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One-Pot Synthesis of Dimethyl Carbonate from Methanol, Propylene Oxide and Carbon Dioxide Over Supported Choline hydroxide/MgO

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Abstract A basic ionic liquid, namely choline hydroxide, was prepared and supported on MgO to form Choline hydroxide/MgO material. The supported ionic liquid material was characterized by XRD, FT–IR and TG and used as a catalyst in one-pot synthesis of dimethyl carbonate from propylene oxide, methanol and carbon dioxide. A good catalytic performance was obtained with 98% conversion of epoxide and selectivity of above 90% to DMC + PC over the composite catalyst. However, the catalyst could be reused three times without a significant change in its catalytic activity.

Keywords Ionic liquid · Dimethyl carbonate · Methanol · Carbon dioxide · Propylene oxide

1 Introduction

Dimethyl carbonate (DMC) is a green chemical that has been paid too much attention in recent years. It can be effectively used as an environmentally benign substitute for highly toxic phosgene and dimethyl sulfate in carbonylation and methylation reaction, as monomer for several types of polymers and an intermediate in the synthesis of pharmaceutical and agricultural chemicals [1]. Also, DMC can be used as a promising octane booster due to its high oxygen content [2]. Currently, DMC is produced by phosgene and non-phosgene route, but phosgene route is limited for the use of toxic phosgene. For the non-phosgene route, DMC is mainly prepared by the oxidative carbonylation of methanol and the two-step transesterification from epoxide, methanol and CO_2 in the bulk production. However, the oxidative carbonylation of methanol suffers from the low production rate, the need for corrosion resistant reactors, the toxicity and potential explosion of carbon monoxide. Besides, the major disadvantages of this two-step process are high energy consumption, high investment and production costs due to the requirement of the intermediate separation, i.e., cyclic carbonate. The one-pot synthesis of DMC from carbon dioxide, methanol and ethylene or propylene oxide shown in Scheme 1 was, therefore, developed in order to avoid the separation of the intermediate ethylene or propylene carbonate in the two step trans-esterification. Several catalysts, such as inorganic base composites and/or basic metal oxide [3–6], $Re(CO)_5Cl/K_2CO_3$ [7], KOH/4A molecular sieve [8], n-Bu_4NBr/n-Bu_3 N [9], [bmim]/BF_4 [10], Mg containing.

Smectite [11], heterogeneous anion exchange resins [12] and inorganic base/phosphonium halide functionalized polyethylene glycol [13] etc. have been employed for the one-pot synthesis of DMC. But, most of these systems suffer from several drawbacks such as lower activity and selectivity to DMC, difficult recycle of these catalysts and rigorous reaction conditions from a practical point of view.

In the present investigation, a supported basic ionic liquid-choline hydroxide/MgO was prepared and used as a catalyst for the direct synthesis of DMC from CO_2, methanol and propylene oxide under milder conditions. The effect of various reaction and catalyst preparing conditions on the reaction was investigated. Recycle and reusability of the catalyst was carried out.

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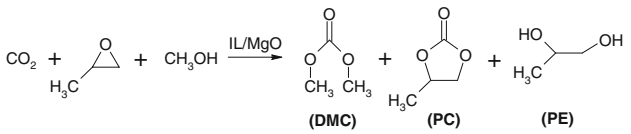


Scheme 1 Reaction equation

2 Experimental

2.1 Preparation of Supported Ionic Liquid Material

Methanol, choline chloride and KOH in term of molar ratio of 1:1 were charged in a three-neck flask fixed with a condenser and magnetic stirrer. The reactor was then heated to 60 °C in water bath under stirring strongly for 12 h. After cooling to room temperature, the mixture reaction solution was filtered to remove solid KCl and choline hydroxide solution was obtained (Fig. 1). Then MgO was added to the solution and stirred strongly at room temperature for 4 h. The mixture solution was vaporized under reduced pressure to afford a yellow solid. The obtained solid was calcined at 120 °C to yield supported basic ionic liquid choline hydroxide on MgO, nominated as CH/MgO in the next section.

