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Characterization and Cracking Activity of Zeolite Prepared from Local Kaolin

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Abstract

The synthesis of zeolite NaX from locally available kaolin has been studied. The operating conditions for zeolite NaX production from kaolin with good crystallinity were as follows; a gel formation step of metakaolin in alkaline medium in presence of additional silica to crystallize the zeolite was achieved at 60 oC for 1 hr,and with stirring. In ageing step of the reactants at room temperature for 5 days and crystallization step at 87±2 oC for 24 hr. The catalytic activity of catalyst prepared from local kaolin was studied by using cumene cracking as a model for catalytic cracking and compared with standard HY zeolite and HX zeolite catalysts. The activity test was carried out in a laboratory continuous flow unit with fixed bed reactor at duration time in the range 10-240 minutes, temperature 823 K, and LHSV 1 h-1. The prepared and the standard catalysts were characterized by atomic absorption, X-Ray Diffraction Analysis, Fourier Transform Infrared Spectroscopy, surface area and pore volume.

Introduction

Most catalysts used in commercial catalytic cracking units today are either amorphous synthetic silica-alumina combinations or mixtures of amorphous synthetic silica-alumina and crystalline synthetic silica-alumina catalysts called zeolites or moleculars sieves[1]. The advantages of the zeolite catalysts over the natural and synthetic amorphous catalysts are: higher activity, higher gasoline yields at a given conversion, production of gasoline containing a larger percentage of paraffinic and aromatic hydrocarbons, lower coke yield (and therefore usually a larger throughput at a given conversion level), increased isobutane production, and ability to go to higher conversions per pass without overcracking[1,2].

Despite the fact that activated natural clays have not been used as cracking catalysts for a long time, awareness of their characteristics is important since natural clays continue to be included in the composition of synthetic catalysts in order to reduce their cost. This technique, initially used in the production of silica alumina catalysts, is used today on a large scale in the production of zeolitic catalysts [3].

Clay minerals of the kaolin group are convenient starting materials for the synthesis of zeolites. Kaolin clay must be sufficient plastic so that is can be molded and remain strong in the green and dry state, must not be so plastic that it shrinks and distorts on drying [4]. Kaolin type clays or clay minerals have the general composition $Al_2O_3.2SiO_2.2-4H_2O$, which makes such clays preferred for synthesis of zeolite types [5]. Kaolin is inexpensive, naturally occurring, abundant material and was employed as the sole source of silica and alumina [6]. It is largely available in Iraq; particularly in Al-Ga'ara areas of western Iraq that have four regions (Dewkkla, Samhat, Tel- Afef and Bir Mlusi) [4]. Kaolinite is the major mineral component of kaolin, which may contain impurities such as quartz, illites, smectites, and feldspars [7].

When kaolin –type clay is heated, it will undergo several transitions. The first of these takes place at about (550-600°C), and produces the disordered metakaolin phase (metastable phase) by an endothermic dehydroxylation reaction [8], and it has been reported that metakaolin is more reactive under chemical treatments, this transformation occurs with the loss of structural water with a reorganization of the structure; only a small part of AlO6 octahedral is maintained, while the rest are transformed into much more reactive tetra- and penta coordinated units [7].

The metakaolin is then stable to about 935-950°C where it rearranges to give a defect aluminum–silicon spinel, which is also referred to as a γ-alumina type structure. The so called γ-Al2O3 phase converts to mullite 3Al2O3.2SiO2 at 1050°C, as shown in the following equations [9]:

$$\underset{\text{Kaolin}}{2Al2Si2O5\ (OH)\ 4} \xrightarrow{550-600^{\circ}C} \underset{\text{metakaolin}}{2Al2Si2O7} + 4H2O$$

$$\underset{\text{metakaolin}}{2Al2Si2O7} \xrightarrow{925-950^{\circ}C} \underset{\text{spinel}}{Si3Al4O12} + SiO2$$

$$\underset{\text{spinel}}{3Si3Al4O12} \xrightarrow{1015^{o}C} \underset{\text{mulli}}{2Si2Al6O13} + \underset{\text{cristablite}}{5SiO5}$$

Metakaolin is believed to be a defect phase in which the tetrahedral silica layers of the original clay structure are largely retained. It is know to be more reactive, therefore it is used as a starting material for the synthesis of zeolite [9].

