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Tuning the acidity and reducibility of Fe/ZSM-5 catalysts for methane dehydroaromatization

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ABSTRACT

Methane dehydroaromatization was studied over Fe/ZSM-5 promoted catalysts. Transition metals (Cu, Ni, Co, and Zn) were used as promoters aiming to alter the Fe reducibility whereas alkali metals (Ca, Mg, and La) were used with the purpose of decreasing the acidity of ZSM-5. The samples were characterized by surface area measurements (S_{BET}), TPR, XRD, TPD- NH_3 and TPO. Activity tests were carried out at 750 °C in a fixed-bed quartz tubular reactor with on-line GC analysis. The addition of transition metal or alkali metal to Fe/ZSM-5 alters to a greater or lesser extent both the reducibility and the acidity of the catalyst. Among the transition metals, Cu-promoted catalyst showed a shorter induction time and high rate of benzene formation. Among the alkali metals, Ca-promoted catalyst produced a significant decrease in coke formation and formed significant amounts of aromatics.

1. Introduction

The world has an abundant amount of methane resources including natural gas, coal-bed gas and biogas. Methane reserves in form of shale gas are turning cost-effective to extract with recent technological advances. Shale deposits are estimated to have between $14.16 \times 10^{12} \text{ m}^3$ and $28.3 \times 10^{12} \text{ m}^3$ potential gas resource in the US alone [1], with world reserves reaching up to $220.72 \times 10^{12} \text{ m}^3$ [2]. Shale gas extraction has boosted U.S. gas production to a point that led to low natural gas and oil prices [3] and there is still room to enhance shale gas production in U.S. for the years to come [4]. Similar repercussions are expected for the world methane gas prices as the world shale reserves start becoming extracted. Moreover, methane hydrates, which are deposits of natural gas trapped within the crystalline structure of frozen water, are another potential future source of methane with reserves estimated between 50% and 15 times more than all global shale deposits combined [5].

The abundance of natural gas makes methane a cheap and readily available feedstock. However, the energy density of natural gas is three orders of magnitude lower than that of oil, making the handling and transportation an economic issue to the point that flaring portions of the methane extracted is a common practice [6]. The catalytic conversion of methane into more valuable chemicals at the production site is a possible solution to justify transportation costs and make use of this abundant feedstock.

There are several possible routes to convert methane, including indirect routes that involve the production of syngas as intermediate and direct routes. Among these, the methane dehydroaromatization (MDA) is a promising direct route for the production of aromatics. For this reaction non-oxidative conditions are preferred, producing aromatics with higher selectivity. Nonetheless, the direct conversion of methane to aromatics becomes thermodynamically unfavorable, requiring reaction temperatures above 700 °C.

The Mo/HZSM-5 catalyst is the most studied catalyst for MDA with the first report back in 1993 [7]. However, the Mo-based zeolite catalyst has relatively low stability to coke formation [8–10]. Various supported transition metals have since been tested for the MDA reaction. Among them, Fe showed to be a promising low cost and active alternative, although with lower conversion when compared to the Mo-based catalyst [11–13]. Fe is most prominently used as a promoter for Mo/HZSM-5 based catalysts [13,14]. Recently some research has been conducted studying Fe for the MDA reaction [15,16]. However, the high rate of carbon formation seems to be the major disadvantage of this system. In addition, Fe-based catalysts have longer induction times than Mo-based catalysts [14,16]. The modification of Fe/HZSM-5 with other metals for the MDA reaction was not reported yet.

In the present work, the methane dehydroaromatization over Fe/ZSM-5 catalysts promoted by two different metal groups was studied: a) transition metals (Cu, Ni, Co and Zn) aiming to alter the Fe reducibility; b) metals with alkaline properties (Ca, Mg and La) with the purpose of

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decreasing the acidic properties of Fe/ZSM-5 catalyst.

2. Experimental

2.1. Catalysts preparation

The parent zeolite ZSM-5 used as support was supplied by Zeolyst with Si/Al ratio of 30. All metals were impregnated by the incipient wetness method using the appropriate amount of the following precursors: nitrates of calcium and copper (Synth), nitrates of nickel, cobalt, lanthanum, iron and magnesium (Vetec) and zinc nitrate (Merck). After impregnation, the samples were dried overnight at 80 °C and calcined in 50 ml min⁻¹ of synthetic air at 600 °C for 2 h with heating rate of 10 °C min⁻¹. The parent zeolite is denoted ZSM-5, the 5% Fe impregnated zeolite is denoted Fe5 and the promoted samples with 5% Fe and 1% M (M = Cu, Ni, Zn, Co, Mg, La and Ca) are denoted Fe-M.

2.2. Catalyst characterization

Powder X-ray diffraction (XRD) measurements were performed for the fresh and spent samples using a Bruker D2-Phaser diffractometer with Cu-K α radiation at 30 kV and 10 mA. The diffraction patterns were recorded with a step of 0.02° (2 θ) in the range of 5–70°.

