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Communication

Core-shell $\text{TiO}_2@\text{SiO}_2$ catalyst for transesterification of dimethyl carbonate and phenol to diphenyl carbonate

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ABSTRACT

Core-shell $\text{TiO}_2@\text{SiO}_2$ was prepared using a combination of reverse microemulsion and precipitation methods and used as a heterogeneous catalyst for the transesterification of dimethyl carbonate and phenol. $\text{TiO}_2@\text{SiO}_2$ calcined at 200 °C gave the best catalytic performance. When the amount of catalyst was 0.20 g, the phenol conversion and transesterification selectivity were 41.8% and 100%, respectively. Transmission electron microscopy was used to characterize the core-shell $\text{TiO}_2@\text{SiO}_2$ structure, and the results showed that $\text{TiO}_2@\text{SiO}_2$ is bilayer with a TiO_2 core of diameter 220–300 nm and SiO_2 shell of thickness 40–60 nm. The $\text{TiO}_2@\text{SiO}_2$ was reusable, and phenol conversion remained above 40% when the $\text{TiO}_2@\text{SiO}_2$ was used four times. The catalytic performance of $\text{TiO}_2@\text{SiO}_2$ in the transesterification of dimethyl carbonate and phenol was promoted by the formation of Ti–O–Si bonds.

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Diphenyl carbonate (DPC) is a green engineering thermoplastic intermediate, which has low toxicity and is non-polluting. It is used to synthesize various organic compounds and polymers by halogenation, nitrification, hydrolysis and ammonolysis, and particularly for the preparation of polycarbonates by melt transesterification without the use of phosgene [1]. The transesterification of dimethyl carbonate (DMC) and phenol is the most promising method for the industrial production of DPC [2]. In view of the difficulties in separating and recycling homogeneous catalysts, increasing attention is being focused on highly active heterogeneous catalysts for the transesterification of DMC and phenol. The heterogeneous catalysts reported to date are single or composite oxides [3], zeolites [4], hydroxalate-like compounds [5], and heteropoly compounds [6].

Although up to 40% yields have been obtained, these catalysts display poor selectivity or reusability. Among them, $\text{TiO}_2/\text{SiO}_2$ showed outstanding catalytic activity but was rapidly deactivated as a result of TiO_2 leaching [7]. The core-shell technique is the method most commonly used to obtain shell-protected TiO_2 materials to avoid instability of the active component in the core [8,9].

In this study, core-shell $\text{TiO}_2@\text{SiO}_2$ [10] was prepared using a combination of reverse microemulsion and precipitation methods and was used, for the first time, to catalyze the transesterification of DMC and phenol. The core-shell structure prevents leaching of the active component, i.e., TiO_2 , and increases the reusability.

The preparation of $\text{TiO}_2@\text{SiO}_2$ is different from that of

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TiO₂@void@SiO₂ [11,12], which is used in photocatalysis. First, the TiO₂ core was precipitated from peroxo-titanium with ammonia water, and SiO₂ was coated on the TiO₂ by hydrolysis of tetraethoxysilane under alkaline conditions. The transesterification of DMC and phenol was carried out in a 100 mL three-necked round-bottomed flask, equipped with a N₂ inlet, magnetic stirring bar, dropping funnel, and fractionating column connected to a liquid-dividing head. Phenol (AR, Guangdong Guanghua Sci-tech Co., Ltd., China) and the catalyst were introduced into the flask under N₂. DMC ($\geq 99\%$, Huasheng Co., Ltd., Shandong University of Petroleum, China) was added dropwise after the mixture was heated to 175 °C. Qualitative and quantitative analyses of the products were conducted using gas chromatography-mass spectrometry (Agilent 6890/5973) and gas chromatography (Agilent 7820A), respectively.

A transmission electron microscopy (TEM) image of TiO₂@SiO₂ is shown in Fig. 1. TiO₂@SiO₂ has a clear bilayer structure with a TiO₂ core of diameter 220–300 nm and a SiO₂ shell of thickness 40–60 nm. N₂ adsorption (BET) analysis showed that the SiO₂ shell has a mesoporous structure and an average pore diameter of 4.6 nm, which is favorable for the diffusion of reactants and products.