Zeolites (aluminosilicates) are crystalline clays that can be either natural minerals or prepared synthetically by crystallizing silica and alumina solutions [10].

At present some 39 naturally occurring zeolite species have been recorded and their structures determined. In addition more than 100 synthetic species with no know natural counterparts have been confirmed as new zeolite and the majority a wait full structural determination [11].

Cumene (isopropyl-benzene) is a typical aromatic compound in the gasoline pool. Thus the reactions of these important aromatics are quite significant for refiners [12].

The chemistry and kinetics of cumene cracking have been received the largest attraction form researchers due to its simplicity. Corma and Wojeiechowski have reviewed this reaction in detail [13]. Long-chain aromatics also draw the attention of researchers because they represent the aromatics in gas oil. Corma and co-workers [14,15] reported that these compounds crack by a number of competing reaction pathways including dealkylation, side chain cracking, and self alkylation.

Thus, although cumene cracking has been used extensively as a test reaction to investigate the characteristics of newly developed cracking catalysts [12], locally limited research has developed on the cracking of cumene.

Frillete et al. [16] studied the cumene cracking and found that the conversion was low at 510oC over NaX-zeolite (6 mole%), more extensive over CaX-zeolite (59 mole% at 470°C), but not so extensive over amorphous aluminosilicate.

Kazuo and Hiroshi [17] examined the effects of the degree of ion exchange and the silica to alumina mole ratio on the cumene cracking activity of faujasite- type zeolite. When they studied the activity of five different faujasite –type zeolites with different silica /alumina mole ratio; (Na-X2.5, Na-Y5,Na-Y3.25 ,Na-Y3.85 , and Na-Y4.6) by cumene cracking ,and treated the Zeolites under the same conditions ,they found that when the SiO2/Al2O3 mole ratio was 5.1 and the reaction temperatures 300, 350, 400, and 450°C the cumene conversion (mole%) would be 0.5, 10.8, 35.2, and 62.5, respectively.

And they found that when sodium ions in Na-form zeolite are replace with polyvalent metal ions or NH4 ions, the order of activity is La>NH4>Ca>Na; where the activity would be determined by both the acidity and the acid strength. The catalytic activity of La-Na-Y at 350°C becomes notable after the cation exchange exceed 50%, and reached the maximum value 100mol% cumene conversion at 87% exchange . The same phenomenon was observe by James [18] who examined the cumene cracking for a series of faujasites ion-exchange with alkali and alkaline earth elements (K, Na, Li, Ba, Sr, Ca, and Mg) using micro-reactor. The order of cumene conversion is Mg>Ca>Sr>Ba>Li>Na>K.

Peter et al. [19] studied dealkylation of cumene over Zeolite Y in hydrogen form pretreated at temperatures between 500 and 800°C and they found that the main products were benzene and propylene and they calculated the conversion data from the concentration of benzene in the product.

Donald and Wojciechowski [20] used cumene cracking reaction to evaluate the activity of 100/140 mesh of LaY zeolite catalyst. Cumene accumulative conversion increases as the temperature increases from 360 to 500°C and increasing catalyst/oil (wt/wt) ratio from 0.004 – 0.016 at the same time on stream. Also it was observed that the accumulative conversion increases and reach a stable value at 200 sec time on stream at the same above conditions.

Lin et al. [21] studied the cumene fractional conversion over LaY zeolite vs. time on stream at several reaction temperatures (360-500°C), several space times (2.5- 10 ×10-3 gs/mol), and two particle sizes (-20 + 40 mesh) and (-60+80 mesh). A 10.8 mol% initial cumene conversion was observed at 360°C and 5.2×10-3 gs/mol. during the first 5 min and the rate of reaction decline as the time on stream increases at the same conditions, the conversion reaches 7.5 mol% at 141 min time on stream.

This work deal with the production of HX zeolite from locally kaolin and test it is cracking activity by cumene cracking.