Ammonia temperature-programmed desorption (TPD-NH₃), hydrogen temperature-programmed reduction (TPR-H₂) and nitrogen adsorption experiments were obtained using a bench flow system with thermal conductivity detector. Prior to each TPD-NH₃ run, 0.2 g of the sample was heated to 250 °C for 30 min under pure He (30 sccm, ramp 10 °C min⁻¹). The sample was then cooled to 100 °C and a flow of 30 sccm 5% NH₃ was used to adsorb ammonia for 30 min. The sample was purged with pure He (30 sccm, 100 °C) for 30 min to remove excess ammonia before obtaining the TPD profile, where the temperature was ramped up to 750 °C at 10 °C min⁻¹ with 30 sccm of He. For the TPR analysis 0.1 g of the sample was pretreated at 150 °C in a 30 sccm flow of nitrogen before ramping up to 800 °C at 10 °C min⁻¹ under 30 sccm flow of N₂ and H₂ with 5% H₂.

The surface area was determined via nitrogen adsorption using a Nova 4200e analyzer (Quantachrome Instruments). The sample (0.2 g) was degassed for 180 min at 300 °C under vacuum prior to each analysis. Multi-point B.E.T. was used to calculate the specific surface area.

Temperature-programmed oxidation analysis (TPO) was carried out in a thermobalance (TA Instruments, SDT-Q600). For each test 10 mg of the spent catalyst was heated to 800 °C at 10 °C min⁻¹ under 100 sccm of synthetic air flow.

2.3. Activity tests

The MDA reactions were carried out in a fixed-bed tubular quartz reactor (1/2 in diameter) with heating provided by a resistive electric oven and quartz wool as the support of the catalyst bed. Typically, 0.2 g catalyst was heated to 750 °C at 10 °C min⁻¹ under 100 sccm of N₂/CH₄ 90:10 mixture. The chromatographic analysis of the products started when the reactor reached 750 °C and was carried out on-line by a gas chromatograph Varian 3600cx with a packed column Porapak Q, using a thermal conductivity detector (TCD) and a flame ionization detector (FID). The reactions were carried out for 360 min before stopping the methane feed and cooling the reactor.

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of the calcined samples. For all samples the peaks relative to the ZSM-5 framework were observed, indicating that the framework retained the ZSM-5 structure regardless of the metal utilized in the impregnation. For the Fe-Cu and Fe-Mg samples two peaks ascribed to the Fe₂O₃ were observed at 33.2 and 35.6°, which indicates particle aggregation during the sample

calcination. No additional peaks were observed for the other samples, thus the iron and its co-impregnated metals are highly dispersed on the ZSM-5 surface.

The Scherrer equation was used to calculate the crystallite sizes of the peak at 7.9°, perpendicular to plane (0 1 1) of ZSM-5, and the results are listed in Table 1. Concerning the intensity of the HZSM-5 reflections and its crystallite size, it is noticed that the impregnation with Fe significantly decreases the crystallinity of the support, which indicates a partial destruction of the HZSM-5 structure [17,18]. The addition of a second metal improves the crystallinity of the Fe5 catalyst, indicating a better dispersion of the metals on the support. The presence of transition and alkaline metals might offer better alternatives for iron to interact and stabilize in the zeolite surface without disrupting its structure. The interaction of Fe with other metals is further discussed below in TPR-H₂ results. The sample containing Cu exhibits the highest crystallinity. In general, samples promoted with alkali metals show higher crystallinity than samples promoted by transition metals.

The BET surface area and the total acidity of the materials are listed in Table 1. The BET area for the parent zeolite was 345 m²/g. For all the modified ZSM-5 samples a decrease in the surface area was observed, most notably for Fe-Mg, which is in agreement with the observed sintering of iron in the XRD pattern for this sample.

The TPD-NH₃ profiles of the samples are presented in Fig. 2. The results were deconvoluted into three peaks (Table 1). Two desorption peaks were observed for the parent ZSM-5 at around 250 and 450 °C. The peak at low temperatures is assigned to weakly bound NH₃ on Lewis acidic sites. At higher temperatures, above 350 °C, the desorption peak is assigned to NH₃ bound on Brønsted acidic sites [15,19,20]. The addition of Fe increases the total acidity of the HZSM-5 zeolite and shifts the second peak to higher temperatures, around 480 °C, indicating an increase in the strength of the strong acid sites [14]. The deconvolution of the TPD-NH₃ traces for Fe5 indicates three types of acid sites [18].

The impregnation of transition metals with Fe over ZSM-5 decreases the second peak relative to strong acidity, except for the Fe-Ni sample. The incorporation of Cu with Fe in ZSM-5 causes a split of the second desorption peak in two, one centered at 450 °C and the other shifted to high temperatures, around 620 °C. The development of strong acid sites above 500 °C with the incorporation of Cu in ZSM-5 was observed before [21,22]. The addition of Ni promotes an increase of the total amount of acid sites. On the other hand, the impregnation of Co causes a smoothing and broadening of the second desorption peak, without significantly modifying the total amount of acid sites. The addition of Zn also causes a smoothing of the second peak, but shifting the maximum to a lower temperature, which indicates a decrease in the acid strength.

