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Chemoselective hydrogenation of 3-nitrostyrene over Pt/FeOx pseudo-single-atom-catalyst in CO_2-expanded liquids

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Gang Xu,[a,b] Haisheng Wei,[b] Yujing Ren,[b] Jianzhong Yin,*[a] Aiqin Wang,*[b] and Tao Zhang[b]

Chemoselective hydrogenation of substituted nitroarenes containing two reducible groups in one molecule is a highly desired approach to the synthesis of functionalized anilines. To make this process environmentally benign, we used pseudo-single-atom-catalyst Pt/FeOx and investigated the reaction in supercritical CO_2 and CO_2-expanded toluene. The results showed that supercritical CO_2 afforded excellent selectivity but low reactivity due to the limit of substrate solubility in the reaction medium. By contrast, when the reaction proceeded in CO_2 expanded toluene, both the conversion of 3-nitrostyrene and the selectivity of 3-vinylaniline reached above 95% under optimum conditions while the organic tolune amount could be reduced by 90% comparied to that without CO_2. The thermodynamic calculations revealed that the solubility of H_2 increased while the viscosity of the reaction system decreased with the CO_2 pressure, which facilitated the mass transfer and therefore increased the reaction rate meanwhile kept the selectivity at a high level.

Introduction

Functionalized anilines are important intermediates for the production of agrochemicals, pharmaceuticals, dyes, and pigments.[1, 2] They are typically synthesized by reduction of the corresponding substituted nitroarenes. Different from simple nitroarene molecule (e.g., nitrobenzene) whose reduction is easily implemented through catalytic hydrogenation over Group VIII metal catalysts (e.g., Raney Ni, Pt, etc.),[3] chemoselective hydrogenation of substituted niroarenes, especially those containing two or more reducible groups (e.g., C=C, C≡C, C≡N, etc.), is still a challenging topic.[4] Currently, the commercial production of functionalized anilines containing these highly reducible groups is accomplished through non-catalytic methods using a stoichiometric amount of iron, tin, or other reducing reagents,[5] which produces a large amount of solid wastes and brings about serious environmental issues. Therefore, there is a strong incentive to develop an environmentally benign approach to the manufacture of functionalized anilines. Indeed, in the past decade, many encouraging attempts have been made towards the chemoselective hydrogenation of substituted nitroarenes.[6-14] For example, Corma et al. reported gold nanoparticles supported on TiO_2 or Fe_2O_3 served as a highly chemoselective catalyst for hydrogenation of substituted nitroarenes, giving rise to > 95% selectivity at nearly 100% conversion for a variety of substrates.[6] After that, many gold and silver nanocatalysts with tunable nanostructures and particle sizes were investigated for this reaction,[7-10] and in most cases good to excellent chemoselectivity could be obtained. However, either gold or silver had a poor capability for H_2 activation,[11] which led to at least one order of magnitude lower activity than Pt-group metal catalysts. For that reason, interest is steered towards the modification of supported Pt catalysts, e.g., through alloying Au with a minor amount of Pt,[12] or via strengthening the interaction between Pt and the underneath support by elevating the reduction temperature.[13] As a result, both high activity and chemoselectivity could be obtained over these modified Pt catalysts, although these modifications inevitably led to loss of some intrinsic activities of the Pt catalysts.

In 2011 we reported a single-atom-catalyst (SAC) where all the Pt species are dispersed as single atoms such that the utilization of Pt in reactions is ideally 100%.[15] Using this strategy, we recently synthesized FeOx supported Pt SAC and pseudo-SAC and then used them for chemoselective hydrogenation of substituted nitroarenes. To our delight, the Pt/FeOx SAC and pseudo-SAC afforded a turnover frequency (TOF) of 1500 h^{-1} and a selectivity close to 99% in the chemoselective hydrogenation of 3-nitrostyrene to 3-aminostyrene,[16] which was the best result reported so far. This exciting result motivated us to further explore the reactions catalysed by SAC and pseudo SAC, in particular regarding the environmental friendliness of the reaction.

