Characterization of the balance between metallic and acidic properties of Cu–MFI catalysts by using the transformation of haloaromatic compounds: effect of copper loading and Si/Al ratio

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Abstract

The transformation of equimolar mixtures of *m*-bromofluorobenzene and chlorobenzene was carried out over Cu–MFI catalysts at 400°C under atmospheric pressure in a fixed bed reactor. A reversible exchange of halogen atoms occurred between *m*-bromofluorobenzene and chlorobenzene leading to *m*-chlorofluorobenzene and bromobenzene. The isomerization of *m*-bromofluorobenzene into *o*- and *p*-bromofluorobenzene was also observed. It was found that the activity in halogen exchange increased linearly with increasing copper content up to a loading corresponding to the cationic exchange capacity of the zeolite, while the isomerization activity decreased symmetrically. It was concluded that the halogen exchange reaction between the aromatic compounds was catalyzed by the copper species located in the cationic exchange sites of the zeolite and that the isomerization reaction was catalyzed by the residual protonic acidity. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Cu–MFI catalysts are widely used in NO_x decomposition and NO reduction [1,2]. But, these catalysts are also among the most active in the production of phenols from haloaromatics [3–6]. In a previous work [7,8], we reported that a reversible exchange of halogen atoms occurred between *m*-bromofluorobenzene and chlorobenzene in the presence of Cu–MFI catalysts (Scheme 1) under the conditions of the hydrolysis of chlorobenzene. Under these conditions, it was shown that the displacement of fluorine did not occur.

For the hydrolysis of chlorobenzene into phenol, the best catalyst was found to be a protonic MFI catalyst with a Si/Al ratio equal to about 40, impregnated with 2 wt.% of copper [9,10]. This catalyst seems to be also a good catalyst for the halogen exchange reaction between haloaromatic compounds. As reported in the literature, the substitution of halogen atoms in aromatic compounds can be promoted by copper(I) or (II) [11–13], by nickel(I) or (II) [14–16] or by a phase-transfer catalyst [17]. Generally, the substitution proceeds by exchange of a halogen atom from an aromatic compound with another halogen atom issuing from various inorganic sources: CuCl [11–13], $NiCl_2$ [14], aryl nickel chloride [14,15], NaOCl [15,16]. However, Tsou and Kochi [15] reported the exchange of halogen atoms between *p*-bromomethoxybenzene and iodobenzene to give *p*-iodomethoxybenzene and

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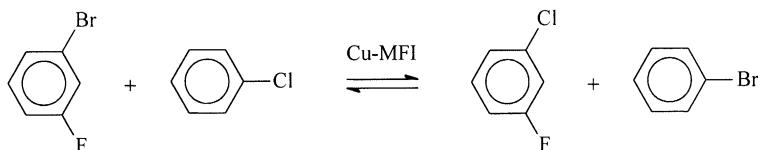
Scheme 1. Reversible exchange of halogen atoms between *m*-bromofluorobenzene and chlorobenzene.

bromobenzene in the presence of nickel(I). According to the literature [17,18], a S_{RN} mechanism can be involved in the reaction. As proposed previously [8], Cu(I) could give one electron to initiate a catalytic cycle through such a mechanism. However, a mechanism involving aryl copper complexes cannot be excluded [7,13,19,20]. Under our reaction conditions, it seems that Cu(I) ions are the species which catalyze the halogen exchange reaction [7]. Without a catalyst or in the presence of MFI there was less than 4% exchange. The nature of the copper catalytic sites in Cu–MFI catalysts is still debated. However, it was shown that Cu^{2+} species can be reduced to Cu^+ species during heat treatment at high temperature ($>200°C$) under vacuum [21–23].

In this work, the influence of the composition of Cu–MFI catalysts on their activity in the halogen exchange reaction between *m*-bromofluorobenzene and chlorobenzene as well as in the isomerization of *m*-bromofluorobenzene into *o*- and *p*-bromofluorobenzene was investigated. For this purpose, the copper loading and the Si/Al ratio of the Cu–MFI catalysts were varied.

2. Experimental

2.1. Chemicals

The chemicals were supplied by Sigma–Aldrich and were used without further purification.

2.2. Catalysts

The protonic MFI zeolite with a Si/Al ratio of 43 was synthesized according to the procedure described by Guth et al. [24] using colloidal silica, sodium aluminate and tetrapropylammonium bromide. The sodium form of the zeolite was then exchanged with an ammonium chloride solution and calcined at 520°C under dry air flow to obtain the protonic form (in bold in Table 1).

