

Study of catalytic activities of nanostructure copper and cobalt supported ZSM-5 catalysts for conversion of volatile organic compounds

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This paper reports the comparison of the activities of nanostructure Cu-ZSM-5 and Co-ZSM-5 catalysts for conversion of ethyl acetate and toluene and deals with the relationship between activity and structure of catalysts. The catalysts were characterized by ICP-AES, XPS, EDX, XRD, SEM, and TEM techniques. Catalytic studies were carried out under atmospheric pressure and in a temperature range of 200-500 °C. Cu-ZSM-5 catalysts showed better activity than Co-ZSM-5, revealing higher activity of copper cations. The higher activity was ascribed to higher electro-negativity, smaller cation radius, good distribution, and specific coordination of copper cations inside Cu-ZSM-5 catalysts. The activity of catalysts increased with the increase in loading at the range of metal loading (<5 wt %). Ethyl acetate showed higher reactivity than toluene on these catalysts.

Key Words: Catalytic oxidation, volatile organic compound, ethyl acetate, toluene, Cu-ZSM-5, Co-ZSM-5.

Introduction

Volatile organic compounds (VOCs) are a type of toxic environmental pollutant and are produced in a variety of small and medium size industries. Several chemicals as well as printing processes emit volatile organic compounds such as toluene and ethyl acetate. Toluene and ethyl acetate are common volatile organic compounds present in various gas exhaust streams. These compounds can cause severe environmental hazards and be harmful to the health of human beings.¹

Catalysis plays a major role in improving our atmosphere and reducing pollution. Catalytic oxidation is an effective way to control air pollution. In recent years, the use of catalytic oxidation has been investigated

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for a variety of applications, such as the control or removal of CO, NO, volatile organic compounds (VOCs), automobile exhaust emissions, by-products from chemical production, and toxic organics in wastewater. While thermal oxidation requires temperatures in excess of 1023 K, with the attendant disadvantages of high fuel cost, need for special material, and production of undesirable by-products, catalytic oxidation requires much lower temperatures in the range of 523-723 K and is therefore given more attention because of its energy saving characteristics. The catalysts used for abatement of VOC emissions are mainly divided into 2 categories: noble metals and transition metal oxides. Noble metal catalysts are generally more active and more tolerant to sulfur poisoning.² Despite having less activity than precious metals at low temperatures, transition metal oxides are much cheaper, allowing a higher catalyst loading. They are commonly deposited on suitable supports. Among all catalyst supports, zeolites have gained interest as potential active catalysts for combustion of hydrocarbons because of their pore structure, acidic properties, good thermal stability, ion exchange properties, and inherent catalytic properties.³ They have traditionally received great interest because of their optimum performances. Many papers have reported methods of enhancing the activity of zeolites by modifying the support.^{4,5}

X-type, Y-type, and ZSM-5 are common zeolites used as catalysts in the elimination of volatile organic compounds. The transition metal-modified ZSM-5 catalysts have exhibited excellent catalytic activities in reactions.^{6,7} For example, these types of catalysts have been studied for catalytic oxidation of organic compounds.⁸⁻¹¹ It has been revealed that the position and cationic sites inside different zeolites are not the same, and a particular cation in zeolites has a definite location. For instance, it has been found that for CH₄-SCR the activity of Co-ferrierites and Co-ZSM-5 is not linearly proportional to concentration of cobalt cations.^{12,13} This indicates the presence of cobalt cations with different activities. The approach to the estimation of the cationic sites of cobalt cations in mordenite, ferrierite, and ZSM-5 zeolites was based on the determination of characteristic Vis spectra of the Co(II) ions in these zeolites.¹⁴⁻¹⁶

On the other hand, it has been confirmed that different transition metals on the same support may have different activities.¹⁷⁻¹⁹ In this work, copper and cobalt were selected because of their high activity and stability in catalytic reactions.^{19,20} Toluene and ethyl acetate were selected as VOC model compounds with different natures.

