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Sustainable catalysts for methanol carbonylation

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Methanol carbonylation is the most important process for manufacturing C2 molecules from methanol. The present industrial carbonylation has been proven to be the most successful process on economical grounds. However, there is a request to develop more sustainable and 'green' processes to overcome the inherent drawbacks. Well-designed cross-linked copolymers were prepared and used as support for the simultaneous immobilization of rhodium and iodide species. The resulting catalyst was proven to be highly active in CH_3I-free methanol carbonylation and methyl acetate was the main product. Approximately 90% of methanol was converted after a two-hour reaction time at 120 °C under a CO pressure of 3.0 MPa. The immobilization strategy of the active species works efficiently and the present methanol carbonylation catalyst shows good recyclability. After regenerating the catalyst twice over a fifteen-batches test, the catalyst keeps an acceptable activity. The process based on the present catalyst is evidently a promising sustainable methanol carbonylation.

Introduction

The homogeneous carbonylation of methanol is one of the major industrial applications of homogeneous catalysis.[1] Its products, methyl acetate and acetic acid, are important aliphatic intermediates which are used for the manufacture of many industrially significant secondary products such as acetate esters, acetate salts, chloroacetic acids, acetic anhydride and ketene. In the late 1950s, Reppe and coworkers at BASF developed and commercialized a cobalt iodide-based methanol carbonylation process under relatively high reaction temperatures and pressures.[2] A more efficient iodide-promoted rhodium complex catalyst was discovered by Paulik and Roth at Mosanto[3] and this process has become the main technology for methanol carbonylation with the licensed operation of BP Chemicals and Hoechst-Celanese. In the early 1990s, BP Chemicals developed and commercialized an iridium-complex catalyst as the Cativa™ process.[4] In China, the catalysts of our research group have been commercialized in Jiangsu (1.2×10^6 tonnes per annum) and Henan (0.6×10^6 tonnes per annum). Homogeneous methanol carbonylation has been intensively investigated and numerous reviews cover this subject.[5]

Although the present industrial processes have excellent catalytic activity and selectivity, there is plenty of room for improvement. Iodide is employed as the main cocatalyst for both the rhodium and iridium catalysts. Expensive materials are required to construct equipment to resist the corrosion of HI. Halide-free methanol carbonylation processes may lead to a considerable decrease in plant construction costs. In the present homogeneous processes, the product separation and catalyst recycling are carried out through continuous distillation columns and catalyst recycling stream systems. A heterogeneous catalyst, which has competitive activity and selectivity with the existing homogeneous catalysts, could overcome the engineering concerns about product–catalyst separation which hamper homogeneous processes. Various solid supports, including carbon materials, inorganic oxides, zeolites and polymeric materials, have been employed to immobilize expensive rhodium catalysts for liquid or vapor phase heterogeneous methanol carbonylation.[5] It was revealed that the ionic attachment strategy was the most efficient supporting model for rhodium catalysts.[6] In 1998, Chiyoda and UOP claimed the commercialization of heterogeneous methanol carbonylation as *Acetica*™ process, which is based on the support of polyvinylpyridine resin.[7] Our research group has reported many results of heterogeneous methanol carbonylation and a pilot system was built up.[8] In all heterogeneous processes, iodide cocatalyst must be added to the reactant stream and then separated from the catalytic system with the product. The problems with recycling the iodide cocatalyst actually limit the scale of heterogeneous methanol carbonylation. Some efforts have been made to address these issues, such as the development of halide-free dimethyl ether carbonylation, methylformate isomerization and oxidative carbonylation of

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methane or ethane. However, their activity cannot compete with iodide-cocatalyzed rhodium catalysts.

Catalysis plays a critical role in promoting the sustainability and eco-efficiency of methanol carbonylation processes. The sustainability of chemical processes, as promoted by the European Technology Platform on Sustainable Chemistry (ETP SusChem),[9] is relevant to process intensification. A core technology of process intensification is utilised to develop new catalysts, which allow improvements in yields/productivity and abate process costs through longer catalyst life, milder reaction conditions, and reduction of separation and environmental costs.[10,11] In this work, sustainable methanol carbonylation was achieved by the simultaneous immobilization of rhodium and iodide species over well-designed cross-linked copolymeric materials. In the catalytic cycle, the terminal groups of copolymeric supports are involved as cocatalysts. The immobilization strategy works effectively and very low rhodium and iodide concentrations are observed in the product stream. The catalyst shows good recyclability. After the fifteen-run test, no significant loss of catalytic activity was observed. This process is evidently a promising sustainable methanol carbonylation.

