NaY 分子筛超笼内离子液体和金属配合物自组装制备溶剂分子和金属配合物一体化催化剂

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摘要: 采用自组装-瓶中造船法在 NaY 分子筛超笼内, 将溴化 1-癸基-3-甲基咪唑离子液体和邻菲罗啉钯组合成一体化催化剂, 并用于苯胺羰化反应。结果表明, 相对于以离子液体为溶剂, 邻菲罗啉钯配合物/NaY 分子筛为催化剂的体系, 该一体化催化剂在离子液体和邻菲罗啉钯配合物用量显著降低的条件下, TOF 可达 23 000 h⁻¹, 而相应均相催化体系的 TOF 仅为 3 060 h⁻¹。

关键词: 活性位; 离子液体; 金属配合物; 羰化; 苯胺; 苯胺基甲酸甲酯; 转化频率

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Self-Assembly of Ionic Liquids and Metal Complexes in Super-Cages of NaY: Integration of Free Catalysts and Solvent Molecules into Confined Catalytic Sites

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Abstract: The integration of a free metal complex, Pd(phen)²⁺, and a room temperature ionic liquid (IL) solvent molecule, 1-decyl-3-methylimidazolium bromide, into a complete catalytically active site and confined in a NaY zeolite super-cage with an appropriate spatial arrangement was investigated. This integration was achieved through a molecular self-assembly method. A preliminary test of this catalyst system for the carbonylation of aniline to methyl phenyl carbamate indicated that far higher catalytic activity could be achieved (TOF increased from 3 000 to 23 000 h⁻¹) with far lower amounts of the IL solvent and the Pd complex in comparison with a simple mixture of Pd(phen)Cl₂/IL/NaY as the catalyst. This new system can also be applied to other areas of catalysis.

Key words: active site; ionic liquid; metal complex; carbonylation; aniline; phenyl methyl carbamate; turn over frequency

典型的均相催化体系通常由金属配合物催化剂和溶剂组成, 其中溶剂作为反应介质对提高催化剂活性具有重要作用。但我们推测, 在一个实际反应中, 大部分溶剂分子仅仅起反应介质的作用, 少量具有合适空间位置的溶剂分子有可能参与形成活性位 (见图 1(a))。那么, 如果将溶剂分子和金属配合物固

定在适当的位置上, 就有可能使用少量溶剂就可形成同样多的活性位 (见图 1(b))。

与有机溶剂相比, 离子液体具有低蒸气压和强静电场等特点, 因而可用于均相催化体系^[1]。近年来, 人们将离子液体固载^[2,3]或包载在多孔材料中^[4]进行催化反应。

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图 1 溶剂参与形成催化活性位 (a) 和空间限制下溶剂分子与金属配合物形成催化活性位假想图 (b)

Fig. 1. Illustration of (a) a whole catalytically active site in a homogeneous reaction and (b) an isolated catalytically active site confined in a nano-pore.

因此, 本文尝试原位自组装-瓶中造船法^[5], 将 1-癸基-3-甲基咪唑离子液体和邻菲罗啉钯配合物组装在 NaY 分子筛的超笼内, 制得金属配合物和溶剂分子一体化的催化剂. 首先将甲基咪唑、溴癸烷、 Pd^{2+} 和邻菲罗啉依次引入到 NaY 分子筛超笼中(超笼直径 1.2 nm, 通道直径 0.74 nm^[6]), 原位形成离子液体和钯的邻菲罗啉配合物(见图 2), 然后在自组装材料间的相互作用下, 离子液体和邻菲罗啉钯配合物分子可较为有序地分布于分子筛超笼中^[7].

本文制备了 Pd-phen-NaY (邻菲罗啉钯被组装于 NaY 分子筛超笼), Im-NaY (离子液体 1-癸基-3-甲基咪唑被组装于 NaY 分子筛超笼), Pd-Im-NaY (钯和离子液体被组装于分子筛超笼) 和 Pd-phen-

图 2 NaY 分子筛超笼中自组装/瓶中造船法合成离子液体和邻菲罗啉钯示意图

Fig. 2. The process for the self-assembly of IL and Pd complex in the super-cage of NaY.