The objectives were to compare the catalytic activities of nanostructure Co-ZSM-5 and Cu-ZSM-5 catalysts for conversion of different nature VOCs (ethyl acetate and toluene) and to relate the catalytic activities of cations inside exchanged ZSM-5 with their coordination and other factors. Firstly, the Si/Al ratio of parent zeolite was determined using ICP-AES, EDX, and XPS. The nanostructure of zeolite was investigated using XRD, SEM, and TEM. Then the catalytic activities of catalysts were investigated and finally the catalyst structures were studied. In addition, the effects of the amount of cation loading and organic compound molecular structure on conversion efficiency were studied.

Experimental

Preparation of metal-exchanged ZSM-5

Parent ZSM-5 (Na-ZSM-5) with a SiO₂/Al₂O₃ mole ratio of 12, BET surface area of 3.13×10^5 m²/kg, and pore volume of 1.6×10^{-4} m³/kg was supplied by the Research Center of the Iranian Petroleum Industry. Cobalt and copper supported ZSM-5 catalysts were prepared as follows: first, samples in the NH₄-form were

prepared by ion-exchange with a 1M NH_4NO_3 solution at 70 °C for 12 h, according to the procedure outlined in the literature.^{21,22} The HZSM-5 was obtained by calcinations of NH_4 -zeolites in air at 500 °C for 4 h. Copper and cobalt-supported catalysts were prepared by wet impregnation of the supports with an aqueous solution of copper and cobalt acetates (Merck). Applying different impregnation times yielded catalysts with different amounts of loading.

After these materials were left for 12 h, they were filtered and dried at 120 °C for 6 h, followed by calcinations in a furnace 500 °C for 4 h.

Characterization of catalyst

The content of copper and cobalt loadings in exchanged ZSM-5 was determined by ICP-AES (Integra XL, GBC Australia).

X-ray diffraction (XRD) studies were carried out on a Siemens D500 diffractometer, working with Cu K_α radiation operated at 40 kV and 30 mA with a 2θ scanning speed of 1°/min. Measurements of the samples were carried out in the range 2θ of 0-70°.

Scanning electron images of catalysts were obtained using a SEM model EQ-CL1. TEM images of parent ZSM-5 were used for determining the average crystal size of ZSM-5, which was carried out with a Philips CM 200 FEG. X-ray photoelectron spectroscopy (XPS) analysis of parent ZSM-5 was carried out using an ESCALAB 200R (Fissions instrument).

Evaluation of catalytic activity

Oxidation reactions were carried out in a conventional fixed bed U-shaped reactor under atmospheric pressure and different temperatures. Figure 1 shows a schematic of the experimental setup used for catalytic studies. The total flow rate through the reactor was set at 100 $\text{cm}^3 \text{min}^{-1}$. The VOC-laden air stream at a fixed concentration as feed to the reactor was generated by bubbling the nitrogen gas at suitable flow rate through the VOC saturators. The catalytic activity tests and the preparation of aged catalyst samples were performed in a 0.008 m intra diameter and 0.6 m long cylindrical quartz reactor heated with an electrical furnace. The gas hourly space velocity (GHSV) was measured at inlet conditions of about 32,000 h^{-1} .

The catalytic reactions were operated under steady state in which all process variables remained constant with time at any given point in the reactor before any measurement was made. The feed and product gases were analyzed using an off-line Shimadzu 2010 gas chromatograph (GC) equipped with a FID detector and a CBP20 column (l = 25 m, i.d. = 0.25 mm). Helium gas was used as carrier gas. The samples were injected using a 0.1 μL Hamilton syringe.

Results and discussion

Elemental composition

EDX, ICP-AES, and XPS techniques were used for the elemental composition analysis of parent ZSM-5. The Si/Al atomic ratios that resulted from these techniques are listed in Table 1. The analysis confirmed a Si/Al

ratio of 12 for ZSM-5, which is in agreement with the ratio of Si/Al stated by the zeolite catalogue.

