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Article

Reaction kinetics and phase behavior in the chemoselective hydrogenation of 3-nitrostyrene over Co-N-C single-atom catalyst in compressed CO₂

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ABSTRACT

Single-atom catalysts (SACs) have demonstrated excellent performances in chemoselective hydrogenation reactions. However, the employment of precious metals and/or organic solvents compromises their sustainability. Herein, we for the first time report the chemoselective hydrogenation of 3-nitrostyrene over noble-metal-free Co-N-C SAC in green solvent — compressed CO₂. An interesting inverted V-curve relation is observed between the catalytic activity and CO₂ pressure, where the conversion of 3-nitrostyrene reaches the maximum of 100% at 5.0 MPa CO₂ (total pressure of 8.1 MPa). Meanwhile, the selectivities to 3-vinylaniline at all pressures remain high (> 99%). Phase behavior studies reveal that, in sharp contrast with the single phase which is formed at total pressure above 10.8 MPa, bi-phase composed of CO₂/H₂ gas-rich phase and CO₂-expanded substrate liquid phase forms at total pressure of 8.1 MPa, which dramatically changes the reaction kinetics of the catalytic system. The reaction order with respect to H₂ pressure decreases from ~0.5 to zero at total pressure of 8.1 MPa, suggesting the dissolved CO₂ in 3-nitrostyrene greatly promotes the dissolution of H₂ in the substrate, which is responsible for the high catalytic activity at the peak of the inverted V-curve.

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1. Introduction

With an output of 4 million tons per year, functionalized anilines represent key intermediates for the production of dyes, agrochemicals, pharmaceuticals, polymers and various other fine chemicals [1,2]. Traditionally, functionalized anilines are synthesized by non-catalytic reduction of their corresponding

nitroarenes using stoichiometric reagents such as sodium hydrosulfite, iron, tin, or zinc [3]. However, this process has been prohibited due to serious environmental concerns. Among the environmentally benign approaches developed thus far, the catalytic hydrogenation by supported metal nanoparticles is the preferred one since H₂ is a green and cost-effective reducing reagent and the only by-product is H₂O. This methodology

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works well for simple nitroarenes, yet encounters problems for those with diverse reducible functional groups on the benzene ring because of the over-hydrogenation side-reactions, especially for nitrostyrenes where the $-C=C$ group is much more sensitive than $-NO_2$. Generally, most of the nano-catalysts exhibit poor chemoselectivity [4], and only when those catalysts are modified by organic molecules (e.g., Pt/TiO₂-thiols [5]), or metal salts (such as Pt/C-H₃PO₂-VO(acac)₂, Pt-Pb/CaCO₃-FeCl₂-*n*-Bu₄NCl, Rh/C-Fe(OAc)₂) [6,7], could high chemoselectivity be achieved. However, these modifications by soluble reagents bring about additional environmental problems associated with the production of waste water.

Great efforts have been devoted to developing true heterogeneous and selective catalysts for the hydrogenation of functionalized nitroarenes [8,9]. Au nanoparticles supported on Fe₂O₃ [10], as well as modified Pt, Ru and Ni nano-catalysts through strong metal-support interaction (SMSI) were reported to be highly selective for the hydrogenation of 3-nitrostyrene [11–17]. However, the catalytic activity was still not satisfactory enough due to either the low intrinsic capability of IB metals for activating H₂ [18], or the decreased number of active sites for platinum-group metals resulting from the covering by the support or catalytically inert metals. To improve the catalytic efficiency, we previously developed FeO_x-supported platinum single-atom and pseudo-single-atom as catalysts for the hydrogenation of 3-nitrostyrene, and a TOF as high as 11064 h⁻¹ was achieved [19], which was 20-fold higher than the nano-particulate counterpart (Pt/TiO₂, the best catalyst reported before our Pt₁/FeO_x SACs) developed by Corma's group [12]. In addition, the selectivity to 3-vinylaniline reached as high as ~99%, far superior to the NPs counterpart. Recently, the catalytic activity of Pt₁/FeO_x was further enhanced by 2-fold through engineering the coordination environment of Pt single atoms while the chemoselectivity remained at 98% [20], demonstrating the unrivalled capability of SACs for chemoselective hydrogenations [21–23]. Based on these achievements, we became interested in developing non-precious metal SACs for the hydrogenation of nitroarenes given the high price and limited availability of noble metals. Previously, we reported that single-atom catalyst Co-N-C demonstrated good catalytic performance in the hydrogenative coupling of nitroarenes to produce azo compounds with the assistance of NaOH [24]. Compared with the Co-based nano-catalysts reported (e.g., Co₃O₄@N-C) [25], our Co-N-C SAC bear the merits of mild reaction conditions (e.g., reaction temperature 110 °C vs 80 °C). However, the addition of NaOH caused additional environmental concerns. Therefore, it is highly desirable to develop noble-metal-free and additive-free single-atom catalytic system for the hydrogenation of functionalized nitroarenes.

