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Article

TiO₂-based green heterogeneous catalysts for the cycloaddition of CO₂ to epoxides

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ABSTRACT

TiO₂ doped with metal ions (M-TiO₂, M = Zn²⁺, Cu²⁺, Co²⁺, Mn²⁺, or Ni²⁺) was investigated as a heterogeneous catalyst for the coupling reaction of CO₂ and epoxides, using tetrabutylammonium iodide (TBAI) as a co-catalyst under solvent-free conditions. These compounds were found to exhibit high catalytic activities. The effects of reaction temperature, reaction time, and CO₂ pressure on the effectiveness of a Zn-TiO₂/TBAI catalyst system were also examined. Zn-TiO₂ represents a nontoxic, heterogeneous catalyst that can be reutilized up to five times without a significant loss of catalytic activity.

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1. Introduction

In recent years, the greenhouse gas effect and associated climate change impact of carbon dioxide have received increasing attention. Thus, the efficient transformation of CO₂ into useful chemicals is an attractive research area in view of the feature of CO₂, such as non-toxicity, worldwide being, and as a renewable carbon resource. One of the most promising means of using CO₂ synthetically is its coupling with epoxides to form cyclic carbonates, a process which is a good example of 100% atom economy [1–4].

The cyclic carbonates represent CO₂ fixation products and are widely applied as monomers, aprotic polar solvents, and pharmaceutical intermediates [5–8]. A number of homogeneous catalysts have been developed for the synthesis of cyclic carbonates from epoxides and CO₂, such as quaternary ammonium salts [9,10], ionic liquids [11–13], oxychlorides [14], organic bases [15], and organometallic compounds [16–20].

However, homogeneous catalysts are undesirable, in which it is difficult to separate the catalyst from the products following completion of the reaction. Although there are several heterogeneous catalysts that have been reported for this reaction, including metal oxides [21,22], ion-exchange resins [23], mesoporous materials [24–26], inorganic oxides [27], metal-organic frameworks [28], and biopolymers [29], most of these systems currently suffer from low activities or the use of toxic solvents, high pressures, or high temperatures. Therefore, the development of heterogeneous catalysts that are both green and efficient remains a challenge.

TiO₂ is an inexpensive, readily prepared, and environmentally benign material and is widely made use of in pigments, sunscreens, toothpastes, and ointments as well as in the working electrodes of dye-sensitized solar cells [30–32]. However, there have been few reports on reactions using TiO₂ as catalyst in the absence of light irradiation [33].

In this study, a series of metal ion-doped TiO₂ (M-TiO₂) ma-

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Scheme 1. Coupling of CO₂ and epoxides.

terials were prepared *via* a co-precipitation procedure and employed as nontoxic heterogeneous catalysts in conjunction with tetrabutylammonium iodide (TBAI) in the cycloaddition reaction of CO₂ and epoxides under solvent-free conditions (Scheme 1).

2. Experimental

2.1. Preparation of catalysts

Propylene oxide (PO), tetrabutyl titanate, TBAI, and other chemicals were purchased from the Sinopharm Chemical Reagent Co., Ltd. The PO was purified and dried over CaH₂ before use, while all other chemicals were used as-received without further purification.

The typical procedure for fabricating the M-TiO₂ catalysts was as follows. The metal nitrate (5.86 mmol) was dissolved in ethanol (40 mL) to produce a clear solution, following which another solution of Ti(OBu)₄ (58.6 mmol, 20 mL) in ethanol (80 mL) was added in one portion with vigorous stirring. Ammonium hydroxide (40 mL) was then added dropwise to adjust the pH of the mixture to 9 to precipitate the product, after which the mixture was stirred for another 20 h at room temperature. Finally, the precipitate was filtered, washed with deionized water and ethanol, and dried at 80 °C overnight in a vacuum oven.