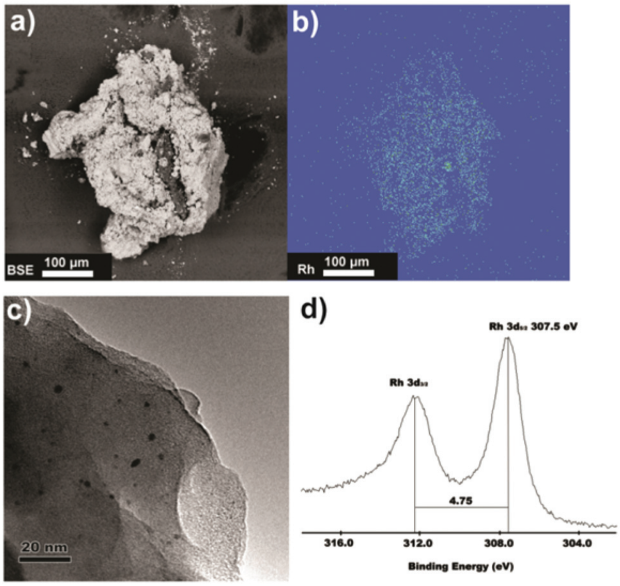
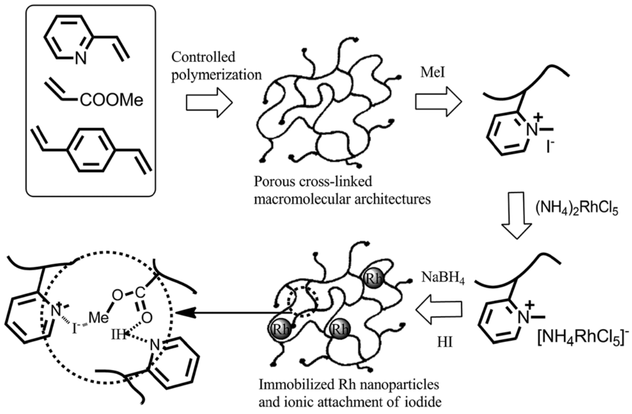


Fig. 1 (a) A selected catalyst particle. (b) EMPA image of the dispersion of Rh species over the copolymeric support. (c) TEM image of Rh nanoparticles over the copolymeric support. (d) XPS peaks of Rh species over the copolymeric support.

Results and discussion

Heterogenizing Rh and iodide species over cross-linked polymeric materials

Rh catalytic species and the iodide cocatalyst were simultaneously immobilized over cross-linked polymeric supports through the route in Scheme 1. Porous cross-linked macromolecular architectures were synthesized by controlled polymerization. Approximately 30% of pyridine groups were methylated. Rh species and iodide ions were immobilized through strong ion-pair interactions and the steric effect of cross-linked polymeric architectures. Supported Rh species were converted to zero-valent metal nanoparticles. The dispersion state of Rh nanoparticles was characterized by EMPA. Fig. 1a shows the selected sample and Fig. 1b is the dispersion of Rh nanoparticles over copolymeric supports. There is some negligible background noise in Fig. 1b. The bright points are Rh-enriched spots. The TEM image (Fig. 1c) demonstrates that Rh nanoparticles are kept in a monodispersed state. Their size distribution is in the range of 1–3 nm. Fig. 1d shows the XPS peaks of Rh nanoparticles. The binding energy of Rh $3d_{5/2}$ is 307.5 eV, which is attributed to zero-valent Rh species.



Scheme 1 Schematic illustration of the preparation procedure of cross-linked copolymer supported Rh nanoparticles and iodide species.