Im-NaY (邻菲罗啉钯和离子液体被组装于分子筛超笼) 四种催化剂. 为了便于比较, 本文还采用 Pd-phen-NaY 浸渍离子液体的方法合成了 Pd-phen-NaY-Im 催化剂.

Pd-phen-Im-NaY 催化剂的制备方法如下. 将 10 g 的 NaY (Aldrich, 铝含量 6.8%) 和 25 ml 甲基咪唑依次加入到 250 ml 锥形瓶中, 在室温搅拌 12 h 后, 加入 75 ml 溴癸烷, 在 60°C 再搅拌 12 h (甲基咪唑和溴癸烷在使用前进行蒸馏处理). 将上述混合物过滤, 用 30 ml 热乙醇洗三次, 可获得约 11 g 的 Im-NaY 样品. 将该样品加入到 100 ml 锥形瓶中, 再加入 30 ml 蒸馏水和 4.8 ml 的 H_2PdCl_4 溶液 (0.028 mol/L), 在室温搅拌 12 h 后, 加入 1 g 邻菲罗啉, 并在室温下再搅拌 12 h. 最后将上述混合物过滤, 用乙醇和丙酮洗涤, 在 180°C 干燥 3 h, 即制得约 10 g 的 Pd-phen-Im-NaY 催化剂.

样品的原子发射光谱 (3520 ICP AES) 结果表明, 制得催化剂中 Pd 含量为 0.07%~0.09%. 红外光谱 (FT-IR) 结果表明, 催化剂 Im-NaY 在 1466 和 1571 cm^{-1} 处出现离子液体两个特征峰, 而它在 1169 cm^{-1} 处的特征峰被 Si-O-Si 的吸收峰覆盖. 这表明在 NaY 分子筛超笼中原位形成了离子液体和钯的邻菲罗啉配合物.

图 3 为各样品的拉曼 (Raman) (Nicolet 5700) 光谱. 可以看出, Im-NaY 表现出与纯离子液体不同的 Raman 谱. 这是由于有机金属配合物和离子液体被限制在纳米孔中, 可能导致分子对称性和几何结构发生变化所致^[8,9]. 可见, 在 NaY 分子筛超笼中可能形成了含有钯配合物和离子液体分子一体化催化剂. 进一步的 FT-IR 和 Raman 结果表明, Pd-phen-NaY 表现出与邻菲罗啉、氯化菲罗啉钯和 phen-NaY 催化剂不同的光谱特征. 这表明在 NaY 分子筛超笼中形成了不同于氯化菲罗啉的钯配合物, 但其结构还有待确定. 而 Pd-phen-Im-NaY 催化剂则表现出和 Im-NaY 相同的 FT-IR 和 Raman 光谱特征. 这可能是由于 Pd 担载量较低, 邻菲罗啉钯的光谱被离子液体的所掩盖. 而 Pd-phen-NaY-Im 的 Raman 光谱和离子液体的几乎一样, 但与 Pd-phen-Im-NaY 则明显不同. 这表明 Pd-phen-NaY-Im 中的离子液体处于 NaY 分子筛超笼的外部.

元素分析 (Elementar Vario EL) 结果表明, 这些

图3 不同样品的 Raman 谱

Fig. 3. Raman spectra of different samples. (1) Pd-phen-Im-NaY; (2) Im-NaY; (3) Pd-phen-NaY-Im; (4) Im (1-decyl-3-methyl imidazolium bromide).

催化剂中离子液体含量为 8.7%~11.2% ($(1.7\sim2.2) \times 10^{20}$ 离子液体分子/g). 在 Pd-phen-NaY 中, 邻菲罗啉含量为 0.2% ($\sim 6 \times 10^{18}$ 邻菲罗啉分子/g). 由于 1 g 的 Pd-phen-Im-NaY 中含有 $\sim 2.6 \times 10^{20}$ 个超笼^[6], 因此每 100 个分子筛超笼中含 65~85 个离子液体分子, 仅 2.1 个钯配合物.

