The influence of the acid sites on the methylamines synthesis with Cu-HZSM-5 zeolite

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There is a high industrial demand for MMA and DMA, however, the production of TMA is favored with the commercial catalysts. This work tested the methanol amination reaction with HZSM-5 and Cu/HZSM-5 zeolites (%Cu = 1.2, 3.7 and 6.0). Regarding the MMA selectivity, light differences were observed among Cu/HZSM-5 catalysts and pure zeolite, although the catalysts containing 3.7% copper was slightly more selective to MMA than the other metallic catalysts studied. From these results it is suggested that the metal loading present in the catalysts leads to a modification in the nature of the acidic sites, in particular, the selectivity depends on ratio Brönsted/Lewis acid sites. This modifications would facilitate the amines desorption during the reaction.

KEY WORDS: acid sites; methylamines synthesis; Cu-HZSM-5 zeolite.

1. Introduction

Methanol conversion in valuable products makes it an important raw material to the wide miscellaneous chemicals. Acetic acid, propionic acid, acetic anhydride, ethylene glycol, ethanol and amines are good examples of products that have already been successfully synthesized using methanol as feedstock [1]. Among the materials that can be obtained from methanol, the low molecular weight aliphatic amines occupy an important place in modern society because of their large application possibilities. Mono-, di- and tri-methylamines (MMA, DMA and TMA) are normally used as corrosion inhibitors, probe molecules to characterize superficial acidity of solid materials, softeners for synthetic fibers, scatters to paints and pigments and like intermediates in chemical and pharmaceutical industries (production of pharmaceutical product, pesticides, explosives and animals feed).

Methylamines are synthesized industrially, using methanol and ammonia and acid catalysts (e.g. alumina or silica–alumina) that approaches the thermodynamic equilibrium molar ratio MMA : DMA : TMA (17 : 21 : 62 at $T = 673$ K and molar ratio $NH_3/CH_3OH = 1$). Close to the thermodynamic equilibrium the TMA production is favored, and therefore the demanding products MMA and the DMA become more important [2]. For increasing production of MMA and DMA it is necessary to recycle TMA, but it makes the process more expensive. To minimize costs involved for separation of TMA and to increase the production of MMA and DMA, recent research have developed zeolite catalysts [3,4]. According to literature, the product distribution and the enhancement of MMA selectivity are related to pore sizes of zeolites in this reaction (shape selectivity). It can be explained either by the retention of TMA in the pores or by the reaction of these molecules inside the pores.

The literature did not present new catalysts able to increase the MMA and DMA selectivity to reach the molar ratio 33 : 53 : 14 (MMA : DMA : TMA) required in industrial processes. There are continuously publications in this area [5]. An interesting observation is that there are only few reports concerning the employment of transition metals modified zeolites for this kind of reaction, although copper catalysts on different supports, such as Al_2O_3, Cr_2O_3 and Cr_2O_3–SiO_2, are highly efficient for the catalytic amination of alcohols [6].

The main goal of this paper is to test the Cu/HZSM-5 catalysts and how it affects the molar relation of amines produced in methanol amination reaction. Besides, different characterization techniques were employed to determine the effect of the metal and acidic properties on the selectivity and activity.

2. Experimental

2.1. Catalysts preparation

HZSM-5 zeolite from DEGUSSA (SAR = 28.4) was previously calcined at 803 K for 4 h (5 K min^{-1}) in a pyrex glass calcinator under continuous air flow

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(30 mL min^{-1}) before the preparation. This prior treatment was necessary to stabilize the zeolite structure and to eliminate undesirable materials, like as residual templates.

The catalysts were prepared using three different methodologies of preparation:

(1) Ionic exchange
(2) Step 1: Ionic exchange
    Step 2: Precipitation (pH = 7.0 with NH_4OH)
(3) Step 1: Ionic exchange
    Step 2: Precipitation (pH = 9.0 with NH_4OH and pH = 7.0 with HNO_3)

The ionic exchange step consisted by adding a known amount of HZSM-5 zeolite (SAR = 28.4) to a copper nitrate solution (0.90 N) and maintaining the mixture under agitation during 20 h at 353 K. Methods (2) and (3) were applied after ionic exchange and submitted to a second step, the precipitation (step 2). This later one consisted by adjusting the pH solution to the desired value (7.0 or 9.0) with NH_4OH, according the procedure defined by Iwamoto *et al.* [7]. Then the samples were filtered, washed, dried at 373 K (16 h) and calcined (under air flow) for 6 h up to 773 K (30 mL min^{-1}). Another catalyst was prepared adjusting the pH to 9.0 with NH_4OH and then to 7.0 with HNO_3.