One important factor to be considered is the solvent, which is well known to affect both the performance of the catalyst and the greenness of the process.[17] Indeed, solvents

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[a] *State Key Laboratory of Fine Chemicals, School of Chemical Machinery, Dalian University of Technology, Dalian 116024, China. E-mail: jzyin@dlut.edu.cn*

[b] *State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China. E-mail: aqwang@dicp.ac.cn; taozhang@dicp.ac.cn*

† Footnotes relating to the title and/or authors should appear here.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x have become one of the major contributors to industrial waste streams. In the above reviewed chemoselective hydrogenation reactions, organic solvents (toluene, ethanol, etc.) were always used in a high solvent/substrate volume ratio (typically > 500). To make the process greener, partly or complete replacement of organic solvents by environmentally benign solvents is thus highly desirable. Among others, CO_2-expanded liquids (also called gas expanded liquids, GXLs) offers prominent advantages due to greatly reduced solvent amount and tunable solvent properties in a wide range.[18-27] In earlier studies, Yoshida et al. investigated the hydrogenation of nitrostyrene in CO_2-expanded ethanol and toluene at 323 K over Pt/TiO_2,[28] but either the conversion or the selectivity was not satisfactory (< 50%), probably due to the intrinsic nature of Pt/TiO_2.

In the present work, we for the first time report the performance of pseudo SAC Pt/FeOx for chemoselective hydrogenation of 3-nitrostyrene in CO_2-expanded toluene. To our delight, both high conversion and excellent selectivity (>95%) were obtained while the toluene amount was decreased by 90% in comparison with earlier reports, thus demonstrating a green and atom-economic route for the production of functionalized anilines.

Experimental section

Preparation of catalysts

The Pt/FeOx pseudo-single-atom-catalyst was prepared as reported previously.[16] In brief, 0.15 ml of an aqueous solution of chloroplatinic acid ($H_2PtCl_6{\cdot}6H_2O$, 7.59×10^{-2} mol/L) was added to 20 ml of an aqueous solution of ferric nitrate ($Fe(NO_3)_3{\cdot}9H_2O$, 1 mol/L), and the resulting mixture was added dropwise to 60 ml of an aqueous solution of sodium carbonate (1 mol/L) while vigorous stirring at 50 °C for 3 h. The pH value of the mixture was maintained at 8. After further aging for 3 h at 50 °C, the precipitate was recovered by filtration and washing, and then dried at 60 °C overnight, calcined at 400 °C in air for 5 h, and reduced at 250 °C in 10 % H_2/N_2 for 0.5 h to obtain the pseudo-SAC Pt/FeOx catalyst with Pt loading of 0.08 wt%.

For comparison, Pt/SiO_2, Pt/Al_2O_3, and Pt/TiO_2 were prepared with an incipient wetness impregnation method, followed by the same calcination and reduction treatments as that for Pt/FeOx, except for Pt/TiO_2 which was reduced in H_2 at 450 °C for 3 h. The Pt loadings in all the samples were kept at 0.08 wt%.

Hydrogenation reaction test

The chemoselective hydrogenation of 3-nitrostyrene was carried out in a 15 ml stainless steel autoclave equipped with glass undersleeve and pressure control system. For each reaction, 0.1 g of catalyst, 0.5 mmol of 3-nitrostyrene, and 0.5 ml toluene were loaded into the reactor, and then the reactor was sealed and flushed with 1 MPa H_2 for 5 times. After that, the reactor was charged with H_2 until 3 MPa, and then CO_2 was filled into the reactor to the specified pressure. After sealing the reactor, the mixture was heated to 40 °C in a water bath with a magnetic stirrer to initiate the reaction. The H_2 pressure decreased gradually during the reaction as a result of hydrogenation. After reaction, the product was analyzed by GC-MS.

Calculation of the system viscosity

The viscosity of the liquid phase in equilibrium with CO_2 is predicted using Grunberg and Nissan equation [29-31]

$$ln\,\eta_m = \sum m_i\, ln(\eta_i) + \sum\sum_{i\neq j} \omega_i\, \omega_j G_{ij} \qquad (1)$$

η_m — mixture viscosity (mPa·s).
m_i — mass fraction of component *i* which is calculated by the PR-BM equation described in supporting information.
η_i — viscosity of pure component *i* at the system conditions.
G_{ij} — interaction parameter.