Cross-linked polymeric supports contain functional groups that act as promoters or anchoring sites for catalysts. Heterogenizing the homogeneous methanol carbonylation catalyst by immobilization over these functional groups is the key to developing chemically homogeneous but physically heterogeneous catalysts. Fitting of C 1s envelope in the XPS spectrum of the cross-linked polymeric support resulted in the identification of four chemical states of carbon. Peaks at the higher binding energy of 287.4 eV and 288.5 eV are attributed to methylated pyridine groups and methyl carboxylate groups (Fig. 2a). Fitting of N 1s resulted in the identification of two chemical states of nitrogen: one with a binding energy of 399.7 eV with an atomic concentration of 34.6% and another at 398.6 eV with an atomic concentration of 65.4% (Fig. 2b). The peak at the higher binding energy is attributed to the methylated pyridine groups, which are anchoring sites for active Rh species. Other pyridine groups are base sites for adsorbing HI. Methyl carboxylate groups are cocatalysts for converting methanol to methyl iodide, which is the rate-determining step in the catalytic cycle of methanol carbonylation (Scheme 1).

Catalytic activity and mechanistic aspects of methanol carbonylation over copolymeric catalysts

Methanol carbonylation to give acetic acid involves formal insertion of carbon monoxide into the C–O bond of methanol.

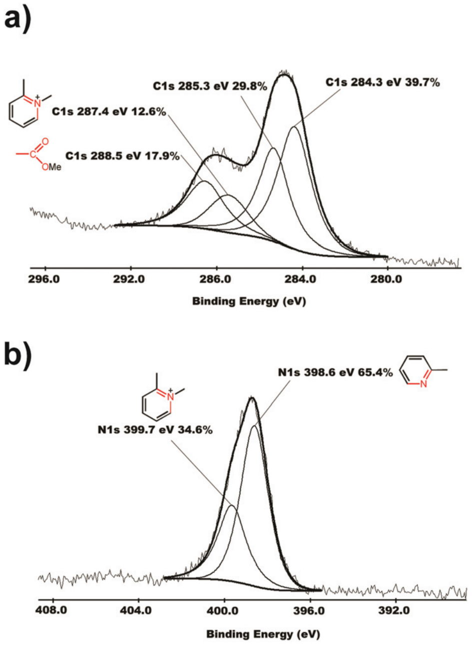
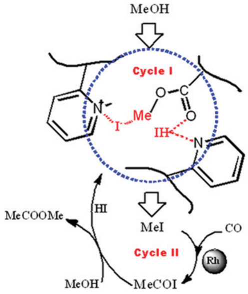


Fig. 2 (a) Fitting of C 1s envelope in the XPS spectrum of the copolymeric support. (b) Fitting of N 1s envelope in the XPS spectrum of the copolymeric support.



Scheme 2 Proposed catalytic cycle of methanol carbonylation over the copolymeric catalyst.

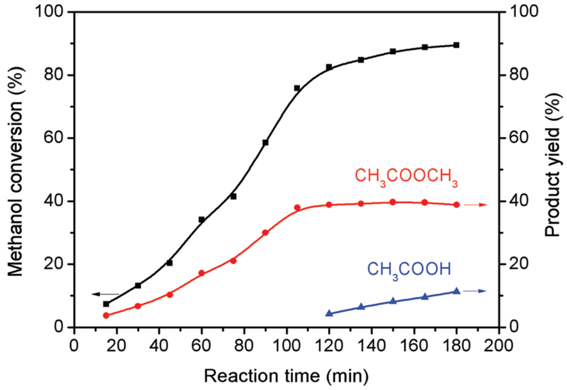


Fig. 3 Methanol carbonylation over the copolymeric catalyst.

The Rh catalyst does not activate methanol directly. More active methyl substrates must be generated *in situ* as the reactants. Under the typical industrial conditions, methyl iodide is added as a cocatalyst and the iodide promoter is recycled in the form of HI to convert methanol into methyl iodide. In a working catalytic system, the reaction medium is acetic acid and methanol is converted into methyl acetate. Methyl acetate is activated to form methyl iodide with the aid of the iodide promoter. As shown in Scheme 2, side-groups (methyl acetate) and anchored iodide promoters over the cross-linked polymeric architectures facilitate the catalytic cycle of converting methanol to methyl iodide. The methyl iodide undergoes carbonylation by the Rh catalyst to give acetyl iodide, which is rapidly hydrolyzed or alcoholyzed to acetic acid or acetate ester. The activity of the polymeric catalyst was tested by directly suspending it in pure methanol under carbon monoxide (3.0 MPa). Methanol was gradually converted into methyl acetate and acetic acid. After 180 min under 3.0 MPa CO with a continuous feeding flow, the methanol conversion reached approximately 90% (Fig. 3). Methyl acetate was the main carbonylation product. The yield to acetic acid was approximately 10%. This methanol carbonylation process proceeded without the addition of iodide promoters (methyl iodide or HI).