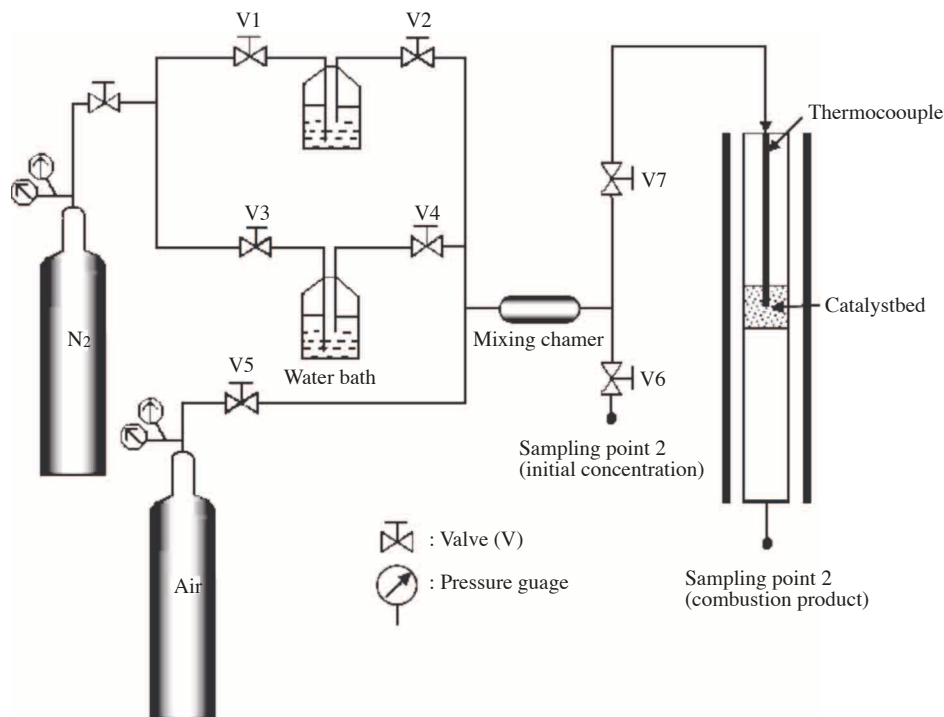


Figure 1. Schematic of the experimental setup.

Table 1. Elemental composition of ZSM-5.

Technique	Si/Al in parent ZSM-5
XPS	11.92
ICP-AES	12.043
EDX	11.96

XRD pattern of catalysts

It should be noted that in all characterization and catalytic studies we used high loading and it was the same in the 2 catalysts, i.e. 2.5 wt %. The XRD patterns of a series of HZSM-5, Cu-ZSM-5 (2.5 wt. %), and Co-ZSM-5 (2.5 wt. %) are compared in Figure 2. In order to distinguish between peaks, the XRD patterns of these materials are shown within 2θ range of $7-33^\circ$. All the characteristic peaks of HZSM-5 were observed in copper and cobalt exchanged ZSM-5 samples. XRD peaks remain sharp and intense for Cu-ZSM-5 and Co-ZSM-5, but a slight decrease in intensity of main peaks can be observed. This reveals a decrease in crystallinity of catalysts compared to HZSM-5. No other identified phase in the XRD patterns of Cu-ZSM-5 and Co-ZSM-5 was observed when compared with HZSM-5. This indicates that there are not any cobalt and copper oxides and they are ionic forms, which are well distributed. Furthermore, the XRD pattern of HZSM-5 was used to estimate the crystal size of zeolite through the Debye-Scherrer equation. Using this equation, the mean particle size of HZSM-5 was estimated to be approximately 28 nm.

