Effect of Additives on Isomerization of Hexane over PtGa-Mordenite Catalysts

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Abstract

PtGa (or Zn)/mordenite catalysts were prepared by incipient wetness impregnation of mordenite (H-MOR) with 1.0%Pt and Ga (or Zn) solutions, respectively. The catalysts were calcined, activated under flowing N_2 then reduced in H_2. They were characterized by X-ray diffraction (XRD), nitrogen adsorption method (BET) and temperature programmed desorption (TPD). The influence of various parameters affecting on the conversion of hexane was investigated. The reaction products are formed from isomerization, cracking and aromatization reactions. Effect of additives: MgO, ZrO_2 and MgAlO was studied.

Keywords: n-hexane, mordenite, platinum, gallium

1. Introduction

Isomerization of linear alkanes to branched counterparts has attracted attention since increasing the degree of branching of alkanes can boost the octane quality of a gasoline fraction. The application of branched hydrocarbons is an environmentally more acceptable alternative compared with other techniques, such as blending with aromatics or oxygenates. The iso-alkanes can be obtained via two processes: (1) alkylation process, where light alkanes are alkylated with lower iso-alkanes and (2) hydroisomerization process in which linear alkanes are converted into the branched ones. There are four distinct noble metal-loaded catalysts available commercially to increase the octane number of the feedstocks: (1) chlorinated alumina [1], (2) MOR-type zeolites [2], (3) sulfated zirconia [3] and (4) tungstenated zirconia [4].

The mechanism of an isomerization reaction on a zeolitic catalyst involves the formation of an alkene by dehydrogenation of the alkane at a metal site. Subsequently, the alkene forms a carbenium ion by protonatiion at an acid site and the ion undergoes chain isomerization or β-cleavage. Zeolites have been widely used as catalysts for the isomerization of alkanes, since undesirable side effects observed with other catalysts, like corrosion can be avoided [5]. Platinum dispersed mordenite is a bifunctional catalyst, active for isomerization of n-alkanes and aromatization of paraffins [6]. In order to prepare a suitable catalyst for conversion of alkanes, good balance between the two functions has to be obtained. Rapid molecular transfer between the metal and acid site is necessary for selective conversion of alkanes into desirable products. Activity and selectivity of bimetallic catalysts were much higher than those over monometallic [7, 8].

Mordenite is a naturally-occurring silica-rich aluminosilicate zeolite with 12-membered (0.65 x 0.70 nm) channels. They are in parallel to each other along the z direction and interconnected by 0.48 nm deep 8-membered pockets [9], as shown in

Figure 1. Dealumination causes decrease in the total number of acid sites, but the strength of remaining sites increase as a result of the decrease in the number of atoms sharing the charge (media effect). Mordenite has been successfully operating in industrial processes, e.g. Shell's process for hydroisomerization of linear alkanes.

The strength and the density of the acid sites, metal loading and the textural properties of the zeolite are important parameters controlling the performance of the catalyst. Ways of modifying the acidity of zeolites are dealumination and cation exchange [10]. Dealuminated mordenite (Si/Al = 32) loaded with Pt resulted in high isomer yield (97%) in the n-hexane hydroisomerization and higher conversion (43%) than that of the parent mordenite (Si/Al = 18) (20%) due to the optimum acidity [6].

Various techniques are available to introduce metals into zeolites, for example, impregnation and solution ion exchange [11]. The presence of metal on these catalysts may modify the Bronsted centers of the zeolite and the metal state may be modified by the influence of the support [12]. Mordenite promoted with Pt was reported for isomerization of n-butane [13]. The Ni and Pd loaded-mordenite (Si/Al = 7.5) catalysts prepared by impregnation and ion-exchange method were reported to yield high selectivity to isobutane in the isomerization of n-butane [10]. Coke formation in the H-mordenite/0.5%Pd catalyst was reported to affect catalytic activity and product selectivity in hexane isomerization [14].

Using H-ZSM5 (Si/Al = 40) with ZnO, Ga_2O_3 and Fe_2O_3 as a promoter (3 wt.%) in the conversion of n-hexane, it was found that the H-ZSM5/ZnO and H-ZSM5/ Ga_2O_3 yielded higher aromatics [15].