A model reaction was performed to investigate the involvement of the functional polymeric catalyst in the methanol carbonylation. The catalyst (0.5 g) was suspended in 20 ml reaction medium of 1,2-dichlorobenzene–water (v/v 5 : 1). The reaction was performed under typical conditions. Acetic acid was detected after the reaction. The amount of acetic acid in the resulted mixture is a function of the load of iodide promoters over the cross-linked polymeric architectures (Fig. 4a). The methyl acetate groups of the copolymeric chains were converted to methyl iodide (Scheme 2). The carbonylation over Rh sites and the subsequent hydrolysis led to the formation of acetic acid. The presence of iodide promoter over the copolymeric is the key to activating the methyl acetate to form more active methyl iodide. As revealed by Fig. 4a, the conversion of methyl acetate is determined by the load of iodide promoters, which is represented by the XPS intensity ratio of I 3d peak to N 1s peak. The calculated maximum amount of acetic acid was derived from the proportion of methacrylate ester monomer in the copolymeric chains on the supposition that methyl acetate groups were totally converted. The production of acetic acid in the methanol-free medium proved that methyl acetate groups and iodide promoters over the copolymeric chains were involved in the catalytic cycle as shown in Scheme 2.

Methanol from the reaction medium was activated to methyl iodide with the aid of methyl acetate groups and iodide promoters over the copolymeric chains. Methanol was smoothly carbonylated according to the mechanism depicted in Scheme 2. The load of iodide promoters over the cross-linked copolymeric architectures directly affects the reaction rate of methanol activation, which is the rate-determining step of methanol carbonylation. Fig. 4b shows that the TOF of methanol carbonylation increases sharply with the increase of the iodide promoter load. The presence of methyl acetate side-groups was indispensable to methanol activation. Model

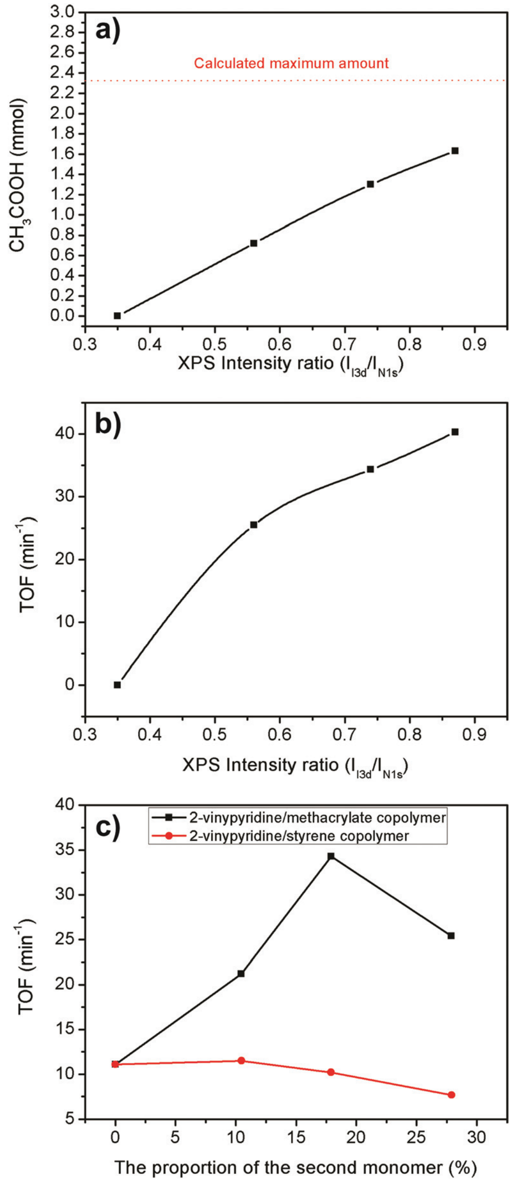


Fig. 4 (a) Experimental results about the involvement of methyl acetate groups over copolymeric chains in the carbonylation process. (b) The relationship between methanol carbonylation activity and the load of iodide promoters over the copolymeric support. (c) The relationship between methanol carbonylation activity and the proportion of methacrylate ester monomer in the copolymeric chain.

catalysts with various proportions of methacrylate ester monomer in the copolymeric chains were investigated to address this relationship. As shown in Fig. 4c, when methacrylate ester monomer is replaced with styrene, the copolymeric support of vinyl pyridine–styrene exhibits low catalytic activity. There is an optimum proportion of methacrylate ester monomer in the copolymeric chains. Methanol carbonylation exhibits the highest TOF at the proportion of approximately 18 mol% under typical reaction conditions. When the proportion reaches 25 mol%, a sharp decrease in the TOF value is observed. The resulting decrease in the proportion of vinyl pyridine lowers the local concentration of iodide promoters over the copolymeric architectures, and then leads to the loss of catalytic activity.