The effect of alkaline promoters had different effects on the acidic properties of Fe5. A decrease in acidity was observed and the effect was in the following order: Mg > Ca > La. A shift to lower temperatures of the desorbed ammonia was observed for Ca, indicating a decrease in acid strength. The deconvolution of this curve shows a second peak with maximum at 413 °C which can be related to medium acid sites [14,18] and a third peak at 549 °C. These temperatures are considerably lower than for Fe5 which were 480 and 620 °C, respectively, and demonstrate the decrease in the strength of the acid sites. The addition of La did not change the acidic properties considerably, which can be attributed to the small amount of La in mols, due to the high molecular weight of La, and to the size of La cation. The addition of Mg caused a greater modification on the zeolite acidity, strongly decreasing the total number of acid sites and also decreasing the strength of the medium and strong acid sites. The deconvolution of TPD curve shows that the medium and strong acid sites occurs at 388 and 578 °C, respectively. These temperatures are around of 100 °C and 40 °C lower, respectively, than for the Fe5 sample, which evidences the strong decrease of the acid strength with the addition of Mg.

The difference of the alkali metal effect seems to be related to the

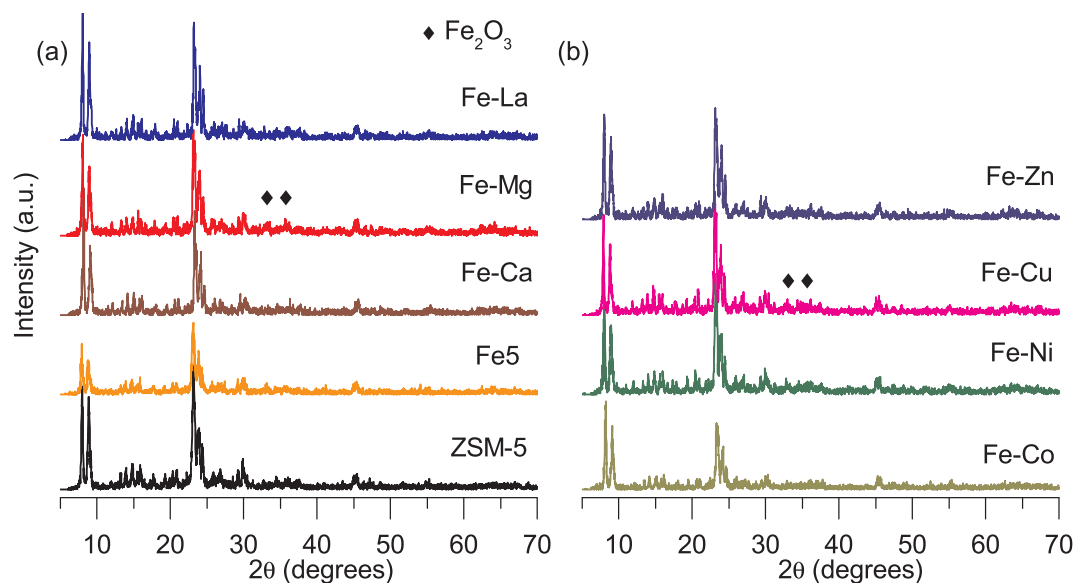


Fig. 1. XRD of the Fe/ZSM-5 samples modified by: (a) Alkali metals, (b) transition metals.

Table 1

BET surface area, crystallite size and TPD-NH₃ characterization results.

Sample	BET (m ² g _{cat} ⁻¹)	ZSM-5 crystallite size (nm)	Desorption temp. (°C)			Acidity (mmol _{NH3} g _{cat} ⁻¹)			
			T ₁	T ₂	T ₃	Peak 1	Peak 2	Peak 3	Total
ZSM-5	345	32.2	243	442	–	0.55	0.34	0.00	0.89
Fe5	307	24.6	254	481	618	0.67	0.57	0.06	1.30
Fe-Co	289	36.5	231	381	563	0.55	0.44	0.21	1.20
Fe-Ni	285	28.4	236	438	628	0.67	0.78	0.05	1.49
Fe-Cu	310	44.8	240	454	618	0.68	0.34	0.09	1.11
Fe-Zn	290	35.4	238	424	595	0.58	0.51	0.08	1.16
Fe-Mg	261	41.3	242	388	578	0.51	0.45	0.19	1.16
Fe-Ca	277	44.7	243	413	549	0.56	0.55	0.07	1.18
Fe-La	308	40.8	255	483	630	0.64	0.54	0.02	1.21

size of the cations which follows the order Mg < Ca < La. Thus, the effect is inversely proportional to the size of the cation: Mg > Ca > La. Taking into account that Mg has the smallest cation size (0.13 nm), it is reasonable to suppose that Mg cations are dispersed within the ZSM-5, neutralizing the strong acid sites. In addition, the electronegativity of Mg²⁺ is the largest among these cations. On the other hand, the larger size of lanthanum indicates that La cation is dispersed only externally, therefore without affecting the acidity of ZSM-5.

From the TPD-NH₃ experiments it can be concluded that the impregnation of promoter metal affects the balance of acidity in both peaks differently.