苯胺羰化反应是非光气合成异氰酸酯中间体的一个重要方法, 而离子液体又是苯胺羰化反应的有效溶剂^[10,11]. 因此, 本文以苯胺羰化为探针反应考察了所合成催化剂的性能, 结果列于表 1. 可以看出, 当以 Pd-phen-NaY 或 Pd-Im-NaY 为催化剂时, 苯胺转化率仅为 27% 或 21%; 而以 Pd-phen-Im-NaY 为催化剂时, 苯胺转化率达到 81%, TOF 值高达 $23\,000\text{ h}^{-1}$. 当催化剂 Pd-phen-Im-NaY 用量由 50 mg 提高到 100 mg 时, 苯胺转化率可达 95%. 当以 Pd-phen-NaY-Im 为催化剂时, 苯胺转化率仅为 10%. 以机械混合的 Pd(phen)Cl₂/Im/NaY 为催化剂时, 苯胺转化率为 67%, 而此时 Pd 和离子液体用量分别为 Pd-phen-Im-NaY 催化剂时的 20 和 200 倍. 当重复使用一次 Pd-phen-Im-NaY 催化剂时, 苯胺转化率仍可达 73%.

表 1 苯胺氧化羰化制备 N-苯基氨基甲酸酯

Table 1 Oxidative carbonylation of aniline over NaY confined Pd-ionic liquid catalysts to phenyl methyl carbamate

$\text{C}_6\text{H}_5\text{NH}_2 + \text{CO} + \text{O}_2 \xrightarrow[\text{catalyst}]{\text{MeOH}} \text{C}_6\text{H}_5\text{NHCO}_2\text{Me}$				
Entry	Catalyst	Conversion (%)	Selectivity (%)	TOF ^c (h ⁻¹)
1	Pd-phen-NaY	27	~99	8500
2	Pd-Im-NaY	21	~99	6600
3	Pd-phen-Im-NaY	81	~99	23000
4 ^a	Pd-phen-Im-NaY	95	~99	13000
5	Pd-phen-NaY-Im	10	~99	2400
6 ^b	Pd(phen)Cl ₂ /Im/NaY	67	~98	3060
7	Pd-phen-Im-NaY	73	~99	20000

Reaction conditions: catalyst 50 mg, aniline 1 ml, MeOH 5 ml, CO 5.5 MPa, O₂ 0.5 MPa, 150 °C, 1 h; ^acatalyst 100 mg; ^bPd(phen)Cl₂ 1 mg, IL 1 ml, NaY 50 mg.

^cDefined as the moles of substrate converted per mole of Pd per hour.

综上所述, 与 Pd-phen-NaY, Pd-Im-NaY 和机械混合的 Pd(phen)Cl₂/Im/NaY 相比, 一体化催化剂 Pd-phen-Im-NaY 表现出更高的催化苯胺氧化羰化活性. 这表明离子液体和 Pd 配合物被固载于分子筛超笼后, 其催化性能明显改善; 而高活性的催化体系, 除了需要 Pd 配合物、离子液体和 NaY 之间的协同作用外, 空间协同效应也是必需的. 结果还表明, 钯、邻菲罗啉、甲基咪唑和溴癸烷可能在分子筛超笼中原位形成了 Pd(phen)²⁺ 配合物和离子液体分子, 且在分子筛超笼的作用下形成了高活性的活性位, 而所形成活性位的数量约占分子筛所有超笼的 2% 以下.

本文进一步对该催化剂进行了计算机模型化 (Forcite Plus/Materials Studio, Accelrys), 结果示于图 4. 结果表明, 在同一个分子筛超笼中组装一个离子液体分子和一个 Pd(phen)²⁺ 配合物是可能的. 离子液体分子和 Pd(phen)²⁺ 配合物平行分布, 两者之间

图4 离子液体分子和 Pd(phen)²⁺ 在 NaY 分子筛超笼中的空间排布

Fig. 4. The spatial arrangement of the ionic liquid molecule and the Pd(phen)²⁺ complex in the super-cage of NaY.

