Esterification of acetic acid over mesoporous Al-MCM-41 molecular sieves

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Abstract

Al-MCM-41 molecular sieves with Si/Al ratios 25, 50, 75 and 100 were synthesised and characterised by XRD, FT-IR, ^{27}Al-MAS NMR and BET techniques. Their catalytic activity in the esterification of acetic acid with amyl alcohol was studied in the vapour phase between 150 and 250 °C. The activity of the catalysts followed the order Al-MCM-41 (100) > Al-MCM-41 (75) > Al-MCM-41 (50) > Al-MCM-41 (25). The study of time on stream at 250 °C showed about 25% decrease in conversion at the end of 5 h. The influence of feed rate and feed ratio on conversion was also studied and the results are discussed.
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Keywords: Al-MCM-41 molecular sieves; Amyl alcohol; Esterification; Acetic acid; Amyl acetate

1. Introduction

Organic esters are important intermediates in the synthesis of fine chemicals, drugs, plasticisers, food preservatives, pharmaceuticals, solvents, perfumes, cosmetics and chiral auxiliaries [1]. Esterification is also an important reaction in synthetic organic chemistry, since it is a technique to protect carboxylic acid group in a molecule [2]. Commonly employed catalysts for this reaction are sulphuric acid, hydrogen chloride or sulphonic acid [3]. All these catalysts are hazardous and hence undesirable from the environmental point of view. Therefore, there is global effort to replace hazardous and environmentally harmful catalysts with ecofriendly alternatives [4]. Solid acid catalysts such as microporous crystalline aluminosilicate namely zeolites are convenient alternatives to such conventional acids. They have been used as catalysts since 1960s and although they are widely exploited in petrochemicals manufacture [5], their applications as catalysts are also expanding into areas of speciality and fine chemical synthesis [6,7]. But zeolites are microporous materials with much diffusional resistance both for reactants and products. It leads to unnecessary increase in the time requirement for establishment of equilibration in the liquid phase reactions. In this context compared to zeolites, the mesoporous Al-MCM-41 materials discovered by the researchers of Mobil oil company [8] may be convenient candidates as they have high surface area and large pore diameters with nearly nil diffusion constraint for both the reactants to enter and the products to leave their mesopores. Their activity for esterification in liquid phase has already been documented in the literature [9]. Generally in liquid phase esterification the equilibrium for the stoichiometric mixture is reached at about 66–68% [10] conversion for straight chain saturated alcohol; complete conversion can only be achieved by elimination of the water formed. But it is known that the same reaction may be thermodynamically favoured when performed in the vapour phase due to the higher values of equilibrium constants in comparison with those of the liquid phase [11].

Based on these reports in the present investigation it has been planned to study esterification of acetic acid with amyl alcohol in the vapour phase over Al-MCM-41 molecular sieves. The reaction was also studied earlier by Berg and Yeh [12] by extractive distillation techniques. Ternary azeotropes were found in the mixtures of amyl alcohol, amyl acetate and water. Lee et al. [13–15] studied the kinetics

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of the reaction and the data were correlated by a quasi-homogeneous model. The reaction was also studied by Lee et al. [16] over Amberlyst-15 and the kinetics was correlated by a modified Langmuir–Hinshelwood model. There is much demand for amyl acetate, as it has been widely employed as solvents. Amyl alcohol conversion of more than 90% is reached in this study and the reaction parameters that have control on the conversion are presented and discussed.

2. Experimental

2.1. Materials and methods

Al-MCM-41 molecular sieves with Si/Al ratios 25, 50, 75 and 100 were synthesised hydrothermally according to the following reported procedure. Sodium metasilicate (E-Merck) and aluminium sulphate (E-Merck) were used as the sources for silicon and aluminium respectively and CTAB (E-Merck) was used as structure-directing template. The mesoporous materials were crystallised from the gel of composition SiO_2:0.2 $CTAB$:X Al_2O_3:0.89 H_2SO_4:120 H_2O (X varies with the Si/Al ratio).

