

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-methyl imidazolium 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; turnover frequency

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

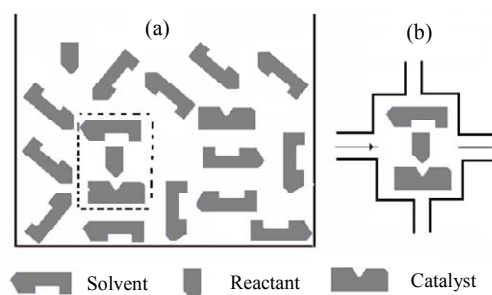


Fig. 1. Illustration of (a) a whole catalytically active site in a homogeneous reaction and (b) an isolated catalytically active site confined in a nano-pore.

Received date: 14 March 2010.

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Foundation item: Supported by the National Natural Science Foundation of China (20533080).

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DOI: 10.1016/S1872-2067(09)60090-5

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-methyl imidazolium 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 ($30 \text{ ml} \times 3$) with hot ethanol. A white solid powder ($\sim 11 \text{ g}$) 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 $\sim 10 \text{ g}$ Pd-phen-Im-NaY. The other catalysts were

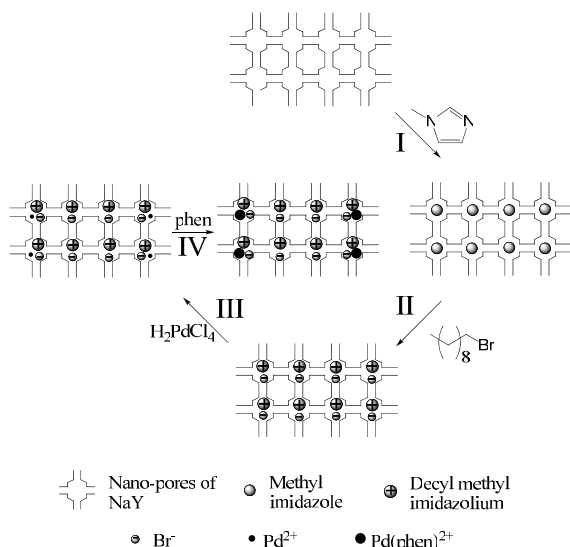


Fig. 2. The process for the self-assembly of IL and Pd complex in the super-cage of NaY.

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 1466 and 1571 cm^{-1} were also observed for Im-NaY. The peak at 1169 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, $\text{Pd}(\text{phen})\text{Cl}_2$, 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.

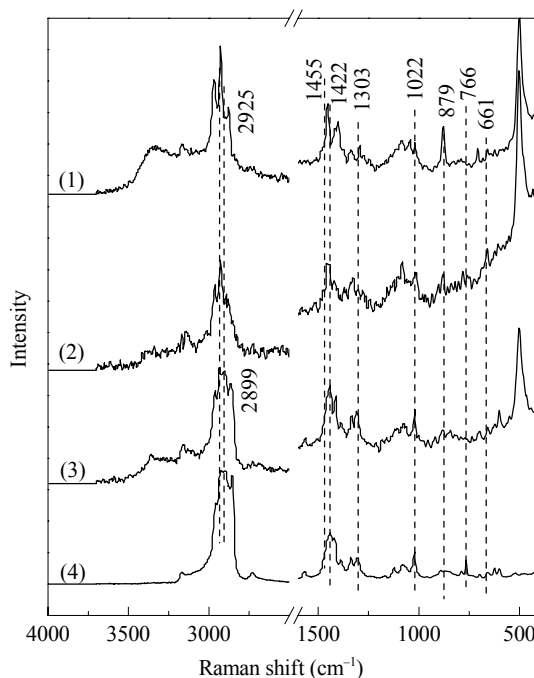
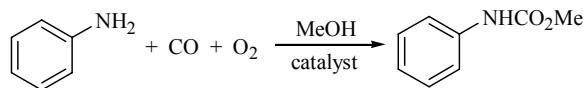


Fig. 3. Raman spectra of different samples. (1) Pd-phen-Im-NaY; (2) Im-NaY; (3) Pd-phen-NaY-Im; (4) Im.

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

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.

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 syn-

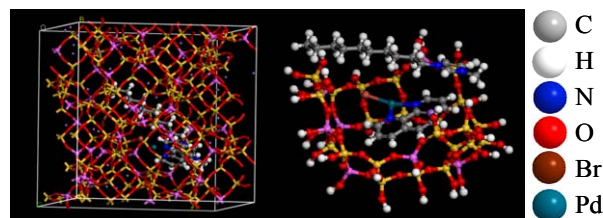


Fig. 4. The spatial arrangement of the ionic liquid molecule and the Pd(phen)²⁺ complex in the super-cage of NaY.

ergism 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.

Acknowledgements

We thank NeoTrident Technology Limited for helping with computer modeling.

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