For nonpolar mixtures, a simplified Arrhenius relation is used:[32]

$$ln\,\eta_m = \sum m_i\, ln(\eta_i) \qquad (2)$$

For pure toluene, the General DIPPER equation[33] is used:

$$ln(\eta) = C_1 + C_2/T + C_3 lnT + C_4 T^{C_5} \qquad (3)$$

T — Temperature (K).

The coefficients are taken from DIPPER database and listed as follows:

component	parameters				
	C_1	C_2	C_3	C_4	C_5
C_7H_8	-219.172	6805.7	37.542	-0.06085	1

For pure CO_2 or H_2, the Jossi–Stiel–Thodos empirical correlation [34] is used:

$$[(\eta-\eta^*)\varepsilon + 10^{-4}]^{1/4} = 0.10230 + 0.023364\rho_{ri} + 0.058533\rho_{ri}^2 - 0.040758\rho_{ri}^3 + 0.0093324\rho_{ri}^4 \qquad (4)$$

$$\varepsilon = \left(\frac{T_{ci}}{M_{wi}^3 P_{ci}^4}\right)^{1/6}$$

$$\eta^* = \frac{34\times10^{-5} T_{ri}^{0.94}}{\varepsilon}$$

η^* — viscosity in the normal pressure (0.1–5 bar).
ρ_{ri} — reduced density，$\rho_{ri} = \rho_i/\rho_{ci}$.
ρ_i — density of pure component *i* at the system conditions.
ρ_{ci} — critical density.
T_{ci} — critical temperature.
M_{wi} — molar mass.
P_{ci} — critical pressure.
T_{ri} — reduced temperature，$T_{ri} = T/T_{ci}$.

Results and discussion

Solvent effect

As we reported in previous work,[16] the employment of pseudo-SAC resulted in both exceptionally high activity and selectivity for the chemoselective hydrogenation of 3-nitrostyrene in toluene. Nevertheless, the solvent to substrate molar ratio was pretty high (around 1000). In order to make the process more environmentally friendly, we firstly investigated the reaction in supercritical CO_2 without any addition of organic solvent. As shown in Fig.1, the conversion of 3-nitrostyrene increased with the CO_2 pressure while the selectivity remained essentially unchanged, at approximately 98%, demonstrating that the pseudo-SAC was a highly selective catalyst whatever the solvent used. When the total pressure was 11.6 MPa and the H_2 partial pressure was 2.0 MPa, the 3-nitrostyrene conversion attained 61.9% and the selectivity of 3-vinylstyrene was 98.2%. In order to explain the increasing trend of the substrate conversion with CO_2 pressure, we further measured the 3-nitrostyrene solubility in supercritical CO_2, and the experimental details were described in supporting information. As shown in Fig. S1-3 and Fig. 2, the solubility of 3-nitrostyrene in $scCO_2$ increased with the CO_2 pressure but decreased with the reaction temperature. At the reaction temperature of 50 ^{o}C and the CO_2 pressure of 10.3 MPa, all the substrate (0.5 mmol 3-nitrostyrene) could be completely dissolved in $scCO_2$. Then with a further increase of the CO_2 pressure, more 3-nitrostyrene and H_2 could be dissolved in the $scCO_2$ such that the reaction rate was increased.

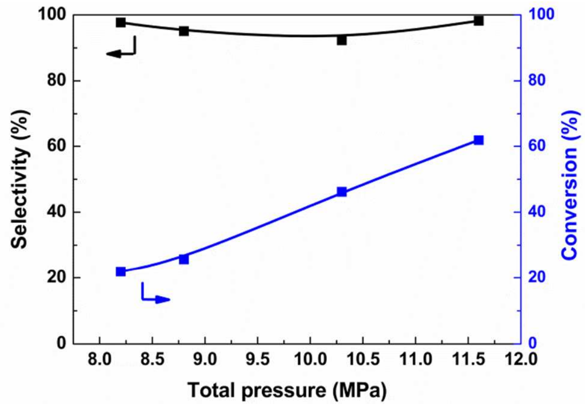


Fig. 1 Influence of total pressure on the conversion of 3-nitrostyrene and the selectivity of 3-vinylaniline for the hydrogenation of 3-nitrostyrene in supercritical CO_2. Reaction conditions : 0.5 mmol 3-nitrostyrene, 0.1 g catalyst, 2 MPa H_2 pressure, 50 ^{o}C, 60 min.

