

EFFECT OF THE MODIFICATION WITH Sn, Zr AND Ce ON THE PHYSICO-CHEMICAL AND CATALYTIC PERFORMANCES OF H-ZSM-5 ZEOLITE

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abstract: The physico-chemical and catalytic activities of Zr-, Sn- and Ce- modified HZSM-5 zeolite catalysts utilised in n-butene conversion were analysed and correlated with the nature of the modifying agent. In modified catalysts prepared by impregnation technique, the modifying element is found mainly as an oxide on the external surface of the zeolite. Its presence generates modifications of the acidity and of the specific surface area of the zeolite. The highest selectivity for n-butene aromatisation was obtained with the catalyst modified by Sn, which was the element with the lowest ionic radius and the highest electronegativity. The modification with Sn generates the catalyst with the highest surface area and the highest proportion of strong acid sites.

keywords: Sn-H-ZSM-5, Zr-H-ZSM-5, Ce-H-ZSM-5, aromatisation of n-butene, NH₃-TPD.

Introduction

Due to its high protonic acidity and unique shape-selective behaviour, ZSM-5 zeolite has been proved to be a highly active and stable catalyst for the conversion of light olefins in oligomers (at low temperatures, 200-300°C) and aromatics (at higher temperatures). The formation of aromatics from olefins in the presence of H-ZSM-5 catalysts is accompanied by production of light alkanes since aromatisation takes place simultaneously with hydrogen transfer and cracking reactions [1,2]. Different authors showed that when the zeolite is modified with different metal oxides such as Ga₂O₃ or ZnO [3÷5], aromatics formation is improved while that of the alkanes is decreased and the hydrogen is directly eliminated from the reaction system. It has been assumed that this fact would be a consequence of the dehydrogenating activity of the modifying oxide. Several other studies showed that the performances of H-ZSM-5 zeolite in the aromatisation of light olefins (C₂-C₄) are improved when it is modified by other cations, such as In³⁺, Sc³⁺, Ni²⁺, or Ag⁺ [6÷8]. In an earlier study, we showed that in the case of H-ZSM-5 zeolite modified with bivalent cations, the catalytic activity for the aromatisation of butane and butene depends on the acid-base character of the modifying oxide and on the pathway of hydrogen transfer [8]. Up to now, the effect of the modification with tetravalent cations on the physico-chemical and catalytic performances of H-ZSM-5 type zeolite utilised in the

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aromatisation of light hydrocarbons (C₂-C₄) has been investigated only for Ce⁴⁺ [9] and Ge⁴⁺ [10], while Sn⁴⁺ effect has been investigated only when it is added to Pt [11,12]. However, the results of these researches cannot be correlated since different parent zeolites, concentrations of modifying agents, and reactants were utilised. Therefore, in this paper we considered it would be interesting to investigate the consequences of the modification with Zr⁴⁺, Sn⁴⁺ and Ce⁺ on the properties of a H-ZSM-5 zeolite modified with equivalent concentrations of modifying element. The physico-chemical and catalytic activities of several modified zeolite catalysts M/HZ (M=Zr, Sn, Ce, HZ=H-ZSM-5) were analysed and correlated with the specific features of the modifying agent.

Experimental

Since the number of Al atoms in the lattice of H-ZSM-5 is known to be responsible for the acidity and ionic exchange capacity of this solid, this value characteristic to the parent zeolite was calculated based on its composition. Aiming to study the effect of the modifying agent, for all M/HZ (M=Zr, Sn, Ce) modified catalysts, a concentration of modifying element representing approximately half of the total amount of Al per gram of zeolite was chosen.

Modified H-ZSM-5 catalysts, (M/HZ, where M=Zr, Sn, Ce), were prepared using a parent zeolite HZ (SiO₂ /Al₂O₃ = 45, Al_{conc.}= 4.8 x 10²⁰ atoms/gram). The parent zeolite, was impregnated with aqueous solutions of Zr, Sn, and Ce salts, (e.g. SnCl₄, Zr(NO₃)₄ and Ce(NO₃)₄), containing the appropriate amounts of modifying agent. After impregnation, the solids were dried at 105°C for 12 hours, and then submitted to calcination under airflow at 550°C for 4 h. This treatment allowed the thermal decomposition of the modifying elements salts into the corresponding metal oxides (MO₂). The concentrations of the modifying elements as determined by AAS were: Zr - 3.6 wt.% in Zr/HZ; Sn - 4.7 wt.% in Sn/HZ; Ce - 5.5 wt.% in Ce/HZ. These values corresponded to: 2.35 x 10²⁰ Zr-atoms /gram of catalyst; 2.36 x 10²⁰ Sn-atoms/gram of catalyst; 2.37x10²⁰ Ce-atoms/gram of catalyst.