It has been reported that the binder could change the acid properties of a zeolite as a result of changes in proton-exchange efficiency [16]. The effect of the bentonite in the n-octane hydroisomerization in vapor phase over mordenite and ZSM-5 using Pd was reported. A decrease in conversion was observed due to agglomeration [17].

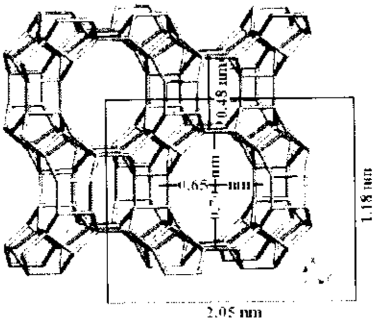


Figure 1.Structure of mordenite [13]

In this work, catalytic performances of 1.0%Pt 1.0%Ga (or Zn)/mordenites on conversion of n-hexane were investigated. The 1.0% Pt 1.0%Ga/mordenite was mixed with additives: MgO, ZrO_2 and MgAlO and catalytic activity and product distribution of the mixture on conversion of n-hexane were studied.

2. Experimental

Mordenite, H-MOR (SiO_2/Al_2O_3 = 90) was obtained from Zeolyst International Co. Ltd., USA. $Pt(NH_3)_4Cl_2.xH_2O$, $Ga(NO_3)_3.xH_2O$, $ZnCl_2$ and n-hexane (> 99%) were obtained from Fluka.

2.1 Catalyst preparation and characterization

Mordenite (5 g) was impregnated with minimum amount of aqueous $Pt(NH_3)_4Cl_2$ solution (1.0%Pt) and dried at 120°C, the resulting solid was further impregnated with $Ga(NO_3)_3$ or $ZnCl_2$ solution (1.0% Ga(or Zn)), dried at 120°C and calcined in air at 350°C for 5 h.

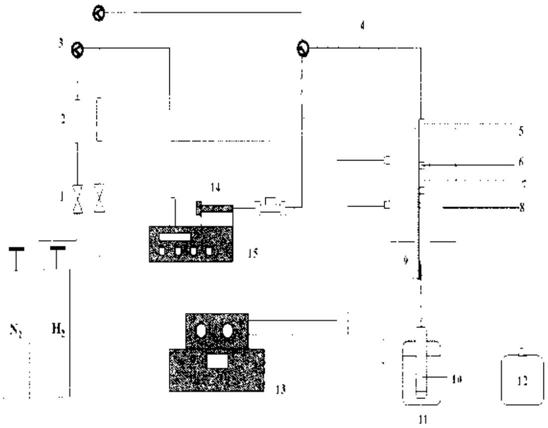
The 1.0%Pt 1.0%Ga/H-MOR catalyst was mixed with additive: MgO, ZrO_2 or MgAlO (obtained from calcination of MgAl hydrotalcite) in a 1:1 ratio (by weight).

MgAl hydrotalcite was prepared by co-precipitation of an aqueous solution (60 mL) of $Mg(NO_3)_2.6H_2O$ (72 mmol) and $Al(NO_3)_3.9H_2O$ (18 mmol). This solution was added slowly to 90 mL of an aqueous solution of $(NH_4)_2CO_3$ (0.11 mol). The pH was adjusted to 8 using NH_4OH. The reaction mixture was held at 65°C while stirring for 3 h. The solid was filtered, washed with distilled water, dried and calcined at 450°C for 35 h to obtain MgAlO.

The structure of the catalysts was analysed with Rigaku, DMAX 2002/Ultima Plus diffractometer equipped with a rotating anode using Ni filtered Cu-Kα radiation between 2 and 30° (with a scanning rate of 2° min^{-1}. The BET surface area, pore volume and pore size distributions were obtained from nitrogen adsorption-desorption isotherm measured at 77K by a micromeritics adsorptometer, model Flowsorb 2300. The concentration of the acid sites was measured by temperature-programmed desorption of ammonia (NH_3-TPD) using a Micromeritics TPD/TPR 2900 analyzer. The sample was firstly heated from room temperature to 400°C at 10°C min^{-1} under a flow of helium. After cooling to room temperature ammonia was then flowed over the sample. Then the sample was purged with helium at 100°C for 1 h in order to eliminate physisorbed species. The temperature was ramped a 10°C min^{-1} to 700°C. A thermal conducting detector was used to detect the desorbing molecules. The amount of coke deposited during reaction was measured by thermogravimetric analysis (TGA) on a TA instrument thermogravimetric analyzer (SDT 2960) at the heating rate of 10°C min^{-1} under nitrogen atmosphere.

