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An Escape from Noble Metals for Generating Urethanes via Reductive Carboxylation of Nitroarenes over FeSe$_2$/γ-Al$_2$O$_3$†

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Abstract: The reaction of FeCl$_3$, SeO$_2$, and Pyridine (Py) in the presence of methanol (MeOH) under CO pressure generates a black precipitate, which has been confirmed as ferric di-selenide, FeSe$_2$ through different structure characterization methods. Furthermore, impregnation of 5 wt% of FeSe$_2$ onto γ-Al$_2$O$_3$ exhibits better catalytic performance than FeSe$_2$ due to the highly dispersed and smaller particle sizes ca. 200–300 nm. The reductive carboxylation of nitrobenzene (NB) was investigated over FeSe$_2$/γ-Al$_2$O$_3$ as a heterogeneous catalyst, delivering an excellent yield and high selectivity of methyl-N-phenyl carbamate (MPC). Moreover, a set of reactions was performed with variation in the reaction time, temperature, and pressure to investigate the effects of these factors. In particular, FeSe$_2$/γ-Al$_2$O$_3$ is highly stable and can be recycled for up to five cycles without significant loss in catalytic performance. A mechanistic study was also conducted on this low-cost catalyst system, especially proposing a crucial role of FeSe$_2$ (μ-CO) active species.

Keywords: ferrous selenide; nitrobenzene; reductive carboxylation; urethane

1. Introduction

Urethanes (carbamates) are essential precursors for producing isocyanates, the main material for manufacturing polyurethane, due to their transformation ability into isocyanates via thermal cracking. Conventionally, the production of urethanes involves the employment of phosgene, which is extremely toxic and harmful to the environment and human beings. Therefore, there have been tons of endeavors for producing carbamates via phosgene-free pathways [1–19]. Among them, the catalytic reductive carboxylation of nitroarenes is regarded as one of the promising routes [6–8,20–27]. Noble metal complexes containing Ru, Rh, and Pd have been commonly employed as main catalysts in this process [5,9,10,24,28–37]. Ragaini’s research group showed that [Pd(phen)$_2$][BF$_4$]$_2$ could produce 71.05% yield of methyl-N-phenyl carbamate (MPC). In his work, the use of [Pd(phen)$_2$][BF$_4$]$_2$ resulted in ca. 6000 h$^{-1}$ turnover frequency (TOF), which is the highest reported record to date [6,38]. Even though these catalyst systems showed high efficiency, there are still some limits in recyclability and leaching problems of noble metals-based catalysts. Meanwhile, selenium metal or selenium compounds have been widely used in catalytic reductive or oxidative carboxylation processes to produce carbamates from the corresponding aliphatic and aromatic
amines. In the oxidative carboxylation of aromatic amine compounds, the active species were confirmed as Se(IV) such as SeO₂, MSeO, MSeO₂(OR), M₂SeO₃, and QSeO₂(OR) (with M = alkali metal; Q = imidazolium, phosphonium) [1,2,39]; however, Se(0) is applied in reductive carboxylation [40–44]. Indeed, it has been reported that only Se(0) can convert nitrobenzene (NB) to urethanes and/or disubstituted ureas through reductive carboxylation [41,45].

Throughout our study on the reductive carboxylation of NB over different catalyst combinations consisting of Se-based and other metal halides to prepare MPC, we found that not only Cu²⁺Se₂⁺, which has been already found by our research group as an active and novel heterogeneous catalyst [46], but also Fe²⁺Se₂⁺ is found to be far more active than Cu²⁺Se₂⁺ species. Like the case of Cu²⁺Se₂⁺, the ferrous diselenide (FeSe₂) is also generated during the carboxylation reaction using the catalyst system consisting of FeCl₃ and SeO₂, but its activity was enhanced with the co-presence of pyridine. Additionally, FeSe₂ is a heterogeneous system that gives a simple separation and high selectivity toward urethanes. Furthermore, the catalyst can be prepared from the first-row transition metals, providing a promising route for replacing the precious metals in the reductive carboxylation of nitroarenes.

In this work, the authors provide the preparation of FeSe₂ and FeSe₂/γ-Al₂O₃ and characterization by various spectroscopic methods. Additionally, the catalytic activities of the FeSe₂/γ-Al₂O₃ in the reductive carboxylation will be investigated (Scheme 1). A plausible mechanism is also provided based on this active heterogeneous catalyst system, especially emphasizing the critical role of FeSe₂(μ-CO) species.

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\text{ArNO}_2 + \text{MeOH} + 3 \text{CO} \xrightarrow{T, P, t} \frac{5 \text{wt% FeSe}_2/\gamma-\text{Al}_2\text{O}_3}{\text{ArNHC(O)OMe} + 2 \text{CO}_2}
\]

Scheme 1. The reductive carboxylation of nitroarenes over FeSe₂/γ-Al₂O₃.