In Fig. 3 the temperature-programmed reduction profiles for all samples are shown. The TPR-H₂ was used to investigate the influence of the promoter metal on the Fe5 reducibility. The iron loaded sample show three reduction peaks at 390 °C, 520 °C and 660 °C. The low temperature peak is ascribed to the reduction of Fe₂O₃ to Fe₃O₄, the middle temperature peak shows the reduction of Fe₃O₄ to FeO and the high temperature peak corresponds to the reduction to metallic Fe [21,23,24]. The broad peak above 700 °C can be ascribed to the reduction of iron oxide nanoparticles or to the slow reduction of Fe²⁺ in ion exchange positions [25].

For catalysts promoted with transition metals, the reduction profile of Fe-Cu shows an increase in the peak at 520 °C, which may be due to the improved reducibility of FeO to Fe⁰ promoted by Cu [21,26]. It is very well established that Cu has a promoter effect on the reducibility of metal oxides. For the Fe-Co sample a new peak was observed at

780 °C which can be related to reduction of cobalt oxide. According to Panahi et al. (2017) this peak corresponds to the reduction of monoatomic Co²⁺ at exchangeable sites which are stabilized under the effect of the zeolite framework [22]. The Co loading also showed to increase the reduction peak at 660 °C, which may be ascribed to a higher proportion of Fe ions being completely reduced in the Fe-Co sample. No significant differences in TPR were observed with the Zn loading in the sample. It was reported before that TPR profiles of Fe-Zn oxides display similar features to the zinc free iron oxide [26]. An unusual behavior is observed for the Ni-promoted sample, which shows a broad and strong peak between 350 and 600 °C, indicating that the reduction of all iron oxide phases takes place in a single step. Nickel can promote iron reduction due to spill over effect, as Ni easily dissociates hydrogen [27]. The higher amount of reduction sites can be explained by a higher dispersion of Fe ions with the Ni co-impregnation. Similar effect was observed for Ni-Fe supported in Al₂O₃ with Fe/Ni ratio of 1.5 and indicates the presence of NiFe₂O₄ phase [28–30]. The Fe-Ni profile is completely different than that of Fe5, no reduction peaks are observed at high temperatures indicating that the mixed oxide phase NiFe₂O₄ should be the most abundant metallic phase in Fe-Ni. Therefore, the influence of transition metals as reduction promoters was in the following order: Fe-Ni >> Fe-Cu > Fe-Co ~ Fe-Zn.

Interestingly, there was a significant modification in the reducibility of Fe5 with the addition of alkali metals. Both Fe-Ca and Fe-Mg presented a more pronounced hydrogen uptake at the region between 550 and 750 °C, indicating a strong interaction with iron oxides species. The addition of La affected the reduction properties of iron, promoting the