2.2 Catalytic studies

The catalytic apparatus is shown in Figure 2. Catalytic test reactions were carried out in a fixed bed downstream quartz tubular reactor of 10 mm inner diameter. The catalyst powders (pressed and crushed into 2x2x0.7 mm) were loaded into a middle part of a reactor and held in place using quartz wool support. The catalyst portion was covered with small amount of quartz wool. The height of the catalyst portion was 25 mm. The catalyst was activated under flowing N_2 at 500°C for 1 h and then reduced in a hydrogen flow at 500°C for 1 h. The hexane was fed using a Milton Roy syringe pump into nitrogen stream, passed from the top through the catalyst (1 g) at N_2 flow rate of 20 ml $min^{-1}$and a WHSV (weight hourly space velocity) of 1 h^{-1}.



1 = needle valve 2 = flow controller 3 = two-way valve
4 = heater cable 5 = tubular reactor 6 = quartz
7 = catalyst 8 = electric furnace 9 = thermostat
10 = cold trap 11 = dry ice-acetone bath
12 = Tedlar bag 13 = temperature programmed controller
14 = syringe 15 = syringe pump

Figure 2. Reaction apparatus.

The whole gas line was heated to avoid condensation of gases along the line. The temperature of the catalyst bed was monitored using a thermocouple located at the center of the reactor. The reaction products were passed through a cooling system to condense products which were analyzed by gas chromatography. Three runs were performed for each experiment. The activity data are reported in terms of n-hexane conversion (%). A blank test without a catalyst showed negligible conversion of hexane. Gas products were analyzed by a Hewlett-Packard gas chromatograph, using a fused silica PLOT Al_2O_3/KCl column and an FID detector. Liquid products were analyzed with a Shimadzu GC-8A gas chromatograph equipped with a 30-m long and 0.32-mm diameter DB-1 column. The product selectivities were calculated as equation 1.

$$Selection(\%) = \frac{product \text{ x } 100}{consume\ n-hexane} \qquad (1)$$

At the end of the reaction, the catalyst was removed and the coke deposited on the catalyst was estimated from the weight loss in thermogravimetric analysis.

2.3 Catalyst regeneration

Catalyst regeneration was performed by oxidizing coke deposited onto the catalyst in air flow at 550°C for 2 h. The regenerated catalyst was reused in the reaction.

3. Results and discussion

3.1 Catalyst characterization

X-ray diffraction patterns of all metal loaded mordenite catalysts exhibit similar X-ray diffraction patterns (Figure 3) with mordenite indicating the structural integrity of the mordenite [18]. The intense peaks appear at 2 Theta (degree) = 6.55, 8.67, 9.71, 19.61, 22.25, 25.73 and 27.69. The structures of the metal loaded mordenites did not show any presence of the metal due to the small amount of metal loading.

The specific surface area, pore volume and pore diameter of the metal loaded mordenite catalysts are presented in Table 1 compared to the mordenite in order to assess the influence of the presence of metal on the catalyst surface. The mordenite has specific surface area of 551 $m^2 g^{-1}$ with pore volume 0.35 $cm^3 g^{-1}$ and pore radius 2.56 nm. The specific surface area was reduced after impregnation of Pt and Ga or Zn.

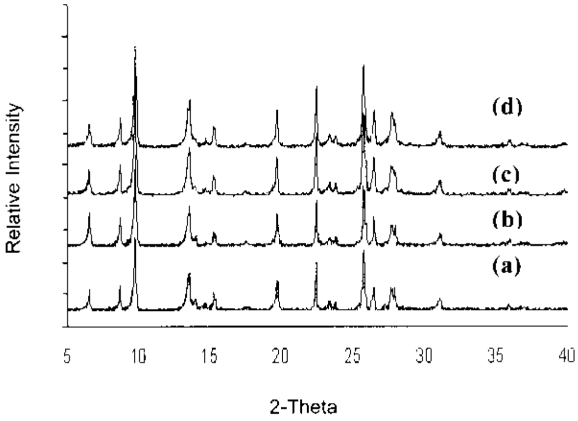


Figure 3. X-ray diffraction patterns of
(a) H-MOR
(b) 1.0%Pt/H-MOR
(c) 1.0%Pt 0.5%Ga/H-MOR
(d) 1.0%Pt 1.0%Zn/H-MOR