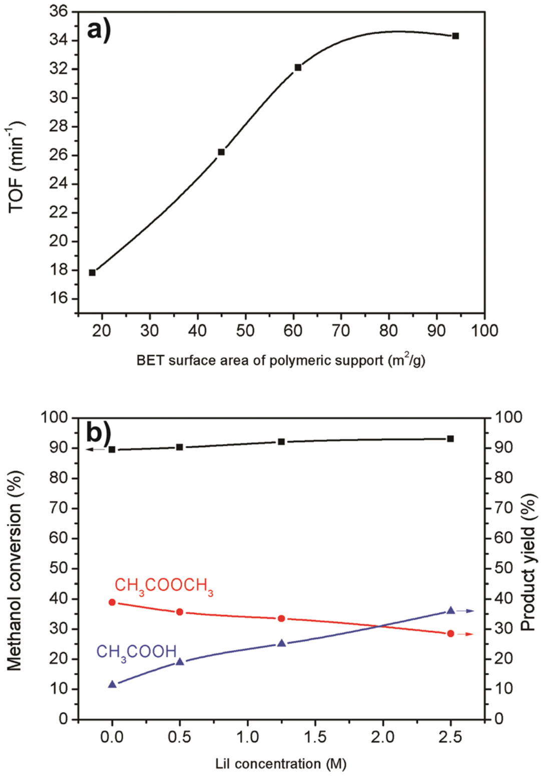


Fig. 5 (a) The TOF of methanol carbonylation as a function of the surface area of the copolymeric support. (b) The influence of adding LiI into the methanol carbonylation mixture.

Porosity of the copolymeric support is another important factor in controlling the mass transfer of methanol activation. The surface area of the copolymeric support was adjusted by controlling the addition of pore templates during the synthetic procedure. Fig. 5a shows the TOF of methanol carbonylation as a function of the surface area of the copolymeric support. The increase in the surface area markedly improves the catalytic activity in methanol carbonylation. When the surface area reaches 70 m^2 g^{-1}, the TOF of methanol carbonylation exhibits little fluctuating.

As exemplified by the Celanese Acid Optimization (AO Plus) technology,[12] lithium iodide was implemented to increase the productivity of rhodium-complex-catalyzed methanol carbonylation at very low water concentrations. It has been found that lithium iodide promotes the activation of methyl acetate to methyl iodide[13] and the subsequent oxidative addition of methyl iodide to rhodium catalysts.[14] In this work, the promoting effect of lithium iodide was investigated under different concentrations in the reaction solution. As shown in Fig. 5b, the addition of lithium iodide exercised very little influence upon the conversion of methanol. However, the selectivity toward acetic acid increased with the concentration of lithium iodide.

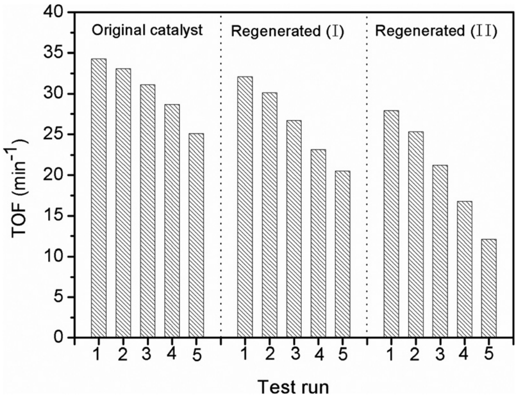


Fig. 6 The recyclability of the cross-linked copolymer supported catalyst.

