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The role of copper species and Brønsted acidity in CuCl/ZSM-5 catalysts during the selective catalytic reduction of NO by propene

M.J. Jia[a,b], W.X. Zhang[a,*], T.H. Wu[a]

[a] Department of Chemistry, Jilin University, 130023 Changchun, China
[b] Institute of Catalysis and Petrochemistry, C.S.I.C., 28049 Madrid, Spain

Abstract

The role of copper species and Brønsted acidity in the selective catalytic reduction (SCR) of NO by propene over CuCl/ZSM-5 catalysts prepared by dispersion method has been investigated. The results of IR and H_2-TPR show that the main active species of CuCl/H-ZSM-5 catalyst are isolated copper ions (Cu^{2+} and Cu^+) located in the ion exchange sites of ZSM-5, which formed during the high-temperature solid-state exchange reaction occurred between CuCl and the Brønsted acid sites of H-ZSM-5. While the high dispersed CuCl on the surface of ZSM-5 is inactive for this reaction. Some direct evidences indicate that the initial Brønsted acidity of the starting zeolite is useful to produce active copper ions species during the preparation process of catalysts. However, it is not necessary for the SCR of NO over Cu-ZSM-5 catalysts. © 2002 Published by Elsevier Science B.V.

Keywords: CuCl/ZSM-5; SCR of NO; Copper ions; Brønsted acidity

1. Introduction

Copper-exchanged ZSM-5 have been widely studied for the selective catalytic reduction (SCR) of NO by hydrocarbon since the first reported by Held et al. [1] and Iwamoto et al. [2]. It is also known that Cu-ZSM-5 catalysts deactivate rapidly under lean-burn conditions, which means these catalysts may not be used commercially. However, this discovery was vital, since it clearly demonstrated that lean NO conversion could be made a reality. Besides, as a kind of model catalysts, the studies on

the Cu-ZSM-5 will help us to identify the nature of the active sites, to understand the reaction and deactivation mechanism, then to provide some guidance to the search for more active and durable catalysts [3–8]. To date, there are still some controversial questions, such as the nature of the active copper species, and what is the role of Brønsted acidity contributes to the reaction.

Shelf et al. [9] proposed that the active sites for lean NO reaction are isolated, irreducible, Cu^{2+} ions, and Petunchi and Hall [10,11] reported that it is important to have oxidising conditions in order to prevent the reduction of Cu^{2+} to lower oxidation states. But some other authors [12,13] identified the presence of Cu^+ species under reaction conditions, and proposed that Cu^+ is the main active species for the reaction, the hydrocarbon reductant is responsible for maintain-

* Corresponding author. Tel.: +86-431-8922331-3214;
fax: +86-431-8949334.
E-mail addresses: mjia@icp.csic.es (M.J. Jia),
wth@mail.jlu.edu.cn (W.X. Zhang).

ing a reasonable concentration of active Cu^+ sites. Whatever, it is has been generally accepted that the copper ions species (Cu^{2+} and/or Cu^+), which exist in the exchange sites of ZSM-5, play an important role in the reaction of NO-SCR with hydrocarbons [14].

Besides, some early contributions assumed an important role of Brønsted acidity in the SCR of NO over ion-exchanged Cu-ZSM-5 [15]. This was inferred by the superiority of alkenes reductants over alkanes, and the appreciable SCR activity of acidic solids, e.g. H-ZSM-5, Al_2O_3, even undoped. Inui et al. [16] suggested a bifunctional mechanism involving an acid function and a redox function. On the other hand, sets of evidences were provided to suggest that Brønsted acidity may not be necessary for SCR-HC at least over Cu-ZSM-5. Such conclusion was reached by Jen et al. [5] in a study of Cu-ZSM-5 with high Cu/Si or Si/Al ratio and by Centi et al. [17], who compared Cu-ZSM-5 with catalysts in which copper was dispersed in the boralite analogue to ZSM-5, which is only mildly Brønsted acidic. However, the direct evidence is difficult to be obtained, because the Brønsted acidity still exists even in the over-exchanged Cu-ZSM-5 [3].