2. Results and Discussion

2.1. Screening of the Catalyst Systems

The reductive carboxylation of NB for producing MPC was conducted over a catalyst system consisting of three compounds, FeCl₃, SeO₂, and pyridine (Py) in MeOH at 160 °C, 8.3 MPa of CO for 4 h. Table 1 shows that this catalyst combination generates MPC with a remarkable yield of 93.8% with complete conversion of NB (Entry 1). It is worth mention that the reductive carboxylation of NB is only effective when three components of FeCl₃, SeO₂, and Py are applied concomitantly. The absence of any components results in a decrease in the activities (Entry 2–4). Moreover, the single system (Entry 5–7) gives even worse outcomes. However, SeO₂ itself delivers 25.8% yield of MPC (Entry 6), (SeO₂ + Py), affording 37.8% (Entry 3), and (FeCl₃ + SeO₂) delivers 32.1% (Entry 2), demonstrating the importance of the presence of selenium in the reductive carboxylation. Furthermore, Se(0) itself could deliver 50.3% yield of MPC (Entry 8). Hence, 25.8% yield of MPC obtained from SeO₂ could be explained from an incomplete reduction of SeO₂ to Se(0) under this reducing conditions [41,42]. On the other hand, an insoluble solid was always formed during the reductive carboxylation of NB using the three-compound catalyst system. Being encouraged by this phenomenon, a reaction of FeCl₃ and SeO₂ in the methanolic Py solution is conducted without NB under otherwise identical conditions. After the reaction, the insoluble solid was collected by filtration, washed with methanol, and vacuum dried. The FT-IR results of this compound show there are no organic moieties; thus, it is thought to be an inorganic compound, and we tentatively named it as Fe₂Se₇.
Table 1. Screening of the catalysts system.

| Entry | Catalyst Composition | NB Conv. (%) | MPC Yield (%) | AN Yield. (%) | TON |
|-------|----------------------|--------------|---------------|---------------|-----|
| 1     | FeCl₃ SeO₂ Py        | >99          | 93.8          | 6.2           | 11.7 |
| 2     | FeCl₃ SeO₂           | 50.3         | 32.1          | 18.2          | 4.0  |
| 3     | SeO₂ Py              | 46.5         | 37.8          | 8.7           | 4.7  |
| 4     | FeCl₃ - Py           | 0            | 0             | 0             | 0    |
| 5     | FeCl₃ -              | 0            | 0             | 0             | 0    |
| 6     | - SeO₂ -             | 30.5         | 25.8          | 4.7           | 3.2  |
| 7     | - - Py               | 0            | 0             | 0             | 0    |
| 8     | - - Se²              | 66.9         | 50.3          | 16.6          | 6.3  |

*Conditions: NB (2.46 g, 20 mmol), FeCl₃ (0.054 g, 0.4 mmol), SeO₂ (0.177 g, 1.6 mmol), Py (0.158 g, 2 mmol), molar ratio of NB/[Se] = 12.5, MeOH 30 mL, T = 160 °C, pCO = 8.3 MPa, t = 4 h.

2.2. Characterization of Active Species and Its Supported System

Figure 1 shows that XRD spectra of Fe₅₇₀ contains mainly ferroselite Fe₅₇₀ phase [JCPDS 65-1455, Figure S1] [47,48]. To find out the stoichiometry of Fe₅₇₀, EDX/EDS analysis was carried out. The EDX/EDS spectra indicate the appearance of only Fe and Se, and Fe is combined with Se in the ratio of 1:2 (Supplementary Materials, Figure S3); thus, the stoichiometry of Fe₅₇₀ is assumed to be FeSe₂.

Figure 1. X-ray diffraction spectra (XRD) of (a) Fe₅₇₀, which is the black solid synthesized from the reaction of FeCl₃, SeO₂ in the presence of methanolic Py solution under CO pressure, and (b) standard pattern of ferroselite Fe₅₇₀.

XPS analysis of FeSe₂ was conducted to examine the oxidation state of Fe and Se elements (Supplementary Materials, Figure S5). As shown in Figure S5, the XPS survey of FeSe₂ indicates that it comprises only Fe and Se. Furthermore, the Fe2p region depicted in Figure S7a shows that the band of Fe 2p₁/₂ and Fe 2p₃/₂ at 711.5 and 724.8 eV exhibits the presence of Fe²⁺ [49]. The minor peak at 707.1 eV is attributed to metallic Fe⁰ which could be resulting from the further reduction of Fe²⁺ to Fe⁰ [49]. Meanwhile, the peak at 55.07 eV and 59.1 eV in Figure S7b belong to Se 3d₅/₂ and Se 3d₇/₂ of Se²⁻ species in FeSe₂ [49,50]. The C 1s XPS spectra was also investigated to check the formation of carbonaceous species of the sample. As can be seen in Figure S7c, the spectra did not exhibit the
presence of peaks belonging to carbonaceous compounds except the standard carbon peak at 284.8 eV for XPS calibration. These studies clearly demonstrate that the black compound generated during the reductive carboxylation is defined as ferrous diselenide (Fe\textsubscript{2}Se\textsubscript{2}).