Experimental work

Materials

Materials	Properties
Cumene	
Supplied by	BDH with 98% purity
Molecular weight	120.20 g/mol
Density	0.860 g/cm^3
Boiling point	423K
HY-Zeolite(CBV600)	Zeolyst International (UWE
Supplied by	Ohlrogge (VF)) as a powder .
	0.2
Na_2O(wt %)	5
SiO_2/Al_2O_3 mole ratio	24.3 Å
Unit cell	0.92
pore volume	660 m^2/g.
surface area	Linde company as pellets
Synthetic Zeolite type 13X	(3*5)mm .
Supplied by	14
Na_2O(wt%)	2.2
SiO_2/Al_2O_3 mole ratio	24.9 Å
Unit cell	0.35
pore volume	340 (m^2/g)
surface area	Al-Dewekhala Quarry in Al-
Kaolin(locally)	Enbar region.
The used kaolin is available in	53.49
SiO_2(wt%)	30.83
Al_2O_3(wt%)	0.22
Na_2O(wt%)	2.15
Fe_2O_3(wt%)	2.82
TiO_2(wt%)	0.056
CaO(wt%)	0.056
MgO(wt%)	0.422
K_2O(wt%)	9.956
L.O.I(wt%)	
Colloidal sodium silicate	
Ammonium Nitrate	BDH limited Poole England
Supplied by	.80.04 g/mole .
molecular weight	BDH limited Poole England
Sodium Hydroxide	40 g/mole .
Supplied by	High grade quality (purity 99.9
molecular weight	%) of nitrogen obtained from
Nitrogen	Al-Mansor factory

Preparation of H-X zeolite from kaolin

H-X zeolite is prepared by steps consisting essentially of:

1. Calcination of the raw kaolin at 550°C for 1 hr in a programmable electrical furnace (Model N_2O/H,Max. Temp. 1340^{o}C), after that, the kaolinite can be transformed to metakaolinite.
2. Sieving the metakaolinite to a particle size ≤75 µm.
3. The gel was prepared by mixing 5 ml of NaOH solution (10 wt% NaOH) with 1g colloidal sodium silicate. At low alkali concentration the reaction did not take place, because the crystallization speed was so low that no crystalline species were obtained as observed by Caballero et al. [22], and De Lucas et al. [23, 24]. So, at sodium hydroxide concentrations below 10%, the desired zeolite may not form [25].

The resulting solution was mixed with 1 g of metakaolinite in a 1000 ml round –bottom flask with two necks: one neck fitted with water –cooling reflux condenser, and the other neck with thermometer to measure the temperature, where the reaction was carried at atmospheric pressure. Agitation and heating of the flask were done by oil bath on magnetic heater stirrer, where the temperature of the mixture in the heated flask was kept constant by using voltage regulator .

The gel formation step was achieved at 60°C, for 1 hr. Caballero et al. [22] found that the stirring speed does not exert a strong influence on the zeolite relative crystallinity value, and it was only necessary to guarantee good gel homogeneity.

4.The aging step was done at room temperature and for 5 days [26] without agitation. The product will be more crystalline when aging the gel at low temperature before carrying out the high temperature crystallization [26].

5.Crystallization step was done at temperature 87±2°C [27] for 24 hours without agitation. At the end, the flask was quenching in cold water. 6.The next steps were decantation and washing several times with deionezed water until the PH value equal to 10 [28] then the powder was filtered in Buckner funnel with the aid of a vacuum pump. The drying was achieved at 120°C for 12 hr using a programmable electrical furnace(Model N_2O/H,Max. Temp. 1340^{o}C). After that, the product was milled to convert it to a fine powder, which was sieved to a particles size ≤ 75µm.

7. A 100 g of catalyst powder was prepared by mixing 25 g [4,29] of the binding material which is kaolin with 75g of catalyst powder.The resulted dry powder was mixed with deionezed water manually using spatula to form a paste.
8. The paste was placed in a cylindrical cavity of 2 cm inside diameter, and 10 cm long. Extrudates shapes were obtained when the paste was compressed manually. Very uniform spaghetti shaped paste was ejected and put in a porcelain crucible at room temperature overnight.

9. Extrudates were dried in a programmable electrical furnace at 120°C for 2 hr [4, 30]. The calcination was done at 550°C for 2 hr [4, 31]. Then the calcined extrudates were cut into 4-8 mm long.
10. Hydrogen-form catalysts were prepared by ion exchange method of the original catalyst with 3 N ammonium nitrite solution [32, 33]. Thus 120 g of ammonium nitrite in 500 ml deionized water was contacted with 50 g of catalyst in a continuous stirring for 2 hr at 90°C [28]. The pH of the solution was held constant at 7.5, and socking this catalyst in a fresh solution of ammonium nitrite with pH 7.5 at room temperature overnight. The extrudates were washed, filtered, and dried at 120°C for 2 hours [28]. The dried extrudates were calcined at 550°C for 4 hr. During calcination ammonia and water are liberated and decationized H-form zeolite is formed.