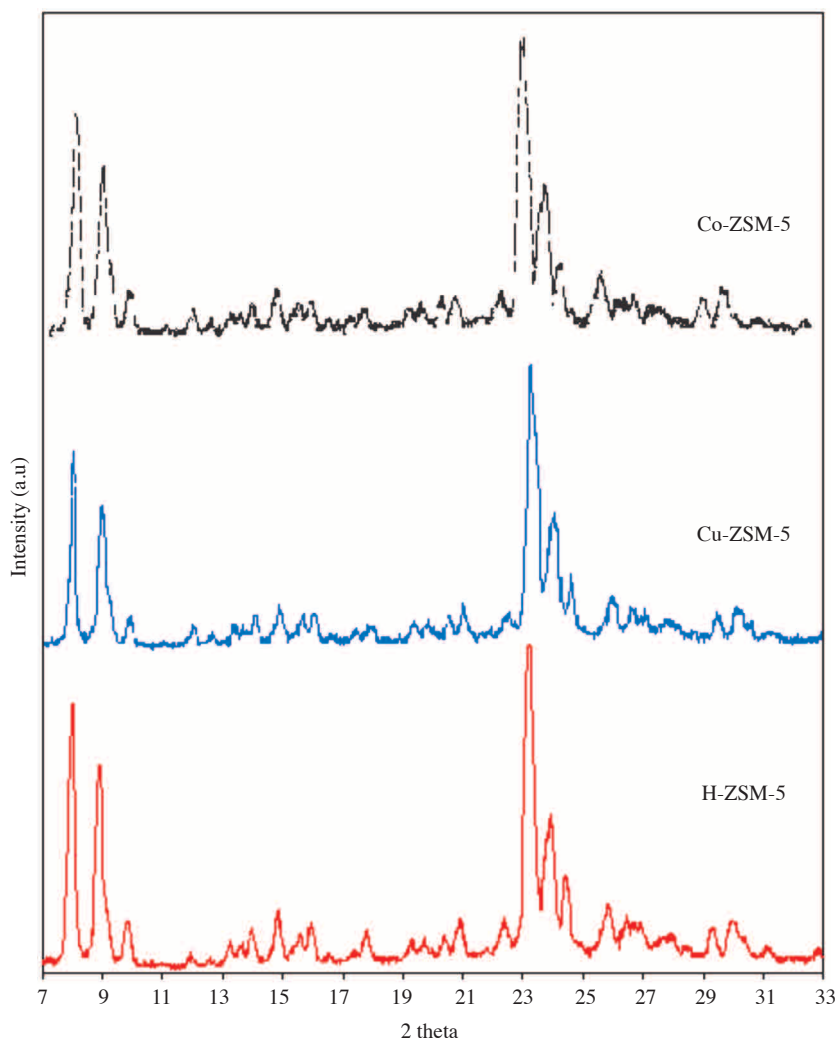


Figure 2. XRD patterns of HZSM-5, Cu-ZSM-5, and Co-ZSM-5.

Results of XRD patterns of Cu-ZSM-5 and Co-ZSM-5 catalysts are presented in Table 2.

The Table shows that the spacing of crystalline materials (d) remains fixed for Co-ZSM-5 catalysts. However, there is a slight decrease in the spacing of crystalline materials for Cu-ZSM-5 catalysts. The intensities of XRD lines decreased comparing to HZSM-5. From the XRD pattern, relative crystallinity was calculated based on comparison of the average intensities of the most intense peaks of the HZSM-5 versus treated zeolite catalysts. The HZSM-5 was assumed to be 100% crystalline. Herein, the degree of crystallinity of Co-ZSM-5 and Cu-ZSM-5 catalysts was identified utilizing the main X-ray diffraction peak ($20\text{--}25^\circ$) using the following equation:

$$\text{Crystallinity (\%)} = \frac{\text{peak intensity of product}}{\text{peak intensity of reference sample}} \times 100$$

The relative crystallinity for Co-ZSM-5 and Cu-ZSM-5 catalysts is shown in Table 2. It is observed the relative crystallinity decreases with increasing cationic sites. The greater decrease in crystallinity of Cu-ZSM-5 indicates

that copper cations penetrate more deeply into pores of zeolite than cobalt cations.

Table 2. Results of XRD patterns of catalysts.

Catalyst	$I_{M-ZSM-5}/I_{HZSM-5}$	$d_{M-ZSM-5}/d_{HZSM-5}$	Relative crystallinity (%)
Co-ZSM-5 (0.75 wt %)	0.89	≈ 1	89
Co-ZSM-5 (1.5 wt %)	0.86	≈ 1	86
Co-ZSM-5 (2.5 wt %)	0.83	≈ 1	83
Cu-ZSM-5 (0.75 wt %)	0.875	≈ 1	87.5
Cu-ZSM-5 (1.5 wt %)	0.852	≈ 1	85.20
Cu-ZSM-5 (2.5 wt %)	0.81	0.9986	81
Cu-ZSM-5 (5 wt %)	0.79	0.9968	79

Characterization of zeolite using TEM

Transmission electron microscopy (TEM) was used to give more confidence in the case of average crystal size of parent ZSM-5 zeolite. TEM images confirmed the nanostructure of ZSM-5 zeolite. Using TEM, the particle size of ZSM-5 was determined to be approximately 20-30 nm. TEM images are shown in Figure 3. The particles of ZSM-5 are agglomerate and detection of discrete particles is difficult.