The heterogeneous catalyst FeSe\textsubscript{2} was employed as the catalyst in the reductive carboxylation of NB for producing MPC. Table 2 reveals that FeSe\textsubscript{2} exhibits the best catalytic performance that shows 96.6% of MPC yield at the complete conversion of NB (Entry 1). After the reaction, aniline (AN, about 3.4%) was found as the only by-product, regarded as an intermediate in the reductive carboxylation of NB. Furthermore, when similar process is performed over FeSe\textsubscript{2} which was prepared without Py, the MPC yield is reduced to 85.3%, suggesting the important role of Py, which is thought to render the particle size of the FeSe\textsubscript{2} smaller and uniformed (Entry 2). In comparison with the catalytic performance of other Se\textsuperscript{2−} species, a commercial chemical of Fe\textsuperscript{II}Se\textsubscript{2} was tested. However, it shows poorer activity in terms of both conversion and yield (Entry 3). A reported catalyst, CuSe\textsubscript{2}/CeO\textsubscript{2} was also tested at the same conditions; however, it gives lower yield (63.5% yield of MPC at 68% conversion of NB) than that of FeSe\textsubscript{2} (Entry 9) [46].

From these observations, it is concluded that Se\textsuperscript{2−} is the most responsible species for providing high activity toward MPC, and this trend is significantly noticeable when using ferrous diselenide (FeSe\textsubscript{2}).

**Table 2. Activities of various MSe\textsubscript{2} and their supported systems.**

| Entry | Catalyst | Molar Ratio (NB/Cat) | NB Conv. (%) | MPC Yield (%) | AN Yield (%) | TON |
|-------|----------|-----------------------|--------------|---------------|--------------|-----|
| 1     | Fe\textsuperscript{II}Se\textsubscript{2} | 4                     | >99          | 96.6          | 3.4          | 3.9 |
| 2     | Fe\textsuperscript{II}Se\textsubscript{2} | 4                     | 97.4         | 85.3          | 12.1         | 3.4 |
| 3     | Fe\textsuperscript{II}Se | 4                     | 79.4         | 69.1          | 10.3         | 2.8 |
| 4     | Fe\textsuperscript{II}Se | 85                    | 25.8         | 21.7          | 4.1          | 18.4|
| 5     | FeSe\textsubscript{2}/γ-Al\textsubscript{2}O\textsubscript{3} | 85                    | >99          | 98.9          | 1.1          | 84.1|
| 6     | FeSe\textsubscript{2}/basic Al\textsubscript{2}O\textsubscript{3} | 85                    | >99          | 91.6          | 8.4          | 77.9|
| 7     | FeSe\textsubscript{2}/α-Al\textsubscript{2}O\textsubscript{3} | 85                    | 98.1         | 87.8          | 10.3         | 74.6|
| 8     | FeSe\textsubscript{2}/AlPO\textsubscript{4} | 85                    | 87.0         | 85.7          | 1.3          | 72.8|
| 9     | CuSe\textsubscript{2}/CeO\textsubscript{2} | 85                    | 68           | 63.5          | 4.5          | 53.9|

\*Conditions: NB (2.46 g, 20 mmol), catalyst (5 mmol), molar ratio of NB/catalyst = 4, MeOH (30 mL), T = 160 °C, P (CO) = 8.3 MPa, t = 4 h. \textsuperscript{b} NB (2.46 g, 20 mmol), FeSe\textsubscript{2} synthesized without Py (1.07 g, 5 mmol). \textsuperscript{c} MeOH (30 mL), T = 160 °C, P (CO) = 8.3 MPa, t = 4 h. \textsuperscript{d} NB (2.46 g, 20 mmol), 4-5 wt% FeSe\textsubscript{2}/support (1 g, [FeSe\textsubscript{2}]: 0.2338 mmol), molar ratio of NB/FeSe\textsubscript{2} = 85. MeOH (30 mL), T = 160 °C, P (CO) = 8.3 MPa, t = 4 h. \textsuperscript{e} NB (2.46 g, 20 mmol), 4-5 wt% CuSe\textsubscript{2}/CeO\textsubscript{2} (1.04 g, [CuSe\textsubscript{2}]: 0.235 mmol).

Molar ratio of NB/CuSe\textsubscript{2} = 85, MeOH (30 mL), T = 160 °C, P (CO) = 8.3 MPa, t = 4 h.

To enhance the catalytic performance of FeSe\textsubscript{2} by an impregnation approach, a wet impregnation technique has been adopted with different types of supports such as γ-Al\textsubscript{2}O\textsubscript{3}, basic Al\textsubscript{2}O\textsubscript{3}, α-Al\textsubscript{2}O\textsubscript{3}, and AlPO\textsubscript{4} with 5wt% of FeSe\textsubscript{2} loadings. As shown in entries from 5 to 9 in Table 2, γ-Al\textsubscript{2}O\textsubscript{3} supported FeSe\textsubscript{2} exhibits the highest catalytic activity toward MPC (98.9% yield, Entry 5). It is noteworthy to mention that the molar ratio of NB/FeSe\textsubscript{2} of this reaction over FeSe\textsubscript{2}/γ-Al\textsubscript{2}O\textsubscript{3} is almost twenty times higher than that of the neat FeSe\textsubscript{2} in terms of the molar ratio basis (Entry 1), indicating that the catalytic performance of FeSe\textsubscript{2}/γ-Al\textsubscript{2}O\textsubscript{3} was enhanced without any loss of selectivity. Indeed, the MPC yield when using neat FeSe\textsubscript{2} at the same molar ratio of 85 is found to be very low (21.7%, Entry 4). Basic Al\textsubscript{2}O\textsubscript{3}, α-Al\textsubscript{2}O\textsubscript{3}, and AlPO\textsubscript{4} did not show as good activity as γ-Al\textsubscript{2}O\textsubscript{3} (entries 6-8), and activities of other supporting materials are also provided in the Supplementary Materials (Table S1), and XRD results of FeSe\textsubscript{2}/γ-Al\textsubscript{2}O\textsubscript{3} and its XPS spectra are presented therein (Figures S2 and S6).