2.2. Temperature programmed reduction (TPR)

TPR measurements were performed as described elsewhere [8], with a thermal conductivity detector (TCD) and an acquisition program (Peaksimple II/Chromatography Software). Prior the analysis the samples were dried from 298 to 503 K under Ar flow (10 K min^{-1} and 30 mL min^{-1}) for 30 min and then cooled to room temperature. After this step the Ar flow was switched to a mixture 1.6% H_2/Ar (30 mL min^{-1}) raising the oven temperature from 298 to 803 K at 5 K min^{-1}.

2.3. Temperature programmed reaction (TPSR)

2.3.1. Temperature programmed reaction of NH_3 prior adsorbed and CH_3OH/He flow

Initially the catalyst was reduced by flowing H_2 (30 mL min^{-1}) and rising the temperature from 298 to 803 K (5 K min^{-1}), held constant for 30 min at this temperature and cooled down to room temperature. Then a mixture 4% NH_3/He was admitted to the reactor (50 mL min^{-1}) and maintained for about 1 h. The reactant was outflown with He (50 mL min^{-1}) until total removal of the residual NH_3. Then, the flow was switched to a mixture 21% CH_3OH/He (50 mL min^{-1}) and the temperature raised continuously at 10 K min^{-1} up to 803 K. The reactor downstream was followed by a quadrupole mass spectrometer.

2.3.2. Temperature programmed reaction of CH_3OH prior adsorbed and NH_3/He flow

Similarly, the catalysts were reduced as described above. Then a mixture 21% CH_3OH/He was admitted to the reactor (50 mL min^{-1}) and maintained for about 1 h. The reactant was totally outflown with a He flow (50 mL min^{-1}) prior switching to a mixture 4% NH_3/He (50 mL min^{-1}) flow and the temperature raised continuously at 10 K min^{-1} up to 803 K. The reactor downstream was analyzed by a quadrupole mass spectrometer.

2.4. Oxidation with N_2O (determination metallic surface area)

The methodology for the determination of the metallic surface area was performed according to Bond and Namijo [9]. The first step consisted by reducing the metal as described above in the TPR and then cooling down to 363 K. Then the flowing gas was switched to a mixture 10% N_2O/He (80 mL min^{-1}) where the sample was submitted to an oxidant atmosphere for 20 h (1,2 and 3,7 CuZ) and 24 h (6,0 CuZ). After superficial oxidation the sample was cooled to room temperature under Ar flow and switched to the reduction mixture. This technique is basically the decomposition of N_2O molecules on copper surface according to the reaction

$$N_2O_{(g)} + 2Cu_{(s)} \rightarrow N_{2(g)} + (Cu{-}O{-}Cu)_{(s)}.$$

The H_2 consumption in the second reduction cycle ($Cu_2O + H_2 \rightarrow 2Cu + H_2O$) allows us to calculate the surface copper area, according following equation [8]

$$S_M = \frac{2 \times n_{H_2} \times 6.02 \times 10^{23}(at/gmol)}{1.4 \times 10^{19}(at/m^2) \times m_{cat}(g)},$$

where S_M – Metallic area, m^2/g_{cat}, n_{H_2} – H_2 consumption in the second TPR cycle, gmols, m_{cat} – Catalyst weight, g.

2.5. Infrared of pyridine adsorption (FTIR-Py)

By adsorbing pyridine followed by infrared measurements it was possible to verify the influence of the methodology used in preparation method and the formation and nature of acid sites present in the catalyst. The analysis was performed in a PERKIN-ELMER apparatus (model SYSTEM 2000 FTIR) and the samples were analyzed on a self-made pastille. The IR spectrum registered bands between 450 and 4000 cm^{-1}.