In fact, from the viewpoint of green chemistry, the use of organic solvents represents a critical concern in most of organic transformations. Solvents not only subtly affects the activity and selectivity of catalysts, but also accounts for the vast majority of chemical waste [26]. In the catalytic systems reported for hydrogenation of nitroarenes, toxic and flammable organic solvents (such as toluene, THF) have been widely employed,

which will definitely not recommended by green chemistry. Therefore, it is highly desirable to substitute them with greener ones (such as ionic liquid, supercritical fluids, and water). In particular, supercritical CO₂ (scCO₂) offers prominent advantages such as nontoxicity, non-flammability, and facile regulation of phase behavior which improves the solubility of H₂ and facilitates the separation of the products. Previously, Arai's group investigated the hydrogenation of nitrostyrene in CO₂-expanded liquids with or without extra organic solvents (e.g., ethanol, toluene) [27,28]. However, the conversion (64%) and selectivity to vinylaniline (75%) were not satisfactory owing to the low-efficiency of Pt/TiO₂ nano-catalysts. By contrast, we achieved high conversion and selectivity (both were higher than 95%) using Pt₁/FeO_x SAC for the reaction in CO₂-expanded toluene [29], demonstrating the great power of single-atom catalyst in conjunction with green solvents. Even though, toluene was still indispensable to maintain high conversion level in that work.

In the present work, we have reported the hydrogenation of 3-nitrostyrene in compressed CO₂ without any extra solvent over single-atom Co-N-C catalyst. An interesting inverted V-curve relation was found between the hydrogenation activity and the CO₂ pressure. Under optimal reaction conditions (60 °C, 3 MPa H₂ (RT), 5.0 MPa CO₂), CO₂/H₂ gaseous phase and CO₂-expanded 3-nitrostyrene liquid phase formed in the top and bottom of the reactor, respectively. The biphasic system not only greatly enhanced the solubility of hydrogen in the CO₂-expanded substrate liquid phase, but also changed the reaction order from 0.5 to zero with respect to hydrogen. Consequently, the reaction rate was dramatically increased. Our work has demonstrated a green, efficient and cost-effective route to the synthesis of functionalized anilines by combining the compressed CO₂ solvent with the noble-metal-free single-atom catalyst.

2. Experimental

2.1. Preparation of Co-N-C

The catalyst was prepared according to the procedure we previously reported [24]. Briefly, Cobalt (II) acetate tetrahydrate (0.5 mmol, 125 mg), 1,10-phenanthroline hydrate (1.5 mmol, 300 mg) and ethanol (50 mL) were added to a round bottom flask. The mixture was stirred for 0.5 h at room temperature, followed by addition of 4.0 g Mg(OH)₂ and refluxing at 60 °C for 4 h. After ethanol was removed by rotary evaporation, the remaining solid was dried at 60 °C, and was subjected to pyrolysis at 700 °C for 2 h under N₂ atmosphere (100 mL/min) with ramp rate of 2 °C/min. After Mg(OH)₂ was removed by washing with HCl solution (200 mL, 1 mol/L) twice, the remaining black solid was dried at 80 °C, and was denoted as Co-N-C catalyst.