To examine the role of Py, the possible correlation between morphologies and activities of the catalysts was studied using SEM image and MPC yields. As shown in Figure 2, FeSe\textsubscript{2} synthesized without Py exhibits the irregular rod-typed morphology, whereas the one made with Py exhibits the identical flake typed and well-dispersed morphologies. The observed size of FeSe\textsubscript{2} without Py is
about 1–1.1 µm (Figure 2a), while that of FeSe₂ prepared with Py decreased to ca. 400–450 nm (Figure 2c). The catalytic activity is also correlated with the size of catalysts, that is, the smaller the particle size, the better the performance on the formation of MPC (see Table 3). When we compare the SEM images of the supported system, FeSe₂/γ-Al₂O₃ prepared without Py shows irregular rod and flake typed structures with a size of 0.75 µm (Figure 2b). However, FeSe₂/γ-Al₂O₃ prepared with the presence of Py exhibits regular and well-dispersed particles of 200–300 nm (Figure 2d), almost two times smaller than the prepared with Py without the support. These results indicate that the presence of Py helps to render the size of FeSe₂ regular and smaller. Therefore, it is concluded that the improvement of catalytic activity in the FeSe₂/γ-Al₂O₃ system is attributed to the higher dispersion of FeSe₂ particles onto γ-Al₂O₃. High-resolution TEM images of FeSe₂ and FeSe₂/γ-Al₂O₃ are also provided in Figure S9.

![Figure 2. Scanning Electron Microscopy (SEM) images of (a) FeSe₂ prepared without pyridine, (b) FeSe₂/γ-Al₂O₃ prepared without pyridine, (c) FeSe₂ prepared with pyridine, and (d) FeSe₂/γ-Al₂O₃ prepared with pyridine.](image)

**Table 3. Correlation between morphologies and activities**

| Entry | Catalyst | Molar Ratio (NB/Cat) | NB Conversion (%) | MPC Yield (%) | Morphology | Size |
|-------|----------|----------------------|------------------|---------------|------------|------|
| 1     | FeSe₂ without Py | 4 | 97.4 | 85.3 | Irregular rod-type and aggregated flakes | 1–1.1 µm |
| 2     | FeSe₂ with Py | 4 | >99 | 96.6 | Uniformed flake-type | 400–450 nm |
2.3. Catalytic Activities of FeSe$_2$/γ-Al$_2$O$_3$

To investigate product profile as a span of reaction time in the reductive carbonylation of NB over FeSe$_2$/γ-Al$_2$O$_3$, a set of experiments was conducted with variable reaction time ranging from 0.5 h to 6.0 h. The results illustrated in Figure 3 show that the amount of MPC arises upon elevating time from 0.5 to 4 h and then keeps constant. Upon prolonging the time to 4 h, the amount of NB reduced rapidly. Moreover, this time-course study also shows that aniline (AN) is the only by-product during the conversion of NB, and it is suppressed within 0.14 mmol level.

![Figure 3. Product compositional changes as a function of time in the reductive carbonylation of NB at 160 °C, 8.3 MPa of CO in the presence of 1 g of 5wt% FeSe$_2$/γ-Al$_2$O$_3$. Conditions: NB (20 mmol), 5 wt% FeSe$_2$/γ-Al$_2$O$_3$ (1 g, [FeSe$_2$]: 0.2338 mmol), molar ratio of NB/FeSe$_2$ = 85, MeOH (30 mL), T = 160 °C, P (CO) = 8.3 MPa, t = 4 h.](image)

The influence of the reaction temperature on the reductive carbonylation of NB over FeSe$_2$/γ-Al$_2$O$_3$ was tested with a variable thermal scale from 120–180 °C. As shown in Figure 4, the higher MPC yield was obtained when elevating the temperature until 160 °C, thereafter both conversion and yield are decreased. The generation of AN could not be neglected at a low temperature of 120 °C, which is ascribed to a simple reduction of NB to AN. However, AN reduces with a further increase in the temperature up to 160 °C. The lower yield of MPC, together with the increase in the aniline (AN) formation at 180 °C might be due to the thermal decomposition of MPC.
Figure 4. Effect of temperature on the formation of MPC at 8.3 MPa of CO for 4 h in the presence of 1 g of 5 wt% FeSe₂/γ-Al₂O₃. Conditions: NB (20 mmol), 5 wt% FeSe₂/γ-Al₂O₃ (1 g, [FeSe₂]: 0.2338 mmol), molar ratio of NB/FeSe₂ = 85, MeOH (30 mL), \( p = 8.3 \) MPa of CO, \( t = 4 \) h.