2.2 Procedures of the Reaction

All experiments were carried out in a stainless reactor with inner volume of 500 mL provided with a mechanical stirrer and an electric heater. Certain amounts of methanol, propylene oxide (PO) and the catalyst (CH/MgO) were added to the reactor. After being purged three times with CO_2, the reactor was pressured to a certain pressure and heated to the desired temperature under stirring. After the required time of 2–10 h, the reaction mixture was cooled, distilled, sampled and analyzed by GC and GC–MS.

2.3 Characterization

IR spectrum of the supported material and CH was recorded on Nicolet 360 FT-IR spectrophotometer with pressed KBr pellet and liquid film in the 4,000–400 cm^{-1} region; its thermal stability was analyzed with thermogravimetric analysis performed on a PE Diamond instrument (Perkin–Elmer) in static air with a heating rate of 5 °C/min from 25 to 400 °C. Powder X-ray diffraction pattern of the sample was recorded on a D/max-rB X-ray diffractometer (RIGAKU) using Cu Kα radiation.

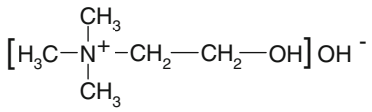


Fig. 1 Choline hydroxide molecule

3 Results and Discussion

3.1 Characterization of the Catalyst

3.1.1 XRD

Figure 2 illustrates X-ray powder diffraction pattern of CH/MgO sample as compared with pattern of MgO. The results showed that the two diffraction patterns are almost the same except for several peaks that are ascribed to amorphous organic CH found in the range from 15 to 30°, exhibiting that this catalyst is a composite composed from crystalloid MgO and amorphous CH.

3.1.2 FT–IR

Figure 3 shows the IR spectra of composite CH/MgO and CH recorded by pressed KBr pellet and liquid film, respectively. As can be seen by comparison of the two spectra, both are elementally the same (Fig. 3a, b). This implies that the composition and structure of CH was retained in the composite, although the composite has already been heated in the course of the preparation. This material is surely formed by CH supported on MgO.

3.2 Influence of the Catalyst Preparing Conditions on the Synthesis

3.2.1 Calcined Temperature

It was known from previous reports that the one-pot synthesis of DMC from methanol, PO and CO_2 was carried out by the following two steps: PO firstly reacts with CO_2 to form intermediate propylene carbonate (PC), then the trans-esterification of PC with methanol successively takes place to generate DMC accompanied with propylene glycol

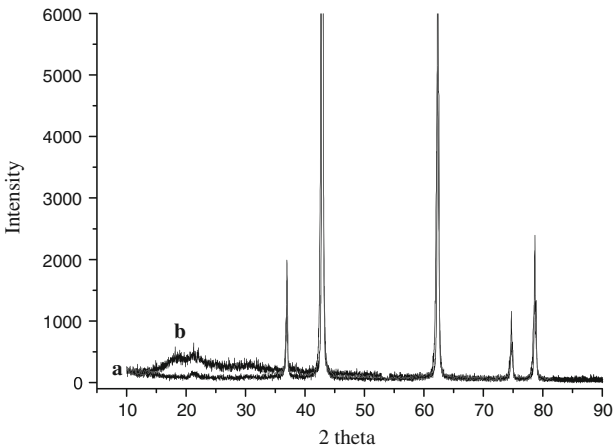


Fig. 2 XRD patterns of CH/MgO *b* and MgO *a*

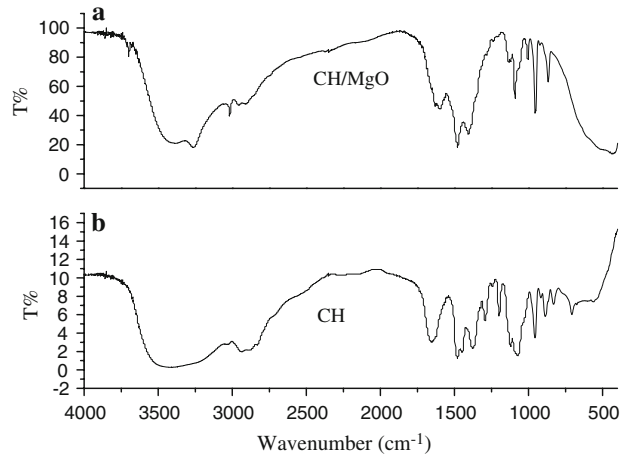
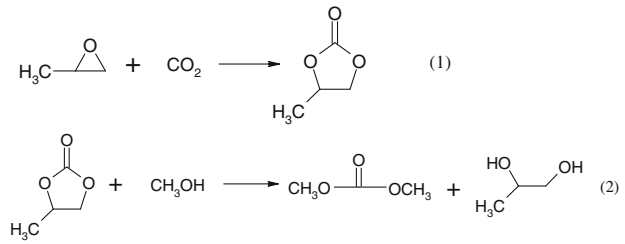