MFI zeolites with various Si/Al ratios were purchased from Conteka. Their composition and characteristics are given in Table 1. Cu–MFI catalysts were obtained by impregnation of the zeolite with aqueous solutions ($1 \, cm^3 \, g^{-1}$ of zeolite) of $Cu(NO_3)_2$ in appropriate concentrations. The water was evaporated by heating at 80°C for 2 h and then at 120°C for 12 h. The samples were calcined at 520°C under a dry air flow for 12 h. The main characteristics of the Cu–MFI catalysts are given in Table 2. The catalysts are designated by a formula representing "wt.% copper–zeolite structure–Si/Al ratio".

2.3. Procedure

The reaction between *m*-bromofluorobenzene and chlorobenzene (equimolar mixtures) was carried out at 400°C under atmospheric pressure using a fixed-bed glass reactor. The weight of catalyst was 25 or 50 mg. The partial pressure of each reactant was 0.1 bar, the diluting gas was nitrogen (0.8 bar).

Table 1
Characteristics of the MFI catalysts (in bold MFI catalyst synthesized in our laboratory)

Catalyst	Si/Al	Unit cell	Surface area ($m^2 \, g^{-1}$)
CBV3020	16	$Na_{0.03}H_{5.62}Al_{5.65}Si_{90.35}O_{192}$	397
CBV5020	28.5	$Na_{0.05}H_{3.20}Al_{3.25}Si_{92.75}O_{192}$	418
CBV8020	36.5	$Na_{0.02}H_{2.53}Al_{2.55}Si_{93.45}O_{192}$	430
CBV2802	159	$Na_{0.01}H_{0.59}Al_{0.60}Si_{95.40}O_{192}$	421
MFI synthesized	**43**	$\mathbf{Na_{0.40}H_{1.77}Al_{2.18}Si_{93.82}O_{192}}$	**535**

Table 2
Characteristics of the Cu–MFI catalysts (in bold the standard catalyst)

Catalysts	Si/Al	Copper loading		
		(wt.%)	Cu/Al	Exchange level[a]
0.2Cu–MFI-43	43	0.23	0.096	19
0.5Cu–MFI-43	43	0.49	0.204	41
0.7Cu–MFI-43	43	0.67	0.279	56
1Cu–MFI-43	43	0.98	0.409	82
1.4Cu–MFI-43	43	1.36	0.567	113
2Cu–MFI-43	**43**	**1.99**	**0.830**	**166**
4.4Cu–MFI-43	43	4.38	1.833	365
6Cu–MFI-43	43	5.95	2.481	496
8Cu–MFI-43	43	7.89	3.29	658
2Cu–MFI-16	16	1.86	0.32	64
4Cu–MFI-16	16	3.97	0.64	128
2Cu–MFI-29	28.5	1.96	0.56	112
2Cu–MFI-37	36.5	1.95	0.71	142
2Cu–MFI-159	159	1.94	3.02	604

[a] Mole percent of the maximum cationic exchange capacity of the zeolite.

The product distribution was determined by gas chromatography using a CP-Sil5 capillary column (25 m, 0.12 mm silicon film thickness). A typical product distribution with the 2Cu–MFI-43 catalyst (weight of catalyst: 50 mg; flow rate of reactants: 2 ml h^{-1}) was: m-bromofluorobenzene (40.9 mol%); chlorobenzene (41.3 mol%); m-chlorofluorobenzene (8.1 mol%); bromobenzene (8.4 mol%); p-bromofluorobenzene (1.1 mol%); p-chlorofluorobenzene (0.2 mol%).

3. Results and discussion

3.1. Effect of the copper loading

The halogen exchange reaction between m-bromofluorobenzene and chlorobenzene was carried out on protonic MFI catalysts (Si/Al atomic ratio: 43) with different copper loadings. The activities were measured under conditions where a linear relationship between conversion and contact time was obtained (conversion lower than 15 mol%). The influence of the copper content of the catalyst on the activities in the bromine–chlorine exchange reaction on the one hand and in m-bromofluorobenzene isomerization on the other is shown in Fig. 1.

Up to a copper loading of 1.3 wt.%, the activity regarding the halogen exchange reaction increased

and the activity concerning isomerization decreased linearly with increasing copper content. Beyond this copper loading, the activity of the catalysts in halogen exchange was about 10 times higher than the activity in isomerization. Actually, the copper content of 1.3 wt.% corresponds to 100% exchange of the protonic sites by cupric ions. The increase in halogen exchange activity with increasing copper content up to 1.3 wt.% can be interpreted by supposing that up to this concentration, copper ions were well dispersed and stabilized in the zeolite. This is in accordance with the results reported in the literature which show that copper deposited by impregnation can migrate inside the zeolite network into exchange centers [25,26]. Copper in excess to the exchange capacity is supposed to form small copper oxide clusters or aggregates outside the crystals [25,27]. This could explain why copper introduced in excess with respect to the exchange capacity seems to play a minor role (if any) in the reaction. In fact, it was found that the copper in excess was not stable in the zeolite structure and was eluted during the reaction. The copper content of the catalyst samples was measured after 8 h on reaction stream (Fig. 2).