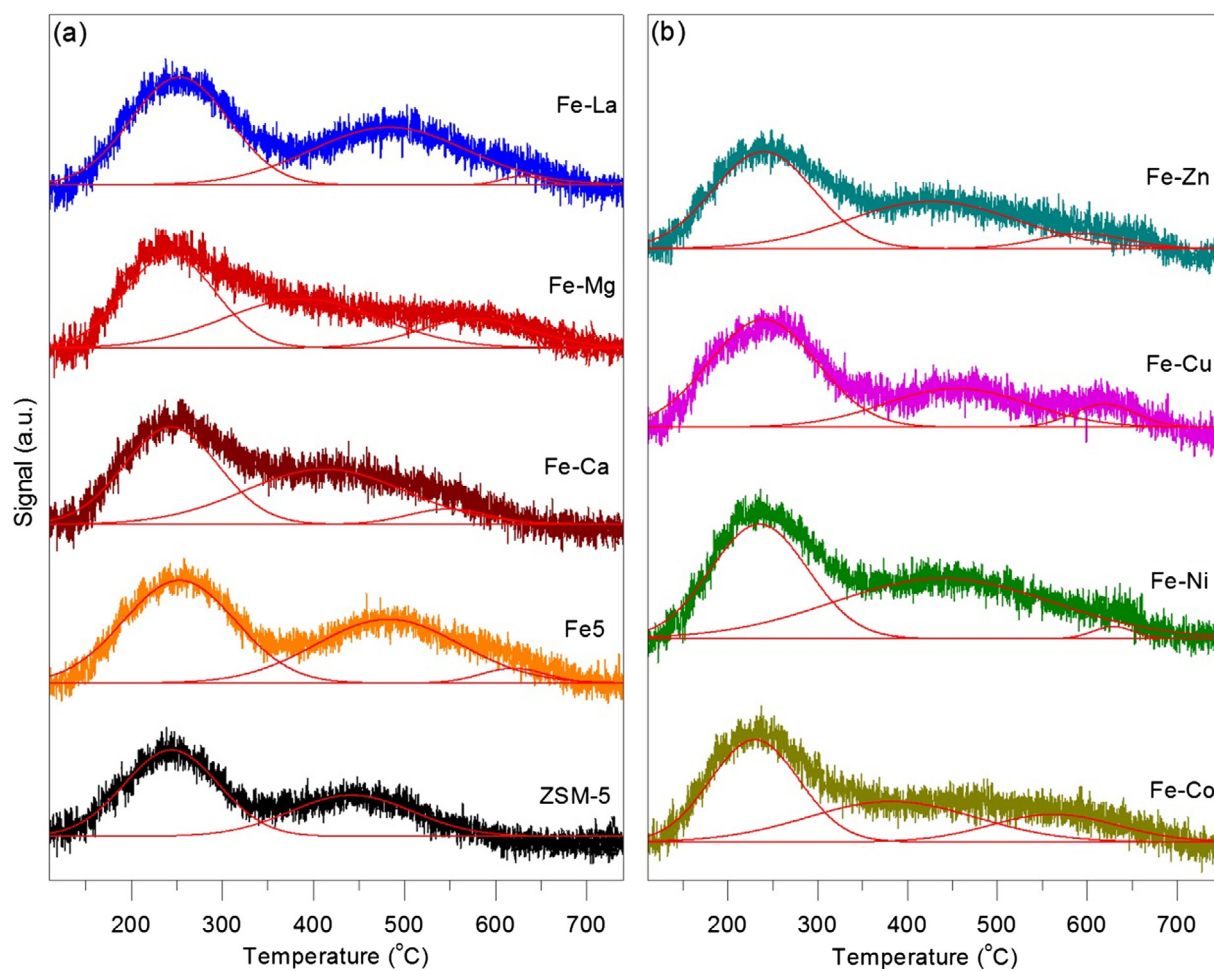


Fig. 2. TPD-NH₃ profiles of the Fe/ZSM-5 samples promoted by: (a) Alkali metals, (b) transition metals.

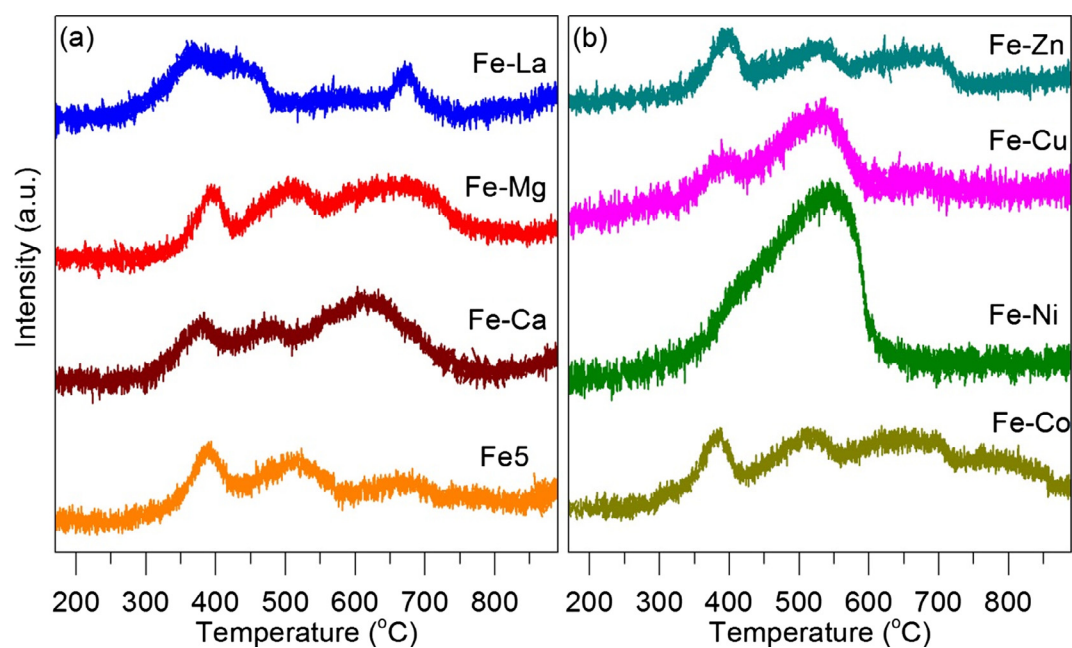


Fig. 3. TPR-H₂ profile of the prepared samples promoted by: (a) Alkali metals, (b) transition metals.

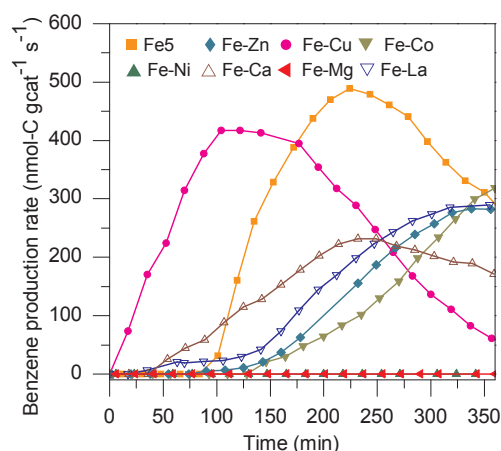


Fig. 4. Benzene production rate with the time on stream at 750 °C and GHSV of 3000 scc g cat⁻¹ h⁻¹ of N₂/CH₄ 90:10.

reduction of Fe₂O₃ → Fe₃O₄ → FeO in a single step and at a lower temperature than Fe5. The lanthanum might be in the form of LaFeO₃, as the mixed oxide reduction peak overlaps with the Fe₂O₃ reduction [31] and the signal at 400 °C seems to show two peaks. The shape of the reduction peak at 660 °C is also more prominent, which could be ascribed to the reduction of FeO to metallic Fe.