2.2. Characterization of catalysts

ICP-AES data were collected on an IRIS ER/S emission spectrometer (American TJA Co.). N₂ adsorption-desorption isotherms were recorded at −195.8 °C on a TriStar II 3020V instrument. The specific surface areas were calculated using the BET equation over the range of relative pressures (p/p_0) between 0.06 and 0.3. The pore size distributions were determined by BJH analyses based on the desorption branch of each isotherm. Powder X-ray diffraction (XRD) patterns were obtained with an X'Pert PRO diffractometer (Holland PANalytical Co.) over the range of $2^\circ \leq 2\theta \leq 90^\circ$ at a scanning rate of 8° min^{-1} using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). X-ray photoelectron spectroscopy (XPS) data were recorded on a Kratos AXIS Ultra spectrometer equipped with a monochromatic Al K α X-ray source and a delay-line detector (DLD) and a work function of 4.59 eV. XPS data were fitted with CasaXPS software.

2.3. Typical procedure for the synthesis of cyclic carbonates from epoxides and CO₂

All experiments were conducted in a 100 mL stainless steel reactor equipped with a magnetic stirrer and immersed in an oil bath. The reactor was charged with known amounts of the

Table 1

ICP-AES data and textural properties of catalysts.

Catalyst	Metal ion content (mol%)		S_{BET} (m ² g ^{−1})	V_p (cm ³ g ^{−1})	D_p (nm)
	Feeding	Measured			
TiO ₂	—	—	205	0.14	2.77
Zn-TiO ₂	10	5.72	351	0.21	2.38
Cu-TiO ₂	10	5.73	210	0.17	3.15
Co-TiO ₂	10	6.12	138	0.16	4.63
Mn-TiO ₂	10	8.41	200	0.17	3.44
Ni-TiO ₂	10	3.89	232	0.19	3.27

epoxide and the desired catalyst at room temperature, and then heated to a specified temperature. CO₂ was subsequently added from a high pressure reservoir tank while maintaining a specified constant pressure over the desired time period. After the reaction, the reactor was cooled in an ice water bath, and residual CO₂ was slowly released from the device. The yield of cyclic carbonate was determined by the subtraction method or by ¹H NMR spectroscopy.

3. Results and discussion

3.1. Catalyst characterization

The ICP-AES analysis results are shown in Table 1. The actual molar ratios of metal ions doped into the TiO₂ are consistently lower than the metal ion feed ratios owing to the solubility in water of the ions, such that some metal was removed during washing with deionized water.

The specific surface areas, pore volumes, and pore diameters of all the metal ion-doped TiO₂ nano-catalysts are also provided in Table 1. It can be seen that the particular metal ion species had an impact on the textural properties of the resulting nano-catalysts, such that Zn-TiO₂ presented the largest specific surface area of 351 m² g^{−1}. The pore diameters of the catalysts ranged from 2.38 to 4.63 nm.

The XRD patterns of these catalysts are depicted in Fig. 1, in which it is obvious from the lack of sharp peaks that these catalysts all had amorphous structures. New peaks did appear

Fig. 1. XRD patterns of catalysts.

Fig. 2. XPS spectrum of Zn-TiO₂.

when Zn-TiO₂ was calcined at 600 °C for 2 h. The resulting 2θ values of 25.3°, 37.9°, 48.4°, and 53.9° were attributed to characteristic reflections from the (101), (103), (200), and (105) planes of anatase TiO₂, respectively.

To confirm the states of the metals, XPS analysis was performed. As shown in Fig. 2, the XPS data obtained for Zn-TiO₂ showed a Zn 2p_{3/2} peak at 1019.0 eV. Because this does not coincide with the expected peak of zinc oxide according to the literature [34], the metals in catalysts must have been present as ions.

3.2. Activities of various catalysts for coupling of CO₂ with PO

The activities of different catalysts for the coupling reaction of CO₂ with PO were investigated with the results shown in Table 2. Initially, several M-TiO₂ catalysts were chosen for investigation with regard to this reaction, using TBAI as a co-catalyst. The results demonstrated that the catalytic efficiency decreased in the order Zn-TiO₂ > Cu-TiO₂ > Co-TiO₂ > Mn-TiO₂ > Ni-TiO₂ (Table 2, entries 1–5). The best catalyst system, Zn-TiO₂/TBAI, gave a propylene carbonate (PC) yield of 92.3% (Table 2, entry 1). Co-catalyst effects were also investigated in this series of reactions, and it was determined that the PC yield decreased in the order TBAI > TBAB > TBAC > PTAT (Table 2, entries 6–8) because of the varying nucleophilic

Table 2

Catalytic activities of various catalysts for the coupling reaction of CO₂ and PO.