Fig. 3 FT-IR of CH/MgO *a* and CH *b*

(PG). The reaction equation was shown in Scheme 2. Figure 4 shows dependence of the calcined temperature in the course of the catalyst preparation on conversion of PO, selectivity of PC and DMC, along with yield of DMC. One can see unconspicuous decrease in PO conversion with the temperature increase. In the case of PC and DMC selectivity, we observed a remarkable decline of DMC selectivity and increase in PC selectivity over 160 °C, showing that higher treated temperatures play a suppressive role for the step (2). This behavior may be relative to decomposition of CH supported on MgO at higher treat temperature and it is validated by TG and DTG of the catalyst, shown in Fig. 5. Three stages of weight loss were observed in TG curve, the first one in the range from 50 to 100 °C stands for loss of water that the IL absorbed; the second from 150 to 200 °C may be attributed to the decomposition of CH supported on MgO and the last one is probably corresponding to the release of water molecules formed by hydroxyl radicals on the surface conjectured by the composition of the material. At last, the yellow solid sample was changed to be white solid MgO. The TG and DTG curves suggested that remarkable decrease in the yield and selectivity of DMC is surely ascribed to decomposition of the catalyst at above 160 °C and the decomposition is almost independent of the reaction of PC formation. 120 °C is found to be a suitable temperature for the catalyst preparation in order to keep its solid state and better catalytic performance.



Scheme 2

3.2.2 CH/MgO Ratio and Other Basic Substances

In order to reveal the influence of amount of CH supported on MgO on the reaction, a series of catalysts composed of various CH/MgO ratios were prepared and used as catalysts for the reaction. As shown in Fig. 6, the increase in amount of CH supported on MgO leads to the decrease of PC selectivity, that is, increase of CH amount can effectively accelerate the step (2). The selectivity and yield of DMC were increased in the range of supported amount from 0.5 to 10 mmol/g; and then excessive amount of CH results in the decrease of DMC selectivity and yield, while the co-reaction was surely promoted to generate by-products such as 1-methoxy-2- propanol and 2-methoxy-1-propanol via the reaction of methanol with epioxide due to the increase in the basicity of the catalyst.