The Fourier-transform infrared (FTIR) spectra of SiO₂ and TiO₂@SiO₂ are shown in Fig. 2. The peak at 1628 cm⁻¹ corresponds to the O–H stretching vibration of adsorbed water, and

Fig. 1. TEM image of TiO₂@SiO₂.

Fig. 2. Fourier-transform infrared spectra of SiO₂, TiO₂@SiO₂, and recycled TiO₂@SiO₂.

the peaks at 1096, 805, and 472 cm⁻¹ are attributed to the asymmetric stretching, symmetric stretching and bending vibrations, respectively, of Si–O–Si bonds. For SiO₂, the weak peak at 956 cm⁻¹ is assigned to the stretching vibration of Si–OH [13]. However, for TiO₂@SiO₂, the Si–O peak at 956 cm⁻¹ is blue-shifted to 964 cm⁻¹; this is considered to be the result of TiO₂ and SiO₂ interacting and forming Ti–O–Si bonds [14]. The peak at 964 cm⁻¹ is clearly observed for TiO₂@SiO₂ that has been used four times.

The X-ray diffraction patterns of TiO₂@SiO₂ calcined at 200–500 °C are shown in Fig. 3. The calcination temperature greatly influences the crystalline structure of TiO₂@SiO₂. Anatase peaks are not detected for the TiO₂@SiO₂ sample calcined at 200 °C, which indicates that TiO₂ is amorphous or microcrystalline. When the calcination temperature is increased to 250 °C, the diffraction peak of anatase at about 25° (2 θ) appears. When the calcination temperature is increased to 300 °C, the peak at 25° strengthens, and anatase peaks at 37.8°, 48.0°, 53.7°, and 62.5° appear. With further increases in the calcination temperature, the diffraction peaks of anatase TiO₂ are further enhanced, and the numbers of crystal defects and intercrystalline disordered structures decrease, indicating that the crystal structure of anatase TiO₂ tends to integrate with increasing calcination temperature. At calcination temperatures of 400 and 500 °C, TiO₂@SiO₂ has an integrated anatase crystal structure.

The catalytic activities of TiO₂@SiO₂ in the transesterification of DMC and phenol are listed in Table 1. The calcination temperature strongly influences the catalytic performance of TiO₂@SiO₂. The catalytic activity declines with increasing calcination temperature from 200 to 500 °C, and phenol conversion reaches 41.8% at 200 °C. The Ti in amorphous TiO₂ is tetracoordinated, and tetracoordinated Ti is highly active in the transesterification of DMC and phenol [15]. However, the Ti in anatase TiO₂ is six-coordinated, and six-coordinated Ti is inactive in this transesterification. The amount of tetracoordinated Ti in TiO₂@SiO₂ decreases, and that of six-coordinated Ti increases with increasing calcination temperature. Consequently, the catalytic activity of TiO₂@SiO₂ decreases with increasing calcination temperature. A comparison of the activities of

Fig. 3. X-ray diffraction patterns of TiO₂@SiO₂ calcined at different temperatures. (1) 200 °C; (2) 250 °C; (3) 300 °C; (4) 400 °C; (5) 500 °C.

Table 1

Effect of calcination temperature on catalytic activity of core-shell $\text{TiO}_2/\text{SiO}_2$.

Calcination temperature (°C)	Phenol conversion (%)	Transesterification selectivity (%)	Yield (%)	
			MPC	DPC
TiO_2^*	23.3	99.8	8.7	14.5
200	41.8	100	17.7	24.1
250	32.1	99.8	17.8	14.3
300	23.9	99.8	12.5	11.3
400	4.5	96.7	3.2	1.1
500	5.0	99.1	3.8	1.2

Reaction conditions: phenol 160 mmol, DMC 160 mmol, catalyst 0.20 g, reaction temperature 150–180 °C, reaction time 9 h.

* Amorphous TiO_2 prepared by the same method as $\text{TiO}_2/\text{SiO}_2$ without adding SiO_2 with calcination temperature of 200 °C.

amorphous TiO_2 and $\text{TiO}_2/\text{SiO}_2$ calcined at 200 °C shows that the phenol conversion with amorphous TiO_2 is just 23.3%, whereas that with $\text{TiO}_2/\text{SiO}_2$ is 41.8%. The FTIR spectra in Fig. 2 show that TiO_2 and SiO_2 interact and form Ti–O–Si bonds. The formation of Ti–O–Si bonds is considered to be an important factor for high catalytic activity of $\text{TiO}_2/\text{SiO}_2$.