The crystalline structure (a=19.92Å, b=19.87Å, c=13.36Å, v=5388.03Å³, β₅₀₁ (°)=0.235, % crystallinity 100%) of the parent zeolite prepared according to the procedure indicated in our previous work [8], was confirmed by the results of XRD analysis performed with a Philips PW 1050 X-ray diffractometer (Cu-K_α radiation, 2θ range 2-60°). In the XRD patterns of the modified catalysts, we could not notice any diffraction lines corresponding to the modifying oxides, probably due to their low concentration.

Modified catalysts were further characterised by FTIR spectroscopy, BET analysis for surface area and pore volume and ammonia thermodesorption (NH₃-TPD). Infrared spectra in the range 400-4400 cm⁻¹ were recorded on a Perkin Elmer 1600 FTIR spectrometer. Resolutions of 4 cm⁻¹ and 64 scans were used. Samples were prepared using the KBr pellet technique and strictly reproducible procedures for obtaining the pellets. The BET surface areas of the catalysts were measured with a Micromeritics ASAP 2000 equipment.

NH₃-TPD experiments allowing to determine the acid properties of catalysts were performed in a continuous flow apparatus, at atmospheric pressure, using a gaseous mixture 5 mol.% NH₃ in helium according to the method described in a previous work [13]. Before adsorption, each sample (*ca.* 300 mg) was kept under helium flow, at 550°C, until the

complete removal of the adsorbed impurities. The sample was cooled down to 150°C and pulses of the adsorbing gas were introduced until the saturation of the surface. The physisorbed gas was removed by passing helium for 30 minutes. The thermodesorption was then performed by heating the sample up to 550°C, at 10°C/min, under helium flow (1 ml/s) and the process was monitored by a thermal conductivity detector (TCD).

The catalytic tests for n-butene conversion were performed in a continuous flow reactor, in the temperature range of 320–540°C at W/F = 22.4 g catalyst · h · (mole n-C₄H₈)⁻¹. For each test, equal amounts of catalyst (3 grams) were utilised. Before each test, catalysts were activated at the reaction temperature under nitrogen flow for 1 h. Reaction products were analysed by gas chromatography according to the method described in a previous work [8].

Results and Discussion

The FTIR spectra of the catalyst samples, in the range of 400–4000 cm⁻¹, are shown in Fig. 1. The lattice vibrations characteristic to H-ZSM-5 zeolite appear in the range of 400–1200 cm⁻¹, while the bands corresponding to OH bonds vibrations appear at wavenumbers higher than 3200 cm⁻¹.

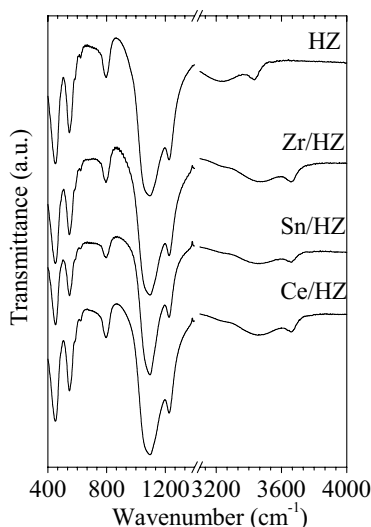


Fig. 1: FTIR spectra of catalysts samples.

According to Flannigen [14], the bands at 545 cm⁻¹, 585 cm⁻¹, and 620 cm⁻¹ are assigned to the structurally sensitive double five-member ring (D5R) vibrations, the band at 450 cm⁻¹, to the bending of the TO₄ tetrahedra, and those at 800 and 1100 cm⁻¹, to the symmetric and respectively, asymmetric stretching vibrations of the T–O–T linkages of the zeolite framework. In the FTIR spectra of the modified catalysts, there were no significant changes in the region of the spectra where the lattice vibrations appear. This fact was consistent with the results obtained by XRD-analysis, which also showed that the crystallinity of the parent zeolite was not affected by the modification with Zr, Sn or Ce.

