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Synthesis and catalytic application of zirconium-substituted aminoethyl phosphonate

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Abstract A new type of zirconium-substituted aminoethyl phosphonate material is prepared and characterized by elemental analysis, ICP, FTIR, XRD, ^{31}P-MAS NMR, TG, DTG and DSC. XRD indicates that the material is amorphous. The ^{31}P-MAS NMR of the material exhibits a single resonance, and thermogravimetry shows that the material has three steps mass loss at temperatures of up to 900 °C. The zirconium phosphonate material as a solid catalyst is investigated in the Knoevenagel condensation of aromatic aldehyde or cyclohexanone with active methylene compounds. The solid catalyst is easily recovered and can be recycled three times without significant loss of its activity. The experimental results imply the catalytic activity of the zirconium phosphonate is different from that of the organic–inorganic hybrid zirconium phosphonate-phosphate.

Introduction

Zirconium phosphate, phosphonate and phosphonate-phosphate have been the object of a growing interest in the fields of ion exchange [1, 2], intercalation chemistry [3, 4], sensor and proton conductivity [5, 6], and catalysis [7–10]. In general, the surface areas of typical zirconium phosphates and phosphonates are in the range of 30–200 m^2/g [11]. No matter they are crystalline, semi-crystalline or amorphous, all organic groups are located on the surface of the layer and in the interlamellar region. The accumulated data indicate that these materials are highly thermal stability and structural versatility. Heterogeneous catalysts are easier to work-up, simpler to separate and purify, and safer to operate in the industrial process, as far as environmental and economic concern, there has been increasing attention on the synthesis and use of new environmentally benign heterogeneous catalysts targeted to minimize the emission of effluents in the chemical industry. Heterogeneous catalysis has received much attention due to its importance in organic reactions, petroleum refining and petrochemical process [12, 13]. In recent years, we and several research groups have reported a variety of organic–inorganic hybrid zirconium phosphonate-phosphates as solid acid catalysts $Zr(HPO_4)_{2-x}(O_3P\text{–}G)_x{\cdot}nH_2O$ (x = 0–2, G: organic groups) such as zirconium sulfophenylphosphonate-phosphate $Zr(HPO_4)_{2-x}(O_3PC_6H_4SO_3H)_x{\cdot}H_2O$ [14, 15], zirconium sulfotolylphosphonate-phosphate $Zr(HPO_4)_{2-x}[O_3PC_6H_3(CH_3)SO_3H]_x{\cdot}H_2O$ [16], zirconium sulfonated 1,4-phenylenediphosphonate-phosphate $Zr(HPO_4)_{2-2x}[O_3PC_6H_3(SO_3H)PO_3]_x$, zirconium-sulfonated 4,4′-biphenylene (phosphonate)-phosphate $Zr(HPO_4)_{2-2x}[O_3PC_6H_4(SO_3H)C_6H_4(SO_3H)PO_3]_x$ [17, 18], zirconium [*N*-(phosphonomethyl) morpholine-phosphate] $Zr(HPO_4)[O_3PCH_2N(CH_2CH_2)_2O]{\cdot}nH_2O$, zirconium [*N*-(phosphonomethyl) iminodiacetic acid-phosphate] $Zr(HPO_4)[O_3PCH_2N(CH_2COOH)_2]{\cdot}nH_2O$ and zirconium [*N*,*N*-di(phosphonomethyl)iminodiacetic acid] $Zr[(O_3PCH_2)_2N(CH_2COOH)]{\cdot}$