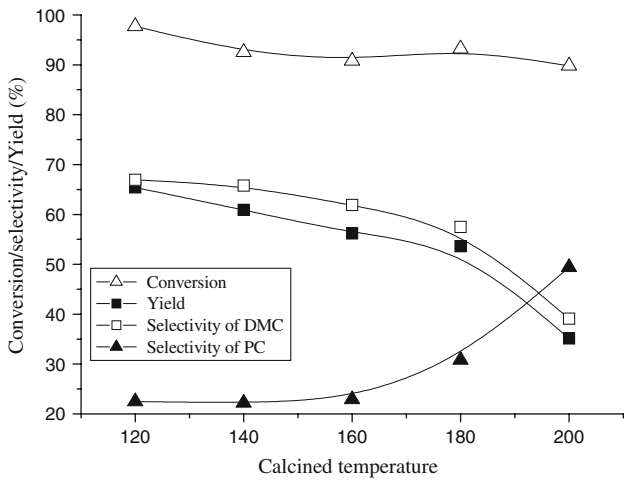


Fig. 4 Effect of calcined temperature on the synthesis of DMC

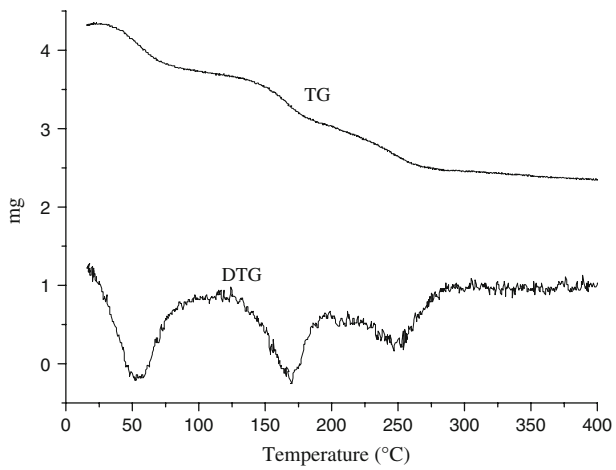


Fig. 5 TG and DTG of the catalyst

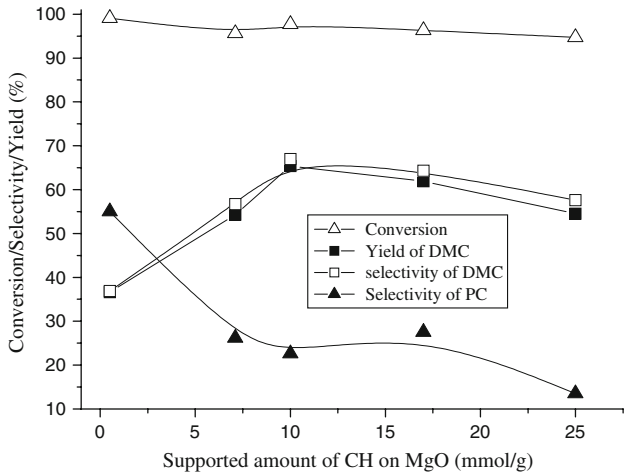


Fig. 6 Effect of supported amount of CH on the synthesis of DMC

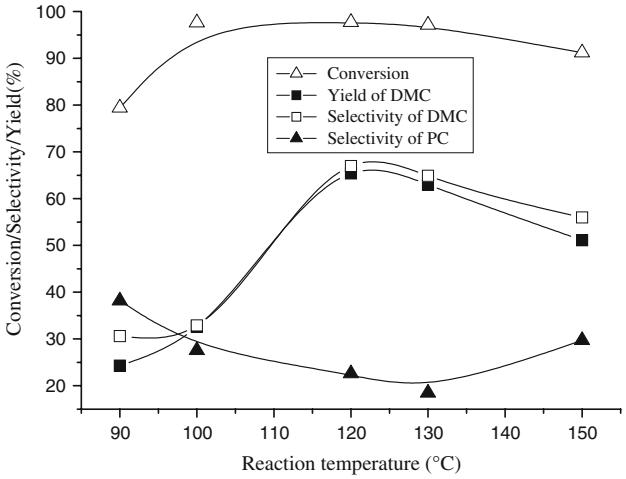


Fig. 7 Effect of reaction temperature on the synthesis of DMC

However, it is noteworthy that the yield of DMC is only 11.2 and 44.1% with the conversion of about 98% under the same conditions when MgO and CH were solely used as catalysts, respectively, and at the same time, the catalytic performance of other basic substances such as bmimOH, bmimOH/MgO and NaOH for the reaction was also investigated. These three basic catalysts displayed lower activity to the one-pot synthetic reaction with 33.8, 48.7 and 20.3% of the yields, respectively, as shown in Table 1. These findings implied that cations composed of ionic liquids have remarkable impact on the reaction and CH/MgO composite has remarkable increment action for the one-pot synthesis of DMC.

3.3 Influence of Various Reaction Conditions

3.3.1 Reaction Temperature

As the reaction temperature was raised, the conversion of PO was increased to the highest value of 98%. Above 120 °C, the conversion was slightly declined as shown in Fig. 7. Optimal yield and selectivity of DMC was obtained at 120 °C. Both the yield and selectivity fallen down over this temperature. Contrarily, the selectivity of PC increased over that temperature. These findings reveal that high reaction temperature accelerates the reaction of steps (1) and (2) in viewpoint of reaction kinetics. But it is changed to be thermodynamic control at higher reaction temperature, where high temperature is mainly disadvantageous of the step (2) by causing the decomposition of the catalyst, resulting in the decrease of the selectivity and yield of DMC. At the same time, high temperature is also advantageous of co-reaction to form ethers. As a result, 120 °C was selected as feasible reaction temperature to achieve higher conversion of PO and yield of DMC.