3.1. Catalytic activity

An induction period was observed for all catalysts that produced benzene (Fig. 4). The induction period changed with the promoter metal used. Two reactions might be involved with this period, one is the reduction and carburization of iron oxides to iron carbide, and the other is the decomposition of CH₄ over the metallic sites resulting in coke and H₂. A number of studies have discussed the induction period in methane aromatization for molybdenum based catalysts during which the molybdenum is gradually reduced by methane in order to form molybdenum carbide [8,32]. Similarly, carburized iron was found as the active species for the conversion of methane to aromatic hydrocarbons [16]. The induction period for Fe-based catalysts is considerably longer than for Mo-based catalysts and, at the same conditions, usually lasts for more than 1 h [14].

The benzene and C₂ production rate with the time-on-stream (TOS) are presented for all samples in Figs. 4 and 5, respectively. The methane conversion with time is shown in Fig. 6. The samples that showed activity for methane aromatization presented an increase in benzene production rate with TOS up to a maximum, after which the benzene

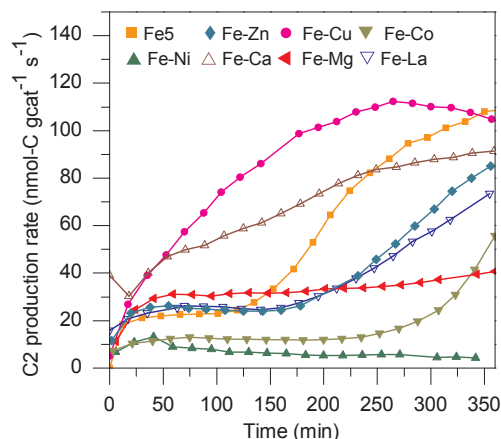


Fig. 5. C₂ production rate with the time on stream at 750 °C and GHSV of 3000 scc g cat⁻¹ h⁻¹ of N₂/CH₄ 90:10.

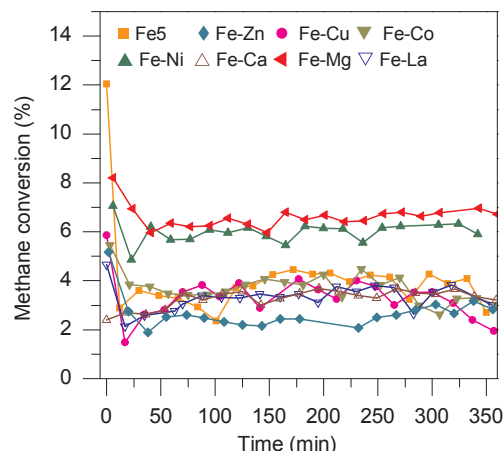


Fig. 6. Methane conversion with time on stream at 750 °C and GHSV of 3000 scc g cat⁻¹ h⁻¹ of N₂/CH₄ 90:10.

selectivity steadily decreased whereas the selectivity to C₂ hydrocarbons slowly increased. The Fe5 catalyst presented the highest production rate of benzene after 220 min of reaction time whereas Fe-Ni did not show any benzene formation. Thus, when comparing the benzene production rate the following order is observed: Fe5 > Fe-Cu > Fe-Co ~ Fe-Zn >> Fe-Ni. On the other hand, the induction time follows the order: Fe-Cu < Fe5 < Fe-Zn ~ Fe-Co. The Cu-promoted sample (Fe-Cu) achieved the maximum benzene rate with only about half the time needed for the unpromoted (Fe5) catalyst. From these results, it can be remarked that the change in the reducibility was more important than the change in the acidity of Fe/ZSM-5 catalyst for the production of benzene with the addition of transition metals. This was most evident with the addition of Ni, which had the most deleterious effect, precisely due to the profound change in Fe reducibility. The changes in reducibility shows that the Fe is strongly interacting with Ni, possibly forming NiFe₂O₄, and the mixture of these metals do not present activity to aromatization. As shown in Table 2, despite having high methane conversion, Fe-Ni showed only selectivity for C₂ compounds and high carbon formation.

The benzene rate production for samples promoted with alkali metals was in the following order: Fe-La > Fe-Ca >> Fe-Mg. This order is exactly opposite to the change produced in the acidity by the addition of the alkali metal, as shown by the TPD-NH₃ results. Since Fe-Mg showed no benzene production, it can be concluded that the addition of Mg was responsible for the neutralization of the strong acidity of the catalyst or inhibition of the iron carbide formation, both essential for

Table 2

Methane conversion, selectivity at peak production and total coke produced.

Sample	Average CH ₄ conversion (%)	Final CH ₄ conversion (% after 360 min)	Selectivity (%) ^a			Coke amount (mg/g) ^c
			C ₂	Benzene	C ₇ + Coke ^b	
Fe5	4.1	3.3	6.9	45.3	4.8	128.8
Fe-Co	3.7	2.9	8.3	40.9	4.6	160.7
Fe-Ni	5.9	5.9	0.8	0	0	185.9
Fe-Cu	3.3	2.4	7.5	38.6	4.0	148.3
Fe-Zn	2.7	2.8	9.3	33.0	4.0	174.5
Fe-Ca	3.3	3.2	8.7	24.9	2.9	63.5
Fe-Mg	6.5	6.6	2.1	0	0	97.9
Fe-La	3.3	3.0	9.4	37.1	4.3	49.3

Conditions: 750 °C reaction temperature; GHSV of 3000 scc g cat⁻¹ h⁻¹ of N₂/CH₄ 90:10.