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nH_2O [19], it is interesting to point out that the organic groups can be designed for special purpose, and organic/inorganic molar ratio (*x* value) may vary and optimize from 0 to 2. However, the report about heterogeneous base catalysis is much less. In previous paper, the hybrid zirconium phosphonate-phosphates $Zr(HPO_4)_{1.35}[O_3PCH_2CH_2N(CH_3)_2]_{0.65}\cdot H_2O$, $Zr(HPO_4)_{1.35}[O_3PCH_2CH_2NHC(=NH)NH_2]_{0.65}\cdot H_2O$ and $Zr(HPO_4)_{1.35}[O_3PCH_2CH_2NHCH(CH_3)_2]_{0.65}\cdot H_2O$ ($x = 0.65$) in which the lamellar surface –OH of α-zirconium phosphate are partially substituted by organic groups are reported, and used as solid base catalysts in high catalytic activity and the reusable nature for the Knoevenagel condensation of benzaldehyde with diethylmalonate or malononitrile, and cyclohexanone with malononitrile [20]. In order to explore the organic group and organic/inorganic molar ratio effect on the catalytic activity of the zirconium phosphonate and the hybrid zirconium phosphonate-phosphate, a new kind of zirconium-substituted aminoethyl phosphonate $Zr(O_3P–G)_2\cdot H_2O$ ($x = 2$) with a basic functional group is prepared (see Scheme 1) in this paper, the lamellar surface –OH of α-zirconium phosphate can be completely substituted by organic groups, the application of the zirconium phosphonate catalyst in Knoevenagel condensation of aromatic aldehyde or cyclohexanone with active methylene compounds has been studied.

Experimential

Materials and methods

All materials used are of analytical grade.

C, H, N elemental analysis are carried out with a Perkin-Elmer 2400 analyzer, and Zr analysis by TPS-7000 ICP analyzer. ^1H-NMR is performed on a dpx-300 NMR instrument. FTIR spectra are recorded on Spectrum GX (KBr pellet). X-ray powder diffractions are performed on a D/MAX-3C automatic diffractometer with Cu-Kα radiation. ^{31}P-MAS NMR spectra are recoded on Bruker AV-300 spectrometer with NaH_2PO_4 as reference. Thermal analysis is performed on a DELTA SERIES instrument. GC and HPLC analysis are carried out with GC-9A and LC-6A instrument, respectively.

Preparation of substituted aminoethyl phosphonic acid

$H_2O_3PCH_2CH_2NR^1R^2$ is prepared according to reference [21], substituted aminoethyl phosphonic acids 1a and 1b yield 85.6% and 84.0%, respectively.

1 a ^1H-NMR (D_2O): δ 2.51–2.75 (8H, m). ^{31}P-NMR: δ 6.76 (s). IR (KBr): 3474 (w), 2,857 (m), 2,450 (w), 2,217 (m), 1,657 (w), 1,568 (m), 1,478 (w), 1,368 (w), 1,161 (s), 1,078 (s), 963 (m), 899 (m), 860 (m), 548 (m) cm^{-1}. Found: C, 28.37; H, 7.86; N, 16.62. Anal. calc.: C, 28.28; H, 7.79; N, 16.66.

1 b ^1H-NMR (D_2O): δ 1.50–1.65 (PCH_2, m), 3.50–3.52 (NCH_2, m). ^{31}P-NMR: δ 6.47 (s). IR (KBr): 3,383 (w), 2,895 (w), 2,444 (w), 1,780 (w), 1,670 (w), 1,364 (w), 1,157(s), 1,074 (s), 949 (m), 858 (s), 546 (m) cm^{-1}. Found: C, 21.52; H, 6.10; N, 25.05. Anal. calc.: C, 21.56; H, 6.03; N, 25.15.

Preparation of solid zirconium phosphonate

$ZrOCl_2\cdot 8H_2O$ (6.45 g, 20 mmol) in water (100 mL) is added to the solution of $H_2O_3PCH_2CH_2NR^1R^2$ (20 mmol) in water (100 mL). After 1 h of stirring, 5 mL of concentrated HCl is added to the reaction mixture, the mixture is stirred under N_2 for 12 h at 60–70 °C, cooled to room temperature, filtered, washed with water and dried in vacuo. White solids of 2 a and 2 b are obtained [22]. Eighty mL of 5% sodium hydroxide is added to 2 a or 2 b, the reaction mixture is stirred for 18 h at room temperature, filtered, washed with water and dried in vacuo. White solids of 3 a and 3 b are obtained in yield of 92.6% and 91.0%, respectively.

Found for 3 a: C, 21.57; H, 5.33; N, 12.53; Zr, 20.55. Anal. calc.: C, 21.76; H, 5.48; N, 12.69; Zr, 20.66.

Found for 3 b: C, 16.32; H, 4.02; N, 19.04; Zr, 20.61. Anal. calc.: C, 16.40; H, 4.10; N, 19.13; Zr, 20.76.