The effects of the amount of $\text{TiO}_2/\text{SiO}_2$ on the transesterification of DMC and phenol are shown in Fig. 4. The phenol conversion increases with increasing catalyst amount, and the phenol conversion and transesterification selectivity reach 41.8% and 100%, respectively, with 0.20 g of $\text{TiO}_2/\text{SiO}_2$. When the amount of $\text{TiO}_2/\text{SiO}_2$ is higher than 0.20 g, the phenol conversion changes slightly; 0.20 g is therefore the optimal amount of $\text{TiO}_2/\text{SiO}_2$.

The SiO_2 shell prevents leaching of TiO_2 from $\text{TiO}_2/\text{SiO}_2$ and increases the reusability. The used $\text{TiO}_2/\text{SiO}_2$ was recovered by filtration, washed with DMC, and dried at 200 °C. Figure 5 shows that the catalytic activity of recycled $\text{TiO}_2/\text{SiO}_2$ is similar to that of the fresh catalyst. The phenol conversion is above 40%, and the transesterification selectivity remains at 100% over four runs. These results demonstrate that $\text{TiO}_2/\text{SiO}_2$ has excellent reusability. Moreover, the Ti content is 51.9% for fresh $\text{TiO}_2/\text{SiO}_2$ and is 51.8% for $\text{TiO}_2/\text{SiO}_2$ after four cycles; this shows that the SiO_2 shell effectively prevents leaching of the active component, TiO_2 .

In summary, the $\text{TiO}_2/\text{SiO}_2$ prepared using a combination

Fig. 4. Effect of amount of $\text{TiO}_2/\text{SiO}_2$ on transesterification of DMC and phenol. Reaction conditions: phenol 160 mmol, DMC 160 mmol, calcination temperature 200 °C, reaction temperature 150–180 °C, reaction time 9 h.

Fig. 5. Reusability of $\text{TiO}_2/\text{SiO}_2$. Reaction conditions: phenol 160 mmol, DMC 160 mmol, catalyst 0.20 g, calcination temperature 200 °C, reaction temperature 150–180 °C, reaction time 9 h.

of reverse microemulsion and precipitation methods can be used as a heterogeneous catalyst for the transesterification of DMC and phenol. When $\text{TiO}_2/\text{SiO}_2$ was calcined at 200 °C and the catalyst amount was 0.20 g, the phenol conversion and transesterification selectivity were 41.8% and 100%, respectively. TiO_2 and SiO_2 interact and form Ti–O–Si bonds, and this improves the catalytic performance of $\text{TiO}_2/\text{SiO}_2$. The core-shell structure effectively prevents leaching of TiO_2 and increases the $\text{TiO}_2/\text{SiO}_2$ reusability. Core-shell $\text{TiO}_2/\text{SiO}_2$ is therefore a highly efficient heterogeneous catalyst for the transesterification of DMC and phenol and has promising applications.