Preparation of H-X zeolite from Na-X standard zeolite

Hydrogen-form standard Na- X zeolite was prepared by ion exchange method of the original Na-X catalyst with 3 N ammonium nitrite solution [32,33]. Thus ,120 g of ammonium nitrite in 500 ml deionized water was contacted with 50 g of catalyst in a continuous stirring for 2 hr at 90°C [28]. The pH of the solution was held constant at 7.5, and socking this catalyst in a fresh solution of ammonium nitrite with pH 7.5 at room temperature overnight. This procedure repeated twice.

The extrudates were washed , filtered, and dried at 120°C for 2 hours [28]. The dried extrudates were calcined at 550°C for 4 hr. During calcination ammonia and water are liberated and decationized H-form is formed.

HY-Zeolite Shaping

1. A 70 g of HY-zeolite as a powder was mixed with 30 g montmorillonite clay as binder. The preferred binder content percent of mixing is between 15-30% as noticed by Allain et al. [34], Martens et al. [35]. The chemical composition of montmorillonite is: 51.3%SiO_2, 28.73%Al_2O_3, 1.3%Na_2O, 3.4% CaO, and 3.3 % MgO. The resulting mixture was mixed with water to form a paste.
2. Steps 8 and 9 used for prepared NaX zeolite were repeated to finalize HY-zeolite preparation.

Activity test

The cracking activity tests were performed in a continuous laboratory unit. The unit consists of feed tank, flow meter , feed pump, evaporator , reactor, separator , collector and cooler with appropriate control system for heating.The reactor was a carbon steel tube with an outside diameter of 1.9 cm, 2 mm thick and 80 cm length .A fresh catalyst was charged to the reactor between two layers of inert materials (glass balls).The activity was carried out at 823K, LHSV 1 h^{-1} , atmospheric pressure and at duration time ranging from 10-240 minutes.

Test method for liquid product analysis

Liquid products were trapped by condenser at -5C, collected periodically and analyzed by using gas chromatography. The gas chromatography model Packard 438A was used for the analysis .This device equipped with column of 0.25mm diameter ,50 m length and FID detector.

Results and Discussion

X-Ray Diffraction

The XRD test was used in the present work to study the crystal structure of the prepared catalysts.

Figure1. represent the X-ray pattern of the prepared Na -X zeolite. This pattern was compared with X-ray data of standard zeolites reported by [9] ,X-ray pattern of standard zeolite for HY (Figure 1) and HX (Figure 2). It was found that prepared NaX zeolite has a 52.17% crystallinity at D spacing 14.64e^{-8} ±0.1 , and has approximately the same crystal structure as the standard type NaX-zeolite .

Some differences are found among the X-ray diffraction data which can be attributed to the distribution of cation (sodium), different in silica to alumina mole ratio, and different in a mode of preparation.

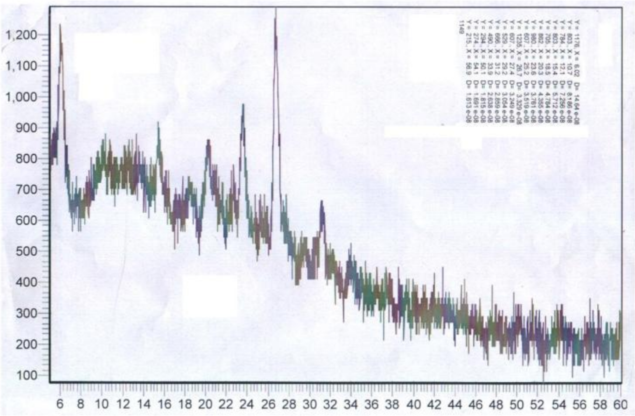

Fig. 1 X-Ray Diffraction Spectrum for the PreparedNa-X zeolite Catalyst After Adding the Binder .