General procedure for Knoevenagel condensation

Benzaldehyde (5.3 g, 50 mmol) is added dropwise to the solution of diethyl malonate (8.1 g, 50 mmol) and white solid 3 a or 3 b (2.0 g) in solvent (40 mL) with stirring, then the reaction mixture is stirred for appropriate time at reflux temperature, cooled to room temperature after water

$$H_2O_3PCH_2CH_2NR^1R^2 \xrightarrow{1} Zr(O_3PCH_2CH_2NH^+R^1R^2)_2 \cdot 2\,Cl^- \xrightarrow{2} Zr(O_3PCH_2CH_2NR^1R^2)_2 \cdot H_2O$$

1 a-1 b 2 a-2 b 3 a-3 b

1, 2,3	a	b
R^1	H	H
R^2	$CH_2CH_2NH_2$	$C(=NH)NH_2$

Scheme 1

separation, filtrated, the condensation product is given by the solvent removal, purified and affirmed by chromatography, ^{1}H-NMR and IR [20].

The reaction of substituted benzaldehyde or cyclohexanone with other active methylene compounds is the same as the above procedure.

Results and discussion

Synthesis, basic strength, and basic number of zirconium phosphonate

The crystalline zirconium phosphonate can be usually prepared by adding a strong complexing agent to solubilize the material. HF is the most common complexing agent, forming a soluble ZrF_6^{2-}. The ZrF_6^{2-} decomposes when the HF is removed from the reaction system, the zirconium phosphonate slowly crystallizes, and the zirconium phosphonate is extremely insoluble. Therefore, soluble $ZrOCl_2 \cdot 8H_2O$ is added to phosphonic acid solution without HF, resulting in rapid precipitation of zirconium phosphonate. Zirconium-substituted aminoethyl phosphonates $Zr(O_3PCH_2CH_2NHCH_2CH_2NH_2)_2 \cdot H_2O$ (3 a) and $Zr[O_3PCH_2CH_2NHC(=NH)NH_2]_2 \cdot H_2O$ (3 b) are obtained in this work. For XRD analysis, both of them are amorphous.

The solid zirconium phosphonate shows that the basic strength (H_-) is stronger than $H_- = 12.2$ by indicator methods.

The basic numbers of solid zirconium phosphonate materials can be measured by titration with benzoic acid [12]. The basic number with $H_- = 9.3$ is 1.86, 2.13 mmol/g for 3 a and 3 b, respectively.

Infrared spectra of zirconium phosphonate

The infrared spectrum of the zirconium phosphonate 3 a is shown in Fig. 1. The broad band at 3,430 cm^{-1} is due to N–H, and water stretching vibrations. In comparison with substituted aminoethyl phosphonic acid 1 a, the bands at 2,857, 1,568, 1,478 and 1,368 cm^{-1} disappear for 3 a. The weak band at 1,653 cm^{-1} is due to water bending vibration. The broad overlapping bands at 987–1,200 cm^{-1} can be ascribed to phosphate stretching vibration. The infrared spectra of the zirconium phosphonate 3 b (Fig. 2) is similar to that of 3 a. In general, IR spectra indicate that there are some differences between phosphonic acid and solid zirconium phosphonate in the vibration frequencies, and the quantity of band of zirconium phosphonate material is much less than that of the substituted aminoethyl phosphonic acid.

XRD and ^{31}P-MAS NMR of zirconium phosphonate

The zirconium phosphonates don't diffract (Fig. 3), which reveal that the materials are amorphous. In order to obtain detailed structure information of the solid materials, ^{31}P-MAS NMR measurements are performed (Fig. 4), each