In the FTIR spectrum of Zr/HZ, a very weak band was noticed at 740 cm^{-1} corresponding to Zr-O vibrations in monoclinic ZrO_2 . The bands at 510 cm^{-1} and 590 cm^{-1} corresponding to Zr-O vibrations in tetragonal ZrO_2 were not noticed in the spectrum of the modified zeolite. This would be probably happened because the intense bands of the parent zeolite overlapped the bands characteristic to tetragonal ZrO_2 [15].

In the FTIR spectra of Sn/HZ and Ce/HZ catalysts, the bands corresponding to D5R vibrations are slightly shifted to lower wavenumbers, 542 cm^{-1} , 582 cm^{-1} , and 617 cm^{-1} in the case of Sn/HZ, and respectively, 543 cm^{-1} , 584 cm^{-1} , and 618 cm^{-1} in the case of Ce/HZ.

The main differences between the FTIR spectra of the unmodified and modified zeolite catalysts appear in the region where the bands ascribed to OH bonds are detected. Thus, in the spectrum of the neat H-ZSM-5 zeolite, these bands appear at 3235 cm^{-1} , and 3425 cm^{-1} , while in the spectra of M/HZ samples, these bands are shifted to higher wavenumbers as it follows: 3454 and 3653 cm^{-1} in the case of Zr/HZ, 3428 and 3656 cm^{-1} in the spectrum of Sn/HZ, and respectively 3455 and 3656 cm^{-1} in the spectrum of Ce/HZ. The intensity of these bands increases in the order: Sn/HZ < Zr/HZ < Ce/HZ.

Based on the results of FTIR analysis, it may be assumed that in Sn, Zr and Ce/HZ, the modifying oxide is disposed mainly on the external surface of the zeolite. This assumption is consistent with the fact that ionic exchange reactions between the parent zeolite and tetravalent cations cannot take place easily. Besides, the impregnation method employed for the preparation of the modified catalysts favours the deposition of the modifying element on the external surface of the zeolite.

In Table 1, data concerning the specific surface area ($\text{m}^2\cdot\text{g}^{-1}$), the pore volume ($\text{mm}^3\cdot\text{g}^{-1}$) and the acidity determined by ammonia TPD for the studied catalysts are presented. The acidity was expressed as miliequivalents of NH_3 per gram of catalyst.

The modification of the H-ZSM-5 zeolite with Zr, Sn, or Ce oxides leads to a decrease of its specific surface area. The specific surface areas and the pores volumes of the modified catalysts are decreasing with the increase of the ionic radius of the tetravalent cation modifier.

NH_3 -TPD analysis showed that modifying the zeolite with tetravalent cations leads to a decrease of the total acidity of the catalyst, this decrease being more drastic as the ionic radius of the modifying element decreases, probably because a small ionic radius would allow their entrance into the zeolites channels. The partial loss of the total acidity of the parent zeolite after modification could be due to a masking effect induced by the presence of the modifying oxide that covers some of the acid sites of the zeolite. Thus, the lowest acidity value is obtained for the catalyst modified with Sn which has the shortest ionic radius. This observation is rather surprising, since Sn has also the highest electronegativity, e.g. 1.8. and it is known that CeO_2 has a basic character, ZrO_2 has a weak basic character and SnO_2 has weak acid character [17]. Hence, it would be expected that the increase of the electronegativity would be accompanied by an increase of the acidity.

However, from the acid sites strength distribution it may be seen that indeed, the concentration of strong acid sites in the modified catalysts increases with the increase of the

electronegativity of the modifying element and with the acid character of the modifying oxide, in the order $Ce/HZ < Zr/HZ < Sn/HZ$.

Table 1. Specific surface area, pore volume and acidity of HZ and M/HZ catalysts (M=Zr, Sn, Ce) and some characteristics of the modifying elements.