In a typical synthesis, 10.6 g of sodium metasilicate dissolved in demineralised water was added to appropriate amount of aluminium sulphate. It was then acidified with 1 M H_2SO_4 to bring down the pH of the solution to 10.5. After 30 min of stirring, CTAB in 20 ml of water was added and the stirring continued for another 60 min. The resultant gel was autoclaved and kept in an oven for 2 days at 145 °C. The solid obtained was filtered and dried at 100 °C. The sample was then calcined at 525 °C in air for 5 h in muffle furnace to remove the template present in the catalyst.

2.2. Characterisation

The XRD powder diffraction patterns of the calcined mesoporous Al-MCM-41 (Si/Al ratio 25, 50, 75 and 100) molecular sieves were obtained from Stereo Scan diffractometer using nickel-filtered Cu Kα ($\lambda = 1.54$ nm) radiation and a liquid nitrogen cooled germanium solid-state detector. The diffractograms were recorded in the 2θ range of 0–10° in the steps of 0.02° with a count time of 10 s at each point.

Surface area, pore volume and pore size distribution were measured by nitrogen adsorption at 77 K with ASAP-2010 porosimeter from Micromeritics Corporation Norcross, GA. The samples were degassed at 350 °C and 10^{-5} Torr overnight prior to the adsorption experiments. The mesopore volume was estimated from the amount of nitrogen adsorbed at a relative pressure of 0.4 by assuming that all the mesopores were filled with condensed nitrogen in the normal liquid state. Pore size distribution was estimated using the Barrett, Joyner and Halenda (BJH) algorithm (ASAP-2010) built-in software from Micromeritics.

FT-IR spectra of the mesoporous Al-MCM-41 molecular sieves were collected on Nicolet (Avatar 360) instrument using KBr pellet technique. About 10 mg of the sample was ground with about 200 mg of spectral grade KBr to form a pellet under hydraulic pressure to record the IR spectrum in the range 400–4000 cm^{-1}.

Solid-state ^{27}Al-MAS NMR spectra of Al-MCM-41 (25, 50, 75 and 100) were recorded using MSL 400 spectrometer equipped with a magic angel spinning (MAS) mass unit to analyse the aluminium environment. The ^{27}Al chemical shifts are reported in relation to liquid solution of aluminium nitrate.

2.3. Acidity measurements

The acidity of Al-MCM-41 was analysed by pyridine adsorption followed by FT-IR study. The catalyst sample was finely ground and pressed into a self-supporting wafer. The wafers were calcined under vacuum at 500 °C for 2 h, followed by exposure of pyridine vapour. The wafers were allowed for 1 h to adsorb the pyridine. The thin wafer was placed in the FT-IR cell and the spectrum was recorded on a Nicolet 800 (Avatar) FT-IR spectrometer. The difference between the spectra of pyridine adsorbed on the samples and that of reference was obtained by subtraction.

2.4. Esterification of acetic acid

Esterification of acetic acid with amyl alcohol was carried out in a fixed-bed, vertical-flow type reactor made up of a glass tube 40 cm in length and 2 cm in internal diameter. About 0.5 g of the catalyst was placed in the middle of the reactor and supported on either side with a thin layer of quartz wool and ceramic beads. The glass reactor was heated to the requisite temperature with the help of a tubular furnace controlled by a digital temperature controller cum indicator. The reactants were fed into the reactor using a syringe infusion pump (SAGE instruments) that could be operated at different flow rates. The reaction was carried out at atmospheric pressure. The bottom of the reactor was connected to a coiled condenser and a receiver to collect the products. The products collected in the first 10 min were discarded, and the products collected after 1 h were analysed for identification. After each catalytic run, the catalyst was regenerated by passing moisture and carbon dioxide free air through the reactor for 6 h at 500 °C.

The percent conversion of amyl alcohol was analysed in a gas chromatograph (Shimadzu GC-17A) with FID detector equipped with a 25 m capillary column (cross-linked 5% phenyl methyl polysiloxane).