In previous works [19], we have investigated the catalytic performances of CuCl/ZSM-5 prepared by dispersion method [18] for the SCR of NO with propene. It was found that two kinds of catalyst system, prepared from H-ZSM-5 and Na-ZSM-5, respectively, exhibited quite different catalytic properties on the reaction. The catalytic activity of CuCl/H-ZSM-5 was substantially higher than that of CuCl/Na-ZSM-5 with similar copper amount. At lower reaction temperature (e.g. 300 °C), the activity of CuCl/H-ZSM-5 (with copper loading above 4 wt.%) was even higher than that of ion-exchanged Cu-ZSM-5 prepared by normal liquid phase ion-exchanged method from the same parent zeolite. A similar result has also been observed on $CuCl_2$/ZSM-5 catalysts prepared by the same method [20]. In the present study, we attempt to elucidate the nature of the catalytic active sites of CuCl/ZSM-5 catalysts. Therefore, a combination of FT-IR, H_2-TPR and catalytic data of the NO-SCR with propene has been done in order to identify which kinds of copper species are present, and what is the role of Brønsted acidity in the SCR of NO over CuCl/ZSM-5 catalysts.

2. Experimental

2.1. Catalysts preparation

CuCl/H-ZSM-5 and CuCl/Na-ZSM-5 (Si/Al = 12.5) catalysts were prepared as reported previously [19]. The mechanical mixture of CuCl with H-ZSM-5 or Na-ZSM-5 was first calcined in air at 400 °C for 12 h, then at 600 °C for 2 h.

Reference sample, to be called ion-exchanged CuH-ZSM-5 was prepared from a slurry of H-ZSM-5 and an aqueous solution of copper(II) acetate solution, following the method described elsewhere [21].

The copper content of the samples was determined by atomic adsorption spectroscopy after the sample was dissolved in HF solution. The chloride content was measured by using ion-chromatography.

2.2. Infrared spectra (IR) analysis

IR spectra were recorded by using a Nicolet Impact 410 spectrometer as described previously [21,22]. The sample was pressed into a self-supporting wafer ($4 \, mg/cm^2$) and placed into an infrared cell equipped with CaF_2 windows. After the resulting wafer was treated at 320 °C for 1 h, the IR spectra in the –OH stretching region was recorded. The IR measurements of NO adsorption were performed at room temperature and the spectra of the adsorbed species were obtained by subtracting the spectrum of the wafer.

2.3. Temperature programmed reduction (TPR) analysis

TPR experiments were carried out by flowing 25 ml/min of 5% H_2/Ar mixture and heating from room temperature to 800 °C with a rate of 10 °C/min [22]. Prior to the TPR measurements, about 80 mg samples were pre-treated under Ar flow (30 ml/min) at 200 °C for 1 h and then cooled to room temperature. The change in hydrogen concentration was monitored continuously with a thermal conductivity detector (TCD). The water produced during the reduction was trapped in a 5A molecular sieve column.

2.4. Catalytic tests

The catalytic tests were carried out at atmospheric pressure in a fixed-bed flow reactor [19]. The catalyst

was treated at 500 °C for 2 h in Ar. Then a mixed gas of 0.16% NO, 0.14% C_3H_6, 2 vol.% O_2 (in Ar) was fed over 0.5 g of catalyst at a rate of 100 ml/min, in a temperature range between 300 and 500 °C. The reactants and products were analysed by an on-line gas chromatograph TCD. The catalytic activity for the reduction of NO was evaluated by the conversion of NO to N_2.

3. Results

3.1. Infrared spectra

The infrared spectra (IR) of 20 Torr NO adsorbed on CuCl/H-ZSM-5 (3.3 wt.% Cu) and CuCl/Na-ZSM-5 (4.1 wt.% Cu) at room temperature are presented in Fig. 1. For CuCl/H-ZSM-5 (spectrum a), the strong bands are observed at 1911, 1895, 1826, 1810 and 1734 cm^{-1}. Compared with the previous IR study on ion-exchanged Cu-ZSM-5 [21,23], it can be seen that all the adsorption peaks of NO on CuCl/H-ZSM-5 are almost same as that of on ion-exchanged Cu-ZSM-5. Therefore, the overlapping peaks at 1911 and 1895 cm^{-1} can be assigned to $Cu^{2+}(NO)$ and $Cu^{2+}O^-(NO)$, respectively. The band at 1810 cm^{-1} is assigned to $Cu^+(NO)$, and the couple of peaks at 1826 and 1734 cm^{-1} can be assigned to $Cu^+(NO)_2$. For CuCl/Na-ZSM-5 (spectrum b), only some very weak bands can be found, the peak at 1876 cm^{-1} is due to the presence of gaseous NO, and the weak band at 1895 cm^{-1} shows that a very small amount of $Cu^{2+}O^-(NO)$ species exists in CuCl/Na-ZSM-5. These results indicate that the copper ions (Cu^{2+} and Cu^+), which exist in the ion exchange sites of ZSM-5, can be formed on CuCl/H-ZSM-5 catalysts by this dispersion method. It means a high-temperature solid-state exchange reaction must occurred between CuCl and the proton acid in H-ZSM-5 during the calcination dispersion process [24].