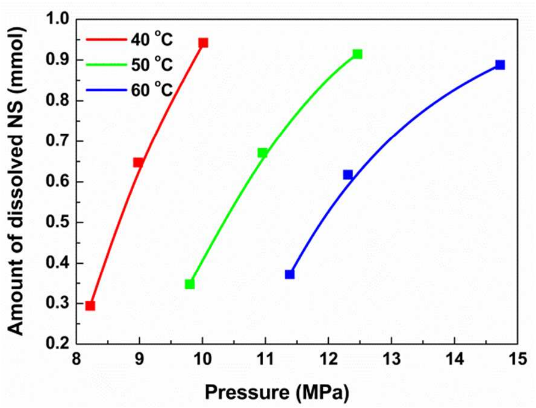


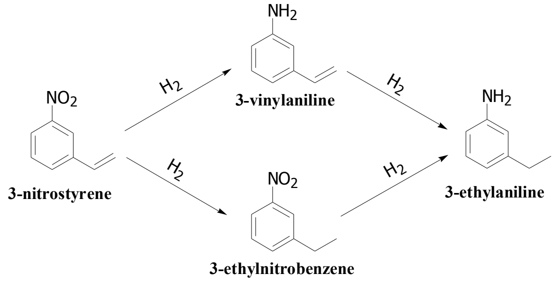
Fig. 2 The solubility of 3-nitrostyrene in supercritical CO_2 at different pressures and temperatures.

Although $scCO_2$ provided a good reaction medium for the chemoselective hydrogenation of 3-nitrostyrene in terms of selectivity, the reaction rate was not satisfactory yet. Therefore, we subsequently investigated the reaction in GXLs, another type of environmentally benign solvents. Three types of GXLs were employed, including CO_2-expanded toluene, ethanol, and tetrahydrofuran (THF). In all cases, the organic solvent volume was 0.5 ml, that is, it was reduced by 90% in comparison with our previous report.[16] The reaction was carried out at a milder condition: 40 ^{o}C, 3 MPa H_2 and the total pressure of 10 MPa. As shown in Table 1, when the reaction proceeded in CO_2-expanded toluene, the conversion of 3-nitrostyrene was 85.9% that was significantly increased in comparison with that in $scCO_2$. At the meanwhile, the selectivity of 3-vinylaniline was 96.2%, again demonstrating the high chemoselectivity of pseudo-SAC. By contrast, in the CO_2-expanded ethanol, both the conversion and the selectivity were relatively lower, while in the CO_2-expanded THF the conversion attained 100% and the selectivity was 84.5% under the same reaction conditions. Considering that the target product 3-vinylaniline was an intermediate in the whole hydrogenation process and it was susceptible to further hydrogenation to the unwanted byproduct 3-ethylaniline (over-hydrogenation, see Scheme 1) at the full conversion of the substrate, we reduced the reaction time to 40 min to ensure that the substrate was not converted completely. In this case, the selectivity of 3-vinylaniline was 94.7% at the substrate conversion of 79.6% in CO_2-expanded THF. Clearly, the CO_2-expanded THF offered better substrate conversion while slightly less selectivity than CO_2-expanded toluene. The result indicates that the solvent nature indeed imposed significant effect on the catalytic performance. As shown in Fig. S4, the solubility of CO_2 in the three solvents as well as the volume expansion follows the order of x_{CO2} (THF) > x_{CO2} (Toluene) > x_{CO2} (ethanol). According to this order, CO_2 in THF offers the best environment to facilitate mass transfer associated with the volume expansion, thus leading to the improved reaction rate. Therefore the conversion of 3-nitrostyrene in CO_2-expanded THF was the highest. Nevertheless, in terms of chemoselectivity, CO_2-expanded toluene appeared as the best solvent among the three GXLs, and it behaved much better than $scCO_2$ regarding the reaction rate, therefore we subsequently optimized the reaction conditions by tuning the pressure and temperature in CO_2-expanded toluene.