	Catalyst			
	HZ	Zr/HZ	Sn/HZ	Ce/HZ
Specific surface area (BET) ($m^2 \cdot g^{-1}$)	418	392	400	367
Pore volume ($mm^3 \cdot g^{-1}$)	191.8	180.3	183.8	169.2
Ionic radius of the modifying cation (\AA) [16]		0.8	0.71	1.01
Total acidity (meq. $NH_3 \cdot g^{-1}$)	1.1	1.02	0.78	1.08
Acid sites distribution (%)				
Weak + Middle-strength (150°C-350°C)	33.64	38.62	23.53	40.56
Strong (350°C-550°C)	66.36	61.38	76.47	59.44
Electronegativity of the modifying element [16]		1.4	1.8	1.2

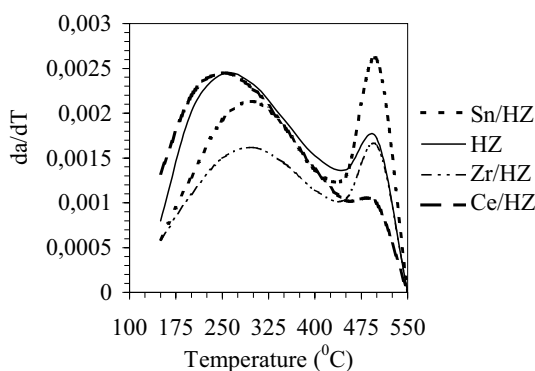


Fig. 2. NH_3 -TPD plots of HZ and M/HZ catalysts (a = acidity expressed as miliequivalents of NH_3 /gram).

The differences between the strength of the acid sites in different catalysts are indicated by the temperatures corresponding to the maximums of the ammonia thermodesorption curves presented in Fig. 2. For all catalysts, the NH_3 -TPD plots present two peaks. The first peak having a broad shape and a maximum intensity at a lower temperature (200-300°C) is ascribed to weak acid sites. The second peak appearing at a higher temperature (above 400°C) is ascribed to strong acid sites. The temperatures where the two maximum intensities of the signal are registered are designated as T_{weak} and T_{strong} respectively. The values of T_{weak} are 225°C for Ce/HZ, 245°C for HZ, 270°C for Zr/HZ and 285°C for Sn/HZ respectively. This suggests that the strength of these weak sites increases in the following order: $Ce/HZ < HZ < Zr/HZ < Sn/HZ$. The values of T_{strong} are 475°C for Ce/HZ, 485°C for Zr/HZ, 490°C for HZ, and 500°C for Sn/HZ, suggesting that the strength of strong acid sites increases in the order: $Ce/HZ < Zr/HZ < HZ < Sn/HZ$. The fact that for the modified catalysts the acid strength varies in the same order as the acid character of the modifying oxide corroborated with the results of FTIR analysis suggests that the modifying element is fixed mainly as oxide on the surface of the parent zeolite.

The results of catalytic activity tests presented in Table 2 show that conversions of butene higher than 90% are obtained at both reaction temperatures (e.g. 320°C favourable for oligomers formation, and 540°C favourable for aromatisation). The differences between the performances of HZ and those of M/HZ concern mainly the distribution of the reaction products and the value of the ratio $R = (\sum \text{moles alkanes } C_2-C_4 / \sum \text{moles BTX})$, which is considered by several authors [4-6] as an indicator of the reaction pathway.

Thus, according to the hydride transfer mechanism on the protonic sites of the zeolite proposed by Poustma for the conversion of propylene to benzene on H-ZSM-5 [18], the formation of each mole of aromatic hydrocarbon should be accompanied by the production of three moles of alkanes. Hence, if the reaction pathway is governed only by the acid sites of the zeolite, the ratio of the alkanes mole number to the aromatics mole number should be equal to 3. On the other hand, it was shown [4-6], that in the case of H-ZSM-5 zeolites modified by metal oxides having dehydrogenating activity, such as Ga_2O_3 and ZnO, R has values much lower than 3. In all cases, our results showed that for M/HZ catalysts the value of the ratio R is lower than 3. Modified catalysts are more selective for oligomerization and aromatisation of n-butene even at 320°C. Their selectivity for aromatisation at 540°C, when aromatics formation prevails, is increased by 10 up to 20% compared to that of HZ. This higher selectivity for aromatisation is accompanied by a higher concentration of H_2 in the reaction products and a lower concentration of alkanes C_2-C_4 . At 320°C, the aromatic fraction was rich in xylenes and ethyl benzene, obtained by dehydrocyclization of C_8 oligomers. At 540°C, the toluene was found to be in higher proportion than C_8 aromatics, while the presence of a high concentration of CH_4 in the reaction products was also noticed, indicating that dealkylation of alkyl benzenes occurs. These observations lead to the conclusion that the formation of aromatics also occurs essentially by the direct dehydrocyclization over the modifying element species that play their own role in the aromatisation process in combination with the zeolitic protons.