Entry	Catalyst	Co-catalyst	Isolated yield (%)
1	Zn-TiO ₂	TBAI	92.3
2	Cu-TiO ₂	TBAI	75.3
3	Co-TiO ₂	TBAI	73.1
4	Mn-TiO ₂	TBAI	71.4
5	Ni-TiO ₂	TBAI	36.3
6	Zn-TiO ₂	TBAB	72.3
7	Zn-TiO ₂	TBAC	69.3
8	Zn-TiO ₂	PTAT	55.3
9	Zn-TiO ₂ *	TBAI	73.7
10	None	TBAI	41.7
11	Zn-TiO ₂	None	13.7

Reaction conditions: catalyst 0.1 g, co-catalyst 0.1 mmol, PO 3.5 mL (50 mmol), CO₂ pressure 2 MPa, 120 °C, 8 h.

* Calcined at 600 °C for 2 h.

TBAB: Tetrabutylammonium bromide; TBAC: Tetrabutylammonium chloride; PTAT: Phenyltrimethylammonium tribromide.

strengths and leaving group tendencies of these compounds. A drop in PC yield was observed when the calcined Zn-TiO₂ was used in this reaction (Table 2, entry 9), which is attributed to the formation of ZnO from Zn²⁺ and a concurrent reduction of the catalyst's Lewis acidity. In addition, poor catalytic activity resulted when either the Zn-TiO₂ or the TBAI were employed alone (Table 2, entries 10 and 11), indicating that there was a synergistic effect between the Lewis acidity of the catalyst and the nucleophilicity of the co-catalyst, which increased the activity of the catalyst system [19,20].

3.3. Influences of reaction conditions on the synthesis of PC

To determine the optimal reaction conditions for our Zn-TiO₂/TBAI catalytic system, the effects of varying the CO₂ pressure, reaction temperature, and reaction time were investigated. Considering that the partitioning behavior of the substrates between phases could affect the reaction rate of a bi-phasic reaction system [35], various CO₂ pressure (0.5–2.5 MPa) were applied to the reaction at 120 °C, with the results presented in Fig. 3. It can be seen that the PC yield increased when the pressure was increased from 0.5 to 2.0 MPa, while the yield decreased when the pressure reached 2.5 MPa. When the reaction was carried out in the low-pressure region, higher CO₂ pressures enhanced the yield owing to the concurrent elevation of CO₂ concentrations in the liquid phase of the reaction system. Too high pressures, however, reduced the PO concentration to give low PC yields. Based on these data, a reaction pressure of 2.0 MPa appears the most suitable.

As shown in Fig. 4, the reaction temperature also has a significant effect on the coupling reaction. With increasing temperatures over the range of 40 to 120 °C, the PC yield was remarkably enhanced from 8.9% to 92.3%, while overly high temperatures reduced the yield as the result of side reactions. Therefore, 120 °C was considered suitable for the target reaction.

The influence of reaction time on the coupling reaction is shown in Fig. 5. The reaction was carried out at 120 °C under 2.0 MPa of CO₂. The yield of PC increased with increasing time and approached 92.3% after 8 h. Further increases in reaction time did not greatly improve PC yield, indicating that 8 h is the optimal time period.

Fig. 3. Effect of CO₂ pressure on the synthesis of propylene carbonate (PC). Reaction conditions: PO 3.5 mL (50 mmol), Zn-TiO₂ 0.1 g, TBAI 0.1 mmol, 120 °C, 8 h.

Fig. 4. Effect of reaction temperature on the synthesis of PC. Reaction conditions: PO 3.5 ml (50 mmol), Zn-TiO₂ 0.1 g, TBAI 0.1 mmol, CO₂ pressure 2 MPa, 8 h.

Fig. 5. Effect of reaction time on the synthesis of PC. Reaction conditions: PO 3.5 ml (50 mmol), Zn-TiO₂ 0.1 g, TBAI 0.1 mmol, 120 °C, CO₂ pressure 2 MPa.