The influence of CO pressure was also studied by elevating pressure from 6.2 to 10.3 MPa at 160 °C for 4 h. As shown in Figure 5, the results reveal that the pressure effect is not as strong as the reaction temperature; however, at least 6.8 MPa of CO is needed to achieve an acceptable MPC yield. It is worth mentioning that the AN formation is suppressed with the increase in the pressure, suggesting that the high pressure of CO is beneficial for the generation of selenium-carbonyl species which might act as an intermediate.

To broaden the scope of applicability of the FeSe₂/γ-Al₂O₃-catalyzed reductive carbonylation, different nitroaromatic compounds were applied as substrates under 160 °C, 8.3 MPa for 4 h (hereafter these conditions will be regarded as standard conditions). As demonstrated in Table 4, 4-nitroanisole having an electron-donating group (EDG) at para position is transformed to methyl-N-(4-methoxyphenyl) carbamate with very high yield (98.5%, Entry 1), while 4-nitrotoluene and 4'-nitroacetophenone is converted to the corresponding carbamates only in 50.1% and 48% yields, respectively (Entry 3 and 4). Additionally, 3-nitroanisole, bearing (EWG) at the meta-position, was transformed to the corresponding carbamate in lower yield (80%, Entry 2). When it was carried out with 4-bromonitrobenzene with an electron-withdrawing group (EWG) at the para position, carbamate yield dropped significantly to 19.7%. These results imply that the EDG/EWG capability of the substituents might affect the catalytic performance of the reductive carbonylation of nitroarenes, i.e., the presence of electron-withdrawing group at the para position tended to reduce the catalyst activity of the carbonylation reaction. The 2,4-dinitrotoluene (2,4-DNT), a main precursor for manufacturing toluene diisocyanate (TDI), is also converted to the corresponding dicarbamate, but the yield was 41.5% even at higher temperature (180 °C), longer reaction time (6 h), and higher catalyst amount (molar ratio of sub/cat = 42), (Entry 6). Surprisingly, the carbonylation of 1,4-nitroaniline gives 40.5% yield of the corresponding diurethane under the optimized conditions. Being encouraged by this outcome, a set of experiments has been conducted by adding a variety amount of aniline (AN) with varying from 20% to 200% based on NB (mol/mol). Figure 6 shows that the MPC yield dramatically increases upon adding AN with 180% (substrate: NB 10 mmol and AN 18 mmol) then reduces. The highest yield of MPC is 204% based on NB, which is almost two times higher than that in the case of without AN. The positive effect of adding AN in the reductive carbonylation has
been reported, and it accelerates the reductive carbyonylation reaction of NB over a palladium-phenanthroline catalyst system [51]; however, this protocol eventually gave rise to a decrease in the selectivity due to the generation of large amounts of azaoyxabenzen [6]. Nevertheless, the FeSe₂/γ-Al₂O₃ catalyst did not show any azoxybenzene as a side-product.

Figure 5. Effect of pressure on the formation of MPC at 160 °C for 4 h in the presence of 1 g of 5 wt% FeSe₂/γ-Al₂O₃. Conditions: NB (20 mmol), 5 wt% FeSe₂/γ-Al₂O₃ (1 g, [FeSe₂]: 0.2338 mmol), molar ratio of NB/FeSe₂ = 85, MeOH (30 mL), T = 160 °C, t = 4 h.

The additional formation of MPC by adding AN can be rationalized by the following in situ cascade reactions: (i) a reaction between AN and isocyanato species produces diphenyl urea (DPU), then (ii) methanolysis of DPU affords MPC (2.5.Mechanism study). This is fairly acceptable because a quantitative production of MPC was verified from the alcoholysis of DPU by methanol in the absence of a catalyst.

It should be clear that the MPC was not obtained when AN was used as a sole substrate (Table 4, Entry 11), which indicates that AN itself cannot be carbyonylated or work as an intermediate in the reductive carbyonylation over FeSe₂ for producing MPC. On the other hand, AN works as a reactant for the generation of DPU via in situ reaction with an isocyanato intermediate, which might be a reasonable explanation about the high reactivity of nitroaniline in the FeSe₂-catalyzed reductive carbyonylation. To confirm this, a reductive carbyonylation over 5 wt% FeSe₂/γ-Al₂O₃ (1 g, with a molar ratio of sub/cat = 170) was conducted by employing the dual substrates system consisting –nitro (20 mmol) and –amino (20 mmol) substrate bearing the same functional group at the para-position of the aromatic ring under standard conditions. After the reaction, the corresponding urethanes were generated in 148.4 and 161.1% yields based on nitro substrate, respectively (Entries 8 and 9, Table 4), which are 1.5 and 3.2 times higher than in the case of the sole substrate system (Entry 1 and 3, Table 4). Moreover, a dual substrates 2,4-dinitrotoluene and 2,4-diaminotoluene were also applied for the reductive carbyonylation, catalyzed by only 1 g of FeSe₂/γ-Al₂O₃ (sub/cat molar ratio = 170) under the standard conditions. Interestingly, the di-carbamate yield was found to be 92.5% (Entry 10, Table 4). Compared to the yield of the nitro substrate (41.5%) at a longer reaction time (6 h), higher temperature (180 °C), and higher catalyst amount, the catalytic performance of this dual substrate system in the standard conditions can be regarded as astonishing.
Table 4. Reductive carbonylation of various nitro compounds