3. Results and discussion

3.1. Characterisation

The XRD powder diffraction patterns of the as-synthesised and calcined mesoporous catalysts show an intense

Table 1
Physical characteristics of Al-MCM-41 (25), Al-MCM-41 (50), Al-MCM-41 (75), Al-MCM-41 (100)

Catalysts	Calcined		Uncalcined		Surface area (m²/g)	Pore size (nm)	Pore volume (cm³/g)
	d_{100} (A°)	Unit cell (nm)	d_{100} (A°)	Unit cell (nm)			
Al-MCM-41 (25)	37.81	4.37	38.47	4.44	951	3.485	0.964
Al-MCM-41 (50)	37.45	4.32	38.47	4.44	982	3.190	0.970
Al-MCM-41 (75)	37.45	4.32	38.19	4.41	1035	2.661	0.952
Al-MCM-41 (100)	37.81	4.36	38.19	4.41	1042	2.665	0.952
Recycled catalyst							
Al-MCM-41 (100)	37.31	4.31	–	–	1030	2.601	0.930

diffraction peak between range 1.8° and 2.2° (2θ) due to [1 0 0] plane and small peaks due to [1 1 0], [2 0 0], [2 1 0] planes confirming the hexagonal mesophase of the materials [17]. The d_{100} spacing and lattice parameter (a_0) calculated as per the literature procedure are presented in Table 1. BET surface area, pore size and pore volume for calcined materials are presented in Table 1. Similar values were also reported for mesoporous materials [18,19]. The FT-IR spectra of the as-synthesised and calcined Al-MCM-41 (Si/Al = 25, 50, 75 and 100) molecular sieves also appear similar to those reported earlier [20].

The FT-IR spectra of Al-MCM-41 (25, 50, 75 and 100) containing adsorbed pyridine are presented in the Fig. 1. The peak at 1545 cm⁻¹ in all the spectra with intensities decreasing from Si/Al (25) to Si/Al (100) is assigned to pyridine adsorbed on the Bronsted acid sites of the catalysts. The peaks at 1455 and 1620 cm⁻¹ whose intensity decreases from Si/Al (25) to Si/Al (100) is assigned to the pyridine adsorbed on the Lewis acid sites. It suggests the presence of more amount of non-frame work aluminium in Al-MCM-41 (25). The peak at 1500 cm⁻¹ indicates the pyridine adsorbed on both Bronsted and Lewis acid sites. The intensities of the peaks due to pyridine adsorbed on Bronsted acid sites correlate with Si/Al ratio of the catalysts [21].

The ²⁷Al-MAS NMR spectra of Al-MCM-41 (25, 50, 75 and 100) are illustrated in the Fig. 2. The spectra of cal-cined samples present a resonance peak close to 53.7 ppm, which is assigned to structural tetrahedrally co-ordinated aluminium [22]. A weak signal around 0.6 ppm represents hexa co-ordinated aluminium belonging to extra-structural species formed during calcination [23,24].

3.2. Catalytic reaction

3.2.1. Effect of temperature

Esterification of acetic acid with amyl alcohol was studied over Al-MCM-41 (25, 50, 75 and 100) at 150, 200 and 250 °C. The reactants ratio (amyl alcohol/acetic acid) was maintained at 2:1, and WHSV at 3.77 h⁻¹. The product was only amyl acetate with 100% selectivity at all the temperatures. The plot of amyl alcohol conversion versus temperature is shown in the Fig. 3. The conversion increased with increase in temperature due to increase in the removal of the by-product water formed in the reaction. Water acting as an adsorption poison over solid acid catalysts has also been reported in the literature [25]. But reaction temperature above 250 °C was not advantageous for this reaction, as the yield of ester was very insignificant.
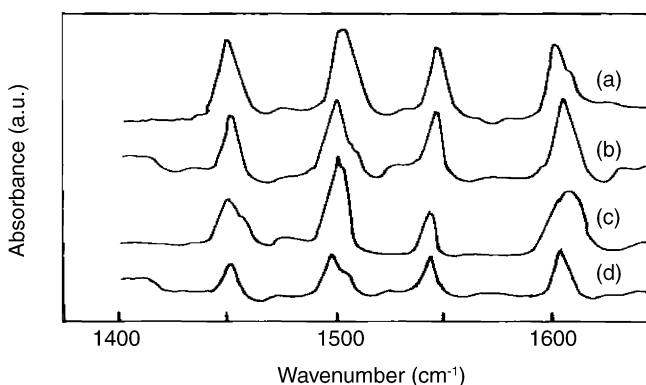