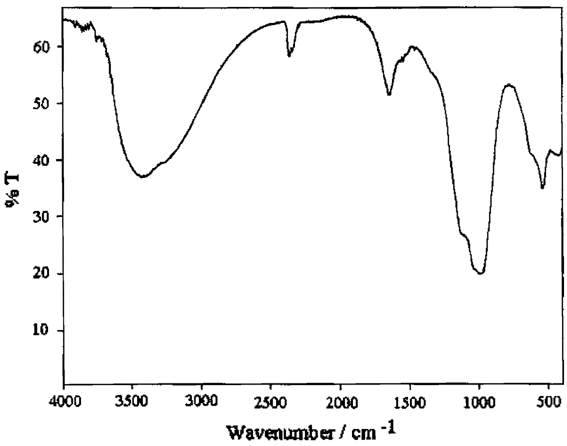

Fig. 1 IR spectrum of 3 a

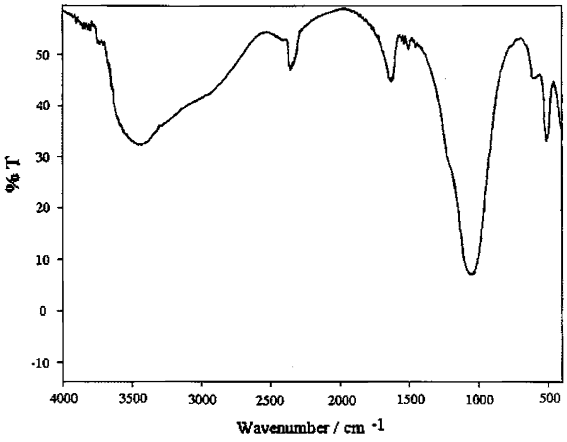

Fig. 2 IR spectrum of 3 b

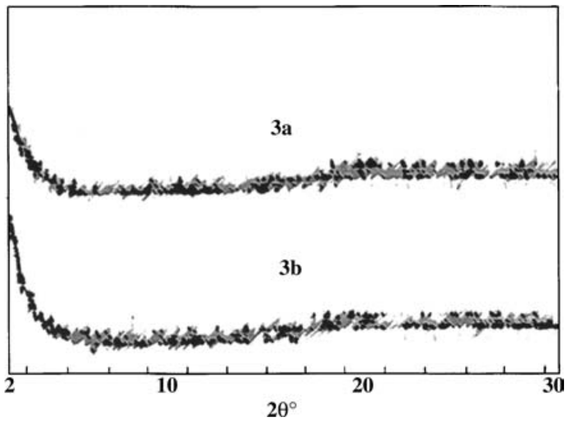

Fig. 3 XRD patterns of 3 a and 3 b

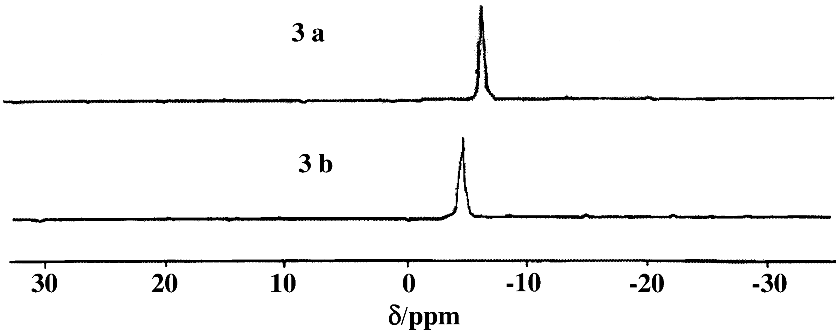

Fig. 4 ^{31}P-MAS NMR spectra of 3 a and 3 b

zirconium phosphonate exhibits a single resonance peak at −7.5 ppm for 3 a and at −5.2 ppm for 3 b. Thus the spectrum indicates that two phosphorus atom of each zirconium phosphonate retain the same microenvironment in the compound.

Thermal behavior of zirconium phosphonate

TG and DTG curves reveal three steps mass loss at temperatures of up to 900 °C, as shown in Figs. 5 and 6. The first mass loss below 200 °C is assigned to the dehydration of the adsorption and crystalline water. The second in the range of 200–610 °C can be ascribed to the decomposition of partial organic groups. DSC curve for 3 a shows the endothermic peak at about 280 °C (Fig. 7). The third in the range of 610–900 °C is primarily due to the decomposition of residual organic moiety, the mass of zirconium phosphonate does not change above 610 °C. The total mass loss is found to be 10.9% and 11.3% for 3 a and 3 b, respectively. This result demonstrates that the thermal stability of the solid material is markedly different from that of α-zirconium phosphate.