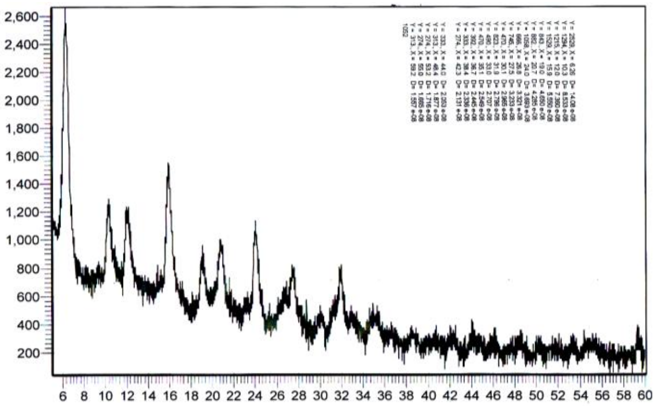

Fig. 2 X-Ray Diffraction Spectrum for the standard H-Y zeolite Catalyst After Adding the Binder .

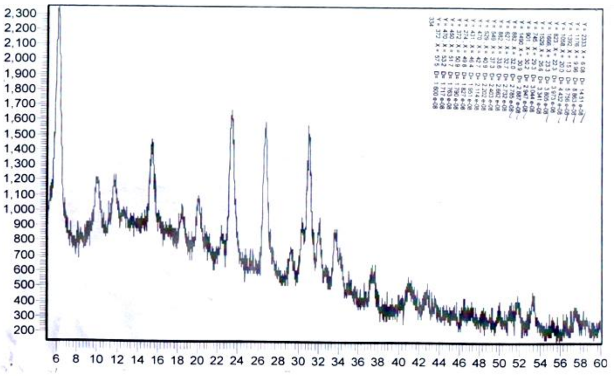

Fig. 3 X-Ray Diffraction Spectrum for the standard Na-X zeolite Catalyst After Adding the Binder.

Fourier Transforms Infra Red Spectroscopy (FTIR)

FTIR was used in this study to identify the structural properties of the catalysts HX-zeolite and prepared NaX zeolite before ion exchange, which contains fundamentals vibrations of the framework of silica-alumina tetrahedral, can be used in characterization of zeolite type. These vibrations include symmetric and asymmetric stretching and bending mode of Si $(Al)_4$ tetrahedral , and double ring vibration. Figures 4 and 5 show the spectrum of HX-zeolite and prepared Na X zeolite (before ion exchanges).

It was observed that the characteristic bands for the vibrations of HX-zeolite (fig.4) and FTIR data from Breack [9] and Chandrasekhar et al. [27], are symmetric due to asymmetric stretch at 970 and 1100 cm^{-1} and symmetric stretch at 750, 670, and 690 cm^{-1}, double ring 560 cm^{-1} and Si(Al)-O bands 455 cm^{-1} are clearly found in the prepared NaX zeolite So, the FTIR spectral analysis results support the XRD inferences.

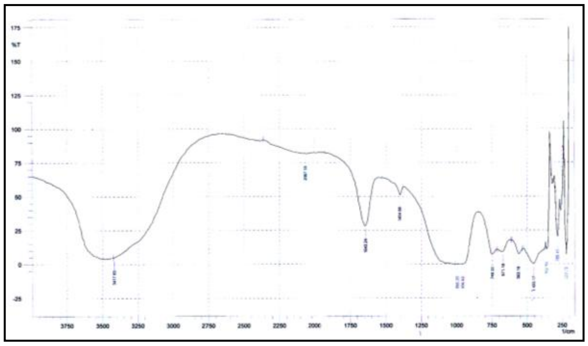

Figure 4 FTIR Spectrum of standard Na-X zeolite Before Ion Exchange.

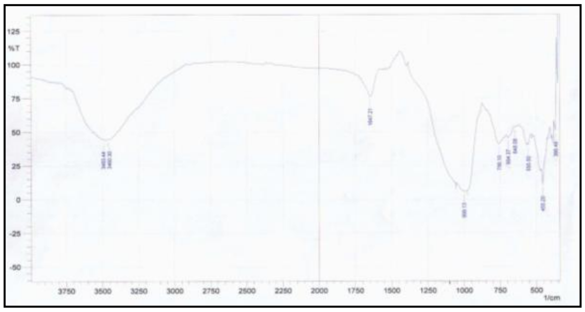

Figure 5 FTIR Spectrum of prepared Na-X zeolite Before Ion Exchange.