Table 1 Comparison of CH/MgO with other basic catalysts

Catalysts	Yield (%)	Selectivity (%)
CH/MgO	65.4	66.9
MgO	11.2	13.8
Choline	44.1	46.0
bmimoh	33.8	36.0
bmimOH/MgO	48.7	49.6
NaOH	20.3	20.5

3.3.2 Molar Ratio of CH_3OH/PO

With CH_3OH/PO molar ratio increase, the conversion and PC selectivity was smoothly increased, as shown in Fig. 8, showing that the decrease in relative amount of PO brings on increase of the percent conversion and accumulation of PC in the system. However, the yield and selectivity of DMC was increased with the CH_3OH/PO ratio up to 20/1, and then

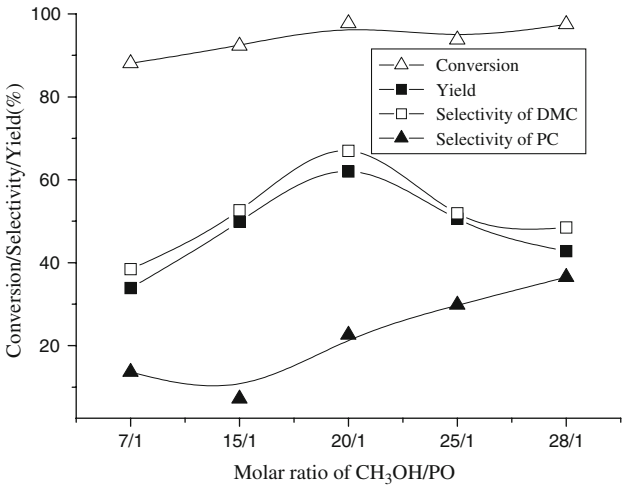


Fig. 8 Effect of CH_3OH/PO molar ratio on the synthesis of DMC

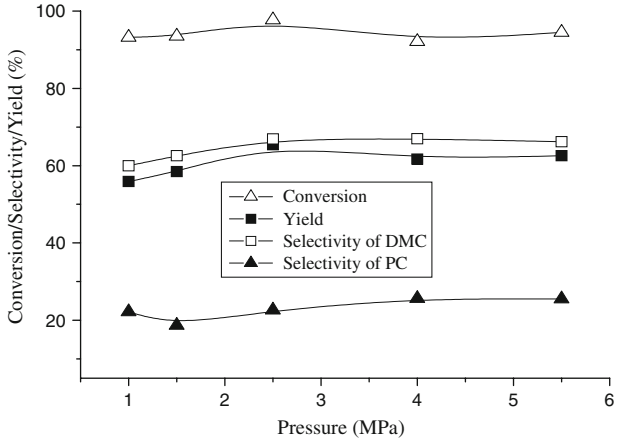


Fig. 9 Effect of reaction pressure on the synthesis of DMC

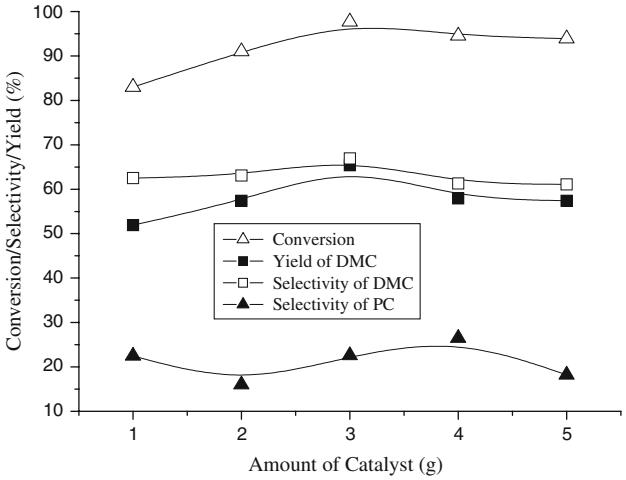


Fig. 10 Effect of catalyst amount on the synthesis of DMC

it falls down when the ratio successively augments. The decrease of DMC yield and selectivity over 20/1 ratio was likely ascribed to high ratio retarding the rate determined step (2) due to the dilute effect of methanol to PC produced in the step (1).