^a Selectivity at maximum benzene production.

^b Estimated based on the converted CH₄.

^c Total coke amount measured by TPO after the reaction.

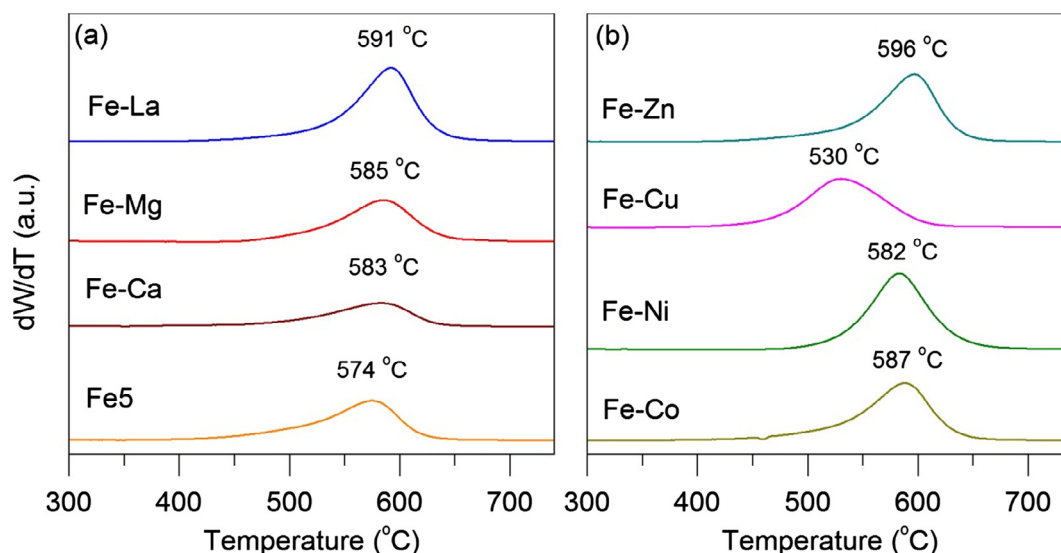


Fig. 7. Temperature programmed oxidation weight loss profiles of samples after the reaction: (a) Alkali metals, (b) transition metals.

the aromatization reactions. Concerning the induction time, both Fe-Ca and Fe-La samples were able to produce benzene approximately after 1 h of TOS, approximately half the time of induction of Fe5.

Table 2 presents the average and final conversion for each catalyst, the selectivity of the products at the maximum benzene production and the total amount of coke produced. It is observed that Fe-Ni and Fe-Mg samples were the ones that showed the highest methane conversion, but at the same time, these samples were those that did not produce aromatics. The Fe-Ni catalyst presented high activity associated with the presence of Ni, which strongly altered the Fe reducibility, promoting reactions of C_2 formation and coke formation. The Fe-Mg catalyst also showed high activity for the formation of C_2 products, but with a low carbon production, due to the strong decrease in the acidity of the catalyst promoted by Mg.

3.2. Characterization of spent catalysts

Coke production is a thermodynamically favored side reaction and the coke accumulation is generally accepted as the main cause of catalyst deactivation in MDA reaction. Fig. 7 present the obtained TPO profiles for the samples after the reaction with their respective peak temperature (T_{max}) and Table 2 shows the total accumulated coke.

The main feature in the TPO profiles is a peak at around 585 °C, which could be assigned to hard coke formed from polynuclear aromatic species associated with the Brønsted acid sites [33–35]. Table 2 shows that coke deposition for samples promoted by transition metals was in the following order: Fe-Ni > Fe-Zn > Fe-Co > Fe-Cu. This sequence corresponds closely to the same order of total amount of acid sites for these samples (Table 1), which evidences that the amount of carbon produced is related to the number of acid sites of the catalyst. The high amount of coke produced in the Fe-Ni sample can also be influenced by the promoted reducibility. In relation to the oxidation temperature, it was observed that the Fe-Ni and Fe-Co samples showed T_{max} close to the Fe5 sample, around 580 °C. The Fe-Zn sample presented an oxidation temperature near 600 °C which is related to the higher acidic strength of the strong acid sites. The Fe-Cu sample presented a T_{max} of 530 °C related to a less hard carbon, which can be attributed to the lower total amount of acidic sites and to the change in the reducing properties of Fe with the addition of Cu.

The amount of coke produced for samples modified with alkali metals was in the following order: Fe-Ca < Fe-Mg < Fe-La. The low amount of carbon produced by the Fe-Ca sample is related to the decrease of the acid strength promoted by the addition of Ca, as shown by

the TPD results. In addition, it is noted that Fe-Ca shows a broad oxidation peak indicating the formation of a less hard carbon that oxidizes at temperatures around 500 °C. On the other hand, Fe-Mg catalyst showed a higher carbon formation, even though the Mg addition had neutralized most of the medium and strong acidity of the Fe/ZSM-5. It is worth noting that this sample did not produce benzene, therefore the carbon produced is not due to aromatization reactions. Among the catalysts promoted by alkali metal, Fe-La presented the highest amount of carbon produced, which was the sample that had the lowest effect on acidity due to the large cation size of La. Among all the samples, Fe-Ca and Fe-Mg were the catalysts that produced less amount of carbon. However, of these only Fe-Ca produced aromatics.