| Entry | Substrates   | Product          | Conv. (%) | Yield (%) |
|-------|--------------|------------------|-----------|-----------|
|       | Nitro        | Amino            | Nitro     | Amino     |
| 1     | \(\text{MeO-}^\text{NO}_2\) | \(\text{MeO-}^\text{N-}^\text{OMe}\) | >99       | 98.5      |
| 2     | \(\text{OMe-}^\text{NO}_2\) | \(\text{OMe-}^\text{N-}^\text{OMe}\) | 92.5      | 80.0      |
| 3     | \(\text{Me-}^\text{NO}_2\) | \(\text{Me-}^\text{N-}^\text{OMe}\) | 56.4      | 50.1      |
| 4     | \(\text{Me-}^\text{CO}\) | \(\text{Me-}^\text{CO-}^\text{N-}^\text{OMe}\) | 50.5      | 48.0      |
| 5     | \(\text{Br-}^\text{NO}_2\) | \(\text{Br-}^\text{N-}^\text{OMe}\) | 35.5      | 19.7      |
| 6\(\text{b}\) | \(\text{Me-}^\text{NO}_2\) | \(\text{Me-}^\text{N-}^\text{OMe}\) | >99       | 41.5      |
| 7     | \(\text{H-N-}^\text{NO}_2\) | \(\text{H-N-}^\text{OMe}\) | 98.5      | 40.5      |
| 8\(\text{c}\) | \(\text{MeO-}^\text{NO}_2\) | \(\text{MeO-}^\text{N-}^\text{NH}_2\) | 87.2      | 90.0      | 148.4    |
| 9\(\text{c}\) | \(\text{Me-}^\text{NO}_2\) | \(\text{Me-}^\text{N-}^\text{NH}_2\) | 99.5      | 74.2      | 161.1    |
| 10\(\text{c}\) | \(\text{Me-}^\text{NO}_2\) | \(\text{Me-}^\text{N-}^\text{NH}_2\) | >99       | >99       | 92.5     |
| 11    | Aniline      | NR               | NR        | 0         |

\(\text{a}\) Conditions: Substrate (20 mmol), 5 wt% FeSe\(\gamma\)/\(\gamma\)-Al\(_2\)O\(_3\) (1 g, [FeSe]: 0.2338 mmol), molar ratio of sub/FeSe = 85, MeOH (30 mL), T = 160 °C, P (CO) = 8.3 MPa, \(t\) = 4 h. \(\text{b}\) Substrate (10 mmol), 5 wt% FeSe\(\gamma\)/\(\gamma\)-Al\(_2\)O\(_3\) (1 g, [FeSe]: 0.2338 mmol), molar ratio of sub/FeSe = 42, MeOH (30 mL), T = 180 °C, P (CO) = 8.3 MPa, \(t\) = 6 h. \(\text{c}\) Nitro compound (20 mmol), aniline compound (20 mmol), 5wt% FeSe\(\gamma\)/\(\gamma\)-Al\(_2\)O\(_3\) (1 g, [FeSe]: 0.2338 mmol), molar ratio of (nitro + aniline)/FeSe = 170, MeOH (30 mL), T = 160 °C, P (CO) = 8.3 MPa, \(t\) = 4 h.
Figure 6. Effect of the addition of aniline on the activity of the reductive carbonylation of nitrobenzene. Conditions: NB (10 mmol), 5 wt% FeSe$_2$/γ-Al$_2$O$_3$ (0.5 g, [FeSe$_2$]: 0.1169 mmol), molar ratio of NB/FeSe$_2$ = 85, MeOH (30 mL), T = 160 °C, $p$ = 8.3 MPa of CO, $t$ = 4 h.

2.4. Catalyst Recyclability

To investigate the reusability of FeSe$_2$/γ-Al$_2$O$_3$, a set of experiments was conducted under milder conditions, that is, 140 °C (original temperature was 160 °C), under 6.8 MPa of CO pressure (original 8.3 MPa) for 2 h (original 4 h), and using 1.0 g of FeSe$_2$/γ-Al$_2$O$_3$ (molar ratio of NB/[FeSe$_2$] = 85) to exclude the effects of high temperature and pressure as well as long reaction time that could maintain high yield of MPC in every cycle. After reaction for 2 h, the solid FeSe$_2$/γ-Al$_2$O$_3$ was filtered and washed with methanol, vacuum dried overnight, and recycled for the subsequent reaction with newly charged NB. The results illustrated in Figure 7 indicate that FeSe$_2$/γ-Al$_2$O$_3$ did not show any loss in the catalytic activity until three consecutive recycles; however, there seems to be a small loss in the activity from the 4th recycling, implying that this low-cost heterogeneous FeSe$_2$/γ-Al$_2$O$_3$ is fairly recyclable. Furthermore, the XRD result of the used catalyst depicted in Figure S22 shows that the diffraction patterns maintained their initial 2-theta value and intensity, demonstrating there is no change in the structure of this catalyst. Furthermore, no remarkable differences in the morphology after the reaction (Figure S21). To examine the change in the oxidation state of the used catalyst, XPS analysis was conducted. As shown in Figure S23, the reused catalyst shows a small shift in the Se 3d region from 54.57 eV to 55.3 eV, implying a partial generation of Se (0) species during reductive carbonylation, which is in high agreement with the generation of the Se$^{0}$-CO as observed using IR analysis (Figure 8), while the oxidation state of Fe did not change. These phenomena will be described in more detailed in the Section 2.5. The possible leaching of ferric or selenium elements was investigated by examining the liquid phase after the reaction using the ICP-MS method. The results show that there are no leached selenium species, indicating that FeSe$_2$/γ-Al$_2$O$_3$ is a highly robust heterogeneous catalyst.
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2.5. Mechanism Study