Table. 1 Influence of solvents on conversion of 3-nitrostyrene and product selectivity.

Solvent	Conv. (%)	Selectivity (%)		
		3-vinylaniline	3-ethylnitrobenzene	3-ethylaniline
CO_2+toluene	85.9	96.2	0.5	3.3
CO_2+ethanol	50.2	84.9	6.0	9.1
CO_2+THF	100.0	84.5	0.2	15.3
CO_2+THF^{a}	79.6	94.7	1.4	3.7

Reaction conditions : 0.5 mmol 3-nitrostyrene, 0.1 g catalyst, 40 ^{o}C, 3 MPa H_2, organic solvent 0.5 ml, total pressure 10 MPa, 60 min. ^{a} 40 min.



Scheme 1 Reaction pathways for hydrogenation of 3-nitrostyrene.

Optimization of reaction conditions

Influence of pressure. It is well known that the properties of CO_2-expanded liquids are dependent on CO_2 pressure, and thereby the reaction conversion and selectivity are tunable by merely adjusting CO_2 pressure. Fig. 3 depicts the effect of total pressure (H_2 pressure was kept at 2 or 3 MPa while CO_2 pressure was altered) at a reaction temperature of 40 ^{o}C. When H_2 pressure was kept at 2 MPa (Fig. 3a), the conversion of 3-nitrostyrene presented a volcano-shape dependence on the total pressure; it first went up and reached the maximum of 52% at 10 MPa and then went down. On the other hand, the selectivity to 3-vinylaniline kept at a high level (~ 98%) over the whole pressure range. When H_2 pressure was increased to 3 MPa (Fig. 3b), the conversion curve presented the similar trend with that at 2MPa H_2, but the reaction rate was enhanced greatly due to the increased H_2 pressure such that the conversion of 3-nitrostyrene reached 100% in the total pressure range of 6-9 MPa. Upon the full conversion of the substrate being reached, over-hydrogenation took place leading to the lower selectivity than that at 2 MPa H_2. It is interesting to observe that the selectivity of 3-vinylstyrene increased monotonically with the total pressure (also CO_2 pressure) at 2 MPa H_2, which suggests that CO_2 may interact with the amino group of the target product so as to facilitate the desorption of 3-vinylaniline and avoid its further hydrogenation to 3-ethylaniline.[35] On the other hand, the decrease of the substrate conversion when the total pressure surpassed 10 MPa was due to the dilution effect of CO_2. In either 2 MPa or 3 MPa H_2, it can be seen that the optimum pressure was 10 MPa at which the selectivity (> 95%) reached promising values.

In addition to CO_2 pressure, the H_2 pressure in the system also affects the solubility of H_2 in the CO_2-expanded toluene based on Henry's law, thereby leads to the change in both conversion and selectivity. Fig. 4 illustrates the effect of H_2 pressure on the conversion and selectivity by keeping the total pressure of 10 MPa. As expected, the conversion increased with the H_2 pressure while the selectivity decreased as a result of the occurrence of complete hydrogenation reaction. The optimum H_2 pressure appeared to be 3.5 MPa at which both conversion and selectivity were greater than 90%.