Table 1. Specific surface area, pore volume and pore diameter of the catalysts

Catalysts	Surface area ($m^2 g^{-1}$)	Total pore volume ($cm^3 g^{-1}$)	pore diameter (nm)
H-MOR	551±0.44	0.35±0.03	2.56±0.05
1.0%Pt/H-MOR	540±0.30	0.32±0.02	2.79±0.05
1.0%Pt 1.0%Ga/ H-MOR	525±0.45	0.35±0.02	2.66±0.04
1.0%Pt 1.0%Zn/ H-MOR	531±0.28	0.34±0.01	2.57±0.05

The acidity of the catalysts were determined by temperature programmed desorption of ammonia, NH_3-TPD. Their results are shown in Table 2. The desorption curves were fitted to two peaks, at low temperature 300-320°C and high temperature 405-450°C, corresponding to the desorption of ammonia on weak and strong acid sites, respectively.

Table 2. Acidity of the catalysts determined by NH_3-TPD

Catalysts	Weak acidity ($mmol\ g_{cat}^{-1}$)	Strong acidity ($mmol\ g_{cat}^{-1}$)	Total acidity ($mmol\ g_{cat}^{-1}$)
H-MOR	0.71$\pm$0.02	0.74$\pm$0.03	1.45$\pm$0.04
1.0%Pt/H-MOR	0.60$\pm$0.03	0.64$\pm$0.04	1.24$\pm$0.02
1.0%Pt1.0%Ga/ H-MOR	0.61$\pm$0.04	0.63$\pm$0.02	1.24$\pm$0.03
1.0%Pt1.0%Zn/ H-MOR	0.70$\pm$0.03	0.60$\pm$0.03	1.30$\pm$0.02

The amount of ammonia desorbed and the desorption temperature were considered as a measure of total acidity and acid strength of catalysts, respectively. [21].

Results show that the 1.0Pt/H-MOR has lower weak and strong acidity compared to the H-MOR. This change in the acid site strength could be due to interactions between Pt crystallites and acid sites [20]. The bimetallc catalysts also possess lower weak and strong acidity. This demonstrates that the metal ions displace the strong acidic protons in the mordenite support.

In this work MgAlO was synthesized from calcination of MgAl hydrotalcite and was characterized. From BET, the MgAlO shows surface area, total pore volume and pore diameter of 243 $m^2\ g^{-1}$, 0.59 $cm^3\ g^{-1}$ and 9.7 nm, respectively. Its XRD pattern was shown in Figure 4 compared with the pattern of MgAl hydrotalcite. Upon calcination, the structure of the MgAl hydrotalcite was destroyed.

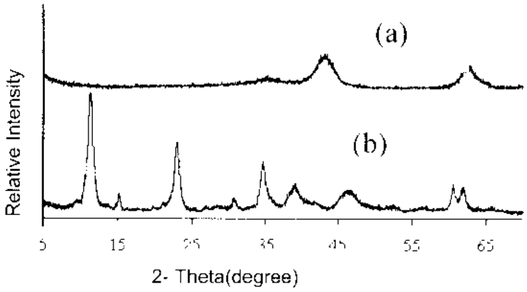


Figure 4. XRD Patterns of (a) MgAlO and (b) MgAl hydrotalcite.

The diffraction peaks of the MgAlO were observed at 2 Theta (degree) = 35.7, 43.2 and 62.6, in good agreement with that in the literature [19].

3.2 Catalytic studies

The reaction was performed under the same condition: catalyst 1.0 g, N_2 flow rate of 20 ml min^{-1}, a weight hourly space velocity (WHSV) 1 h^{-1} and reaction temperature at 400°C. Results of catalytic activity and selectivity of the catalysts studied were shown in Table 4.

The products analyzed by GC-MS were resulted from following reactions: isomerization (i-pentane i.e. 2-methylpentane and 3-methylpentane; i-butane i.e. 2,2-dimethylbutane and 2,3-dimethylbutane); cracking (methane, ethane, propane and butane); dehydrogenation (olefins) and aromatization (BTX: benzene, toluene and xylene).