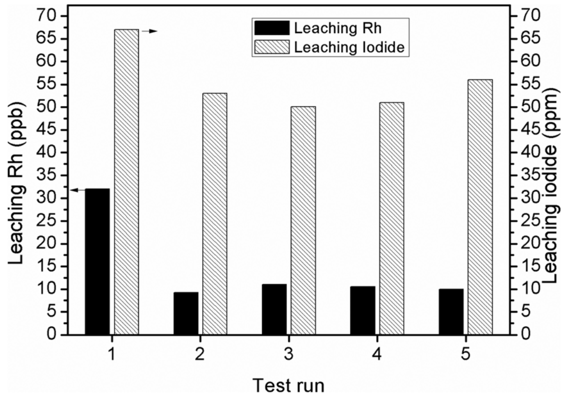
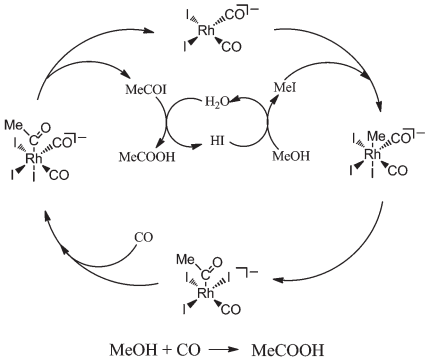


Fig. 7 The leaching amount of rhodium species and iodide promoters in the reaction solution after each test batch of the first five-run test depicted in Fig. 6.

Recyclability and stability of the catalyst

The recyclability of the cross-linked copolymer supported catalyst was explored through a five-run recycling test. Product–catalyst separation was carried out through a simple filtration. In the subsequent batch test, a continuous filter was used to separate the catalyst. The catalyst was recycled into the autoclave with the methanol feedstock stream. The catalyst exhibited an approximately 25% loss of activity after the fifth test (Fig. 6). The used catalyst can be regenerated by impregnation in a diluted methanol solution of HI. The surplus iodide ions were washed out with methanol until there were no iodide ions in the cleaning fluid. In the second five-run consecutive test, a similar downward tendency in catalytic activity was observed. The catalyst was regenerated twice and fifteen batches of activity tests were performed to investigate its recyclability and stability, as shown in Fig. 6. It was found that the gradual leaching of iodide promoters from the copolymeric architectures directly led to the downward tendency in the catalytic activity during each five-run consecutive test. The methanol activation over the copolymeric chains is attributed to the leaching of iodide promoters, as revealed by Scheme 2. However, a simple regeneration process can mitigate this problem. Another inevitable problem is rhodium leaching caused by the formation of carbonyl complexes over the rhodium nanoparticle surface during the methanol carbonylation. After the second regeneration, the reactivated catalyst retained approximately 80% of the catalytic activity of the fresh one (Fig. 6). This decrease is attributed to rhodium leaching.

The leaching degree of rhodium species and iodide promoters was measured by determining their concentrations in the reaction solution after each test batch. Fig. 7 shows the measurement results of the first five-run test depicted in Fig. 6. The concentration of iodide is in the range 50 ppm to 60 ppm, which is approximately 5000 times higher than that of rhodium. The iodide leaching is low and occurs in manageable proportions. It exerts only a small influence on a single batch test, but the cumulative effects lead to a visible loss in the catalytic activity after the five-run overall test. The level of rhodium leaching is relatively high in the incipient batch (32 ppb) due to loosely anchored rhodium species. However, the value in the subsequent batch test is approximately 10 ppb, which is negligible and acceptable in a practical operation. A cumulative effect is observed after the second regeneration and ten-batch tests.



Scheme 3 The catalytic cycle of rhodium-complex-catalyzed homogeneous methanol carbonylation.

As shown by the catalytic cycle of rhodium-complex-catalyzed methanol carbonylation (Scheme 3), rhodium species are heavily involved in several key steps. Transfer between the supported catalyst and the reaction solution is inevitable, which is attributed to the leaching of active metal species. For supported rhodium catalysts (complexes or nanoparticles), the leaching of rhodium from the reaction flow is a serious problem.[15] However, well-designed support structures and attachment strategies can efficiently immobilize the active centers and then greatly mitigate leaching during the catalytic conversion.[16] In this work, the leaching of rhodium was controlled to a negligible scale (Fig. 7). The concentration of leaching rhodium in the reaction solution is approximately 10 ppb. There are two main mechanisms for confining the irreversible transfer of rhodium species: the anchoring and trapping of highly ionized cross-linked copolymeric architectures and the compatible coexistence of iodide promoters with rhodium catalysts over the copolymeric supports (Scheme 1). The pyridine groups were methylated or acidified to give cationic sites,