2.2. Phase behaviour study

The phase behaviour at various pressures and temperatures was visually observed by using a 29.3 mL high-pressure cell

equipped with two quartz windows. After a certain amount of liquid substrate (3-nitrostyrene or nitrobenzene) and a stirring bar were introduced, the cell was sealed and purged for several times with N_2 . Then, hydrogen gas was introduced in the cell until the pressure reached 3 MPa. After the cell was heated to 60 °C with a heating jacket, the liquid CO_2 was pumped into the cell until the designated pressure was reached. The gas-liquid mixture in the cell was stirred for a certain time and then left stand until steady state was achieved. At each pressure, the phase behaviour was visually observed, and a laser pen was used to check the occurrence of Tyndall effect.

2.3. Hydrogenation reaction tests

The hydrogenation reaction was conducted in a Parr autoclave (25 mL). In a typical reaction, 30 mg catalyst, 0.5 mmol 3-nitrostyrene, and 0.25 mmol o-xylene (as an internal standard for GC analysis) were mixed and added into the autoclave before it was sealed. Then, the autoclave was purged with N_2 for several times followed by being charged with 3 MPa H_2 . Subsequently, CO_2 was pumped into the autoclave until the designated pressure was reached. The autoclave was then heated to the reaction temperature of 60 °C in water bath meanwhile the mixture in the autoclave was stirred at a speed of 1200 rpm for 8 h. After the reaction, the autoclave was cooled in icy water and depressurized slowly. The recovered organic liquid was analysed by an Agilent 7890 GC equipped with HP-5 columns and flame ionization detector (FID).

For kinetic measurements, the conversions were controlled below 30% by varying the reaction time between 0.5 ~ 3 h to ensure the reaction proceeded in the kinetically controlled region. For the catalyst durability test, the catalyst was recovered by filtration from the reaction mixture. After rinsing by ethanol and drying, the catalyst was subjected to another batch of reaction.

2.4. Vapour-liquid equilibrium calculation

The gas-liquid equilibrium phase compositions were calculated based on Peng-Robinson equation of state (PR EOS). CO_2 - H_2 binary interaction parameters were obtained by fitting experimental vapour liquid equation data reported in [30], and CO_2 -nitrostyrene and H_2 -nitrostyrene binary interaction parameters were estimated through the group contribution method [31].

3. Results and discussion

3.1. Determination of the dispersion of Co-species

The single-atom Co-N-C catalyst was prepared by the method we reported previously [24]. The as-synthesized catalyst had a specific surface area of 649 m^2/g and a cobalt loading of 4.2 wt%. To determine the dispersion of Co-species, XRD and normal electron microscopy characterizations were first conducted. As shown in Fig. 1, XRD pattern did not show any diffraction peak due to metallic Co or cobalt oxides (Fig. 1(a)),

which was in line with low-magnification TEM image where no any big Co/ CoO_x nanoparticles were observed (Fig. 1(b)), suggesting the high dispersion of Co-containing species. Subsequently, the sub-Ångström-resolution aberration-corrected high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) technique was employed to probe the Co-containing species. As expected, a large number of uniformly dispersed Co single atoms were clearly observed in the image (Fig. 1(c)), and there was no tiny Co/ CoO_x clusters by examination of different regions, demonstrating the single-atom dispersion of cobalt, in good agreement with our previous work [24].

3.2. Effect of H_2 pressure

Having successfully prepared Co-N-C SACs, we then investigated their catalytic performance in the hydrogenation of 3-nitrostyrene in compressed CO_2 medium. Besides the substrate and the internal standard for GC analysis, no extra organic solvent or additive was added for the consideration of environmentally benign process. The influence of H_2 pressure on the catalytic efficiency was first studied, and the total pressure was maintained at about 9.2 MPa. As shown in Fig. 2(a), with an increase of H_2 pressure from 1 to 3 and 5 MPa, the conversion of 3-nitrostyrene increased rapidly from 32% to 84.7% and then to 100%, which could be attributed to the increased solubility of H_2 in the substrate and compressed CO_2 . To our delight, the selectivity to 3-vinylaniline was always kept at 100% even at full conversion, demonstrating the unique advantage of single-atom catalyst in delivering the chemoselective transformations.