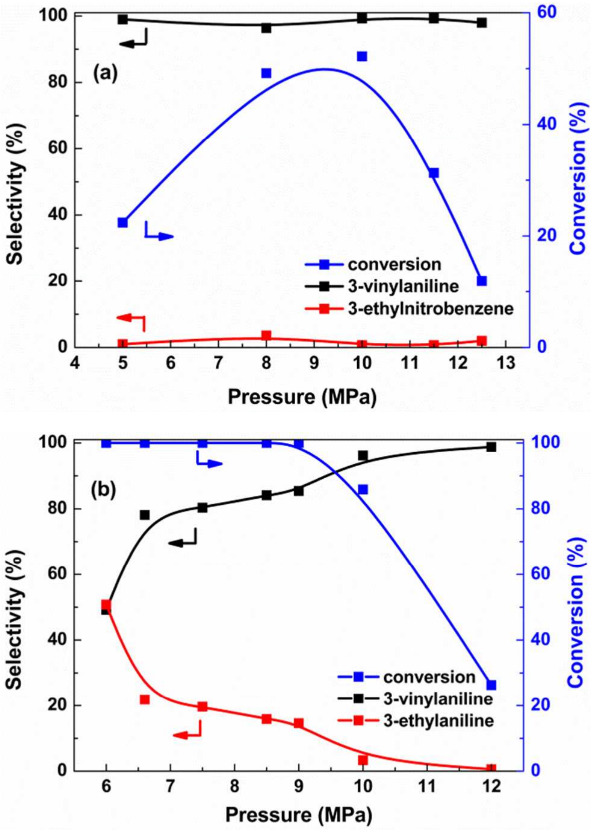


Fig. 3 Influence of total pressure on the conversion of 3-nitrostyrene and the product selectivity. Reaction conditions: 0.5 mmol 3-nitrostyrene, 0.1 g catalyst, 40 ^{o}C, 0.5ml toluene, 60 min. (a) 2 MPa H_2 (b) 3 MPa H_2.

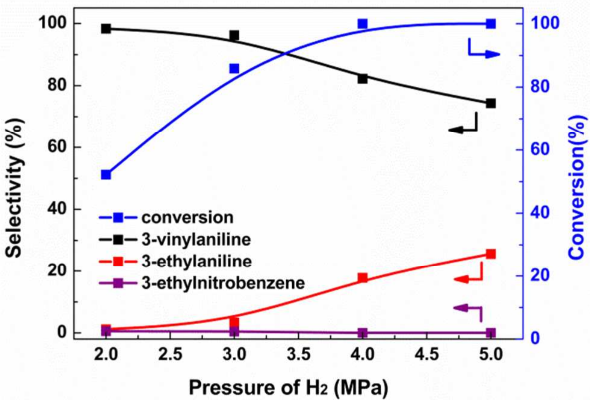


Fig. 4 Influence of pressure of H_2 on the conversion of 3-nitrostyrene and the product selectivity. Reaction conditions: 0.5mmol 3-nitrostyrene, 0.1 g catalyst, 40 ^{o}C, toluene 0.5 ml, total pressure 10 MPa, 60 min.

Influence of reaction time and temperature. The effects of reaction time and temperature are shown in Table 2 and Fig. 5, respectively. As expected, with an increase of the reaction time, the conversion of 3-nitrostyrene increased while the selectivity of 3-vinylaniline remained almost unchanged. At the reaction time of 60 min, the conversion and selectivity reached 85.9% and 96.2%, respectively. For the effect of reaction temperature, to our delight, the conversion increased rapidly when the reaction temperature was raised from 30 to 60 °C while the selectivity of 3-vinylaniline decreased only slightly from 97.6% to 94.2%. At the optimum temperature of 50 °C, the conversion and the selectivity reached 97.8% and 96.0%, respectively. Such a high level is comparable to that obtained in pure toluene solvent (5 ml toluene corresponding to solvent/substrate of 1000),[16] but in our present GXL conditions, the organic solvent was reduced by 90%.

Table. 2 Influence of reaction time on the conversion of 3-nitrostyrene and the product selectivity.

Time (min)	Conversion (%)	Selectivity (%)		
		3-vinylaniline	3-ethylnitrobenzene	3-ethylaniline
20	13.9	97.4	1.6	1.0
30	25.2	98.7	0.9	0.4
40	75.3	95.3	0.9	3.8
60	85.9	96.2	0.5	3.3

Reaction conditions： 0.5 mmol 3-nitrostyrene, 0.1 g catalyst, 0.5 ml toluene, 40 °C, 3 MPa H_2, total pressure 10 MPa.