有 0.5~0.6 nm 的空间, 可满足分子筛超笼中反应物和产物的传输。

综上所述, 本文采用自组装-瓶中造船法在 NaY 分子筛超笼内, 将离子液体分子和钯的邻菲罗啉配合物组装成金属配合物和溶剂分子一体化催化剂。用于苯胺氧化羰化反应时, 所使用的催化剂和溶剂比常规均相反应时的更少, 而催化剂的活性更高。该观念有助于其它反应催化剂的设计。

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英 译 文

English Text

A typical liquid homogeneous catalysis system generally consists of a transition metal complex and a solvent, in which the solvent as a reaction medium plays a very important role in achieving satisfactory catalytic performance. These solvent molecules may participate directly in the catalytic reaction as ‘ligands’ of the metal complex and this may establish an integrated or whole catalytically active site in addition to its role as a reaction medium. This means that only those solvent molecules located in an appropriate spatial position can participate in the formation of active sites with metal complexes (Fig. 1(a)). Large amounts of solvent molecules, however, are not a part of these active sites. Far fewer metal

complexes and solvent molecules would be required if they are fixed at spatially appropriate positions (Fig. 1(b), or part of the dashed line in Fig. 1(a)).

Room temperature ionic liquids (RTILs) possess peculiar physicochemical properties such as very low vapor pressures and strong electrostatic fields in comparison with molecular liquids and they offer great opportunities to develop novel homogeneous catalysis systems [1]. Recently, the immobilization of RTILs onto solid supports [2,3] and the confinement of RTILs in porous materials [4] have been reported.

Herein, we report a new system wherein the integration of the free metal complex and the RTIL solvent molecule into a complete catalytically active site inside the super-cage of a NaY zeolite and with an appropriate spatial arrangement is achieved through molecular self-assembly (MSA) [5]. Initially, the IL (1-methyl-imidazole and decyl bromide) and metal complex (Pd^{2+} and phenanthroline (phen)) fragments are successively introduced into the NaY super-cage (super-cage with a 1.2 nm diameter and channels with a 0.74 nm diameter [6]). The corresponding metal complex ($\text{Pd}(\text{phen})^{2+}$) and the IL (Im, 1-decyl-3-methylimidazolium bromide) are then synthesized in situ, as shown in Fig. 2. Recent studies have suggested that synergistic interactions between self-organizing components and a self-assembling material can lead to hierarchically ordered structures; therefore, these Pd complexes and IL molecules are distributed in an orderly fashion in the NaY super-cage [7].

For comparison, several samples with slightly different loadings of Pd, ligand, and IL were prepared by MSA and these are denoted as Pd-phen-NaY, Im-NaY, Pd-Im-NaY, and Pd-phen-Im-NaY. Pd-phen-NaY-Im was also prepared by the impregnation of the assembled Pd-phen-NaY with the Im IL.

A typical procedure for the preparation of the catalyst Pd-phen-Im-NaY is as follows. A 10 g sample of NaY (Aldrich, aluminum content = 6.8%) and 25 ml methylimidazole were added to a 250 ml round bottom flask and stirred at RT for 12 h. Then, 75 ml of decyl bromide was added and stirred at 60 °C for 12 h. The methyl imidazole and decyl bromide were distilled before use. The mixture was filtered and washed 3 times (30 ml $\times$ 3) with hot ethanol. A white solid powder (~11 g) of Im-NaY was thus obtained and the Im-NaY was transferred into a 100 ml conical flask. Then, 30 ml H_2O and 4.8 ml H_2PdCl_4 solution (0.028 mol/L) were added and stirred at RT for 12 h. Finally, 1 g of phen was added and stirred at RT for another 12 h. The reaction mixture was filtered and washed with ethanol and acetone, upon which it was dried at 180 °C for 3 h to obtain ~10 g Pd-phen-Im-NaY. The other catalysts were prepared using a similar procedure.

Analysis by atomic emission spectrometry (3520 ICP AES) showed that Pd was successfully introduced into the

NaY with varied loadings of 0.07%–0.09% for the different assembled samples. FT-IR characterization (Nicolet Nodule) showed that three characteristic peaks are present for the pure Im IL and two of them at 1 466 and 1 571 cm^{-1} were also observed for Im-NaY. The peak at 1 169 cm^{-1} was overlapped by the strong Si–O–Si peak. This result indicated that an in situ formation of the Im ionic liquid occurred and this probably took place within the NaY super-cage. Raman characterization (Nicolet 5700) of the Im-NaY showed abnormal Raman spectra in comparison with the pure and bulk Im IL (Fig. 3).