The acid sites concentration was calculated for each catalyst using the Lambert–Beer equation: $A = \varepsilon \times L \times C$ where

A – absorbance in a determined wave length, a.u. Brönsted (1540 cm^{-1}), Lewis (1450 cm^{-1}), ε – molar extinction coefficient: Brönsted (0.059 ± 0.004) $cm^2/\mu mol$, Lewis (0.084 ± 0.003) $cm^2/\mu mol$. L – pastille

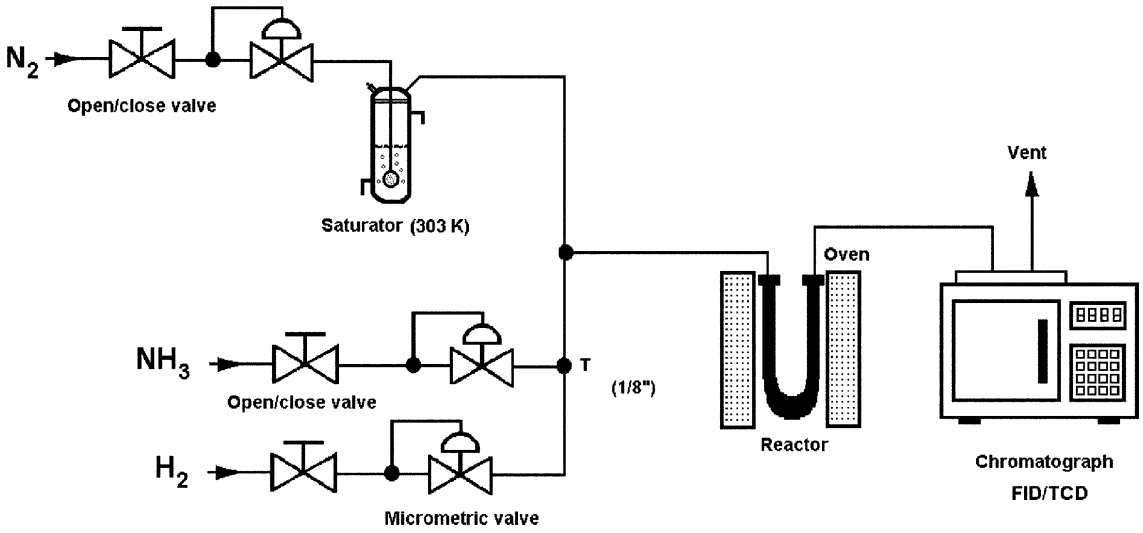

Figure 1. Experimental apparatus scheme.

thickness (or optical way traveled through the incident light).

Prior to the analysis the samples were dried from 298 to 503 K under inert Ar flow (10 K min^{-1} and 30 mL min^{-1}) for 30 min and then cooled to room temperature. After evacuation the sample was cooled to 273 K and pyridine was admitted into the reactor for 1 h. Then, after a second evacuation the temperature was raised continuously up to 298 K and the IR spectrum registered. The analysis was performed using the spectrum of dried samples as background.

2.6. Catalytic tests

The samples were catalytically evaluated in a continuous micro reactor flow specially built for this purpose at atmospheric pressure (figure 1).

Methanol was fed to the reactor through the saturator, kept at 303 K and flowing N_2 as carrier gas. The CH_3OH flow was maintained at 85 mL min^{-1} (NH_3/$CH_3OH = 1$) and the mass of catalyst was 0.4 g. The reaction was studied for five different temperatures (573, 623, 673, 723 and 773 K). Products and the reactants were analyzed by gas chromatography (GC).

Before reaction the catalysts were reduced under flowing H_2, as described above for TPR, and cooled down to the reaction temperature. The products were quantified considering total amines, calibrated previously from reliable pattern solutions. The selectivity values for each amine was calculated using the equation below and compared to the molar ratio 33 : 53 : 14 (MMA : DMA : TMA) required for the industrial processes and used as parameter for the selection of a suitable catalyst for this reaction.

$$S_{MMA} = \frac{Y_{MMA}}{Y_{MMA} + Y_{DMA} + Y_{TMA}},$$

where F_{MeOH} – methanol molar flow, $mols_{MeOH}$ min^{-1}, Y_{MMA} – MMA molar ratio in the reactor downstream, Y_{DMA} – DMA molar ratio in the reactor downstream, Y_{TMA} – TMA molar ratio in the reactor downstream.