3.4. Recycling experiments

To optimize the environmental and economic aspects of the Zn-TiO₂ catalyst, it was recovered and recycled in the coupling reaction of CO₂ and PO (Fig. 6). It was observed that the catalyst could be reused up to five times with little loss of catalytic activity. We also found that the Zn content of Zn-TiO₂ was 3.92% after five reuses, which may be the reason for the observed yield decrease.

Fig. 6. Catalytic stability of recycled Zn-TiO₂. Reaction conditions: PO 3.5 ml (50 mmol), Zn-TiO₂ 0.1 g, TBAI 0.1 mmol, 120 °C, initial pressure 2 MPa, 8 h.

Table 3

Coupling reactions of various epoxides with CO₂ over Zn-TiO₂/TBAI.

Entry	Epoxide	Cyclic carbonate	Yield (%)
1			93.5
2			>99.0
3			91.7
4			78.9
5			24.1

Reaction conditions: Zn-TiO₂ 0.1 g, TBAI 0.1 mmol, epoxide 50 mmol, CO₂ pressure 2 MPa, 120 °C, 8 h.

3.5. Catalytic reactions of various epoxides with CO₂

To further extend the scope of this catalytic coupling reaction, various epoxides were employed in the coupling reaction catalyzed by Zn-TiO₂/TBAI under the optimal reaction conditions. As shown in Table 3, the corresponding cyclic carbonates were achieved in high yields (Table 3, entries 1–3). Although styrene oxide was a low activity substrate due to its electro-negativity, the yield of the corresponding cyclic carbonate was still as high as 78.9% (entry 4). The lowest yield of the cyclic carbonate was obtained when using cyclohexene oxide as the substrate (entry 5) by reason of steric effects.

3.6. Proposed mechanism for the coupling reaction

A proposed mechanism is illustrated in Scheme 2. The epoxide is initially coordinated to the metal center to form an intermediate complex, which is then attacked by the nucleophilic reagent to generate a new intermediate species that re-

Scheme 2. Proposed mechanism for coupling of CO₂ with epoxides.

Graphical Abstract

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TiO₂-based green heterogeneous catalysts for the cycloaddition of CO₂ to epoxidesJing Liu, Anqi Wang, Huanwang Jing*
Lanzhou UniversityZn²⁺-TiO₂ was investigated for the green catalysis of the coupling of CO₂ and epoxides under mild conditions and was found to generate cyclic carbonates in high yields.

acts with CO₂ to yield the cyclic carbonate. The high activity of these catalysts could be attributed to the combination of both a good nucleophile and a good leaving group in the large anion.

4. Conclusions

We have developed a series of green, efficient, recyclable, and heterogeneous catalysts with applications to the cycloaddition of CO₂ to epoxides under mild conditions without the use of an organic solvent. The catalysts exhibit high efficiency when the substrate is inactive styrene oxide and can be reused five times. To the best of our knowledge, this is the first example of the use of a metal ion-doped TiO₂ catalyst in the coupling reaction of CO₂ and epoxides.

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基于TiO₂的绿色多相催化剂催化CO₂与环氧化合物偶联反应

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摘要: 金属离子掺杂纳米TiO₂ (M-TiO₂, M = Zn²⁺, Cu²⁺, Co²⁺, Mn²⁺, Ni²⁺)在CO₂与环氧化合物的偶联反应中表现出较高的催化活性. 反应以四正丁基碘化铵(TBAI)为共催化剂, 在无溶剂条件下进行. 考察了反应温度、反应时间和CO₂压力在Zn-TiO₂/TBAI体系中对反应性能的影响. 作为无毒的多相催化剂, Zn-TiO₂可循环使用5次, 其催化活性没有明显降低.

关键词: 二氧化碳; 环氧化合物; 环碳酸酯; 多相催化剂; 掺杂纳米二氧化钛

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1. 前言

近年来, CO₂越来越受到人们的关注, 部分原因在于温室效应和气候变化, 同时CO₂也被认为是廉价、无毒、可再生的碳资源. 因此, 将CO₂高效转变为有用的有机物成为一个极具吸引力的领域. 其中最希望的途径之一是CO₂与环氧化合物发生偶联反应生成环碳酸酯, 同时该反应也是一个很好的100%原子经济的例子^[1–4].