The change of the Brønsted acidity with the copper loading over CuCl/H-ZSM-5 is also studied by means of infrared spectroscopy (Fig. 2). H-ZSM-5 shows two major hydroxyl peaks at 3740 and 3610 cm^{-1}, which are assigned to the terminal silanol group and the Brønsted acidic hydroxyl group [25,26], respectively. Clearly, the intensity of protonic OH band at 3610 cm^{-1} decreases linearly with increasing copper loading, and disappear completely when the copper loading reached to 10.2 wt.%. These results not only further confirm the solid-state ion-exchange reaction has occurred between CuCl and the proton acid in
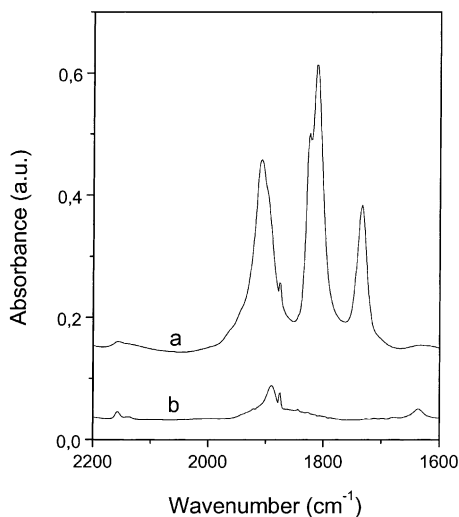

Fig. 1. IR spectra of: (a) CuCl/H-ZSM-5 (3.3 wt.% Cu); (b) CuCl/Na-ZSM-5 (4.1 wt.% Cu) during room temperature exposure to 20 Torr NO for 10 min.
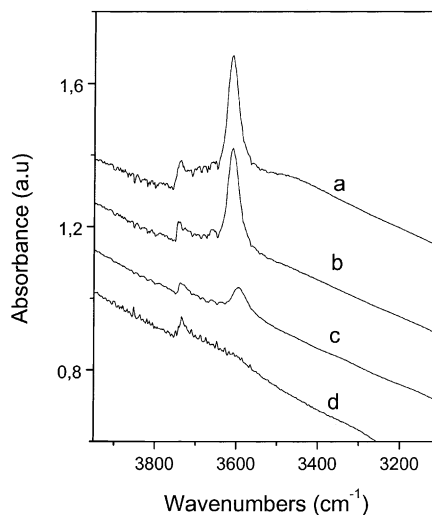

Fig. 2. IR spectra in the –OH stretching region of CuCl/H-ZSM-5 with different copper amounts: (a) 0.0 wt.%; (b) 1.0 wt.%; (c) 5.8 wt.%; (d) 10.2 wt.%.
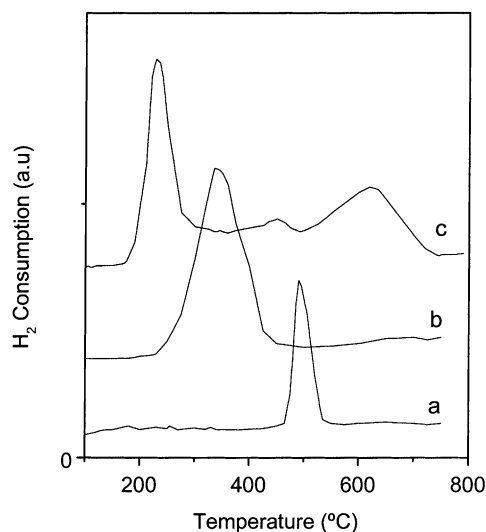
Fig. 3. H_2-TPR profiles of: (a) CuCl; (b) CuCl/Na-ZSM-5 (4.1 wt.% Cu); (c) CuCl/H-ZSM-5 (3.3 wt.% Cu).