3. Results and discussion

3.1. The reduction degree and metallic area

The metal content of the different copper catalysts are presented in table 1. The addition of NH_4OH to the solution after the ion exchange step provided a significant increase of copper amount, as shown in table 1. The possible explanation of this result is the formation of $Cu(OH)^+$ and $Cu(OH)_2$ in neutral pH [10]. After calcination these species are transformed into CuO particles at the external surface of the zeolite. The Cu/HZSM-5 catalyst prepared by wet impregnation [11] presented after calcinations a blue color and small black granules, which are associated to bulk, agglomerated CuO with low interaction with the zeolite at the external surface. On the other hand, when the catalyst was prepared controlling the pH value after ionic exchange, Cu was homogeneously distributed. Interesting is that the Cu content in the sample prepared with successive

Table 1
Chemical analysis of the Cu/ZSM-5 catalysts[a]

Preparation Method	% Cu (p/p)	Designation
Ionic exchange	1.2	1,2 CuZ
Ionic exchange		
Precipitation (pH 7.0)	3.7	3,7 CuZ
Precipitation (pH 9.0)	3.8	3,8 CuZ
Precipitation (pH 9.0 and 7.0)	6.0	6,0 CuZ

[a]The metallic values were obtained by Atomic Absorption.

pH adjustment after ionic exchange (6,0 CuZ) increased 62% when compared to the samples prepared at a fixed pH (3,7 CuZ). This behavior is probably related to the HNO_3 addition during the preparation, because during the pH adjusting, using NH_4OH, part of the copper present in the solution exists as ammoniac complex. It is destroyed during the addition of HNO_3, due to the formation of a more stable complex (NH_4^+). During this process Cu^{2+} ions would be released in the solution and precipitate as $Cu(OH)_2$.

The presence of two distinct copper species in Cu/HZSM-5 catalysts was also confirmed in the TPR results (figure 2).

According to the literature [12,13], Cu^{2+} species in the Cu/HZSM-5 catalysts can be reduced in successive steps with the formation of an intermediate oxidation state ($Cu^{2+} \rightarrow Cu^{1+} \rightarrow Cu^0$). The literature reports that the reduction peaks are associated to following reactions:

$$\text{(A)} \quad (Cu{-}O{-}Cu)^{2+} + H_2 \rightarrow 2Cu^0 + H_2O$$

$$\text{(B)} \quad Cu^{2+} + 1/2\ H_2 \rightarrow Cu^{1+} + H^+$$

$$\text{(C)} \quad CuO + H_2 \rightarrow Cu^0 + H_2O$$

$$\text{(D)} \quad Cu^{1+} + 1/2\ H_2 \rightarrow Cu^0 + H^+$$

The presence of oxocations $[Cu{-}O{-}Cu]^{2+}$ was discarded, because in two successive reduction cycles at room temperature, H_2 consumption was not observed. On the other hand, TPR analysis shows a large amount of H_2 consumption in the first peak, compared to the second one for the catalysts with pH adjust after the ionic exchange step. It suggests the presence of two copper species (probably Cu^{2+} and CuO), which are reduced according to reactions (B) and (C), respectively. Therefore, peak 1 in samples 3,7 and 6,0 CuZ is the overlapping of peaks related to the reactions (B) and (C). It means, Cu^{1+} species would be reduced to Cu^0 like reaction (D), which is represented by curve 2. Comparing the reduction peaks of sample 1,2 CuZ, the maximum temperature is higher than that of the other catalysts. The large peak demonstrates the presence of Cu species, which are more difficult to reduce, due to the strong interaction between Cu species and the zeolite framework.

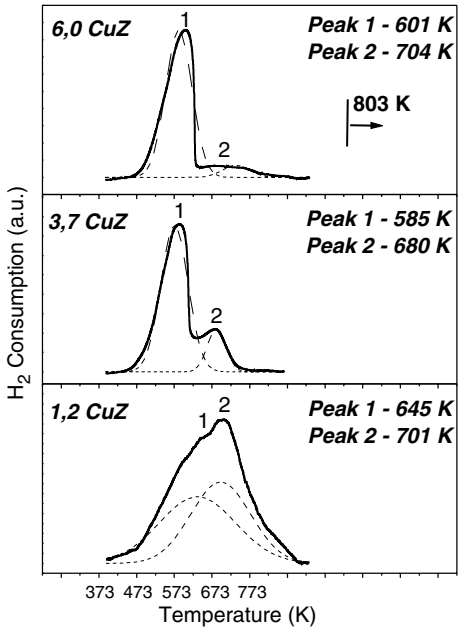

Figure 2. Cu/HZSM-5 catalysts TPR profiles. The dashed curves match to the peaks of deconvolution, considering two reduction peaks.

Table 2 presents the H_2 consumption and degree of reduction from TPR analysis. The degree of reduction was calculated considering the complete reduction of species Cu^{2+}($Cu^{2+} + H_2 \rightarrow Cu^0 + 2H^+$).