Fig. 8 shows XRD patterns of the samples after the reaction, which was carried out at 750 °C for 360 min. Even with lower overall intensity for XRD experiments a new peak has appeared around 43.9° assigned to iron carbide which could be in Fe_3C [16] or $\epsilon-Fe_2C$ form [36]. The intensity of iron carbide peak varied among the catalysts. A more evident signal was observed for Fe-Cu and Fe-Ni, among the samples promoted with transition metals and for Fe-La from the samples promoted by alkalis. Since the formation of iron carbide is expected when using iron for the dehydroaromatization of methane [16], the carbide species must have been formed in all samples that produced aromatics. Its appearance in XRD could be an indicator of either significant carburization of the iron species or the formation of iron carbide clusters during the reaction.

The catalysts promoted with transition metals showed an accentuated decrease in zeolite crystallinity after the reaction, except for the Fe-Cu sample, indicating that the structure of the zeolite could have collapsed. This loss of ZSM-5 structure observed in XRD after the reaction might be one of the reasons for the non-formation of aromatics by Fe-Ni, as the formation of the iron carbide species is not sufficient and the ZSM-5 structure is essential to the generation of aromatic hydrocarbons [37]. It is worth noticing that the Fe_2O_3 peak in Fe-Cu was not observed after the reaction, which indicates that the Fe_2O_3 clusters in Fe-Cu were mostly carburized. For the alkali metal promoted catalysts the zeolite structure was still present in the XRD after the reaction. The Fe-Mg sample presented the highest crystallinity of ZSM-5 structure after the reaction; however no iron carbide peaks were detected in the XRD pattern, which is related to the non-formation of aromatics with this catalyst.

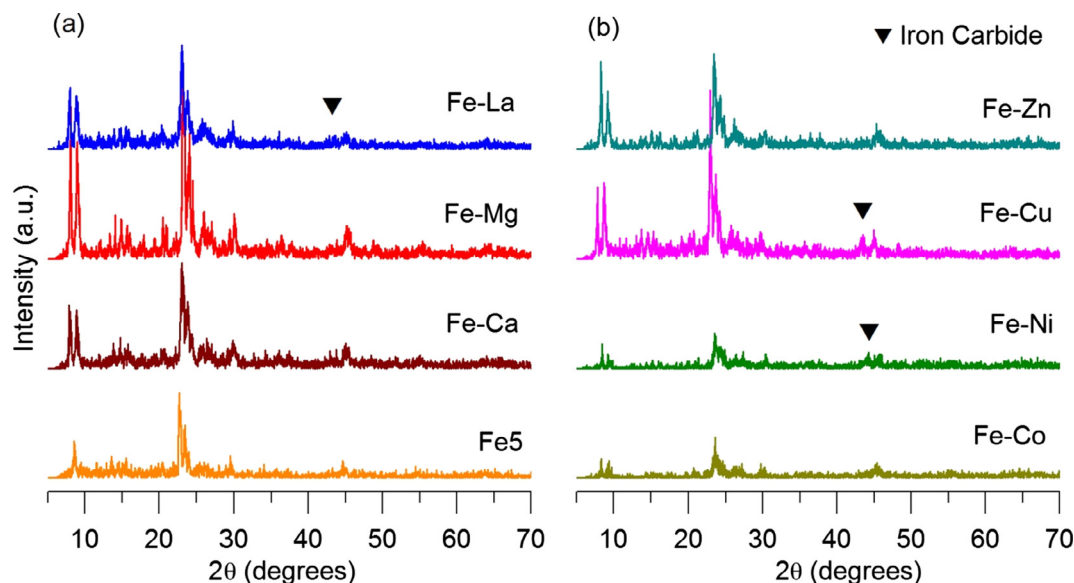


Fig. 8. XRD of the samples after reaction promoted by: (a) Alkali metals, (b) transition metals.

4. Conclusions

The addition of promoters significantly affected the catalytic properties of Fe/ZSM-5 catalysts. It was not possible to change the reducibility and the acidity of the catalyst independently.

Transition metals as promoters affected both the reducibility and acidic properties of the catalyst. Alkali metals as promoters primarily affected the reducibility of the catalyst. The decrease in acidity was lower as the size of the alkaline cation increased. The catalyst promoted by La had no effect on acidity but had a great impact on reducibility.

Among the catalysts promoted with transition metals, the Fe-Cu sample showed a high rate of benzene formation with the shortest induction time, the tuning in the reduction properties of Fe with Cu was essential for this result. Among the alkali metals, Ca caused a significant decrease in coke formation and still formed significant amounts of aromatics.

The reducibility and acidity of Fe/ZSM-5 catalysts are important for the aromatization of methane and therefore both characteristics must be adjusted simultaneously.

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