H-ZSM-5, but also suggest that the exchange reaction is complete when the copper content reached above 10.2 wt.%.

3.2. Temperature programmed reduction

The means of H_2-TPR is also used to identify the copper species present in CuCl/ZSM-5 catalysts. Fig. 3 shows the TPR profiles for CuCl, CuCl/Na-ZSM-5 (4.1 wt.%) and CuCl/H-ZSM-5 (3.3 wt.%), respectively. Under our test condition, the pure CuCl sample shows one reduction peak at 490 °C, assigned to the reduction of CuCl to Cu^0. For CuCl/Na-ZSM-5, only one major reduction peak at about 340 °C can be detected, it should be assigned as the reduction of CuCl to Cu^0 too. Compared with the pure CuCl, the reduction peak of CuCl/Na-ZSM-5 shifts to lower temperature obviously. This can be explained by the high dispersion of CuCl into the surface or the channels of ZSM-5. Then CuCl no longer exists in the crystalline state [18–20]. For CuCl/H-ZSM-5 (3.3 wt.% Cu), two major reduction peaks are observed: the first at ca. 230 °C, and the second in the range 500–700 °C. Besides, a small peak at about 460 °C can also be detected. By comparing the area of two main peaks, also taking into account the related references about ion-exchanged Cu-ZSM-5 [27,28], the peak at 230 °C
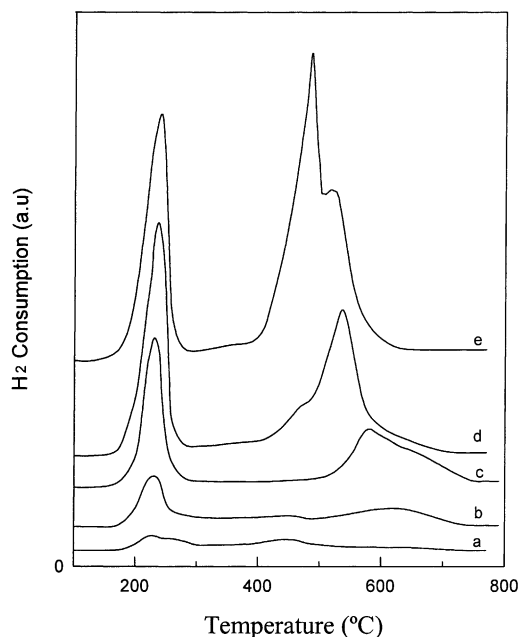

Fig. 4. H_2-TPR profiles of CuCl/H-ZSM-5 catalysts with different copper amounts: (a) 1.0 wt.%; (b) 3.3 wt.%; (c) 5.8 wt.%; (d) 10.2 wt.%; (e) 13.5 wt.%.

can be attributed to the reduction of Cu^{2+} in the ion-exchange sites of ZSM-5 to Cu^+, the peak in the range 500–700 °C corresponds to the reduction of Cu^+ to Cu^0, and the peak at about 460 °C can be assigned to the reduction of small amount of CuCl to Cu^0.

The TPR profiles of CuCl/H-ZSM-5 with different copper contents are showed in Fig. 4. We should point out that all the profiles in this figure present by the same scales in order to compare the concentration changes of copper species in different samples. Obviously, as the copper content increases, the peak area associated with the reduction of Cu^{2+} (230 °C) and Cu^+ (500–700 °C) increases progressively, reached to the highest value when copper loading reached to about 10.2 wt.%. Besides, a strong reduction peak of CuCl can be observed when the copper amount reached to 13.5 wt.%. It should be noted that the high-temperature peak (related to the reduction of Cu^+ ions to Cu^0) shift to lower temperatures as the copper content increases. The reason probably due to the copper ions first occupy the most stable exchange sites in ZSM-5, which are not easy to be reduced by H_2.
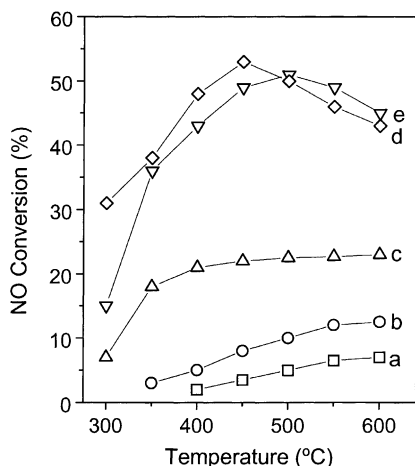
Fig. 5. NO conversion as a function of reaction temperature on different samples: (a) Na-ZSM-5; (b) CuCl/Na-ZSM-5 (4.1 wt.% Cu); (c) H-ZSM-5; (d) CuCl/H-ZSM-5 (4.2 wt.% Cu); (e) CuH-ZSM-5 (2.6 wt.% Cu).