In general, the mechanism of an isomerization reaction on a bifunctional zeolite catalyst involves the formation of hexene by dehydrogenation of the hexane at a metal site. Subsequently the hexene forms a carbenium ion by protonation at an acid site. The carbenium ion further rearranges to more stable tertiary carbenium ion. Finally the tertiary carbenium ion abstract hydride ions from hexane and transform into olefins or undergoes chain isomerization or β-cleavage [22].

From Table 4, the 1.0%Pt/H-MOR yielded the main product from isomerization. The yield of the cracked products was low. This indicates that the ptotolytic cracking of n-hexane as well as hydrogenolysis occurred only to a minor extent. The lack of protolytic cracking can be rationalized, since the concentration of strong acid sites was decreased after Pt introduction into mordenite. This is consistent with the literature, cracking of alkanes requires strongly acidic sites [13].

Table 4. Catalytic activity of PtGa (or Zn)/mordenites

Catalysts	1.0%Pt/ H-MOR	1.0%Pt 1.0%Ga/ H-MOR	1.0%Pt 1.0%Zn/ H-MOR
Conversion (%)	87.0±1.02	93.0±1.15	76.0±0.72
Selectivity (%)			
Cracked products			
Methane	2.0±0.15	0.1±0.02	0.4±0.03
Ethane	5.5±0.08	0.2±0.01	17.4±1.10
Propane	10.5±1.26	0.1±0.01	3.5±0.06
Butane	12.0±0.97	8.7±0.55	0.2±0.01
Pentane	1.0±0.08	0.2±0.01	0.2±0.01
Dehydrogenated products			
Olefins	5.0±0.12	8.8±0.09	40.4±1.75
Isomerized products			
i-Pentane	47.0±2.24	68.1±2.61	35.6±1.38
i-Butane	16.1±2.04	11.3±0.98	0.6±0.14
Aromatized products			
Benzene	0.2±0.01	0.9±0.01	1.1±0.02
Toluene	0.6±0.03	1.4±0.02	0.4±0.01
Xylene	0.1±0.02	0.2±0.03	0.1±0.02

Condition: catalyst 1 g, 400°C, WHSV 1 h^{-1}, time on stream 3 h.

Introduction of Ga or Zn in the 1.0%Pt/H-MOR catalyst affects the n-hexane conversion and product selectivity. The 1.0%Pt 1.0%Ga/H-MOR yielded higher conversion. The product selectivity of 1.0%Pt 1.0%Ga/H-MOR and 1.0%Pt 1.0%Zn/H-MOR catalysts are different. It can be seen that compared with the 1.0%Pt/H-MOR, Ga improves the activity and selectivity to olefins, isomerized product and aromatized products, BTX. The promoting effect of Ga has been attributed to its ability to dehydrogenate alkanes and the production of allylic species. Aromatic was formed from oligomerization and dehydrogenation reactions. It is generally agreed that zeolite Brønsted acid sites catalyze cracking, oligomerization, and cyclization reaction step and that Ga active sites are responsible for dehydrogenation reaction of alkanes and intermediate products of the aromatization reaction steps [23]. For the 1.0%Pt 1.0%Zn/H-MOR, Zn shows higher selectivity to ethane and olefins.

Effect of time-on-stream (TOS) was investigated using 1.0%Pt1.0%Ga/H-MOR. N-hexane conversions and product selectivities at 3 and 8 h time-on-stream are shown in Table 5. A slight decrease in n-hexane conversion was observed with duration of run (time on stream, TOS). This indicates that the deactivation of the catalyst is low. Moreover, deactivation has no influence on the selectivities to different products.