This phenomenon was also observed when an organometallic complex [8] or an IL [9] was confined in nanoporous materials, which resulted from unusual changes in the symmetry and coordination geometry of the molecules confined in a nanoscale space. The FT-IR and Raman spectra of Pd-phen-NaY are quite different from that of free phenanthroline, Pd(phen)Cl₂, and the assembled phen-NaY, which suggests that a different Pd complex forms in the NaY but its structure is not clear at this stage. For Pd-phen-Im-NaY, the same FT-IR and Raman spectra as for Im-NaY are observed and the characteristic peaks of the Pd complex could not be observed because of the overlapping IL peaks and the low loading of Pd. The Raman spectrum of Pd-phen-NaY-Im is almost the same as that of pure Im IL but quite different from that of Pd-phen-Im-NaY suggesting that the Im IL in Pd-phen-NaY-Im was not incorporated into the super-cage of the NaY zeolite.

Elemental analysis (Elementar Vario EL) showed that the IL concentration in all these samples was between 8.7% and 11.2% (or $\sim(1.7\text{--}2.2) \times 10^{20}$ IL molecules/g). The phenanthroline content in Pd-phen-NaY was $\sim 0.2\%$ (or 6×10^{18} phenanthroline molecules/g). Because there are 2.6×10^{20} super-cages per gram of Pd-phen-Im-NaY (pore volume ≈ 0.34 ml/g, 1.3 nm diameter pores) [6], the ratio of IL molecules/super-cages $\approx (65\text{--}85)/100$ and the ratio of Pd atoms/super-cages $\approx 2.1/100$.

The carbonylation of aniline is an important process for the phosgene free synthesis of isocyanate, and RTILs is effective in these reactions [10,11]. Therefore, aniline carbonylation was selected as a model reaction to test the catalysts (Table 1). For the synthesis of methyl phenyl carbamate (MPA) from aniline, the Pd-phen-NaY and Pd-Im-NaY catalysts had lower activity (entries 1 and 2). Pd-phen-Im-NaY greatly increased the catalytic activity and the TOF reached 23 000 h^{-1} (entry 3), while the conversion reached 95% when more catalyst was used (entry 4). However, only $\sim 10\%$ conversion was obtained for Pd-phen-NaY-Im (entry 5). The catalysts prepared by self-assembly had much higher

catalytic activity than the simple mixture of Pd(phen)Cl₂/Im/NaY (entry 6) although ~ 200 times more ionic liquid and ~ 20 times more Pd were used in Pd(phen)Cl₂/Im/NaY. Furthermore, the reuse of Pd-phen-Im-NaY gave a 73% conversion (entry 7), which indicated that the reuse of this catalyst system is possible.

Based on the fact that the catalytic activity of Pd-phen-Im-NaY was far higher than that of Pd-phen-NaY, Pd-Im-NaY, and the simple mixture of Pd(phen)Cl₂/Im/NaY, we suggest that the enhanced catalytic activity results from the formation of an integrated or a whole catalytically active site consisting of the Pd(phen)²⁺ complex and the Im IL in an appropriate spatial arrangement within the super-cage of NaY. Therefore, a synergism between the Pd complex, the IL, and NaY is necessary, and this spatial synergism is required for enhanced catalytic performance. The reaction results also suggest that in addition to the introduction of Pd, phenanthroline, methyl imidazole, and decyl bromide into the NaY and the in situ formation of Pd(phen)²⁺ and Im IL, both the Pd(phen)²⁺ and the Im IL can incorporate into the same NaY super-cage with an appropriate spatial arrangement although these integrated catalytic sites are few (less than 2% of NaY super-cages).

Computer modeling (Forcite Plus/Materials Studio, Accelrys) indicated that the self-assembly of an Im IL molecule and a Pd(phen)²⁺ complex in the same super-cage of NaY was possible and a suitable spatial arrangement was also calculated (Fig. 4). The Im IL and the Pd(phen)²⁺ were located in parallel positions within the super-cage. The computer model also revealed that some space (0.5–0.6 nm between the planes of the phenanthroline and the imidazolium rings) exists for reactant transportation.

In conclusion, a novel method for the integration of a free metal complex and a RTIL molecule into a NaY zeolite super-cage, which formed an effective catalytic site, was developed by molecular self-assembly. Far higher catalytic activity was achieved for the carbonylation of aniline using much lower amounts of ionic liquid as a solvent and less metal complex as well. This new system can be applied to other areas of catalysis.

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