3.3. SCR of NO with propene

Temperature dependencies of the activity of NO reduction on various samples are showed in Fig. 5. The parent H-ZSM-5 zeolite is active for NO reduction in this condition, a 23% NO conversion can be obtained at 500 °C, while the Na-ZSM-5 exhibits very low activity for this reaction. The CuCl/H-ZSM-5 (4.2 wt.% Cu) catalyst exhibits a good activity, even slightly higher than the ion-exchanged CuH-ZSM-5 (2.6 wt.% Cu). In contrast, CuCl/Na-ZSM-5 (4.1 wt.% Cu) is almost inactive for the SCR of NO by propene.

In order to make clear the correlation between the copper species and the catalytic activity, the effect of copper amount on the activities of NO reduction over CuCl/H-ZSM-5 at 300 °C is shown in Fig. 6. It can be seen that the NO conversion increased with copper loading in the region of 0–6 wt.%, further increase of copper loading leads to a slight drop of activity.

According to the H_2-TPR results, we have known that the content of copper ions (Cu^{2+} and Cu^+) has reached to a maximum value at about 10 wt.% copper loading. These results suggest that there should be a direct relationship between the content of copper ions species and catalytic activity of CuCl/H-ZSM-5 catalysts.
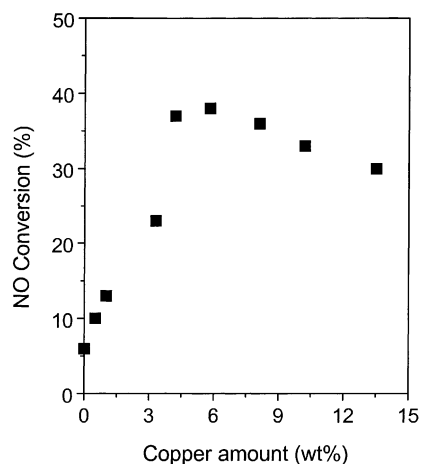

Fig. 6. NO conversion at 300 °C as a function of copper amount over CuCl/H-ZSM-5.

4. Discussion

In our previous work [19], we have found that CuCl/H-ZSM-5, prepared by dispersion method, showed a good activity in the SCR of NO by propene, the conversion of NO was substantially higher than that of CuCl/Na-ZSM-5. According to those results, we may suppose that the initial Brønsted acid sites of parent zeolite should be responsible for the good activity of CuCl/H-ZSM-5. But it is not very clear whether the Brønsted acid has participated the reaction directly, such as activate the propene in the reaction, or it is just useful to produce active copper species during the preparation process of the CuCl/H-ZSM-5 catalysts.

In the present study, the results of infrared spectroscopy of NO adsorption over CuCl/H-ZSM-5 catalysts have proved that the presence of both Cu^{2+} and Cu^+ ions, which located at the ion exchange sites of ZSM-5. The formation of copper ions can be attributed to a high-temperature solid-state exchange reaction occurred between CuCl and the Brønsted acid sites of H-ZSM-5 [24]. This point can also be supported by the results of elemental analysis of CuCl/ZSM-5 catalysts (see Table 1). For the CuCl/H-ZSM-5 catalysts, the ratio of Cl/Cu is much lower than the atom ratio of CuCl, but the ratio of Cl/Cu is still close to 1:1 for the CuCl/Na-ZSM-5.