These results show complete reduction for Cu^{2+} and CuO for catalysts containing more than 3.7% of copper. For low Cu content the reduction degree is almost 83%. In consequence, the surface metallic area increased 10-fold by doubling the Cu content. It turns out that for 3.7% Cu in the zeolite the Cu^{2+} ions are reduced in sequence to Cu^{+1} and Cu^0, while for higher contents only CuO may reduce to Cu^0.

3.2. Activity and selectivity

The activity and selectivity results are shown in table 3. Preliminary tests indicate that the reaction rate can be determined considering a first order reaction.

$$(-r_A) = \frac{-\ln(1 - X_A)}{W_{Catt}/F_{MeOH}}$$

where $(-r_A)$ = Reaction rate, $\text{moles}_{MeOH}\ g_{Cat}^{-1}\ \text{min}^{-1}$, w_{Cat} = Catalysts weight, g.

Table 3 shows the reaction rate for different temperatures, as calculated from this equation. The reaction rate increases 2-fold with the introduction of Cu in the zeolite, but is not very sensitive for higher loading of Cu.

As shown in table 3, the distribution of amines (MMA:DMA:TMA) for different temperatures are still far from the required industrial processes. No significant differences for MMA were observed for pure zeolite and copper containing zeolites. However, comparing the selectivity of MMA at isoconversion, it turns out that the 3,7 CuZ samples was fairly more selective. The high selectivity for TMA at low temperatures is due to the

Table 2
H_2 consumption and degree of reduction results

Sample	H_2 consumption (μmol/g_{Cu})	Degree of reduction (%)	Metallic area $S_{metállic}$ (m^2/g_{cat})
1,2 CuZ	12984 (155.8)	83	1.95
3,7 CuZ	15954 (480.4)	100	20.8
6,0 CuZ	16038 (782.2)	100	31.8

Table 3
Conversion and selectivity and reaction rates results

Catalyst	$T_{Reaction}$(K)	X_{MeOH}(%)	S_{MMA}(%)	S_{DMA}(%)	S_{TMA}(%)	$(-r_A) \times 10^2$ ($moles_{MeOH}$ g_{Cat}^{-1} min^{-1})
HZSM-5	623	14	0	0	100	14
	673	31	0	0	100	35
	723	46	18	12	71	59
	773	48	18	11	70	63
1,2 CuZ	673	20	0	0	100	22
	723	79	16	10	74	150
	773	92	19	11	71	243
3,7 CuZ	573	13	0	0	0	11
	623	54	17	10	73	59
	673	78	21	11	68	117
	673	80	17	13	70	
	723	83	25	11	65	136
	773	87	24	10	66	156
6,0 CuZ	573	6	0	0	0	6
	623	36	0	0	100	43
	673	74	18	10	72	128
	673	63	18	12	70	
	723	89	21	11	67	210
	773	95	23	11	66	285

strong adsorption of MMA and DMA on the acid sites, favoring the transformation of those amines into TMA.

The literature has also reported deactivation of zeolites (coke formation) and zeolites containing copper (nitrite formation) during the methanol amination. Preliminary study was performed at 723 K and after 8 h and no deactivation was observed, contrasting the results of Mochida *et al.* [17]. Our results show similar values of selectivity for Cu catalysts and for pure HZSM-5, which is a strong indication of the absence of side reactions, such as amines desproportionation. In agreement with Jobson *et al.* [18] and Baiker and Kijenski [19] the amines desproportionation may affect strictly the desired product selectivity.

3.3. Influence of the acidity

Although the activity increased with the addition of Cu the selectivity was greatly affected and the main question arises how is the balance between the metallic and acidic sites affecting the selectivity. Therefore, infrared of pyridine adsorption was performed and results show quantitatively the formation of acid sites (Brönsted and Lewis sites) for catalysts HZSM-5 and Cu modified zeolites. The intensity bands 1540 and 1450 cm^{-1} were taken and the concentrations were calculated (ratio between the Brönsted and Lewis acid sites concentration (B/L ratio) was calculated) with the corresponding molar extinction coefficients, as shown in table 4. The Δ parameter is defined as the variation of $A_{Brönsted}$ of CuZ catalysts in relation to pure zeolite

$$\Delta = \frac{A_{Bronsted,HZSM-5} - A_{Bronsted,CuZ}}{A_{Bronsted,HZSM-5}}$$

Table 4
Brönsted/Lewis (B/L) ratio on Cu/HZSM-5 catalysts

Catalyst	$A_{Brönsted}$ (u.a.)	A_{Lewis} (u.a.)	B/L	Δ (%)
HZSM-5	0.7838	0.2260	4.94	–
1,2 CuZ	0.4494	0.2400	2.67	42.66
3,7 CuZ	0.4712	0.6406	1.05	39.88
6,0 CuZ	0.3874	0.9674	0.57	50.57

A_{Lewis} – absorbance related to the Lewis acid sites.
$A_{Brönsted}$ – absorbance related to the Brönsted acid sites.