Fig. 1. FT-IR spectrum of (a) Al-MCM-41 (25), (b) Al-MCM-41 (50), (c) Al-MCM-41 (75) and (d) Al-MCM-41 (100) catalysts containing adsorbed pyridine.
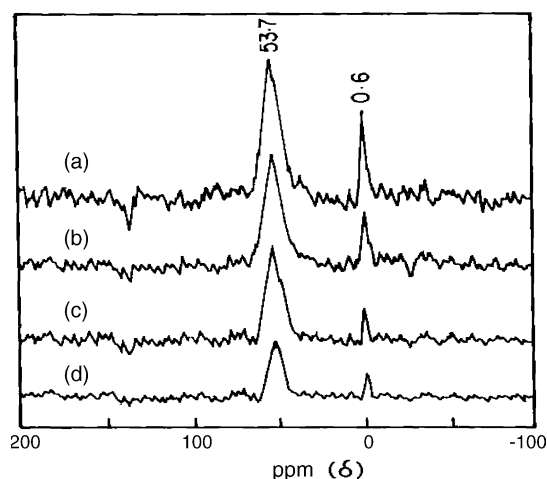

Fig. 2. ²⁷Al-MAS NMR spectrum of Al-MCM-41 molecular sieves after calcination. (a) Al-MCM-41 (25), (b) Al-MCM-41 (50), (c) Al-MCM-41 (75) and (d) Al-MCM-41 (100).
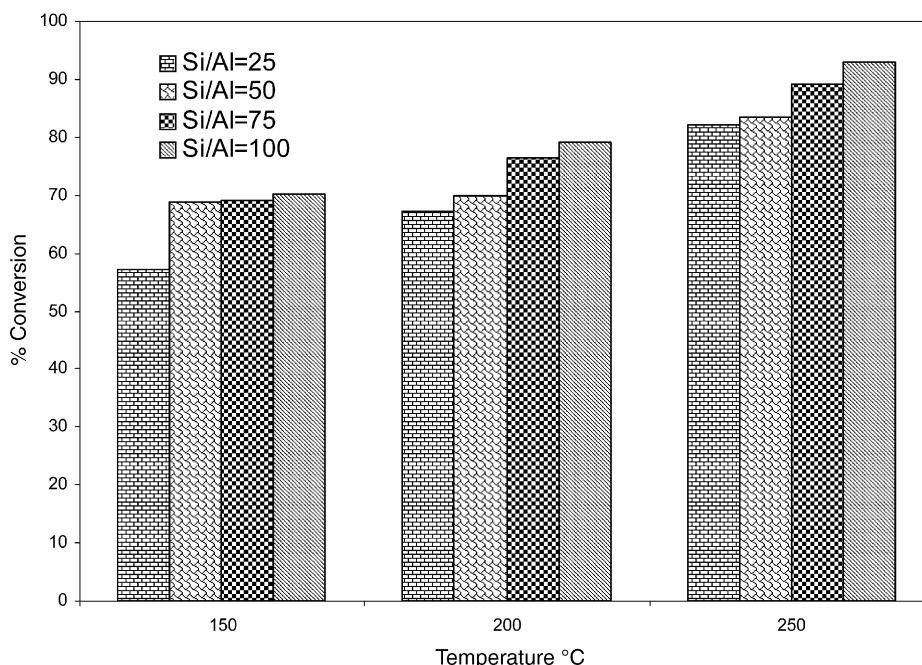
Fig. 3. Variation of temperature in the vapour phase over all the catalysts. Feed ratio (amyl alcohol:acetic acid) 2:1, flow rate 2 ml/h, conversion of amyl alcohol, selectivity 100% amyl acetate.

Hence the alcohol might get decomposed to yield poly olefinic products at high temperatures, but none of such products was observed in the product mixture. High conversion was obtained over MCM-41 with high Si/Al ratios. Since, they are more hydrophobic once water is produced it will be easily be expelled from the pores thus avoiding its poisoning effect. These suggestions account for the order of activity of the catalysts Al-MCM-41 (100) > Al-MCM-41 (75) > Al-MCM-41 (50) > Al-MCM-41 (25). Yet another advantage for high silica materials is the hydrophobic amyl alcohol can better be brought into the pores than those with low Si/Al ratios, which are less hydrophobic. In addition, the strength of Bronsted acid sites of the catalysts with higher Si/Al ratio is also high.