Surface Area

The physical properties of different catalyst were presented in Table 1 shows that commercial Y-zeolite powder has 660 m^2/g surface area and the surface area decreases to 546 m^2/g after adding a binder and shaped from a powder to extradite form. The surface area depends on many parameters such as type of binder used during shaping process and Si/Al ratio. As Si/Al increases the surface area decreases as noted for HY zeolite after adding binder. Bokhoven et al. [36] observed that the external surface area and pore volume for HMOR-26 significantly higher than that of HMOR-57 and found that increase in surface area and pore volume related to lower content of silica.Thus after adding a binder, Si/Al mol ratio increases from 5 to 6 and that surface area and pore volume decrease also because of applying pressure throughout the extrusion to form zeolite extradites was low. This is in agreement with the results published by Gates et al. [37].

Table 2, Physical Characteristics of the Catalysts.

Catalyst	HY Zeolite powder	HY Zeolite + binder	HX Zeolite	Prepared HX zeolite
Pore volume cm^3/gm	0.92	0.850	0.320	0.318
Bulk density g/cm^3		0.356	0.596	0.602
Porosity (%)		88.01	46.03	45.58
Surface area m^2/g	660.0	546.00	299.70	290.20
Si_2O/Al_2O_3 mole ratio	5.0	6.0	2.2	2.8

Catalyst Activity

Cumene cracking was chosen as a model to evaluate the activity of the prepared HX zeolite and to compare the results with the activity of the standard catalysts HY and HX catalysts.

Cumene conversions over the prepared and standard catalysts were determined at different duration times(time on stream).

Figure 6 represents the activity comparison of prepared and standard catalysts at temperature 823 K and LHSV 1 h^{-1}. As shown in this figure that the activity of cracking catalysts take the following order ; standard HY zeolite > prepared HX zeolite > standard HX zeolite . At 10 min, the cumene conversions were 52.38, 33.54 and 49.14 mol% for HY, HX and prepared HX zeolite, respectively . It was observed from this figure as the time on stream increases the cumene conversion decreases. Cumene conversions at 240 min decreased to 33.19, 21.2 and 20 mol%, respectively.

Usually the activity of cracking catalysts declines rapidly because of the accumulation of carbonaceous deposits on the catalyst surface at high time on stream values. The same phenomena was observed and reported in previous studies Donald and Wojciechowski [20],Lin et al. [21], William [38] and Yu Liu and Pinnavaia [39] .

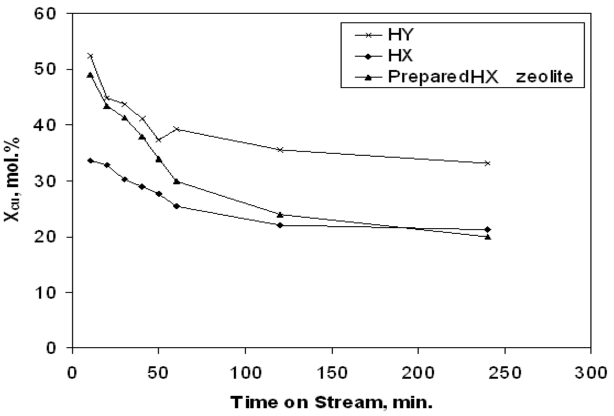

Fig. 6 The activity comparison of prepared and standard catalysts at temperature 823 K and LHSV 1 h^{-1}.

Conclusions:

According to the results obtained from this study, the following conclusions are deduced:

1. It was found from X-ray and FTIR tests that prepared Na X zeolite has a crystallinity 52.17% and nearly has the same crystal structure as the standard type 13X-zeolite with silica to alumina molar ratio 2.8 , and catalyst A did not represented any type of zeolite and it has very low activity.
2. It was observed that the activity of cracking catalysts take the following order ; standard HY zeolite > prepared HX zeolite > standard HX zeolite . At temperature 823 K , LHSV 1 h^{-1}, and 10 min, the cumene conversions were 52.38, 33.54 and 49.14 mol% for HY, HX and prepared HX zeolite, respectively .

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