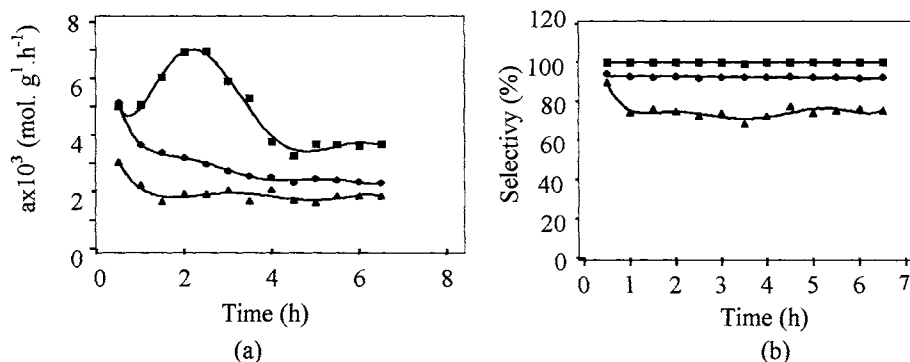

Figure 1. (a) Activity and (b) selectivity to styrene of the catalysts in the dehydrogentaion of ethylbenzene. $\blacklozenge$— α-Fe$_2$O$_3$; $\blacktriangle$— FeMCM-41; $\blacksquare$— FeZSM-5

The TPR profile of pure hematite showed two peaks around 400 °C and 740 °C, ascribed to the reduction of Fe^{3+} and Fe^{2+}, respectively [8]. The TPR curve of FeMCM-41 showed only a peak centered at 500 °C whereas the curve of FeZSM-5 displayed a large peak beginning at the same temperature. As stated early [9] this peak is due to Fe^{3+} reduction in zeolite structure. Therefore, it can conclude that the iron reduction is more difficult on both MCM-41 and ZSM-5 structures as compared to hematite.

The Mössbauer spectra of FeMCM-41 samples were poorly-defined with a low signal-to-noise ratio probably due to the low amount of iron. In the fresh sample a signal related to Fe^{3+} species exchanged and/or superparamagnetic Fe_2O_3 was found. After the reaction, carried out with or without steam, a fraction of iron went into γ-Fe_2O_3 and the sample was attracted by a magnet. This can be explained by considering that during the reaction very small crystallites of magnetite were produced which went into maghemite under the oxidizing conditions of the Mossbauer experiments. Table 2 shows the Mössbauer parameters of the FeMCM-41 catalysts.

Table 2.
Mössbauer hyperfine parameters at 25 °C of FeMCM-41 catalysts. S represents the catalyst tested with steam and WS the catalyst tested without steam

Species	Parameters	FeMCM-41	FeMCM-41(S)	FeMCM-41(WS)
γ-Fe_2O_3	H(T)	————	48 ± 1	47.5 ± 0.4
	δ(mm/s)	————	0.4 ± 0.1	0.41 ± 0.06
	2ϵ(mm/s)	————	0.03 (*)	0.1 ± 0.1
Fe^{3+} exchanged	δ(mm/s)	0.32±0.03	0.33 (*)	0.33 ± 0.02
and/or Fe_2O_3 sp	Δ(mm/s)	0.78±0.04	0.9 ± 0.1	0.94 ± 0.03

*parameter held fixed while fitting; sp: superparamagnetic; H: hyperfine field; δ: isomer shift; 2ϵ: quadrupole shift; Δ: quadrupole splitting.

The fresh FeZSM-5 catalyst shows the Mössbauer parameters which fitted well to hematite.Using the magnetic excitation model [10], the average diameter of the crystallites can be estimated as 17.2 nm, which means that they are outside the channels of the zeolite, in accordance with previous work [11]. After the reaction, performed with steam, these crystallites grew up to 20.1 nm and no other phase, besides hematite, was noted. On the other hand, the reaction carried out without steam caused a phase change, producing maghemite detected by the strong reduction of the hyperfine filed (H) and the zero value of the quadrupole shift (2ϵ). Again, this phase is related to the small crystallites of magnetite that were produced under the reaction conditions. In all spectra, there is a very weak central signal which may correspond to Fe^{3+} species exchanged with the zeolite and/or superparamagnetic hematite related to a fraction of very small crystallites which could be located inside the channels. Table 3 shows the Mössbauer parameters. These results show that magnetite is produced more easily in the FeMCM-41 structure than in the FeZSM-5 one, in the presence of steam. Therefore, MCM-41 is not able to avoid magnetite formation even in the presence of steam. On the

Table 3.
Mössbauer hyperfine parameters at 25 °C of FeZSM-5 catalysts. S represents the catalyst tested with steam and WS the catalyst tested without steam.

Species	Parameters	FeZSM-5	FeZSM-5(S)	FeZSM-5(WS)
α-Fe_2O_3	H(T)	50.9 ± 0.10	51.2 ± 0.10	———
	δ(mm/s)	0.37 ± 0.02	0.37 ± 0.01	———
	2ε(mm/s)	-0.19 ± 0.03	-0.20 ± 0.01	———
γ-Fe_2O_3	H(T)	———	———	49.5 ± 0.10
	δ(mm/s)	———	———	0.32 ± 0.01
	2ε(mm/s)	———	———	-0.06 ± 0.03
Fe^{3+} exchanged and/or Fe_2O_3 sp	δ(mm/s)	0.37(*)	0.37(*)	0.37 (*)

*Parameter held fixed while fitting; sp: superparamagnetic; H: hyperfine field; δ: isomer shift; 2ε: quadrupole shift; Δ: quadrupole splitting.

other hand, the FeZSM-5 catalysts showed only hematite after the reaction (with steam), showing that the zeolite structure is able to stabilize hematite. Without steam, hematite changed to magnetite which went into maghemite during the Mössbauer experiments.