Depending on the nature of the modifying metal oxide, differences in the distribution of reaction products were noticed. Results show that the selectivity to aromatics increased in the order: $Ce/HZ < Zr/HZ < Sn/HZ$ that coincides with the increase of the acid sites strength on the modified catalysts as well as with the increase of their specific surface area (see also Table 1). Since oligomers are known to be precursors in aromatic formation, it would be expected a similar order of increase for the selectivity to oligomers. However, Zr/HZ presents higher selectivity for oligomers than Sn/HZ. This apparent anomaly could be explained taking into account the different types of acid sites involved in oligomerization and dehydrocyclization. Thus, according to Miao [9], when aromatisation takes place in the presence of H-ZSM-5 zeolites modified by metallic oxides which generate strong Lewis – type acid sites on the catalyst surface, the formation of oligomers is due mainly to Brønsted acid sites with high- or middle-strength, while the dehydrocyclization process involves mainly high strength Lewis acid sites. This could explain the higher selectivity for oligomerization of Zr/HZ catalyst when compared to that of Sn/HZ since the former has a higher proportion of middle-strength acid sites accompanied by a lower proportion of strong acid sites. The aromatics distribution was significantly influenced by the modifying oxide whose molecular dimensions determine different diffusion hindrances. The molecular dimensions of the MO_2 oxides increase in the order $SnO_2 < ZrO_2 < CeO_2$. Results showed that, with Ce/HZ an aromatic fraction very rich in

benzene and toluene was obtained, while Sn/HZ leads to higher concentrations of xylenes and heavier aromatics C₉₊.

Table 2. n-Butene conversion at T =320°C and T=540°C, W/F = 22.4 g catalyst· h⁻¹(mole C₄H₈)⁻¹

	Catalyst			
	HZ	Zr/HZ	Sn/HZ	Ce/HZ
T= 320°C				
Conversion (wt. %)	95.3	95.1	94.8	94.7
R = Σ moles alkanes C ₂ -C ₄ / Σ moles BTX	2.9	1.3	1.0	1.7
Products distribution (wt. %)				
H ₂	0.7	1.2	1.4	0.9
CH ₄	2.4	1.0	2.9	3.5
Alkanes C ₂ -C ₄	18.5	14.3	10.4	17.5
Alkenes C ₂ -C ₃	11.3	3.3	6.5	6.2
Oligomers C ₅₊	37.2	48.8	44.4	41.2
Aromatics	27.1	30.0	32.0	28.0
Coke	2.9	1.5	2.4	2.7
Aromatics distribution (wt. %)				
Benzene	8.8	6.5	3.5	12.3
Toluene	13.1	24.0	17.9	28.4
Xylenes+Ethyl-benzene	36.9	44.5	48.6	39.5
C ₉₊	41.2	25.0	30.0	19.7
T=540°C				
Conversion (wt. %)	97.0	97.7	96.4	96.5
R = Σ moles alkanes C ₂ -C ₄ / Σ moles BTX	3.0	1.0	0.8	1.4
Products distribution (wt. %)				
H ₂	0.7	2.8	3.5	2.0
CH ₄	9.4	13.9	17.5	15.3
Alkanes C ₂ -C ₄	35.7	18.0	14.2	24.0
Alkenes C ₂ -C ₃	5.3	5.8	5.6	7.1
Oligomers C ₅₊	13.8	9.5	5.9	5.1
Aromatics	30.7	47.3	50.3	43.0
Coke	4.5	2.7	3.3	3.6
Aromatics distribution (wt. %)				
Benzene	11.6	7.9	5.1	14.9
Toluene	20.3	37.2	33.5	40.3
Xylenes+Ethyl-benzene	43.3	38.5	40.3	33.9
C ₉₊	24.8	16.4	21.1	10.9

Conclusion

The results we obtained entitled us to conclude that the catalytic activity and the physico-chemical properties of H-ZSM-5 zeolite modified with Zr, Sn and Ce were influenced by the nature of the modifying element. Modified catalysts prepared by impregnation technique, contain the modifying element mainly as an oxide on the outer surface of the zeolite, generating modifications of the acidity and of the textural properties of the zeolite. The proportion of strong acid sites increases with the electronegativity of the modifying element, while the specific surface area and the pore volume decrease with the

increase of its ionic radius. The best selectivity for aromatics was obtained with Sn/HZ, the catalyst having the highest specific surface area and the highest proportion of strong acid sites.

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