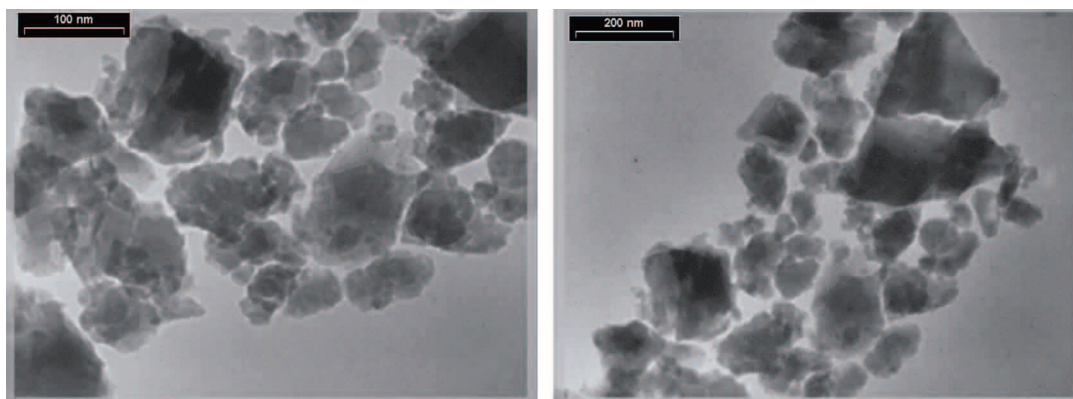


Figure 3. TEM images of parent ZSM-5.

Characterization by SEM

In order to assess the reliability of XRD data and to obtain the catalyst morphologies, we carried out SEM experiments for comparing the structural properties of the materials. The results are shown in Figure 4. The SEM images show pieces of catalysts, which comprised the agglomeration of metal exchanged ZSM-5 particles. The figure shows the SEM images of parent ZSM-5 (a, b), Co-ZSM-5 (2.5 wt. %) (c, d), and also SEM images of Cu-ZSM-5 (2.5 wt. %) (e, f). The only difference in each pair was in their magnitude scales. The geometric features associated with parent ZSM-5, Cu-ZSM-5, and Co-ZSM-5 are not considerably different. This reveals that there are no cobalt and copper oxides inside catalysts as a discrete phase. This manifests the high dispersion

of these cations in the zeolite as evoked by XRD data. The only detectable difference between these catalysts is that the particles of Cu-ZSM-5 are well distributed and therefore have high surface area. Moreover, the particle distribution derived from SEM images was analogous reliably to those calculated from XRD, i.e. $D \leq 100$ nm for particle size.