Table 4 shows the binding energies (BE) of some characteristic core levels of Fe, O and Si in the FeMCM-41 samples as well as the surface amount of Fe^{3+} species. The fresh catalyst showed a binding energy of 710.5 eV which is typical of Fe^{3+} species in hematite [11]. After the catalytic test, carried out with steam, the catalyst surface still showed only Fe^{3+} species. When the reaction was performed without steam, however, a fraction of Fe^{3+} was reduced to Fe^{2+} (45%) as inferred by the BE of 709.7 eV [11]. After the reduction, carried out in the XPS equipment, some Fe^{3+} is reduced to Fe^{2+} in all samples, showing that the Fe^{3+} state was stabilized during the reaction. The surface atomic ratio Fe/Si of the catalyst is also shown in Table 4. It can be seen that the reaction causes an enrichment of iron on the surface. The reduction performed in the XPS equipment increased the amount of iron on the catalyst surface even more.

The binding energies (BE) of some characteristic core-levels of Fe, O, Al and Si in the FeZSM-5 samples as well as the surface amount of Fe^{3+} species are shown in Table 5. The fresh catalyst showed binding energies of 710.0 and 711.7 eV which are typical of Fe^{2+} and Fe^{3+} species respectively [11]. The presence of the reduced species can be explained by an effect of vacuum during the treatment of the samples, in the XPS equipment. The Fe^{3+} reduction, produced by the outgassing, could be due to the dehydroxilation of the zeolite. Similar results have been found by other authors in Fe-zeolite L [12] and Fe-zeolite X [13] systems. After the catalytic tests, the amount of Fe^{3+} species as well as the total amount of iron on the catalyst surface increased. After the reduction, carried out in the XPS equipment, a part of Fe^{3+} is reduced to Fe^{2+} in all samples and the amount of iron on the catalyst surface increased even more. By comparing the Fe/Si ratio of the catalysts, we see that the FeZSM-5 samples have much more iron on the surface, and then more Fe^{3+} species, than the FeMCM-41 catalysts.

Table 4.
Binding energies (eV), surface atomic ratios and surface amount of Fe^{3+} of fresh and spent FeMCM-41 catalysts taken on samples previously treated under vacuum or under hydrogen at 500 °C. S represents the catalyst tested with steam and WS the catalyst tested without steam.

Sample	C1s	Si2p	O1s	Fe2p$_{3/2}$	Fe^{3+} (%)	Fe/Si (atom)
FeMCM-41 (vac)	284.6	103.4	532.9	710.5	100	0.0054
(H$_2$, 500°C)	284.6	103.4	532.0	709.6		0.0069
				711.5	40	
FeMCM-41 (S) (vac)	284.6	103.4	532.9	709.7		0.0075
				711.5	55	
(H$_2$, 500°C)	284.6	103.3	532.0	709.5		0.0078
				711.6	35	
FeMCM-41 (WS)(vac)	284.6	103.4	532.9	711.3	100	0.0068
(H$_2$, 500°C)	284.6	103.4	532.9	709.7		0.0079
				711.7	56	

Table 5.
Binding energies (eV), surface atomic ratios and surface amount of Fe^{3+} of fresh and spent FeZSM-5 catalysts taken on samples previously treated under vacuum or under hydrogen at 500 °C. S represents the catalyst tested with steam and WS the catalyst tested without steam

Sample	C1s	Si2p	Al2p	Fe2p$_{3/2}$	Fe^{3+}	Fe/Si (atom)
FeZSM-5 (vac)	284.6	103.5	74.6	710.0		0.015
				711.7	37	
(H$_2$, 500°C)				709.4		
	284.6	103.3	74.5	711.2	31	0.017
FeZSM-5 (S) (vac)	284.6	103.4	74.4	709.7		0.019
				711.5	43	
(H$_2$, 500°C)	•	103.3	74.5	711.4	33	0.022
	284.6					
FeZSM-5 (WS) (vac)	284.6	103.4	74.5	709.7		0.018
				711.4	43	
(H$_2$, 500°C)				709.7		
	284.6	103.4	74.4	711.6	32	0.020

From these results it can be concluded that the higher activity of FeZSM-5 catalyst, as compared to FeMCM-41 one, can be ascribed to its higher amount of iron on the surface surface However, the FeMCM-41 catalyst seems to be more resistant against deactivation by coke blockage of the pores, since it has larger pores than the other.

CONCLUSIONS

FeMCM-41 and FeZSM-5 catalysts are both active towards ethylbenzene dehydrogenation in the presence of steam. Particularly, FeZSM-5 catalyst is more active and selective than the FeMCM-41 one. The better performance of FeZSM-5 catalyst is due to the higher amount of iron deposited on the external zeolite surface and their ability in stabilizing the active oxidation state (Fe^{3+}) on the surface. Finally, since the FeZSM-5 catalyst is more active and selective than pure hematite and is chromium and potassium-free, it is a promising candidate to commercial applications.

ACKOWLEDGEMENTS

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