References

- [1] Fukuoka S, Kawamura M, Komiya K, Tojo M, Hachiya H, Hasegawa K, Aminaka M, Okamoto H, Fukawa I, Konno S. *Green Chem*, 2003, 5: 497
- [2] Li B J, Ge X, Chen T, Hu X T, Wang G Y. *Chem Ind Eng Prog* (李碧静, 葛鑫, 陈彤, 胡徐腾, 王公应. 化工进展), 2010, 29: 847
- [3] Kim Y T, Park E D. *Appl Catal A*, 2009, 356: 211
- [4] Luo S W, Chen T, Tong D S, Zeng Y, Lei Y C, Wang G Y. *Chin J Catal* (罗淑文, 陈彤, 童东绅, 曾毅, 雷永诚, 王公应. 催化学报), 2007, 28: 937
- [5] Mei F M, Pei Z, Li G X. *Org Process Res Dev*, 2004, 8: 372
- [6] Chen T, Han H J, Yao J, Wang G Y. *Catal Commun*, 2007, 8: 1361
- [7] Chen T, Li B J, Hu X J, Wang G Y, Tang R Z, Yang J, Liu X R, Cai J S (陈彤, 李碧静, 胡晓佳, 王公应, 唐荣芝, 杨建, 刘旭冉, 蔡家胜). CN Patent 103120934A. 2013
- [8] Park O K, Kang Y S. *Colloids Surf A*, 2005, 257–258: 261
- [9] Hwang S T, Hahn Y B, Nahm K S, Lee Y S. *Colloids Surf A*, 2005, 259: 63
- [10] Wu L Z, Yu Y, Zhang Y, Li Y Z, Zhang Y, Zhi J F. *J Colloid Interface Sci*, 2012, 369: 179
- [11] Wang S, Wang T, Chen W X, Hori T. *Chem Commun*, 2008: 3756
- [12] Ren Y, Chen M, Zhang Y, Wu L M. *Langmuir*, 2010, 26: 11391
- [13] Cao T, Sun L T, Shi Y, Hua L, Zhang R, Guo L, Zhu W W, Hou Z S. *Chin J Catal* (曹婷, 孙立婷, 石玉, 华丽, 张然, 郭立, 朱闻闻, 侯震山. 催化学报), 2012, 33: 416
- [14] Zhang H J, Liu Y M, He M Y, Wu P. *Chin J Catal* (张海娇, 刘月明, 何鸣元, 吴鹏. 催化学报), 2006, 27: 749
- [15] Ge X, Li B J, Hu J, Chen T, Wang G Y, Hu X T. *Chem Eng (China)* (葛鑫, 李碧静, 胡静, 陈彤, 王公应, 胡徐腾. 化学工程), 2011, 39: 61

Graphical Abstract

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Core-shell $\text{TiO}_2@\text{SiO}_2$ catalyst for transesterification of dimethyl carbonate and phenol to diphenyl carbonate

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$\text{TiO}_2@\text{SiO}_2$ with a clear core-shell structure exhibits excellent catalytic performance in the transesterification of dimethyl carbonate and phenol. The catalyst was used four times with no loss of catalytic activity.

核壳结构 $\text{TiO}_2@\text{SiO}_2$ 催化碳酸二甲酯与苯酚酯交换合成碳酸二苯酯唐荣芝^{a,c}, 陈彤^{a,*}, 陈勇^b, 张元卓^{a,c}, 王公应^a^a中国科学院成都有机化学研究所, 四川成都610041^b后勤工程学院国防建筑规划与环境工程系, 重庆401311^c中国科学院大学, 北京100049

摘要: 以反相微乳液法和沉淀法相结合制备了核壳结构 $\text{TiO}_2@\text{SiO}_2$, 首次用于碳酸二甲酯与苯酚酯交换合成碳酸二苯酯反应, 显示较好的催化活性. 采用200 °C焙烧的 $\text{TiO}_2@\text{SiO}_2$, 用量0.20 g, 反应9 h, 苯酚转化率达41.8%, 酯交换选择性为100%. 透射电镜显示 $\text{TiO}_2@\text{SiO}_2$ 核厚壳薄, TiO_2 核直径220–300 nm, SiO_2 壳厚度40–60 nm, 具有介孔结构. $\text{TiO}_2@\text{SiO}_2$ 对碳酸二甲酯与苯酚酯交换反应有好的重复使用性, 使用4次苯酚转化率仍保持在40%以上. TiO_2 与 SiO_2 发生相互作用, Ti进入骨架形成Ti–O–Si键, 骨架Ti的形成提高了 $\text{TiO}_2@\text{SiO}_2$ 的催化性能.