3.3. Influence of reaction temperature

The dissolving ability of compressed CO_2 is strongly affected by its density, which can be modulated by both temperature

Fig. 1. XRD pattern (a), low-magnification STEM (b) and high-resolution HAADF-STEM images (c) of the as-synthesized Co-N-C catalyst; HAADF-STEM image of the spent Co-N-C catalyst (d).

Fig. 2. The dependence of conversion and selectivity on H₂ pressure (a), temperature (b) and CO₂ pressure (c). Reaction conditions: 0.5 mmol 3-nitrostyrene, 30 mg Co-N-C catalyst, 60 °C (a,c), 3 MPa H₂ (RT) (b,c), total pressure: 9.2 MPa (a,b), 8 h.

and pressure [32]. Accordingly, the influence of temperature on the catalytic performance was investigated. As shown in Fig. 2(b), the 3-nitrostyrene conversion increased rapidly with the reaction temperature and reached 100% at $T \geq 70$ °C. Meanwhile, the selectivity to 3-vinylaniline was maintained > 99%. Even when the temperature was 80 °C, no byproduct due to over-hydrogenation was detected, suggesting the Co-N-C SAC was chemically inert for the hydrogenation of C=C bond as demonstrated by FTIR measurement and control experiment results we previously reported [24].

3.4. Influence of system pressure

As the system pressure had great impact on the phase behaviour, the dependence of catalytic performance on the total pressure was also studied, and the reaction temperature and H₂ pressure were fixed at 60 °C and 3 MPa (RT), respectively. As shown in Fig. 2(c), an inverted V-curve relation between the 3-nitrostyrene conversion and the CO₂ pressure (as well as the total pressure) was observed. When no CO₂ was charged into the reaction system (i.e., solvent free conditions), the 3-nitrostyrene conversion was only 76.3%. With the introduction of CO₂ and the increase of the total pressure from 3.1 to 8.1 MPa (corresponding to CO₂ pressure of 5.0 MPa), the 3-nitrostyrene conversion increased greatly from 76% to 100%. However, with further increase of total pressure above 8.1 MPa, the conversion dropped dramatically and down to only 69.1% at total pressure of 10.8 MPa. Again, in all cases the chemoselectivity to 3-vinylaniline was maintained high at > 99%, indicating that no over-hydrogenation side-reaction occurred on the single-atom Co-N-C catalyst.

The inverted V-curve relation between catalytic activity and total pressure as well as CO₂ pressure was in sharp contrast with our previous work where the conversion of 3-nitrostyrene over Pt₁/FeO_x SAC increased monotonically with the pressure of CO₂ [29]. It is known that the solubility of 3-nitrostyrene in scCO₂ decreases with the increase of temperature but increases with the pressure of CO₂. In the Pt₁/FeO_x catalytic system, most of the charged 0.5 mmol 3-nitrostyrene could be dissolved in scCO₂ when the pressure was higher than 10.3 MPa at 50 °C [29]. However, in the present work, the total pressure was lower (8.1 MPa) yet the reaction temperature (60 °C) was

higher than that in the Pt₁/FeO_x catalytic system, therefore, 3-nitrostyrene (0.5 mmol) may not be completely dissolved in CO₂, and therefore biphasic system might be formed.