3.3.3 Reaction Pressure

The effect of reaction pressure on the synthesis of DMC was also investigated and the results are shown in Fig. 9. When the pressure increased from 1.0 to 2.5 MPa, the yield slightly increased from 55.9 to 65.4%. The pressure further increase leads to the yield of DMC basically holding invariable. Besides, the effect of CO_2 pressure on the conversion and PC selectivity is very similar to the former. That is, in the presence of CH/MgO composite as catalyst, the one-pot synthesis reaction is changed to be insensitive to the reaction pressure.

3.3.4 Amount of the Catalyst Used

The dependence of the synthesis reaction on catalyst amount used was investigated. As shown in Fig. 10, the shortage or excessive amount of the catalyst should lead to slightly low yield of DMC. The former is ascribed to deficient reaction causing the decrease in the conversion when less amount of the catalyst is used and the latter is due to excessive amount of the catalyst causing the co-reaction, such as the reaction of PO with methanol to produce ethers, accelerated. As a result, the DMC selectivity declined.

3.3.5 Reaction Time

Figure 11 shows the time course of the synthesis reaction of DMC from methanol, PO and CO_2. Obviously, the yield

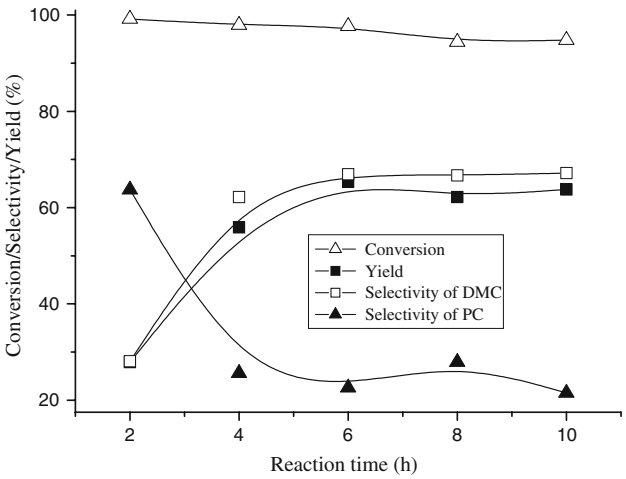


Fig. 11 Effect of reaction time on the synthesis of DMC

and selectivity of DMC were increased gradually with the time prolonging up to 6 h. However, the increase in the yield was small in the period of 6–10 h, suggesting that the reaction thermodynamic equilibrium was achieved. The conversion of PO reached at about 100% at 2 h, indicating the step (1) is really rapid reaction and the (2) is rate determined step.

3.4 Reusability of the Catalyst

In order to evaluate performance of the composite catalyst, reuse experiments of the catalyst were carried out. The catalyst was separated out by distillation under reduced pressure in the end of the reaction and then reused for the next run under the same conditions. The results as shown in Table 2 indicated that the yield and selectivity of DMC was not affected even at the third run with the reused CH/MgO.

Table 2 The reusability of the catalyst

Used times	Yield (%)	Selectivity (%)
1	65.4	67.0
2	60.1	68.5
3	59.0	68.2
4	20.8	22.0

This finding implied that the composite catalyst can be recovered and recycled efficiently. Furthermore, the recovery and reusability of the catalyst will be further improved when the amount of the reactants and catalyst was increased, which needs to be further investigated.

In short, the effect of various reaction conditions on the synthesis of DMC was investigated and the optimal operational conditions for the system was obtained: reaction temperature 120 °C, time 6 h, pressure of CO_2 2.5 MPa, methanol/PO molar ratio 20:1 and amount of the catalyst 3.0 g. The reaction conversion of above 98.0% was achieved; the selectivity and yield of DMC were about 67 and 65% under the optimal conditions. Besides, the catalyst could be simply reused.

4 Conclusion

A basic ionic liquid, namely choline hydroxide, was prepared and supported on MgO to form Choline hydroxide/MgO material. One-pot synthesis of DMC from methanol, CO_2 and PO over this material CH/MgO at milder conditions was investigated. CH/MgO exhibited good catalytic performance with 65.4% of yield and selectivity of above 90% to DMC + PC at 2.5 MPa and 120 °C for 6 h. The effective catalyst should correspond to amorphous CH well dispersed on MgO and the catalyst is easily regenerated and reused.

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