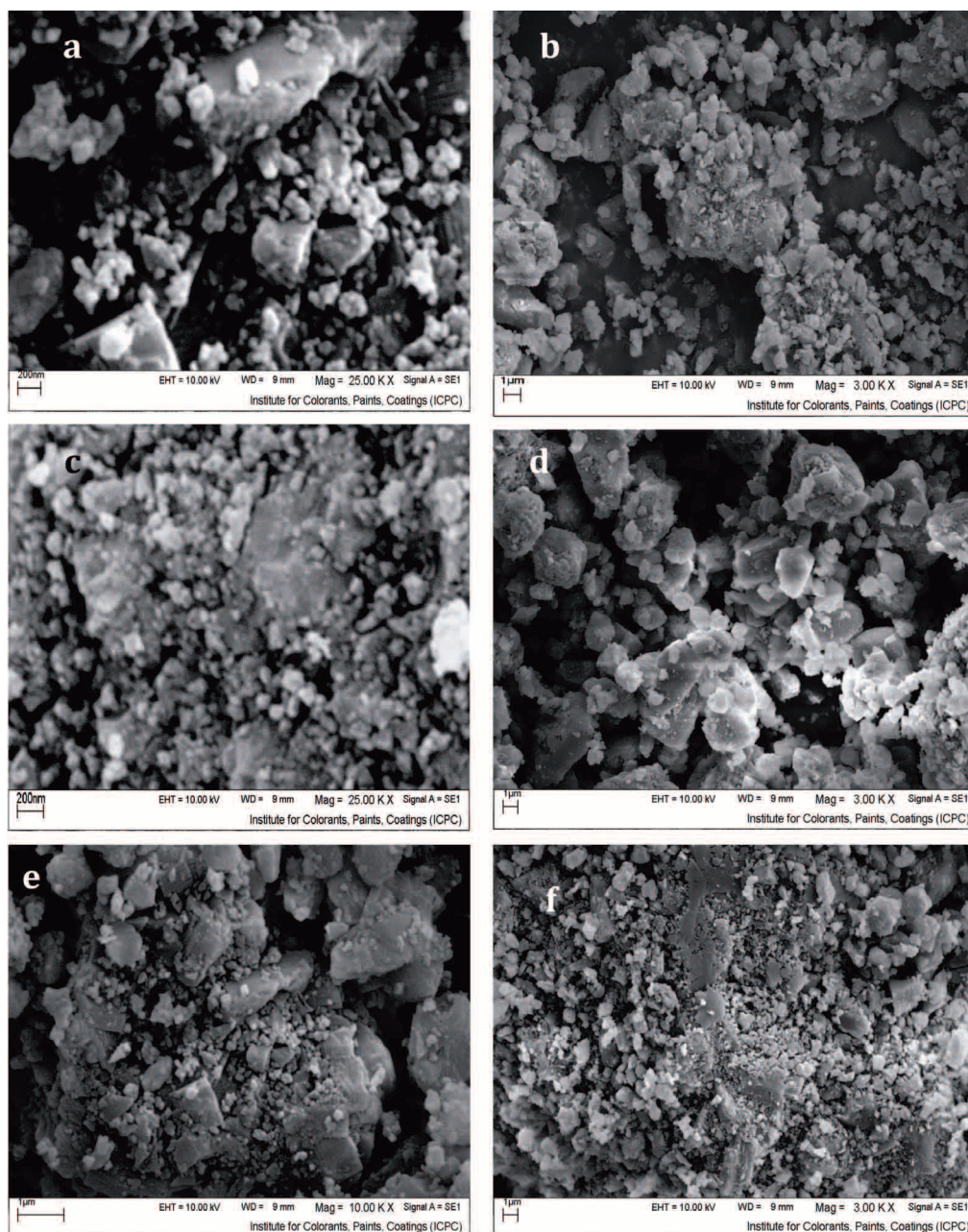


Figure 4. SEM images of catalysts with different magnitude scales; parent ZSM-5 (a,b); Co-ZSM-5 (2.5 wt. %): 200 nm (c), 1 μ m (d); and Cu-ZSM-5 (2.5 wt. %): (e, f) 1 μ m.

Catalytic activity

Catalytic conversions of ethyl acetate and toluene over parent ZSM-5, Co-ZSM-5(2.5 wt. %) and Cu-ZSM-5 (2.5 wt. %) were studied. Light-off curves for ethyl acetate and toluene conversions are shown in Figures 5 and 6, respectively. Conversion of these compounds over Cu-ZSM-5 is higher than conversion over others. In other words, from a catalytic point of view, Cu-ZSM-5 is more active than Co-ZSM-5. The following order is observed for catalytic activity of catalysts for conversion of the organic compounds: Cu-ZSM-5 > Co-ZSM-5 > parent ZSM-5.

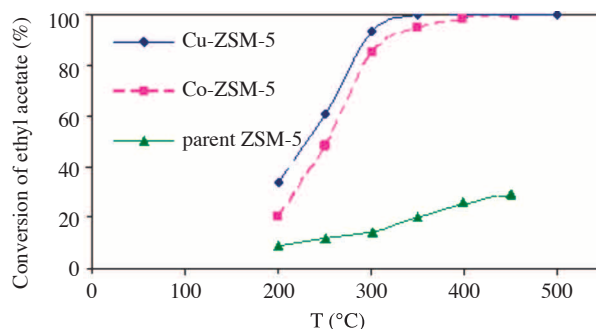


Figure 5. Comparison the activities of Cu-ZSM-5 and Co-ZSM-5 for conversion of ethyl acetate.

The results are in line with other studies.²⁴ To examine the relationship between structure and catalytic activity of catalysts, we investigated in detail the coordination of cations inside catalysts.