To approve the formation of biphasic system, the phase behavior of 3-nitrostyrene-CO₂-H₂ ternary system was investigated by a high pressure view cell. Figs. 3(a), 3(e), and 3(i) displayed the images of 3-nitrostyrene in the absence of CO₂, which clearly showed a pure liquid phase. When CO₂ was charged and the total pressure reached 8.1 MPa, however, a quite different phase phenomenon was observed, and the appearance of a clear interface indicates the formation of biphasic system. The upper phase looked light cloudy and showed a strong Tyndall effect (Figs. 3(b) and (f)), which was indicative of the formation of CO₂/H₂ gas-rich phase where small droplets of the 3-nitrostyrene were dispersed. Meanwhile, the liquid substrate could be observed in the bottom of the cell, indicating the lower part was a 3-nitrostyrene-rich liquid phase (Fig. 3(j)) in which both CO₂ and H₂ were dissolved. Clearly, biphasic system was formed at this stage. Based on these observations, we propose that at the total pressure of ~8 MPa (the corresponding CO₂

Fig. 3. Phase behaviour of 3-nitrostyrene (NS)-CO₂-H₂ ternary system: (a–d) visual observations, (e–h) images of the phase conditions when the view cell was irradiated by a laser beam, and (i–l) the corresponding illustration of the phases at the total pressure of 3.1 MPa (CO₂-free), 8.1, 9.2 and 13.4 MPa, respectively. Other conditions: 0.5 mmol 3-nitrostyrene, 3 MPa H₂ (RT), 60 °C.

pressure of ~ 5 MPa), a part of CO_2 is dissolved in the substrate and facilitates the dissolution of H_2 , similar to what had been reported earlier that CO_2 could be dissolved into organic solvent to form CO_2 -expanded liquid [33]. The fact that no obvious expansion of the 3-nitrostyrene volume was observed at this stage was probably due to the small dosage of the 3-nitrostyrene (0.5 mmol) [34]. When the total pressure was further increased to 9.2 MPa, a dense cloudy phase was observed between the upper gaseous and bottom liquid phases, which presented a thick and diverging light column upon being irradiated by a laser beam (Figs. 3(c) and (g)), suggesting emulsive dispersion of 3-nitrostyrene in CO_2 (Fig. 3(k)). Finally, when the total pressure reached 13.4 MPa, a single transparent phase formed without any interface, indicating the complete dissolution of 3-nitrostyrene in scCO_2 (Figs. 3(d), (h) and (l)).

It was earlier reported that the volume expansion became significant and continuum of CO_2 -expanded solvent was formed when the organic solvent accounted for at least 20 mol% [34,35]. Thereby, to further verify the volume expansion with increasing CO_2 pressure, 6 mL of nitrobenzene was added into the view cell and the phase behaviour of CO_2 -nitrobenzene binary system was investigated. As shown in Fig. 4, the liquid level rose gradually with an increase of CO_2 pressure, indicating that CO_2 was dissolved into nitrobenzene and consequently caused the liquid volume expansion. More interesting, when CO_2 pressure arrived at 5.14 MPa, CO_2 started to penetrate quickly into nitrobenzene at the gas-liquid interface and formed a dilute layer with lighter colour than the bulk, which was more obviously observed at CO_2 pressure of 6.1 MPa. This phase change point was not only in coincidence with the biphasic formation in the 3-nitrostyrene- CO_2 - H_2 ternary system (Fig. 3(b), (f), (g)), but also consistent with the peak conversion of 3-nitrostyrene in Fig. 2(c), thus strongly suggests that at this turning point the concentrations of H_2 and substrate 3-nitrostyrene at the catalyst surface may reach the maxima given that the CO_2 -expanded organic liquid phase improves the dissolution of H_2 in 3-nitrostyrene liquid phase. With further increase of CO_2 pressure from 5.14 to 6.95 MPa, the liquid was continuously expanded until the full volume of the cell at 6.95 MPa.