Besides, the Δ (%) values were used to estimate the degree of exchange of Cu in the Zeolite structure. For this zeolite, 100% corresponds to an exchange of 3.2% Cu. For 1,2 CuZ the exchange was 37.5%, which agrees very well with data presented in table 4. Notice that the catalyst 3,7 CuZ was approximately the same, which indicates the same degree of exchange.

The amounts of Lewis sites increases with Cu content while the Brönsted acid sites decrease, however, the total concentration of acid sites is approximately the same. As shown the Lewis acid sites increase with increasing Cu content, which indicates that the compensation of cations affected the Lewis acid sites.

Therefore, acid sites strength plays a fundamental role in the selectivity performance, however the nature of the acid sites may strongly influence the amines distribution. Figure 3 shows the selectivity as function of the Brönsted/Lewis ratio. For a ratio of approximately B/L = 1.0 the selectivity to MMA is high , but at higher B/L ratio TMA prevails. It turns out that similar concentrations of B and L sites may influence acid

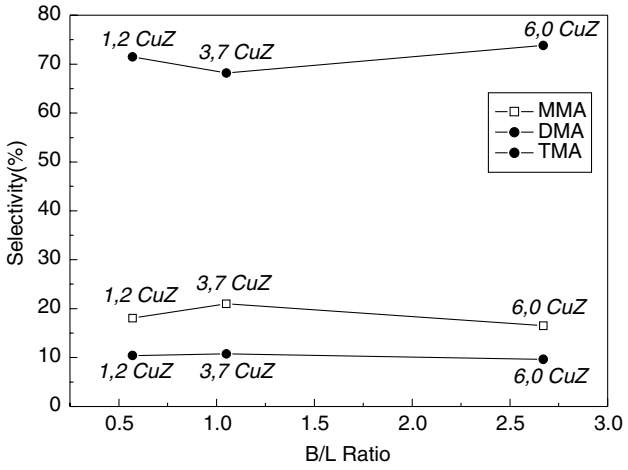

Figure 3. Selectivity as function of the ratio Brönsted/Lewis concentrations.

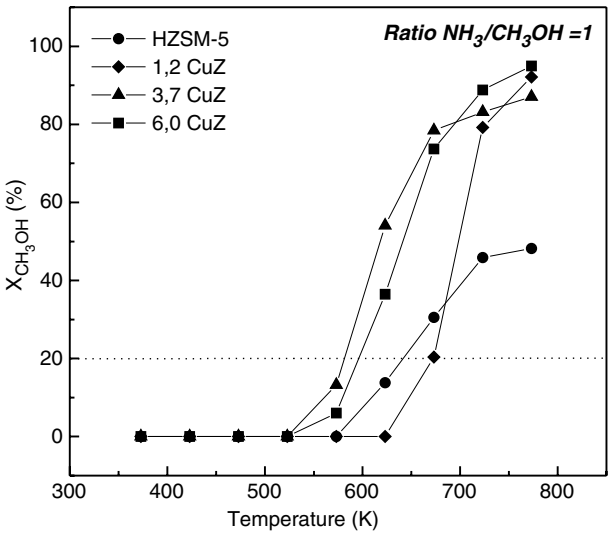

Figure 4. Methanol conversion versus reaction temperature.

strengths, which in turn favors the reaction in terms of activity and selectivity to MMA.

Figure 4 presents the results of methanol conversion versus reaction temperature. As can be seen these catalysts show similar behavior regarding the methanol conversion up to approximately 673 K. However, the 3,7 CuZ and 6,0 CuZ catalysts were more active than HZSM-5 and 1,2 CuZ. Above 673 K the conversion of the 3,7 CuZ sample reach stabilization. The 1,2 CuZ sample presents a significant increase in the methanol conversion above 673 K.