It has been stated in the literature that Co^{+2} cations in Co-ZSM-5 have 3 coordination forms, namely Co- α , Co- β , and Co- γ .^{17,18} The 3 different sites are located inside the main channels for α sites, inside the sinusoidal channels for β sites, and accessible from the sinusoidal sites for γ sites. In Co-ZSM-5 catalysts, β -type Co ions, coordinated to the deformed 6-member ring at the intersection of straight and sinusoidal, possess the highest activity. According to the range of Co loadings in our catalysts, it is seen that the Co cations in Co-ZSM-5 catalysts are in the forms stated above. Since our objective was to compare the difference in coordination of Cu-ZSM-5 and Co-ZSM-5, we did not determine the type of sites in Co-ZSM-5 catalysts.

In the case of Cu-ZSM-5, according to the electron spin resonance (ESR) data, copper cations are thought to be isolated copper cations in 2 types of distorted octahedral coordination: square pyramidal and square plane.²⁰ In addition, copper cations, as XPS analysis confirmed, have more ability to penetrate into the ZSM-5 channels than cobalt cations.¹⁷⁻²⁰ To penetrate the cations into the zeolite microstructure, cation radius, electro negativity, and oxygen partial charge of the relevant oxide play important roles. The cationic radius of Cu^{+2} is smaller than that of Co^{+2} , and it is more electro negative than Co^{+2} . According to XRD and XPS data, there is not any discrete phase of metal oxide of these metals in exchanged catalysts. It should be noted that cobalt and copper cations inside the zeolite are connected to the oxygen of zeolite. The electronic density of Cu^{+2} is higher than that of Co^{+2} and it is more active than Co^{+2} as well. The active Cu^{2+} sites are well distributed in the zeolite, leading to increased catalytic activity. Thus, the difference in distribution and coordination of these cations inside ZSM-5 are important factors in the justification of differences, observed in the ability of organic molecules to adsorb on cationic sites and consequent conversion of organic compounds on catalysts. Thus the factors mentioned above can justify the higher catalytic activity of Cu-ZSM-5 catalyst.

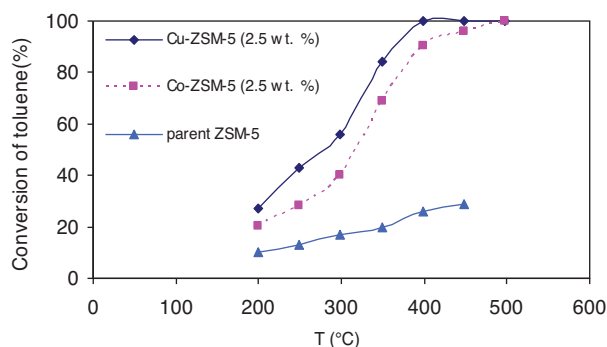


Figure 6. Comparison the activity of Co-ZSM-5 and Cu-ZSM-5 for conversion of toluene.

So far, we have dealt with the relation of difference in activity of catalysts with structure and coordination of Co^{+2} and Cu^{+2} cations inside these catalysts.

For further investigations, the effect of content of metal loading on the conversion of organic compounds was studied. To this end, conversions of ethyl acetate on a series of cobalt exchanged ZSM-5 with 0.75, 1.5, and 2.5 wt % of cobalt loading and a series of copper exchanged ZSM-5 with 0.75, 1.5, 2.5, and 5 wt % of copper loading were studied. Figures 7 and 8 show light-off curves of ethyl acetate conversion over these catalysts.

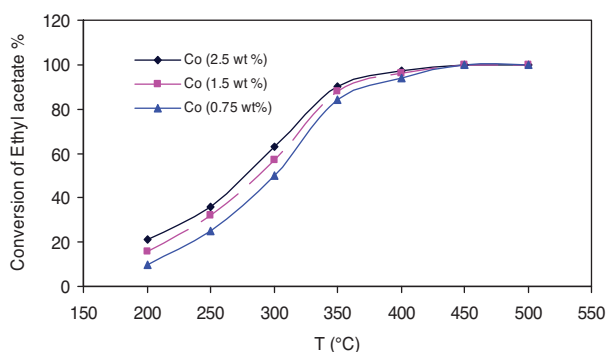


Figure 7. Conversion of ethyl acetate on Co-ZSM-5 with different loadings.