Considering that the dissolving capability of scCO_2 is closely related to its density, we also calculated the density of CO_2 at 60 °C and different pressures. The results showed that the CO_2 had densities of 0.0984, 0.1308, and 0.3165 g/mL at CO_2 pressure of 5.0, 6.2 and 10.4 MPa, respectively [36]. Accordingly, the amount of 3-nitrostyrene dissolved in CO_2 will increase following the same order as CO_2 density with the change of CO_2 pres-

Fig. 4. Photographs of volume expansion in CO_2 -nitrobenzene binary system taken at 60 °C under different pressures.

sure: 5.0 MPa < 6.2 MPa < 10.4 MPa, and the concentration in the liquid phase containing catalyst will adversely decrease in this order. This can explain the descending trend of 3-nitrostyrene with the total pressure at the right side of Fig. 2(c) when the total pressure is higher than 8.1 MPa (corresponding to CO_2 partial pressure of ~ 5 MPa).

To provide a more precise estimation of the hydrogen concentration in the liquid phase at different CO_2 and H_2 pressures, we calculated the solubility of H_2 in the CO_2 -expanded 3-nitrostyrene substrate liquid phase at 60 °C based on the PR EOS, and the result is shown in Fig. 5. It can be seen that the solubility of H_2 firstly increased with the CO_2 pressure and reached maximum at about 5.0 MPa and then decreased rapidly at higher CO_2 pressure. Such an inverted V-curve is well consistent with the activity curve with the CO_2 pressure (Fig. 2(c)), and also agrees well with the report of Devetta *et al.* [37], implying that the solubility of H_2 in the CO_2 -expanded liquid phase is a main factor determining the reaction rate.

To further clarify the impact of CO_2 pressure (as well as total pressure) on the reaction rate, we performed kinetic studies, and the results are summarized in Figs. 6 and 7 as well as Tables S1-S5. The reaction orders with respect to 3-nitrostyrene at total pressure of 8.1 and 11.2 MPa were measured to be 0.7 and 0.8, respectively, both of them were close to first-order dependence, indicating the adsorption/activation of 3-nitrostyrene was involved in the rate-determining step and was almost independent on the total pressure. On the other hand, as shown in Fig. 7, under conditions of CO_2 -free and total pressure of 11.2 MPa, the reaction orders with respect to H_2 pressure were measured to be 0.4 and 0.6, respectively, suggesting the heterolytic dissociation of H_2 and the attack of $-\text{NO}_2$ by proton was involved in the rate-determining step [38,39]. By contrast, at total pressure of 8.1 MPa (corresponding to the CO_2 partial pressure of 5.0 MPa), two-stage relations between $\ln(P_{\text{H}_2})$ and $\ln(r)$ were observed. That is, the reaction order with respect to H_2 was 0.7 in the range of 1–2.5 MPa H_2 , whereas 0.06 when the pressure of H_2 was 3–5 MPa. The nearly zero order at the total pressure of 8.1 MPa suggested that the solubility of H_2 in the liquid phase was greatly enhanced by the dissolved CO_2 such that the catalyst surface was saturated with H_2 . Therefore, by changing the CO_2 partial pressure at a fixed H_2 pressure one can effectively tune the hydrogen solubility in the

Fig. 5. Calculated H_2 solubility in liquid substrate 3-nitrostyrene (NS) at 60 °C under different CO_2 pressures.

Fig. 6. The dependence of reaction rate on the concentration of 3-nitrostyrene at total pressure of 8.1 (a) and 11.2 (b) MPa. Reaction conditions: $P_{\text{total}} = 8.1 \text{ MPa}$, $P_{\text{H}_2} = 3.0 \text{ MPa}$ (RT), 30 mg catalyst, 60 °C, reaction time was varied between 0.5–1 h to maintain the conversions below 30%.

Fig. 7. The dependence of reaction rate on the pressure of H_2 at (a) CO_2 -free condition; (b) total pressure of 8.1 MPa; (c) total pressure of 11.2 MPa. Reaction conditions: 0.5 mmol 3-NS, 0.25 mmol o-xylene, 30 mg catalyst, 60 °C, and the reaction time was varied between 1–3 h to maintain the conversion below 30%.

CO_2 -expanded liquid phase, and consequently change the reaction kinetics towards high catalytic efficiency over the single-atom catalyst.