By the H_2-TPR and IR results in this work, it can be seen that the amount of copper ions (Cu^{2+} and

Table 1
The Cl/Cu ratio in CuCl/ZSM-5 catalysts

Catalysts	CuCl/H-ZSM-5					CuCl/Na-ZSM-5
Content of Cu (wt.%)	1.0	3.3	5.8	10.2	13.5	4.1
Content of Cl (wt.%)	0.28	0.43	1.50	2.17	2.63	2.1
Cl:Cu (mol)	1:2.0	1:4.3	1:2.2	1:2.6	1:2.9	1.0:1.1

Cu^+) in CuCl/H-ZSM-5 catalysts increased with the copper loading, reached to the highest value when copper loading reached to about 10.2%. In contrast, the intensity of Brønsted acid decreases with increasing copper loading, and disappear completely when the copper loading reached to 10.2 wt.% (see Fig. 2). It means that the protons at strong Brønsted acid sites can react with CuCl completely during the calcination treatment process when the copper loading reached to above 10.2 wt.%.

Reaction data show that the activities of CuCl/H-ZSM-5 catalysts increase with the increase of copper ions (Cu^{2+} and Cu^+). The highest catalytic activity is obtained at about 6 wt.% copper loading, while the content of copper ions in this sample is very near to the highest value (see Fig. 4). The catalytic activity dropped somewhat when keep on increasing copper loading. It can be interpreted by the presence of surplus CuCl, which should have dispersed on the surface or channel of ZSM-5, then cover the active centres or block the channel of zeolite [19]. These results suggest that the main active species for this reaction should be the copper ions located at the exchanged sites, while the highly dispersed CuCl is inactive for this reaction. Furthermore, it should be pointed out that the CuCl/H-ZSM-5 still shows a good activity when the Brønsted acidity has disappeared completely (e.g. 10.2 wt.% sample), it means the Brønsted acidity is not necessary for the SCR of NO over CuCl/ZSM-5.

As the characterisation results and the catalytic properties of the CuCl/H-ZSM-5 catalysts are very analogous to a typical aqueous ion-exchange Cu-ZSM-5, then it seems reasonable to propose that the strong Brønsted acidity is also not necessary for the SCR of NO over the usual ion-exchanged Cu-ZSM-5 catalysts.

Then, a question will be raised immediately: if there are no Brønsted acid sites available, how is the hydrocarbon activated? It has been accepted that NO can be activated by the adsorption on ion-exchanged Cu sites. Here, we may assumed that the olefins can also adsorb on the same Cu sites, then both NO and olefin will reside on a single Cu site and the SCR of NO could occur on this site. This speculation is consistent with a study by Parrillo et al. [29], in their work, they found the olefins can be adsorbed on ion-exchanged Cu sites, the formation of olefin complex can be attributed to the Lewis acidity of Cu ions (Cu^+ and Cu^{2+}).

Besides, some authors have pointed out that the presence of proton exchange site plays a crucial role in the Cu-ZSM-5 catalyst deactivation [4,11]. It was found that the presence of Brønsted acidity site provide the point of attack by water molecules in the process of steam-induced dealumination of the zeolite matrix under high-temperature conditions, results into the irreversible deactivation of ion-exchanged Cu-ZSM-5. Thus, we may assume that by using this dispersion method, the stability of Cu-ZSM-5 catalyst could be improved, because all the protons can be removed in a high copper loading sample to avoid such a deactivation process.

In summary, all the results suggest that the active species of CuCl/H-ZSM-5 prepared by dispersion method are mainly related to the copper ions (Cu^{2+} and Cu^+), which exist in the ion-exchange sites of ZSM-5. The initial Brønsted acidity of the starting zeolite is useful to produce active copper ions species for CuCl/H-ZSM-5, however, it is not necessary for the reaction of SCR-HC of NO over Cu/ZSM-5 catalysts.

5. Conclusions

For CuCl/H-ZSM-5 prepared by dispersion method, the main active species in the reaction of SCR of NO are isolated copper ions (Cu^{2+} and Cu^+) located in the ion exchange sites of ZSM-5, while the high dispersed CuCl on the surface of ZSM-5 is inactive for this

reaction. Direct evidences from IR and H_2-TPR show that the initial Brønsted acidity of the starting zeolite is useful to produce active copper ions species during the preparation process of catalysts. However, it is not necessary for the SCR of NO over Cu-ZSM-5 catalysts.

Acknowledgements

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