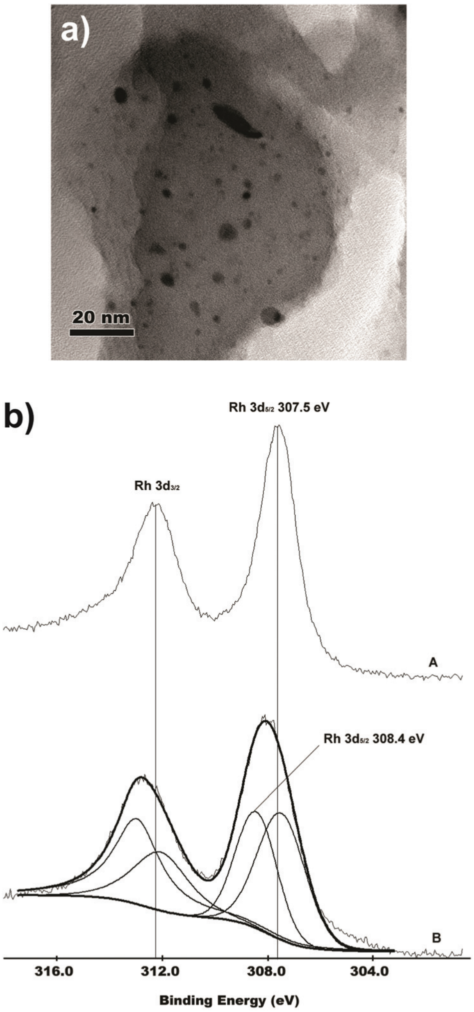


Fig. 8 (a) TEM image of the dispersion state of Rh nanoparticles over the copolymeric support after the recycling test. (b) Rh XPS peaks of the fresh catalyst and the used one.

which could anchor and trap anionic rhodium carbonyl complexes from the catalytic cycle. The coexistence of iodide promoters with rhodium species facilitate completing the entire carbonylation cycle over the copolymeric architectures, and greatly mitigate the rhodium leaching during mass transfer between the catalysts and the reaction solution. The dispersion of rhodium nanoparticles of the used catalyst after ten batches of activity tests (regenerated twice, as shown in Fig. 6) was characterized by TEM (Fig. 8a). Compared with the fresh catalyst (Fig. 1c), rhodium nanoparticles were redispersed. Some nanoparticles exhibited a poorly-defined physical shape and a marked growth in their size. It was clearly revealed that the rhodium species transfer among the nanoparticles in a certain form of rhodium carbonyl intermediate. The rhodium chemical states of the used catalyst were detected by XPS (Fig. 8b). Fitting of the Rh 3d envelope resulted in the identification of two chemical states of rhodium: one with a binding energy of 307.5 eV ($3d_{5/2}$) with an atomic concentration of 56.2% and another at 308.4 eV with an atomic concentration of 43.8%. The $3d_{5/2}$ peak at 307.5 eV was attributed to zero-valent rhodium nanoparticles. Another $3d_{5/2}$ peak at 308.4 eV was indexed to a rhodium carbonyl intermediate ($[Rh(CO)_xI_2]^-$, Scheme 3),[17] which is trapped by cationic sites over copolymeric architectures or over the surface layer of the rhodium nanoparticles. Although this rhodium carbonyl intermediate is dissolvable and transferable, highly ionized cross-linked copolymeric architectures efficiently confine its mobility.

Conclusions

In summary, we have developed an immobilization strategy to simultaneously anchor Rh and iodide species. Well-designed cross-linked copolymers contain functional groups that act as promoters or anchoring sites to heterogenizing homogeneous methanol carbonylation catalyst. Side-groups (methyl acetate) and anchored iodide promoters over the cross-linked polymeric architectures facilitate the catalytic cycle of converting methanol to methyl iodide. Approximately 90% of methanol were converted to methyl acetate and acetic acid after two-hour reaction at 120 °C under CO pressure of 3.0 MPa. The copolymeric catalyst exhibits good recyclability being regenerated twice over a fifteen batch test and could be harnessed as a prototype for developing sustainable methanol carbonylation.