关键词: 核壳结构; $\text{TiO}_2@\text{SiO}_2$; 碳酸二苯酯; 碳酸二甲酯; 酯交换

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碳酸二苯酯(DPC)是一种“绿色”工程塑料中间体, 低毒, 无污染, 可通过卤化、硝化、水解和氨解等反应合成多种有机化合物和高分子材料, 尤其可替代剧毒光气与双酚A通过熔融聚合反应合成性能优良的聚碳酸酯^[1]. 碳酸二甲酯(DMC)与苯酚酯交换反应是非光气路线合成DPC最有前景的方法之一^[2]. 由于均相催化剂分离回收困难, 因此对高活性多相催化剂的研究成为DMC与苯酚酯交换反应的热点. 目前, 已报道的多相催化剂主要是单一或复合金属氧化物^[3]、分子筛类^[4]、类水滑石^[5]和杂多化合物催化剂^[6], 酯交换收率可达40%左右, 但这些催化剂或选择性不好, 或重复使用性不好. 其中 $\text{TiO}_2/\text{SiO}_2$ 显示出较好的催化活性^[7], 但由于活性组分 TiO_2 严重流失而迅速失活. 利用核/壳技术可以通过壳

载体保护核, 避免负载在载体上的活性组分的流失^[8,9].

本文用反相微乳液法和沉淀法相结合制备了核壳结构 $\text{TiO}_2@\text{SiO}_2$ ^[10], 催化DMC与苯酚酯交换合成DPC, 旨在通过核壳结构阻止活性组分 TiO_2 的流失, 提高催化剂的可重复使用性.

$\text{TiO}_2@\text{SiO}_2$ 的制备不同于光催化剂中的 $\text{TiO}_2@\text{void}@\text{SiO}_2$ ^[11,12], 以反相微乳液法和沉淀法相结合, 先用浓氨水使过氧钛沉淀成 TiO_2 核后, 再在碱性条件下通过正硅酸乙酯水解将 SiO_2 包覆于 TiO_2 之上^[10]. DMC与苯酚酯交换反应在100 ml圆底三口烧瓶中进行, 在 N_2 保护下加入苯酚(AR, 广东光华化学厂有限公司)和催化剂, 搅拌下升温至175 °C时开始计时, 逐滴加入DMC ($\geq 99\%$, 石油大学胜华化工股份有限公司), 反应9 h. 反应产物通

过气质联用GC-MS (Agilent 6890/5973)定性, 气相色谱 (Agilent 7820A)校正归一法定量。

所得 $\text{TiO}_2@\text{SiO}_2$ 的透射电镜(TEM)照片如图1所示, 从图中可以看出, $\text{TiO}_2@\text{SiO}_2$ 核壳规整, 具有边界明显的双层结构, 其中作为活性组分的 TiO_2 核直径为220–300 nm, SiO_2 壳的厚度为40–60 nm, 核厚壳薄。同时, N_2 吸附(BET)结果显示 SiO_2 壳具有明显的介孔结构, 平均孔径为4.6 nm, 有利于反应物和产物扩散。

图2为 $\text{TiO}_2@\text{SiO}_2$ 的FTIR谱, 1628 cm^{-1} 处的O–H伸缩振动峰是吸附水产生的, $1096, 805$ 和 472 cm^{-1} 峰分别归属于Si–O–Si键的不对称伸缩振动、对称伸缩振动和弯曲振动。在 SiO_2 中, 位于 956 cm^{-1} 处的弱峰是Si–OH的伸缩振动峰^[13], 而在 $\text{TiO}_2@\text{SiO}_2$ 中, 956 cm^{-1} 处的Si–O峰蓝移至 964 cm^{-1} , 被认为是 TiO_2 与 SiO_2 发生相互作用形成Ti–O–Si键产生的不对称伸缩振动峰^[14]。使用4次的 $\text{TiO}_2@\text{SiO}_2$ 上, 仍可明显观察到 964 cm^{-1} 处的振动峰。

将核壳结构 $\text{TiO}_2@\text{SiO}_2$ 催化剂于200–500 °C焙烧, 其XRD谱如图3所示。可以看出, 焙烧温度对核壳结构 $\text{TiO}_2@\text{SiO}_2$ 的晶相结构有较大影响。200 °C焙烧的 $\text{TiO}_2@\text{SiO}_2$ 样品未出现锐钛矿 TiO_2 的特征峰, 表明 $\text{TiO}_2@\text{SiO}_2$ 中 TiO_2 以无定形或微晶结构存在。当焙烧温度升高至250 °C, 在 2θ 约为 25° 处开始出现锐钛矿 TiO_2 的衍射峰; 继续提高焙烧温度至300 °C, 25° 处的衍射峰增强, 同时在 $37.8^\circ, 48.0^\circ, 53.7^\circ$ 和 62.5° 处观察到锐钛矿 TiO_2 特征峰。继续提高焙烧温度, 锐钛矿 TiO_2 衍射峰强度进一步增大, 特征衍射峰发生锐化, TiO_2 晶粒长大, 晶粒缺陷及晶间无序结构减少, 表明锐钛矿 TiO_2 的晶型结构随焙烧温度提高而趋于完整。当焙烧温度达400和500 °C时, $\text{TiO}_2@\text{SiO}_2$ 的晶型结构完整, 呈典型的锐钛矿晶型结构。