To determine the active species of the reductive carbonylation, FeSe$_2$ was reacted with CO (8.3 MPa) in the presence of methanol at 160 °C for 4 h. The resulting solids were collected and dried under vacuum, and then pelletized with KBr. The sample was analyzed by FT-IR spectroscopy, but no carbonyl band of FeSe$_2$ was observed (Scheme 2, Figure 8a). On the other hand, when the same process was carried out in the presence of O$_2$ with CO, i.e., CO/O$_2$ mixture (v/v = 80:20) (Scheme 3), FT-IR spectra of this sample exhibits a carbonyl peak at 1796 cm$^{-1}$ (Figure 8b).

Scheme 2. The reaction of FeSe$_2$ and CO in the presence of methanol at 160 °C for 4 h.

Scheme 3. The reaction of FeSe$_2$ and CO in the presence of oxidant.

As CO does not tend to bind to Fe(II), it might be bound to Se(0) in FeSe$_2$, which demonstrates that the carbonyl species binds through Se, then forms carbonyl FeSe$_2$ is possible only when Se$^-$ is oxidized to Se$^0$ in the presence of an oxidant (Se$^{-1}$ $\rightarrow$ Se$^0$). In this FeSe$_2$-catalyzed reductive carbonylation, NB contributes as an oxidant. Indeed, the IR experiment conducted on a sample treated in the existence of NB (1 equiv. to FeSe$_2$) under CO pressure in the absence of oxygen also
exhibits the CO band at the same wavelength (Figure 8c). These spectroscopic observations suggest that some part of the Se− species in FeSe₂ seems to be oxidized to pseudo-Se(0), and is then partially converted to Se-CO moiety. In consideration of the fact that the synthesis of the terminal (Se-CO) proceeds in severe conditions such as metal Se reacting with carbon monoxide at 500–700 °C [52] or the reaction between phosgene and Al₂Se₃ at 210 °C [53], the clear observation of Se-CO species using FeSe₂ seems to be very encouraging. In fact, Sonoda et al. reported the vapor phase of prepared Se-CO at ambient condition. Furthermore, the Se-CO was prepared by using distillation at −50 °C/5 torr, then cooling at −196 °C by introducing ammonium selenocarbamate into the mixture of THF/strong acid at −78 °C [54]. Bearing in mind these facts, it seems that the CO peak obtained at 1796 cm⁻¹ from the IR result could be ascribed as bridging form. Based on the well-known fact that the IR stretching vibration of the terminal Se-CO as a vapor phase is around 2009 cm⁻¹ [55], and the IR spectra of CO stretching vibration as bridging form fall to 1720–1850 cm⁻¹ [56], the CO peak at 1796 cm⁻¹ can be defined as bridging form.

Scheme 7 provides a plausible mechanism of the reductive carbonylation of nitroarene catalyzed by FeSe₂. The first step of the carbonylation would be the reaction of FeSe₂ with methanol to form (1a) (Scheme 4), then the generation of active catalyst, FeSe₂(μ-CO) (1b) via the reaction between 1a and CO in the presence of NB. Once again, it is worth emphasizing that 1b is not able to generate by the direct reaction between FeSe₂ and carbon monoxide (Scheme 2) without the presence of an oxidant like oxygen or NB, as studied using FT-IR analysis (Figure 8). The combination of Schemes 4 and 5 generates Scheme 6, indicating that the formation of FeSe₂(μ-CO) (1b) can be assisted by the conditions of the reductive carbonylation of NB.
Although it was not successful in observing 1a by reacting FeSe₂ with MeOH even for a longer time (overnight), the observation of AN and dimethyl carbonate (DMC) was confirmed through GC-MS analysis, as shown in Scheme 6 (SI, Figure S11). Meanwhile, Cotton reported the semi-bridging carbonyl with the CO group is an intermediate between terminal and bridging form [57]. The suggested structure of FeSe₂(μ-CO) (1b) is proposed as semi-bridging carbonyl as well, where the μ-CO is bound asymmetrically to two Se. The length of Se(δ²−)–CO bond might be longer than that of Se(0)–CO, allowing the insertion of NB between Se and carbonyl carbon to be more comfortable through comparatively weaker interaction. Therefore, the reaction of 1b with NB will form 2b via the weaker bond, followed by subsequent decarboxylation (−CO₂) to generate 3b. Then, one CO will be inserted between Se and O bond to generate 4b, and the second decarboxylation will produce a ferrous diselenide nitrido moiety, 5b. The formation of 5b is very important, because it is well known as the formation of LnM = NR in the noble metal-catalyzed reductive carbonylation of nitroarenes [7] This is due to the labile property that can be converted to other compounds such as isocyanates, carbamates, amines, and ureas [7,13,23,24]. Next, 5b is carbonylated with another CO to produce an isocyanato species, 6b. In the end, 6b can aggressively react with methanol to generate urethane with simultaneous regeneration of 1b. We should mention, here, the reason for the noticeable enhancement in the carbamates productivity by employing corresponding amino compounds into the nitro substrate. It can be understood as follows: (i) 6b interacts with RNH₂ to produce disubstituted urea (DSU, (RNH)₂CO), (ii) DSU will be transformed into carbamate and amine via methanoysis, and (iii) the produced amino compound takes part in this small repeated cycle, resulting in an additional generation of carbamates (solid box in Scheme 7).
Scheme 7. Plausible mechanism of FeSe₂-catalyzed reductive carbonylation of nitroarene to produce urethane. The solid box explains about the enhanced urethane productivity when adding corresponding amino compound to the nitro compound-based main catalytic cycle.