Experimental

Preparation of cross-linked polymeric support

Solution A: sodium sulfate (48 g) was dissolved in deionized water (480 ml), and then bentonite (10 g) was added and dispersed with rapid stirring. Solution B: an organic mixture of purified monomers (2-vinylpyridine: 30 g, methacrylate ester: 26 g), cross-linker (DVB: 5.0 g), radical initiator (AVBN: 1.0 g), pore templates (isoamyl alcohol: 6.0 g, diethyl phthalate: 6.0 g), solvents (*o*-xylene: 15.0 g, cyclohexane: 30.0 g).

Solution A was heated to 65 °C and stirred at the speed of 300 r min^{-1}. Solution B was added to solution A over 15 min. The mixture was stirred for 1 h and stored at 75 °C for 24 h. The copolymeric particles were filtered and washed with boiling water for three times to remove bentonite. The dry copolymeric materials were extracted in an acetone stream for 30 h.

Purified copolymeric supports (2.0 g) were suspended in toluene (30 ml). The mixture was sealed in a 100 ml autoclave with a magnetic stirrer and flushed with argon for three times. MeI (0.26 ml) was injected and the autoclave was heated to 90 °C for 3 h under stirring. After the autoclave was cooled to room temperature, the copolymeric supports were filtered and dried under vacuum.

Immobilization of Rh and iodide species over the copolymeric support

$(NH_4)_2RhCl_5$ (34. 85 mg) was dissolved in methanol (30 ml) and methylated copolymeric support (1.0 g) was added. The mixture was stirred for 45 min and the color of the methanol solution disappeared. The solid materials were filtered and washed with deionized water (10 ml) and methanol (10 ml). The washing operation was repeated for three times. The resulting solid was suspended in methanol and $NaBH_4$ (5.5 mg) in water (2 ml) was added under stirring. The solid materials turned light gray. After filtration and washing, the solid materials were dried under vacuum for 3 h. The Rh load was 1.0 wt%.

Before the catalyst test, the catalyst was loaded with HI through direct suspension in a HI methanol solution. The iodide amount was controlled by the concentration of HI in solution. The resulted materials were washed with deionized water until no iodide anion was detected in the eluent through silver cation test. After being washed with methanol and diethyl ether sequentially, the catalyst was dried under vacuum.

Characterization methods

X-ray photoelectron spectroscopy (XPS) was performed over a VG ESCA-Lab200I-XL instrument. All peak positions in XPS experiments were calibrated by the binding energy of C 1s as reference of 284.6 eV. An Eclipse V2.1 data analysis software supplied by the VG ESCA-Lab200I-XL instrument manufacturer was applied for the manipulation of the acquired spectra. Transmission electron microscopy (TEM) was performed on a JEOL 2010 TEM with an accelerating voltage of 200 kV. Electron Probe Microanalysis (EPMA) (carried out on EPMA1600, SHIMADZU) was used to characterize the dispersion state of rhodium nanoparticles. The rhodium concentrations in the reaction mixture were determined by ICP-OES using a Perkin Elmer Optima instrument. The ionic iodide content in the reaction mixture was determined by a 797 VA Computrace polarograph manufactured by Metrohm, the detection limit of which was 0.1 ppb. Trace methyl iodide (CH_3I) in the reaction mixture was measured by a chromatograph with an ECD detector and backflushing technique. Nitrogen-adsorption isothermal and textural properties of the as-synthesized materials were determined by using liquid nitrogen over a Quantachrome Autosorb Automated Gas Sorption System (Quantachrome Corporation).

The products were analyzed by GC and GC-MS. GC was carried out over GC-2014 (SHIMADZU) with a high temperature capillary column (MXT-1, 30 m, 0.25 mm ID) and a FID detector. GC-MS was carried out over GCT Premier/Waters with capillary column (DB-5MS/J&W Scientific, 30 m, 0.25 mm ID).

Test of the catalytic activity for methanol carbonylation

The catalyst tests were carried out in a 50 ml Hastelloy autoclave. Typical reaction conditions: the catalyst; 0.2 g, methanol; 10 ml, reaction temperature; 120 °C, CO pressure; 3.0 MPa, reaction time; 180 min. Product–catalyst separation was carried out through simple filtration in the five-run recyclability test. In consecutive batch tests, a continuous filter was applied to separate the catalyst. The catalyst was recycled into the autoclave with the methanol feedstock stream.

Acknowledgements

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