We can see that for copper contents smaller than 1.3 wt.% (corresponding to an exchange level of 100%) most of the copper remained in the zeolite. For copper contents higher than the exchange capacity, all of the copper in excess with respect to the exchange
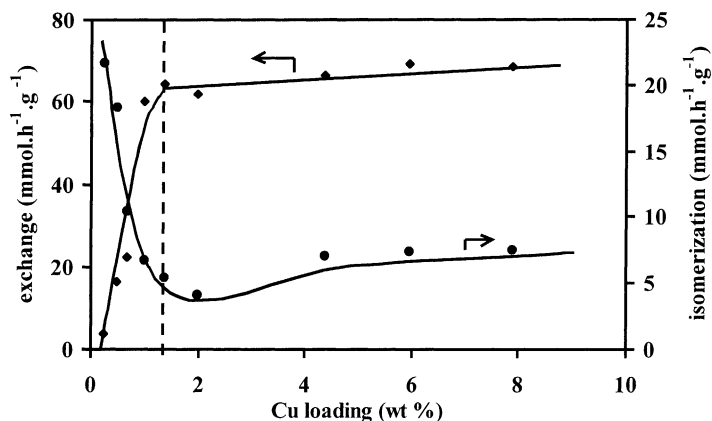
Fig. 1. Influence of the copper loadings of Cu–MFI catalysts (Si/Al atomic ratio: 43) on their initial activity in the bromine–chlorine exchange reaction between *m*-bromofluorobenzene and chlorobenzene at 400°C under atmospheric pressure (◆) and on their initial activity in the isomerization of *m*-bromofluorobenzene (●).

capacity was eliminated. A similar phenomenon was observed in the hydrolysis of chlorobenzene [9,10]. It appears also that the amount of copper remaining in the catalyst after reaction was lower when the amount of copper introduced in excess was larger. Apparently, when the copper was introduced in too large, an excess it did not migrate into the cationic exchange sites of the zeolite so readily and the exchange of the protonic sites by copper ions was probably not complete.

Symmetrically, the activity in isomerization decreased with increasing copper content. This can be easily understood if, as proposed in the literature
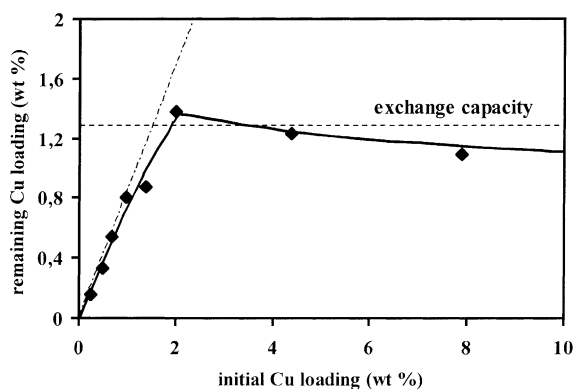

Fig. 2. Amount of copper remaining in the catalyst after 8 h of reaction between *m*-bromofluorobenzene and chlorobenzene (400°C, atmospheric pressure) vs. the initial amount of copper introduced in the zeolite.
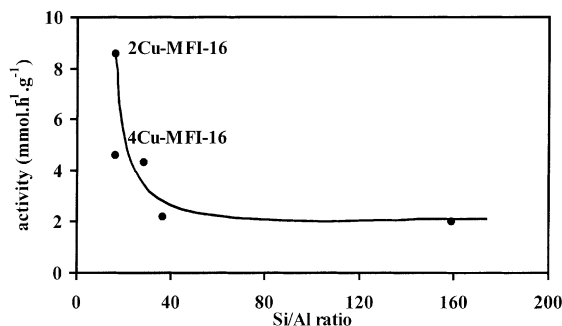
[28], it is assumed that isomerization is catalyzed by protonic centers. Fig. 1 shows also that after having reached a minimum corresponding approximately to the cationic exchange capacity of the zeolite, the isomerization activity increased slightly at higher copper contents. As indicated in the foregoing discussion, this means probably that the cationic exchange did not take place readily when the amount of copper deposited in the zeolite was too high.

3.2. Effect of the Si/Al ratio of Cu–MFI catalysts

The reaction was carried out on four MFI catalysts with Si/Al ratio of 16, 28.5, 36.5 and 159, impregnated with 2 wt.% of copper. A sample with a Si/Al ratio of 16 was impregnated with 4 wt.% of copper in order to obtain a content exceeding the exchange capacity of the zeolite. In this case, the maximum exchange capacity of the zeolite corresponds to a copper content of 3 wt.%.