With increase in temperature conversion increased, hence the reaction might be more activation energy demanding. The formation of the ester can be accounted by the protonation of the acid as the rate determining step of the reaction. It is also supported by the formation of only one product, amyl acetate, without producing isomeric esters. Hence acetic acid might be chemisorbed until 250 °C and above 250 °C, there might be a reversal of adsorption, as the ester was not obtained. Hence, at higher temperatures either the alcohol could be chemisorbed and decomposed, or there might be thermal decomposition to different products. In order to verify this, amyl alcohol was passed through the reactor tube without the catalyst. No decomposition was observed. Hence, above 250 °C, there must be catalyst aided decomposition of amyl alcohol into olefinic oligomers that deactivated the catalysts.

3.2.2. Effect of feed ratio

By considering the economic factor excess of acetic acid, which is cheaper than amyl alcohol, was used to get the maximum yield of ester. The effect of feed ratio (amyl alcohol/acetic acid) was examined with feed ratios 1:1, 1:2, 1:3 and 1:4 over Al-MCM-41 (100) at 250 °C with the feed rate 2 ml/h. The results are illustrated in the Fig. 4. Conversion was less at the feed ratio 1:1 than at other feed ratios. But conversion was nearly 100% with the feed ratio 1:2. But above 1:2, conversion decreased. It might be due to dilution of alcohol by acid. But, dilution effect might not be much important, as the conversion was 91% even at the feed ratio
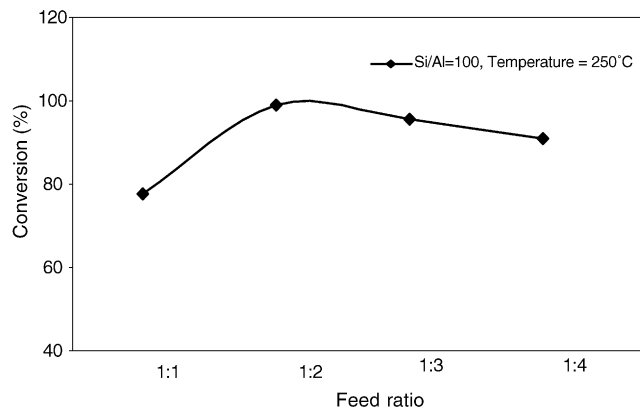

Fig. 4. Effect of feed ratio over Al-MCM-41 (100). Temperature 250 °C, feed ratio (amyl alcohol:acetic acid), conversion of amyl alcohol, selectivity 100% amyl acetate.
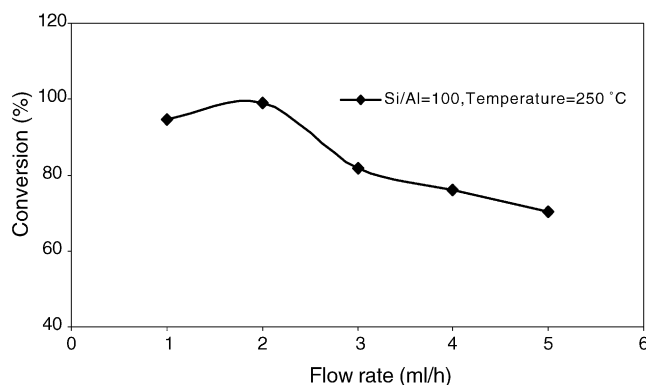
Fig. 5. Effect of feed rate over Al-MCM-41 (100). Temperature 250 °C, feed ratio (amyl alcohol:acetic acid) 1:2, conversion of amyl alcohol, selectivity 100% amyl acetate.

Fig. 7. X-ray diffraction pattern of Al-MCM-41 (100) (a) calcined sample (b) recycled catalyst after calcination.

1:4. In order to verify this dilution effect the reaction was also performed by running the reaction in the presence of 1,4 dioxane, in the feed ratio (amyl alcohol:acetic acid:1,4 diox-ane) 1:4:1. The conversion was reduced to 79% in line with our view.

3.2.3. Effect of flow rate

The effect of flow rate on conversion was studied over Al-MCM-41 (100) with feed ratio 1:2 (amyl alcohol/acetic acid) at 250 °C. The results are illustrated in Fig. 5. At the feed rate 1 ml/h, the conversion was slightly less than that of 2 ml/h, but above 2 ml/h, conversion gradually decreased. The decrease in conversion with increase in the flow rate might be due to rapid diffusion of the reactants with decreased chemisorption on the catalyst surface. The less conversion at 1 ml/h also revealed unattainment of steady state.