$\text{TiO}_2@\text{SiO}_2$ 对DMC与苯酚酯交换反应的催化活性如表1所示。可以看出, 焙烧温度对 $\text{TiO}_2@\text{SiO}_2$ 的催化活性有较大影响。从200 °C升高到500 °C, 催化活性下降, 200 °C活性最好, 苯酚转化率为41.8%。无定形 TiO_2 中钛

以四配位存在, 四配位钛对该酯交换反应有活性^[15], 而锐钛矿 TiO_2 中钛主要以六配位形式存在, 其催化活性极低。随焙烧温度升高, $\text{TiO}_2@\text{SiO}_2$ 中四配位钛减少, 六配位钛增多, 因此 $\text{TiO}_2@\text{SiO}_2$ 的催化活性随焙烧温度升高而下降。进一步对比无定形 TiO_2 和200 °C焙烧的 $\text{TiO}_2@\text{SiO}_2$, 未包覆的无定形 TiO_2 上的苯酚转化率仅为23.3%, 而核壳结构 $\text{TiO}_2@\text{SiO}_2$ 上的苯酚转化率达41.8%。图2的FTIR谱显示, $\text{TiO}_2@\text{SiO}_2$ 中 TiO_2 与 SiO_2 发生相互作用, Ti进入骨架形成了Ti–O–Si键, 可认为是骨架Ti的形成提高了 $\text{TiO}_2@\text{SiO}_2$ 的催化性能, 是 $\text{TiO}_2@\text{SiO}_2$ 具有高活性的重要因素。

考察了 $\text{TiO}_2@\text{SiO}_2$ 的用量对DMC与苯酚酯交换反应的影响, 结果如图4所示。随催化剂用量增加, 苯酚转化率增大, 0.20 g时达最高为41.8%, 酯交换选择性为100%; 继续增加催化剂用量, 苯酚转化率变化不大。适宜的催化剂用量为0.20 g。

采用 SiO_2 包覆 TiO_2 旨在阻止 TiO_2 流失, 提高催化剂的重复使用性。将每次反应后经过滤回收的 $\text{TiO}_2@\text{SiO}_2$ 用DMC洗涤, 于200 °C干燥后直接使用, 其重复使用的测试结果如图5所示。催化剂使用4次, 苯酚转化率均保持在40%以上, 酯交换选择性仍为100%, 表明催化剂具有良好的重复使用性。新鲜 $\text{TiO}_2@\text{SiO}_2$ 中钛含量为51.9%, 4次使用后的 $\text{TiO}_2@\text{SiO}_2$ 中钛含量为51.8%, 显示 SiO_2 壳可有效阻止活性组分 TiO_2 的流失。

总之, 以反相微乳液法和沉淀法相结合制备的核壳结构 $\text{TiO}_2@\text{SiO}_2$ 材料, 可用作DMC与苯酚酯交换合成DPC的多相催化剂, 在200 °C焙烧、用量为0.20 g时, 获得41.8%苯酚转化率和100%酯交换选择性。 TiO_2 与 SiO_2 发生相互作用, Ti进入骨架形成Ti–O–Si键, 该骨架Ti结构提高了催化活性。核壳结构有效地阻止了活性组分 TiO_2 流失, 提高了催化剂的重复使用性, $\text{TiO}_2@\text{SiO}_2$ 使用4次活性没有明显下降。核壳结构 $\text{TiO}_2@\text{SiO}_2$ 是一种高效、有应用前景的DMC与苯酚酯交换反应合成DPC的多相催化剂。