For isoconversion around 20% (dashed line) the 3,7 and 6,0 CuZ catalysts are more active than HZSM-5 zeolite. From these results the following activity pattern becomes

$$3,7\ \mathrm{CuZ}\,(582\,\mathrm{K}) > 6,0\ \mathrm{CuZ}\,(596\,\mathrm{K}) > \mathrm{HZSM\text{-}5}\,(640\,\mathrm{K}) > 1,2\ \mathrm{CuZ}\ (669\,\mathrm{K})$$

3.4. Temperature program surface reaction

Figures 5 and 6 show the TPSR profiles for the HZSM-5, 1,2 CuZ and 3,7 CuZ catalysts. These catalysts presented different behaviors, depending of the adopted experimental procedure in the TPSR analysis. When the sample was submitted first to the

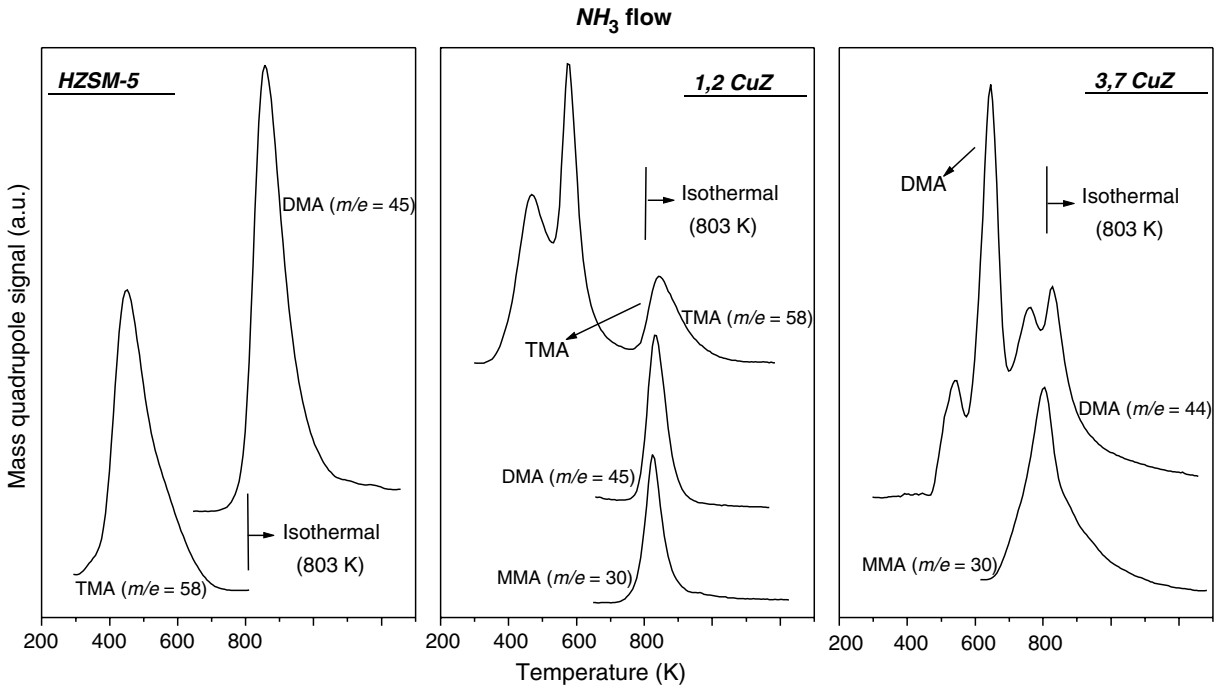

Figure 5. MMA, DMA and TMA profiles obtained during the TPSR analysis.