Taken together, the CO_2 pressure influenced the phase behaviour and consequently the kinetics of the single-atom Co-N-C catalytic system, which made CO_2 expanded substrate liquid rather than the single gaseous phase be the most effective medium for the hydrogenation of 3-nitrostyrene. Similarly, Arai's group reported expanded liquid substrate phase was effective medium for the hydrogenation of cinnamaldehyde to cinnamyl alcohol [40]. The reason was also ascribed to the high concentration of cinnamaldehyde and H_2 , as well as decreased viscosity, however, no kinetic and phase behaviour studies were performed in that work. By contrast, in our previously reported Pt_1/FeO_x system for the hydrogenation of 3-nitrostyrene in scCO_2 , the ideal medium was a single gaseous phase (i.e., the substrate was completely dissolved in scCO_2) [29]. The reason was ascribed to the increased solubility of H_2 as well as the reduced viscosity that facilitated the mass transfer of reactants.

3.5. Durability of Co-N-C catalyst

Catalyst durability is one of the most important concerns for practical utilization. After the reaction, the Co-N-C single-atom catalyst could be easily recovered from the reaction mixture by filtration or centrifugation, and was subjected to another batch

of reaction without additional treatment. As shown in Fig. 8, the catalyst could be recycled for at least 4 times without obvious decay in either catalytic activity or chemo-selectivity. HAADF-STEM image of the recovered catalyst showed that cobalt still existed as single atoms without any aggregation (Fig. 1(d)), demonstrating the high stability of the single-atom Co-N-C catalysts.

4. Conclusions

In summary, compressed CO_2 was explored as environmentally benign medium for the chemoselective hydrogenation of

Fig. 8. Durability of the Co-N-C catalyst. Condition: 3-nitrostyrene (0.5 mmol), Co-N-C catalysts (30 mg), o-xylene (0.25 mmol, as the internal standard), 60 °C, total pressure of 8.1 MPa and H_2 pressure of 3.0 MPa (RT), 8 h.

3-nitrostyrene over single-atom Co-N-C catalyst. An inverted V-curve relation was found between the catalytic activity and the total pressure (or CO₂ pressure), with the conversion peak (100%) being attained at the total pressure of 8.1 MPa (corresponding CO₂ pressure of 5.0 MPa). CO₂-H₂-nitrostyrene ternary system phase behaviour studies revealed that under the optimum total pressure of 8.1 MPa, biphasic system was formed where the upper part was CO₂/H₂ gas-rich phase and the lower part was CO₂-expanded nitrostyrene liquid phase. The formation of CO₂-expanded substrate liquid greatly increased the solubility of H₂, changing the reaction order with respect to H₂ from ~0.5 to nearly zero. The favourable reaction kinetics assisted by the compressed CO₂ led to the complete conversion of 3-nitrostyrene at mild reaction temperature (60 °C), and the single-atom dispersion of Co offered > 99% selectivity to 3-vinylaniline even at full conversions. In addition, the single-atom catalyst could be reused for 4 times without obvious decrease of conversion or chemoselectivity. Our work provides an alternative route to tuning the catalytic performance by jointly using green compressed CO₂ and noble-metal-free single-atom catalysts.

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Graphical Abstract

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Reaction kinetics and phase behavior in the chemoselective hydrogenation of 3-nitrostyrene over Co-N-C single-atom catalyst in compressed CO₂

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An inverted V-curve relation was observed between conversion and P_{CO_2} in hydrogenation of 3-nitrostyrene over Co-N-C SACs in compressed CO₂, where the peak was attributed to the enhanced solubility of H₂ in CO₂-expanded substrate liquid.