Catalytic activity of zirconium phosphonate

Table 1 lists the Knoevenagel condensation results. After each reaction the condensation product is separated from the catalyst, the catalyst washed with dichloromethane and dried in vacuum. The mechanism of Knoevenagel condensation (under basic conditions) is that one proton from the acidic methylene compound is removed by the base to generate a nucleophile that will react with the aldehyde. The zirconium phosphonate materials as solid catalysts possess basic sites stronger than $H_- = 12.2$, their active basic sites are possible to be imine and amine groups. The catalyst 3 b is engaged three times in the condensation of benzaldehyde with diethylmalonate, the condensation product yields 90.7%, 88.7%, 87.1%, respectively. This shows that the catalyst is still efficient after three cycles. In view of the results of Table 1, the reaction times and yields don't show any significant difference between catalyst 3 a and 3 b despite their different organic groups in the same solvent. Compared with the previous catalyst of hybrid zirconium phosphonate-phosphate [20], the present catalyst 3 a or 3 b shows higher yield in the reaction of benzalde-

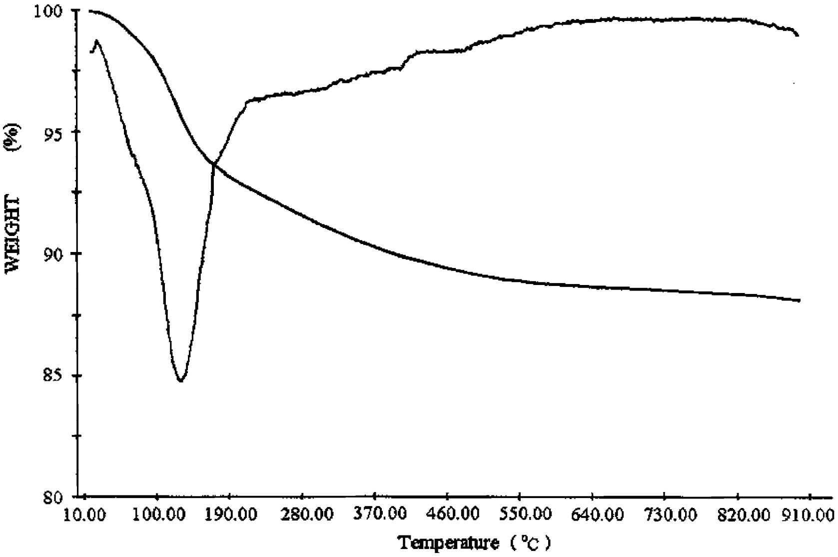

Fig. 5 TG, DTG curves of 3 a

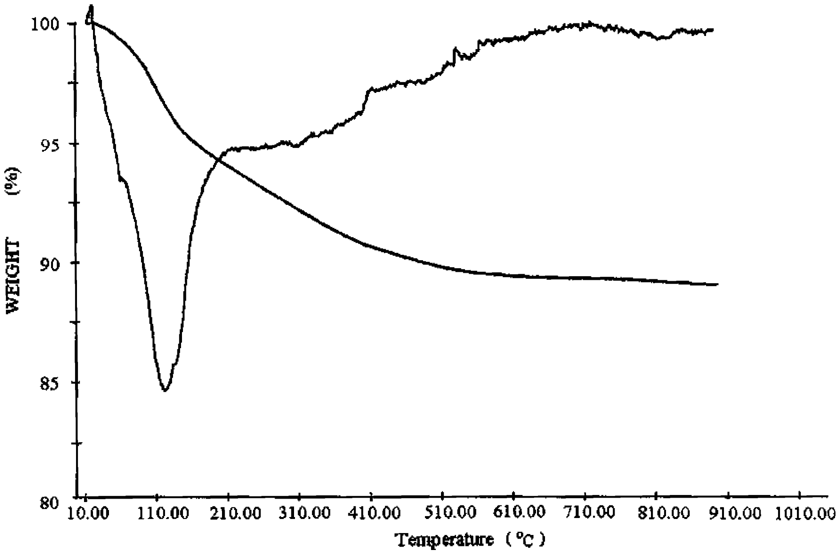

Fig. 6 TG, DTG curves of 3 b

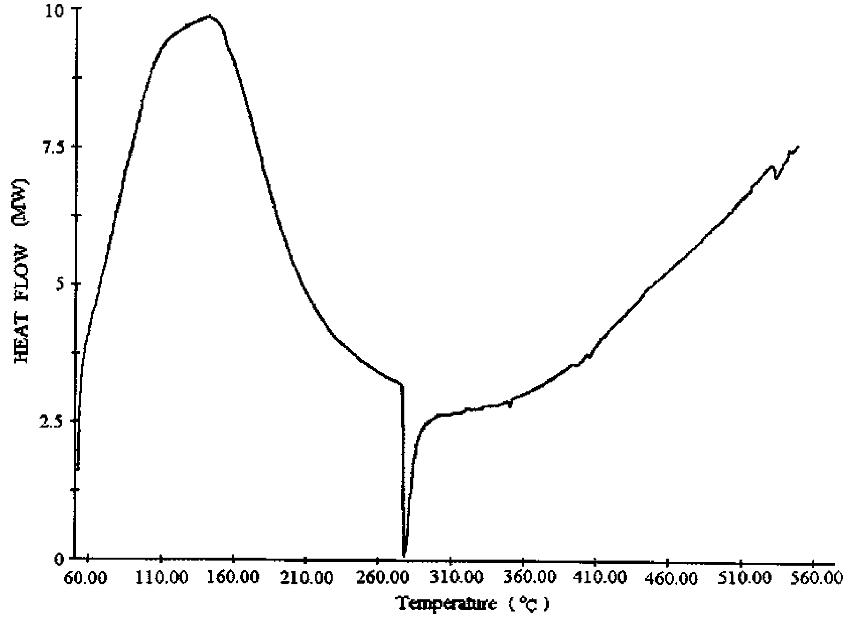

Fig. 7 DSC curve of 3 a

Table 1 Knoevenagel condensation results catalyzed by the solid zirconium phosphonate

Entry	Reactants		Catalyst	Time (h)	Solvent	Yield (%)
1	Benzaldehyde	Diethyl malonate	3 a	4.5	Toluene	88.6
2	Benzaldehyde	Diethyl malonate	3 b	4.5	Toluene	90.7
3	Benzaldehyde	Diethyl malonate	3 a	5.0	Dioxone	86.1