Fig. 3 shows the initial activity in *m*-bromofluorobenzene isomerization versus the Si/Al ratio and confirms that this activity is related to the acidity of the zeolite. We can see that the initial activity decreased when the Si/Al ratio increased. Actually, 2Cu–MFI-16 was the only catalyst that could be expected to have a significant residual acidity. All the other samples had a copper content exceeding the cationic exchange capacity of the zeolites and hence were expected to have

Fig. 3. Effect of the Si/Al ratio of Cu–MFI catalysts (impregnated with 2 wt.% of copper excepted 4Cu–MFI-16) on the initial activity of *m*-bromofluorobenzene isomerization.

Fig. 5. Effect of the Si/Al ratio of Cu–MFI catalysts (impregnated with 2 wt.% of copper) on the amount of carbon after halogen exchange reaction between *m*-bromofluorobenzene and chlorobenzene.

a very low acidity. The 2Cu–MFI-159 was expected to be the less acidic of all the samples and it is also the less active in isomerization.

Fig. 4 shows that the activity of the Cu–MFI catalysts in halogen exchange after 5 h on stream (activity plateau) reached a maximum for Si/Al atomic ratios of about 30–40. If we consider the catalysts with 2 wt.% copper, we would expect 2Cu–MFI-16 to be the most active, since it had the highest cationic exchange capacity and 2Cu–MFI-159 to be the least active, since it had the lowest cationic exchange capacity (corresponding to 0.32 wt.% copper). 2Cu–MFI-159 was actually less active than 2Cu–MFI-29 and 2Cu–MFI-37, but 2Cu–MFI-16 was even less active. This can be attributed to the fact that deactivation due to coke formation was more significant with the catalysts having a low Si/Al atomic ratio (having a more significant
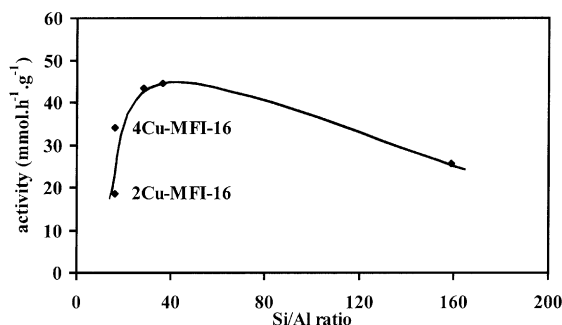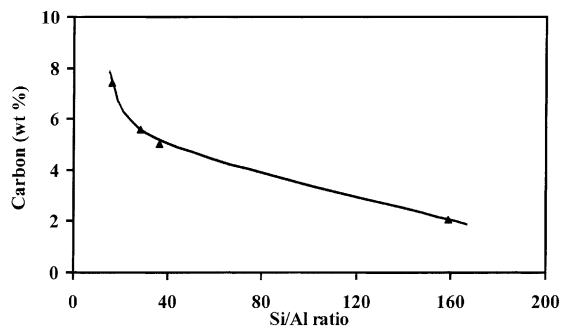

Fig. 4. Effect of the Si/Al ratio of Cu–MFI catalysts (impregnated with 2 wt.% of copper except for 4Cu–MFI-16) on the activity in halogen exchange between *m*-bromofluorobenzene and chlorobenzene after 5 h on reaction stream.

residual acidity). As shown in Fig. 5, the amount of carbonaceous material deposited during the reaction decreased with increasing Si/Al atomic ratio. Consequently, the maximum in activity found with the catalysts having a Si/Al atomic ratio of 30–40 was the result of two antagonistic trends, which occurred when decreasing the Si/Al atomic ratio: the increase in activity due to increasing cationic exchange capacity and the increase in coke formation which caused deactivation. In other words the halogen exchange activity of the Cu–MFI catalysts depended on the balance between the number of copper ions in their cationic sites and their residual acidity. It can also be seen that the MFI catalyst with a Si/Al ratio of 16 impregnated with 4 wt.% of copper was almost twice as active as the same zeolite impregnated with only 2 wt.% of copper (Fig. 4). This shows that the halogen exchange activity really depended on the amount of copper which could be located in cationic exchange sites. At the same time deactivation by coke formation should be lower with 4Cu–MFI-16 than with 2Cu–MFI-16, since the former had in principle less residual acidity.

4. Conclusion

It can be concluded that the species active in the halogen exchange between aromatic compounds over Cu–MFI catalysts are copper ions located in the cationic exchange sites of the zeolite, while the isomerization of the dihaloaromatic reactant is catalyzed by the residual acidity. This explains why the activity

in halogen exchange increased with increasing copper content, while the activity in isomerization of m-bromofluorobenzene decreased symmetrically. It is suggested that this reaction could give useful information about the metallic and acidic functions of Cu–MFI catalysts in view of their application in other reactions.

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