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压缩CO₂中Co-N-C催化3-硝基苯乙烯选择性加氢反应动力学及相行为

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摘要: 对于苯环上含有各种可还原基团(如—C=C, —CN, —C≡C)的硝基芳烃, 通过选择性加氢来制备芳香胺类化合物依然充满挑战。负载型纳米催化剂通常存在过度加氢的缺陷, 虽然通过覆盖部分金属位点等方法可改善其选择性, 但多是以牺牲催化活性为代价。得益于较高的原子利用率以及孤立的活性位结构, 单原子催化剂在硝基芳烃选择性加氢反应中崭露头角。例如Pt₁/FeO_x单原子催化剂在3-硝基苯乙烯加氢反应中对目标产物的选择性高于99%, 且转化频率(TOF)是Pt纳米催化剂的20倍以上。然而, 已报道的单原子催化体系中, 活性组分多为Pt族贵金属, 且以有机溶剂为反应介质, 不符合绿色化学理念。

本文以环境友好型溶剂——压缩CO₂为反应介质, 以氮掺杂碳负载非贵金属Co单原子(Co-N-C)为催化剂, 实现了3-硝基苯乙烯的选择性加氢, 且反应体系中无任何有机溶剂和助剂。在温和(60 °C, 3 MPa H₂(RT), 总压8.1 MPa)的反应条件下, 3-硝基苯乙烯可完全转化, 目标产物3-乙基苯胺的选择性达到> 99%, 且产物可通过简单卸压直接分离。Co-N-C单原子催化剂表现出较高的稳定性, 循环使用4次以后活性并无明显降低。HAADF-STEM表征发现反应后的催化剂中, Co仍然呈单原子分散。

研究发现, 通过改变CO₂压力(即CO₂相行为)可调变H₂在其中的溶解度以及在加氢反应中的反应级数, 进而调变反应速率。通常认为, 催化活性会随CO₂压力增大呈线性增加, 而本文中转化率却随CO₂压力增加呈现“倒V型”曲线关系, 即当体系总压为8.1 MPa(P_{CO₂} = 5.0 MPa)时, 转化率达到最大值(100%), 而升高或降低CO₂压力均会显著降低催化活性。

为解释“倒V型”曲线的成因, 通过含可视窗的高压釜研究了3-硝基苯乙烯/CO₂/H₂三元体系的相行为。发现当总压为13.4 MPa时, 体系为均匀的一相(即3-硝基苯乙烯完全溶解在CO₂中); 而当总压为8.1 MPa时, 却形成了气-液两相。用激光笔照射高压釜上部的气相时, 出现了明显的丁达尔现象, 说明其中溶解有少量的3-硝基苯乙烯, 呈胶体分散; 底部为CO₂膨胀的3-硝基苯乙烯液相, 且该膨胀行为通过硝基苯-CO₂二元相行为研究得到证实(即在一定CO₂压力下, 6 mL硝基苯可被CO₂膨胀至充满整个高压釜(容积为29.3 mL))。动力学研究发现, 在不含CO₂以及总压为11.2 MPa时, H₂的反应级数为~0.5; 而当总压为8.1 MPa(CO₂压力为5.0 MPa)时, H₂的级数降为0, 说明该压力下H₂的溶解度显著增加。通过Peng-Robinson方程计算了不同CO₂压力下H₂的溶解度, 发现H₂溶解度与CO₂压力也呈“倒V型”曲线关系, 且最高点对应的CO₂压力与上述转化率-P_{CO₂}曲线一致。因此, 当总压为8.1 MPa, CO₂分压为5.0 MPa时形成了CO₂膨胀的3-硝基苯乙烯液体, 溶解入该膨胀液体的CO₂促进了H₂的溶解, 进而使H₂的反应级数降为0, 从而促进了加氢反应的进行。

综上, 本文以压缩CO₂为溶剂, 以非贵金属基Co-N-C为催化剂, 发展了一种3-硝基苯乙烯绿色选择性加氢途径。同时发现, 改变CO₂压力可调变反应体系的相行为及反应动力学行为, 进而调变催化性能。该研究结果可为调变压缩CO₂介质中进行的其它催化转化反应性能提供借鉴。

关键词: 单原子催化剂; Co-N-C; CO₂; 相行为; 化学选择性加氢; 3-硝基苯乙烯

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