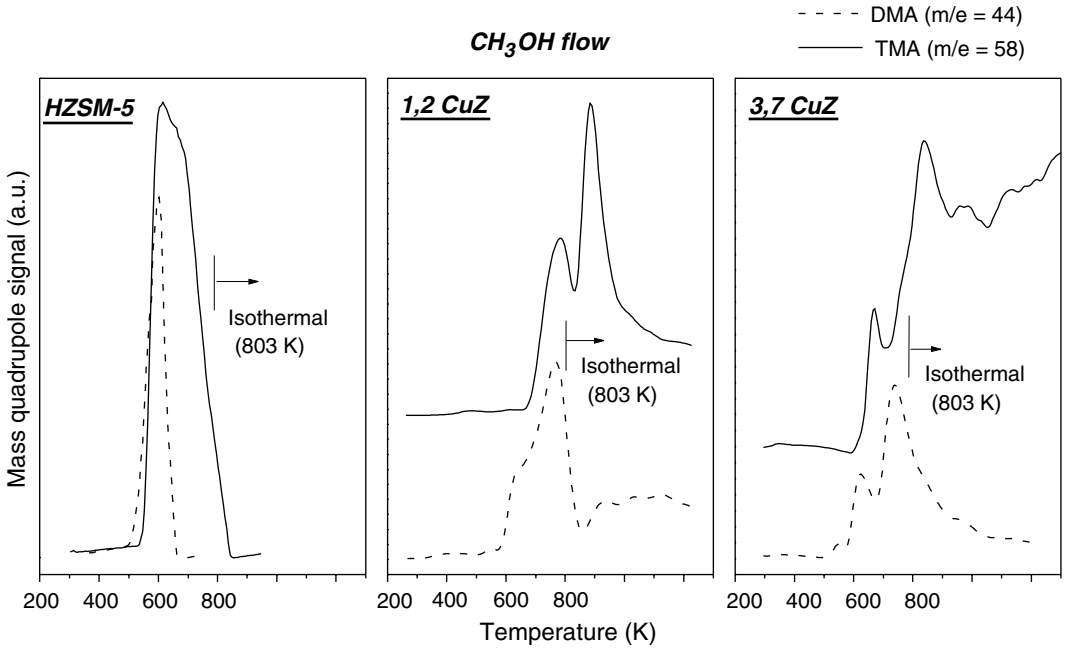

Figure 6. MMA, DMA and TMA profiles obtained during the TPSR analysis.

adsorption of methanol and subsequently to a flowing mixture NH_3/He, then amines desorption with increasing temperature changes with the catalyst. It shows that TMA was desorbed at lower temperature around 450 K on both cases, however, DMA and MMA desorbed at higher temperature around 803 K. However, on Cu catalysts this behavior changed. First, with increasing Cu content, DMA increases and the peaks are shifted to lower temperature, around 400–600 K, compared to the HZSM-5 or 1,2 CuZ catalysts.

The prior adsorption of methanol on the catalysts surface indicates that the amines formation can occur through either ammonia molecules present in gaseous phase and the methanol adsorbed on the catalyst surface. The prior adsorption of NH_3 blocks the surface acid sites, hampers the methanol adsorption. In this case the reaction would occur between the adsorbed NH_3 and the methanol present in the gaseous phase.

TMA is favored for higher Brönsted sites. These results suggest that the water released during the reduction of the CuO species present in the 3,7 and 6,0 CuZ catalysts modified the nature of acid sites, probably due to the dealumination of the zeolitic structure and, as consequence, the formation of extra-framework aluminium species. Then, the later would be the responsible by the increase in selectivity to MMA observed to the mentioned catalysts, in accordance with the literature [20,21].

During the NH_3 adsorption and subsequent flow of a CH_3OH/He mixture, there is possible coke formation, which was also reported in previously for methanol on zeolites HZSM-5 [22–24].

Considering the acid character of these catalysts and the basic nature of the molecules involved in the reaction (ammonia and methylamines), it seems that these molecules would be strongly adsorbed on the acid sites, which explains the inaccessibility of methanol to the acid sites, as described above. When the temperature increases the adsorbed molecules are released and then the conversion increases. Concerning the zeolite HZSM-5 the effect of the temperature increase on the conversion was not sensible. It suggests that this behavior is related to the strong adsorption of molecules on the zeolites acid sites and depends on the nature of the acid sites, in particular the ratio of Brönsted/Lewis acid sites.

4. Conclusion

The preparation of Cu/HZSM-5 catalysts showed that approximately 40% was ion exchanged and because of the pH variation after the ionic exchange step, there are CuO particle deposited at the external surface of the zeolite. However, the selectivity of MMA, DMA and TMA depends on the Cu content. Results showed that the activity increases with Cu and reaches a maximum rates for the 3.7% Cu content, which is also fairly more selective to MMA than the others metallic catalyst. The most important, is that the selectivity depends on the surface Lewis and Brönsted sites and not the total amount of acid sites. With increasing Cu content the Brönsted sites fall while the Lewis sites increases, and the best selectivity was obtained for a B/L ratio of approximately 1.

TPSR results with adsorbed methanol and NH_3 flow confirms that the acid sites affect the selectivity and with the addition of Cu the maximum peak of DMA and MMA are shifted to lower temperatures. TMA is favored for higher Brönsted sites. It suggests that the water released during the reduction of the CuO catalysts change the nature of the acid sites, which in turn would be responsible for the increasing selectivity to MMA.

Acknowledgments

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