4	Benzaldehyde	Diethyl malonate	3 b	5.0	Dioxone	87.3
5	Benzaldehyde	Malononitrile	3 a	5.5	Benzene	87.4
6	Benzaldehyde	Malononitrile	3 b	5.5	Benzene	86.2
7	Benzaldehyde	Malononitrile	3 a	5.0	Toluene	90.2
8	Benzaldehyde	Malononitrile	3 b	5.0	Toluene	89.5
9	Cyclohexanone	Malononitrile	3 a	6.0	Dichloromethane	84.2
10	Cyclohexanone	Malononitrile	3 b	6.0	Dichloromethane	85.8
11	Benzaldehyde	Dimethyl malonate	3 a	5.5	Benzene	88.4
12	Benzaldehyde	Dimethyl malonate	3 b	5.5	Benzene	89.3
13	*p*-Hydroxybenzaldehyde	Dimethyl malonate	3 a	7.0	Toluene	82.9
14	*p*-Methoxybenzaldehyde	Malononitrile	3 b	6.0	Toluene	87.7
15	*p*-Hydroxybenzaldehyde	Malononitrile	3 b	6.5	Benzene	86.3
16	*p*-Nitrobenzaldehyde	Malononitrile	3 b	4.5	Benzene	90.2

hyde with diethylmalonate when dioxone as a solvent, but lower yield and much more reaction times in the reaction of cyclohexanone with malononitrile when dichloromethane as a solvent. Furthermore, the present catalyst 3 a or 3 b allows to achieve in good yields for much more substrates (entries 11–16).

Conclusion

Zirconium-substituted aminoethyl phosphonates $Zr(O_3PCH_2CH_2NHCH_2CH_2NH_2)_2 \cdot H_2O$ and $Zr[O_3PCH_2\text{-}CH_2NHC(=NH)NH_2]_2 \cdot H_2O$ ($x = 2$) are synthesized. The Knoevenagel condensation of aromatic aldehyde or cyclohexanone with active methylene compounds is catalyzed by the zirconium phosphonate material in high catalytic activity and the reusable nature, the results indicate that the catalytic activity of zirconium phosphonate is different from that of the hybrid zirconium phosphonate-phosphate, and the zirconium phosphonate material is a new type of environmentally benign catalyst.

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