环碳酸酯是CO₂固定化的产物, 广泛应用于聚合物的单体、非质子极性溶剂和药物中间体^[5–8]等领域. 许多均相催化剂已被应用于CO₂和环氧化合物生成环碳酸酯的反应中, 包括季铵盐^[9,10]、离子液体^[11–13]、氯化化合物^[14]、有机碱^[15]和金属有机化合物^[16–20]等; 但它们与产物的分离困难, 因而其应用受限. 尽管一些多相催化剂也被报道用于该反应, 例如金属氧化物^[21,22]、离子交换树脂^[23]、介孔材料^[24–26]、无机氧化物^[27]、金属有机骨架化合物^[28]和生物高聚物^[29]等等, 但是它们大都活性低, 使用有毒溶剂, 且在高温和高压下进行. 因此, 开发绿色高效的多相催化剂仍然具有很大的挑战性.

TiO₂是一种廉价易得、环境友好的材料, 广泛应用于色素、遮光剂、牙膏和药膏, 同时也被用作太阳能电池的工作电极^[30–32]. 但是, 将其用于非光照条件下催化反应的报道不多^[33].

本文采用简单的共沉淀方法制备金属掺杂的TiO₂ (M-TiO₂), 并用于CO₂和环氧化合物的偶联反应中, 该反应以TBAI为共催化剂, 在无溶剂条件下进行(图式1).

2. 实验部分

2.1. 催化剂的制备

环氧丙烷(PO)使用前经CaH₂干燥处理, TiO₂, TBAI, 钛酸四丁酯和其他试剂均购买于Sinopharm公司, 未做进一步纯化处理.

将金属硝酸盐(5.86 mmol)溶解于乙醇(40 mL)中, 再加入含有Ti(OBu)₄ (58.6 mmol, 20 mL)乙醇(80 mL)溶液, 强烈搅拌. 然后逐滴加入氨水(40 mL), 调节混合物的pH值到9. 反应物继续在室温下反应20 h. 最后, 过滤沉淀, 并用去离子水和乙醇洗涤, 在80 °C真空干燥过夜.

2.2. 催化剂的表征

ICP-AES数据通过IRIS ER/S发射光谱(American TJA Company)测得. N₂吸附脱附等温线在–195.8 °C下通过TriStar II 3020V设备记录. 比表面积使用BET公式在 $p/p_0 = 0.03–0.6$ 计算得到. 孔径分布从解吸等温线的分支通过BJH分析获得. X射线衍射(XRD)谱通过X' Pert PRO型多晶粉末X射线衍射仪(PANalytical公司)测定. X射线光电子能谱(XPS)在Kratos AXIS Ultra光谱仪上测定, 单色Al K_α射线源, 延迟线检测器. XPS数据通过CasaXPS软件处理得到, 仪器的功函数是4.59 eV.

2.3. 环氧化合物和CO₂生成环碳酸酯实验

所有实验均在配有磁子的100 mL不锈钢反应釜中进行. 先在室温下向反应釜中投入已知量的环氧化合物和适量催化剂, 然后从高压钢瓶充入一定量CO₂, 在油浴中加热至所需温度并反应一定时间. 反应完成后, 反应釜在冰水浴中冷却, 缓慢释放出剩余CO₂. 通过减量法或核磁共振测定环碳酸酯的产率.

3. 结果与讨论

3.1. 催化剂的表征

催化剂的ICP-AES分析结果如表1所示. 可以看出, 各种金属离子掺杂的TiO₂的实际摩尔比率各不相同且总是低于金属离子的投料比. 这是由于当它们用去离子水洗涤时各自在水中的溶解性不同造成的.

所制备的M-TiO₂催化剂的比表面积、孔体积和孔径数据如表1所示. 可以看出, 金属离子的种类对催化剂的结构性质有较大影响. 其中Zn-TiO₂样品比表面积(351 m² g^{–1})最大, 各样品平均孔径在2.38–4.63 nm.