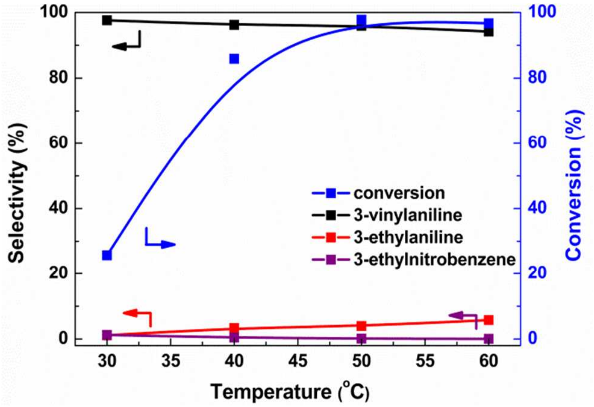


Fig. 5 Influence of temperature on the conversion of 3-nitrostyrene and the product selectivity. Reaction conditions: 0.5 mmol 3-nitrostyrene, 0.1 g catalyst, 3 MPa H_2, toluene 0.5 ml, total pressure 10 MPa, 60 min.

Comparison of different catalysts

From the above result one can see that the FeOx-supported Pt pseudo-single-atom catalyst showed very high (>95%) selectivity towards 3-vinylaniline either in $scCO_2$ or CO_2-expanded toluene. In order to demonstrate the unique property of Pt/FeOx support, we prepared other three different supported Pt catalysts with the same Pt loading as that for Pt/FeOx, including Pt/SiO_2, Pt/Al_2O_3 and Pt/TiO_2. The catalytic performances of these catalysts for the hydrogenation of 3-nitrostyrene were compared under identical reaction conditions. As shown in Table 3, both Pt/SiO_2 and Pt/Al_2O_3 catalysts were poorly selective toward the formation of 3-vinylaniline, while Pt/TiO_2 was highly selective but poorly active. Among the catalysts investigated, only Pt/FeOx catalyst showed both high activity and selectivity. Apparently, the support nature affects significantly the catalytic performance of Pt thereon, with the reducible support more selective towards this reaction[36]. Based on our previous study on the Pt/FeOx single-atom catalyst[16], NO_2-group was preferentially adsorbed on the interface between Pt and the FeOx support, and the electron transfer from Pt to the underlying FeOx support made Pt centers positively charged. The excellent activity and selectivity could be attributed to the isolated and positively charged Pt centers, which limit the hydrogenation of C=C bond to the maximum extent.

Table. 3 Performances of different catalysts in the hydrogenation of 3-nitrostyrene

Catalyst	Conv. (%)	Selectivity (%)		
		3-vinylaniline	3-ethylnitrobenzene	3-ethylaniline
Pt/FeOx	97.8	96.0	3.9	0.1
Pt/SiO_2	79.4	48.8	19.8	31.4
Pt/Al_2O_3	10.3	23.6	76.4	0
Pt/TiO_2	49.7	98.3	1.2	0.5

Reaction conditions: 0.5 mmol 3-nitrostyrene, 0.1 g catalyst, 0.5 ml toluene, 50 °C, 3 MPa H_2, total pressure 10 MPa, 60 min.

Thermodynamic calculation

In order to provide an insightful understanding of the reaction behaviour in GXL, we performed thermodynamic calculations of the volume expansion (ΔV/V) and the viscosity change with the CO_2 pressure. As shown in Fig. 6, the volume of the reaction mixture gradually expanded with an increase of the CO_2 pressure until 9 MPa and there was a sharp volume expansion from 100% to 650% when the total pressure was increased from 10 MPa to 12 MPa, meanwhile the system viscosity decreased almost linearly with the CO_2 pressure, from 219.5 µPa·s to 30.5 µPa·s. The volume expansion to a suitable extent will facilitate the H_2 dissolution while the reduced viscosity will be beneficial to the mass transfer of reactants. As shown in Table S2 in supporting information, the hydrogen solubility in the CO_2-H_2-C_7H_8 ternary system is always larger than that in pure toluene, as shown by the enhancement factor (E) greater than 1 in all cases. These unique thermodynamic properties of CO_2-expanded toluene, in conjunction with the unique function of the Pt/FeOx catalyst, account for the excellent conversion and selectivity for chemoselective hydrogenation of 3-nitrostyrene even at a reduced volume of toluene as high as 90%.