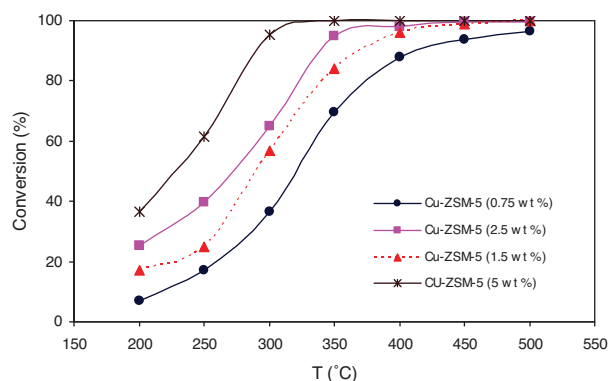


Figure 8. Conversion of ethyl acetate on Cu-ZSM-5 with different loadings.

The results indicate that the increasing of metal loading leads to increases in the catalytic activity of exchanged ZSM-5 catalysts. This is due to increases in the catalytic sites on catalysts, indicating catalytic role of cations in exchanged catalysts. However, higher metal loading decreases the catalytic activity of catalyst²⁵. The difference in catalytic activity of these catalysts is ascribed to different activities of cations in various coordination of metal cations through changing of metal loading.^{17,20} It seems that the interaction intensities of organic molecules and cationic sites in various coordination are the same. In the case of Cu-ZSM-5, isolated Cu^{2+} cations in square pyramidal coordination predominate in Cu-ZSM-5 zeolite with a low exchange level, while those in square-plane coordination are dominant in catalysts with high copper content.

Furthermore, we studied the relation between the molecular structure of organic compounds and its reactivity on Co-ZSM-5 (2.5 wt %). The related light-off curves are shown in Figure 9. Ethyl acetate shows a higher reactivity than toluene for conversion on the catalyst. It is ascribed to ethyl acetate's oxygen-containing

group, a well-known electron-withdrawing group. Since the oxygen atom in ethyl acetate had an unpaired electron, it could easily interact with the vacant p-orbital of cobalt ions in ZSM-5 catalyst, leading to breakage of the C-C bond in the molecule. Meanwhile, toluene was less reactive due to the occurrence of a resonance effect in its ring.

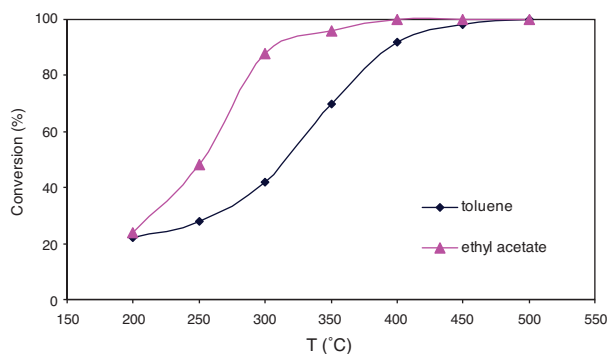


Figure 9. Comparison of ethyl acetate and toluene conversions over Co-ZSM-5 (2.5 wt %).

Conclusions

The relationship between catalytic activities of Cu-ZSM-5 and Co-ZSM-5 with both their structure and cations coordination was studied. The following conclusions are drawn from this study:

- M-ZSM-5 catalysts with different metal cations exhibit different catalytic activities. The difference in catalytic activity is ascribed to various coordinations of metal cations in zeolite, cationic radius, electro negativity, and oxygen partial charge of the relevant oxide.
- Content of metal loading affects the activity of the catalyst, which is related to alterations in metal cations coordination of metal ions in different loadings.
- The molecular structure of the organic compound to be converted is another parameter affecting the conversion efficiency of the compound. This is ascribed to the intensity of the interaction of the organic compound with catalyst sites.

Acknowledgments

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Nomenclature

ICP Inductively Coupled Plasma

TEM	Transmission Electron Microscopy
FTIR	Fourier Transmission Infrared Spectroscopy
VOCs	Volatile Organic Compounds
XRD	X-ray Dispersion
GHSV	Gas hourly space velocity
θ	Diffraction angle in XRD
D	Mean crystal size of ZSM-5
K=	Constant of Scherer equation (0.89)

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