图1为各催化剂的XRD图. 可以看出, 各样品并未出现较尖锐的峰, 表明它们均为无定形的纳米结构. 但是, Zn-TiO₂在600 °C下焙烧2 h后, 于25.3°, 37.9°, 48.4°和53.9°处出现了衍射峰, 分别对应于锐态TiO₂的(101), (103), (200)和(105)晶面.

图2为Zn-TiO₂的XPS谱. 可见Zn 2p_{3/2}的峰在1019.0 eV, 表面催化剂中的Zn呈离子态^[34].

3.2. 不同催化剂对CO₂和环氧丙烷偶联反应催化活性

表2为不同催化剂催化CO₂和PO偶联反应的结果. 可以看出, 当以TBAI为共催化剂时各催化剂的活性大小顺序为Zn-TiO₂>Cu-TiO₂>Co-TiO₂>Mn-TiO₂>Ni-TiO₂,

其中以Zn-TiO₂为催化剂时丙烯环碳酸酯(PC)的产率达92.3% (实验1)。另外, 各共催化剂的活性顺序为TBAI > TBAB > TBAC > PTAT (实验6–8), 这是由于它们的亲核能力和离去能力不同所致。将焙烧过的Zn-TiO₂用于反应(实验9), 发现PC产率明显降低。这是因为Zn²⁺生成ZnO导致其Lewis酸性降低。作为对比, Zn-TiO₂和TBAI分别单独用于催化反应, PC的产率并不高(实验10和11)。这说明催化剂路易斯酸性和共催化剂亲核性的协同催化效应导致催化体系的高效率^[19,20]。

3.3. 反应条件对PC产率的影响

考察了CO₂压力、反应温度和反应时间对反应性能的影响。考虑到底物在不同相态间的性质可能影响两相反应系统的反应速率^[35], 反应中采用了不同的CO₂压力(0.5–2.5 MPa)。如图3所示, 当CO₂压力从0.5 MPa升至2.0 MPa时, PC产率逐渐上升; 至2.5 MPa时, PC产率降低。当反应在低压进行时, 较高的压力能提高反应系统里液相中的CO₂浓度, 从而提高产率。但是太高的CO₂压力降低了PO浓度, 导致产率降低。可见, 在2.0 MPa反应较为适合。

如图4所示, 随着温度从40 °C升到120 °C, PC产率从8.9%迅速增至92.3%。然而太高的温度会导致副反应发生, 从而降低PC产率。因此, 120 °C为适宜的反应温度。

反应时间对偶联反应的影响见图5。可以看出, PC产率随着时间延长而增加, 至8 h后达92.3%。继续延长反应时间产率增加不大, 表面反应8 h较为适宜。

3.4. 循环反应实验

为了考察Zn-TiO₂催化剂的绿色经济性, 图6给出了它的重复使用性能。可以看出, 催化剂可重复使用5次, 其活性略有下降。使用5次后, Zn-TiO₂样品中Zn含量降低至3.92%。这可能是导致产率降低的原因。

3.5. CO₂与多种环氧化合物反应结果

为了进一步扩大催化偶联反应的范围, 将Zn-TiO₂/TBAI用于催化多种环氧化合物与CO₂的偶联反应, 反应在最优条件下进行。如表3所示, 相应的环碳酸酯均达到较高的产率(实验1–3)。值得指出的是, 尽管苯乙烯环氧是一种活性较低的底物, 但是其对应的环碳酸酯产率仍能达到78.9% (实验4)。当以环己烯环氧为底物(实验5)时, 由于空间位阻的影响, 环碳酸酯产率仅为24.1%。

3.6. 可能的反应机理

图式2给出了可能的反应机理。环氧化合物首先与金属中心配位形成中间体, 接着被亲核试剂进攻形成另一个新的中间体, 然后该中间体与CO₂反应形成环碳酸酯。催化剂的高活性归功于良好的亲核性和大阴离子的离去基团。

4. 结论

开发了绿色、高效、可循环的金属离子掺杂纳米TiO₂多相催化剂, 该催化剂能在温和且无溶剂的条件下催化CO₂和环氧化合物的偶联反应。对于较难反应的苯乙烯环氧有较高的催化活性, 且催化剂可循环使用5次。这是首例将掺杂金属离子的TiO₂催化剂在非光照条件下用于催化CO₂和环氧化合物的偶联反应。