3.2.4. Time on stream

The effect of time on stream on amyl alcohol conversion was examined over Al-MCM-41 (100) at 250 °C with the feed ratio 1:2 (amyl alcohol/acetic acid), and flow rate 2 ml/h. The results are illustrated in Fig. 6. Conversion decreased with in-
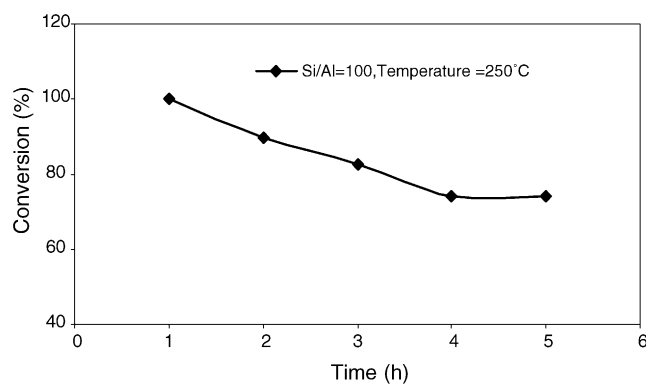

Fig. 6. Time on stream over Al-MCM-41 (100). Temperature 250 °C, feed ratio (amyl alcohol:acetic acid) 1:2, flow rate 2 ml/h, conversion of amyl alcohol, selectivity 100% amyl acetate.
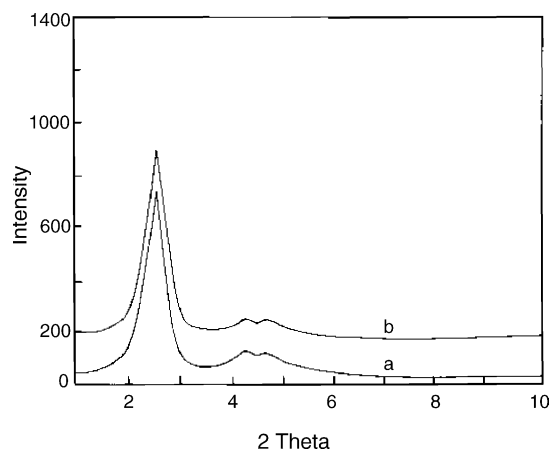
crease in stream due to coke formation. Since the decrease in conversion was slow and the maximum decrease was about 26% at the end of 5 h of stream, there might be diffusional constrain either for the reactant or for the products inside the pores. But the product was only ester, hence the olefinic products that could be formed might have reacted fast to yield the coke based products inside the pores. The hydrophobic property of the channel could assist the coke formation, as the hydrophobic olefins could be better retained inside pores. Although chemisorption of acetic acid on the Bronsted acid sites was suggested for subsequent reaction with amyl alco-hol, chemisorption of the latter might not be avoided due to formation of coke.

In order to establish the sustainability of the catalyst, the catalyst was regenerated after calcination in air for 5 h. Then it was subjected to XRD analysis. The spectrum is shown in Fig. 7. For comparison, the spectrum of calcined material is also presented in the same figure. The spectra illustrate no significant loss in crystallinity and also hexagonal mesopores nature of the catalyst.

4. Conclusion

Study of vapour phase esterification of acetic acid with amyl alcohol over Al-MCM-41 illustrates the process is suc-cessful and more convenient than the liquid phase esterifi-cation. More hydrophobic Al-MCM-41 (100) was found to be more active than other catalysts with less Si/Al ratios. Increase in conversion with increase in temperature estab-lished requirement of high activation energy for the reaction. It might be due to ternary azeotrope formation. Formation of amyl acetate without producing other isomeric esters is an advantage in this study. Although decrease in conversion with increase in stream was observed, the maximum decrease at the end of 5 h of stream was found to be only 26%. It is es-tablished that chemisorption of acetic acid on the active sites of the catalyst is the rate determining step of this reaction.

But chemisorption of amyl alcohol to give olefinic products and their further reaction to give coke was also suggested.

Acknowledgement

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