Table 5. Effect of TOS on catalytic activity of PtGa/mordenite

TOS	3 h	5 h	8 h
Conversion (%)	93.0±1.80	90.0±1.45	89.0±1.28
Selectivity (%)			
Cracked products			
Methane	0.1±0.03	0.1±0.02	0.1±0.02
Ethane	0.2±0.01	1.4±0.04	1.4±0.05
Propane	0.1±0.01	0.2±0.01	0.1±0.01
Butane	8.7±0.93	8.7±0.85	9.0±1.02
Pentane	0.2±0.01	2.2±0.01	2.2±0.02
Dehydrogenated products			
Olefins	8.8±1.09	10.0±0.84	10.0±1.00
Isomerized products			
i-Pentane	68.1±2.06	66.6±1.24	67.0±1.44
i-Butane	11.3±0.85	8.2±1.02	8.0±1.59
Aromatized products			
Benzene	0.9±0.05	1.0±0.01	1.0±0.01
Toluene	1.4±0.08	1.4±0.06	1.0±0.02
Xylene	0.2±0.04	0.2±0.04	0.2±0.02

It was reported earlier that for H-mordenite deactivation does not affected the product distribution [24]. The deactivation is probably caused by coke formation which blocks the pores of mordenite. Access of reactant to both active sites, Pt particles and Bronsted acid sites inside the pores is blocked. In this work %coke determined by thermogravimetric analysis is 5.5-6.0%.

3.3 Catalyst regeneration and usage period

After first use, the amount of coke formed on the spent catalyst was determined. it was 5.5%. In order to regenerate, it was calcined in air at 550°C for 2 h and the activity of the regenerated catalysts was measured. It shows a slight decrease in conversion (90.0%) compared to the fresh catalyst (93.0%).

For the usage period of the catalyst, the results show that the catalysts can be used for about 20 h after regeneration.

3.4 Effect of additives

The 1.0%Pt1.0%Ga/H-MOR was physically mixed with additive: MgO, ZrO_2, and MgAlO in the 1:1 ratio by weight (total weight 1.0 g). Percent conversion and percent product selectivity are shown in Table 6.

Results show that all mixtures gave lower conversion of n-hexane than that of 1.0%Pt1.0%Ga/H-MOR. Additives cause change in the acid property of the mordenite or blocking of the channel of the mordenite during the mixing process. The mixture of 1.0%Pt 1.0%Ga/H-MOR and MgO showed the lowest conversion however the selectivity to aromatized product was high (BTX 15%). This is due to high basicity of MgO which favors aromatization reaction. It was reported that the dehydrogenated species generated by the Pt particles are stabilized by basic oxide ions [23].

For the mixture of the 1.0%Pt 1.0%Ga/H-MOR and ZrO_2 it gave lower selectivity to BTX (1.3%) compared to the MgO. This might be due to the lower basicity of ZrO_2 compared with MgO. For the mixture of the 1.0%Pt 1.0%Ga/H-MOR and MgAlO, the selectivity to BTX was 4.0%.

Table 6. Activity of the 1.0%Pt 1.0%Ga/H-MOR catalyst mixed with additive

Additives	MgO	ZrO_2	MgAlO
Conversion (%)	55.0±1.02	88.2±1.07	74.9±2.05
Selectivity (%)			
Cracked products			
Methane	0.2±0.03	5.5±0.79	2.5±0.63
Ethane	0.3±0.14	6.8±0.62	4.6±0.11
Propane	0.2±0.06	4.2±0.80	1.1±0.68
Butane	1.1±0.06	9.3±1.04	1.6±0.26
Pentane	0.7±0.15	3.4±0.24	0.6±0.03
Dehydrogenated products			
Olefins	11.2+0.52	12.4+0.68	35.2+1.06
Isomerized products			
i-Pentane	40.5+2.12	30.6+1.89	28.1+1.65
i-Butane	30.8+2.10	26.5+1.05	22.3+1.80
Aromatized products			
Benzene (B)	5.8+1.25	0.4+0.03	1.2+0.90
Toluene (T)	8.2+1.34	0.6+0.06	2.2+0.26
Xylene (X)	1.0+0.01	0.3+0.01	0.6+0.01

Condition: catalyst 1.0 g, 400°C, WHSV 1 h^{-1}, time on stream 3 h.

4. Conclusions

The metal loaded mordenites (metal = Pt, Ga or Zn) were prepared and were effective for conversion of n-hexane. The products were resulted from cracking, isomerization, dehydrogenation and aromatization of n-hexane. Results show that catalytic activity and product selectivity depend on type of metal. Ga showed high selectivity to olefins, isomerized product and aromatized products while Zn showed high selectivity to ethane and olefins. Additives possessing basicity have an affect on the conversion. The MgO which has higher basicity compared to ZrO_2 and MgAlO showed higher selectivity to BTX.

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