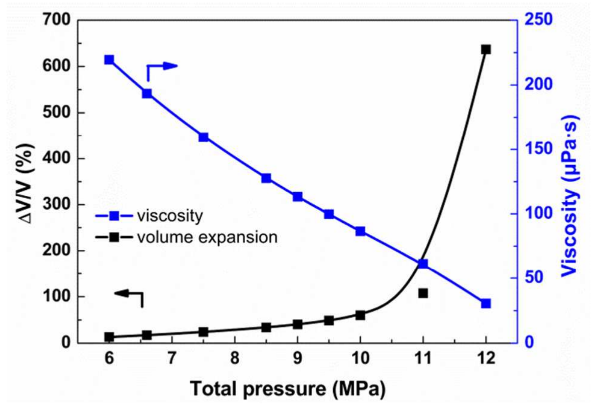


Fig. 6 Calculated volume expansion and viscosity of the reaction system as a function of the total pressure. Ternary system: 0.5 ml toluene, 3 MPa H_2, variable CO_2 pressure..

Conclusions

In summary, the chemoselective hydrogenation of 3-nitrostyrene over Pt/FeOx pseudo-single-atom catalyst proceeded well in both $scCO_2$ and CO_2-expanded toluene. When the reaction was carried out in $scCO_2$, the conversion increased with increasing the CO_2 pressure meanwhile the selectivity of 3-vinylaniline kept at around 98%. In comparison with the reaction in $scCO_2$, CO_2-expanded toluene afforded a much better conversion and good selectivity. In optimum reaction conditions, both the conversion and the selectivity could reach above 95% but the toluene solvent could be reduced by 90%, which provided a green synthesis approach to the functionalized anilines.

Acknowledgements

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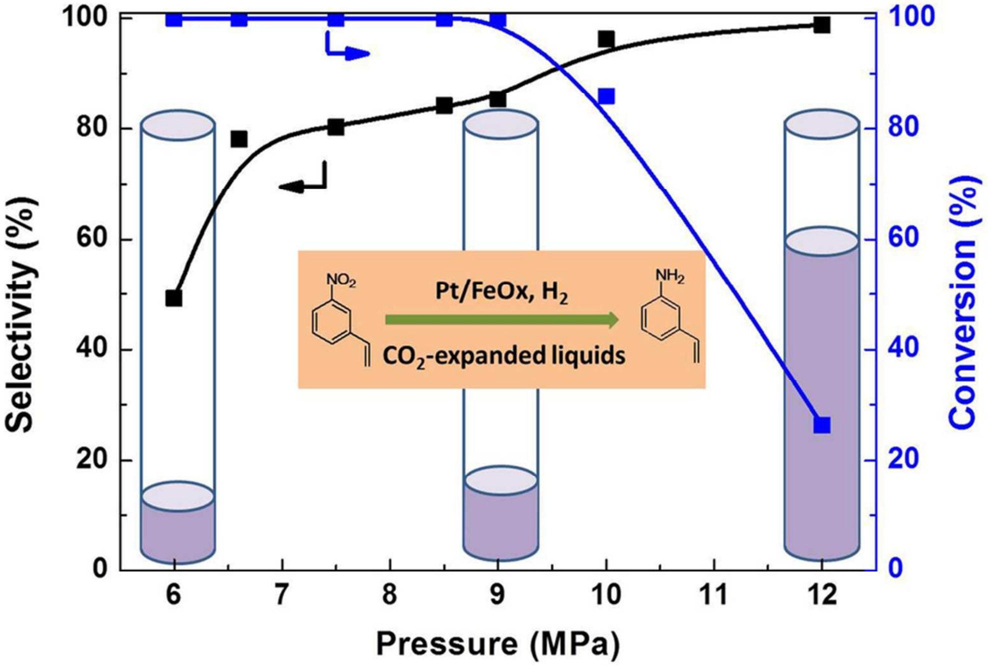

Chemoselective hydrogenation of 3-nitrostyrene over Pt/FeOx pseudo-single-atom-catalyst in CO2-expanded liquids
40x26mm (600 x 600 DPI)