3. Experimental

3.1. Materials

All chemicals, including iron (III) chloride (FeCl₃, 97%), selenium dioxide (SeO₂, 98.0%), pyridine (Py > 99.0%), and nitrobenzene (NB ≥ 99.0%), were purchased from Sigma-Aldrich (St. Louis, MO, USA). The support γ-Al₂O₃ (99.97%), α-alumina (α-Al₂O₃, 99.9%), basic-Al₂O₃ (99.8%), and neutral-Al₂O₃ (99.9%) were obtained from Alfa-Aesar (Ward Hill, MA, USA). Nitrobenzene (NB) and MeOH were freshly distilled under atmosphere of nitrogen. CO with 99.95% purity was supplied from Uniongas (Seoul, South Korea) and without further purification.

3.2. Catalyst Characterization

The surface structure of FeSe₂/γ-Al₂O₃ was examined by using scanning electron microscopy (SEM, JEOL JSM-6701F) and transmission electron microscopy analysis (TEM, JEM-2100F (UHR)). The elemental compositions of catalysts were investigated by the associated EDX system (INCA). The oxidation states of each element on the surface of FeSe₂ and its supports were examined by X-ray photoelectron spectroscopy (XPS) analysis on the Thermo Scientific K-Alpha™ spectrometer (Thermo Fisher Scientific Korea Ltd., Seoul, South Korea). X-ray diffraction (XRD) studies were analyzed on the Bruker D8 Advance (Waltham, MA, USA) to investigate the crystallinity and purity of catalysts. FT-IR analysis was studied by using the Nicolet FT-IR spectrometer (Waltham, MA, USA).
3.3. Catalyst Synthetic Procedure

3.3.1. Preparation of Ferrous Diselenide (FeSe$_2$)

Firstly, FeCl$_3$ (0.98 g, 6.1 mmol) and SeO$_2$ (3.2 g, 24.3 mmol) were dissolved in methanol (30 mL). Subsequently, pyridine (Py) (2.45 g, 31 mmol) was then added to the methanolic solution. The mixture was introduced into the glass-lined high-pressure reactor and filled with 2.5 MPa of CO at room temperature after purging with CO three times to remove air. The system was heated and stirred vigorously at a certain temperature. The reaction system was further charged with 8.3 MPa of CO at 160 °C and maintain during the reaction by using a gas reservoir. After the reaction, the solid part was filtered off and washed with MeOH (20 mL) for five times. The obtained catalyst was soxhleted with methanol in the reflux condenser for 8 h and dried under vacuum overnight. The obtained FeSe$_2$ was ground to get fine powder before applying to the reaction.

3.3.2. Preparation of 5 wt% FeSe$_2$: Supported on γ-Al$_2$O$_3$ (FeSe$_2$/γ-Al$_2$O$_3$)

The preparation of FeSe$_2$/γ-Al$_2$O$_3$ was similar for preparing FeSe$_2$ under otherwise identical conditions except for adding 3.1 g of dried γ-Al$_2$O$_3$ (γ-Al$_2$O$_3$ was firstly dried at 110 °C for 5 h) into the methanolic solution FeCl$_3$, SeO$_2$, and pyridine. The slurry was stirred for 30 min before introducing into the glass liner inside the high-pressure reactor.

3.4. Carbonylation Reaction

As a typical reaction, a carbonylation reaction was performed in a high-pressure reactor installed with a magnetic stirrer and electrical heater. The system was filled with CO (2.5 MPa) at room temperature after purging with CO three times to remove air and then heated to the required temperature with stirring. The system was further charged with 8.3 MPa CO at 160 °C and kept constant during the reaction using a gas reservoir equipped with a pressure regulator and a pressure transducer. After the reaction, the system was cooled to room temperature, followed by depressurization to unseal. The liquid sample obtained from the syringe filter was quantified using a gas chromatography installed with an HP-5 column (30 nm × 0.32 mm × 0.25 μm) and a flame ionization detector (FID), and a constant volume of heptane was added as a standard to calculate the yield of urethane. GC-Mass spectrometer and $^1$H, $^{13}$C NMR spectra (Bruker 300MHz NMR spectrometer) were used for the identities of products.

3.5. FT-IR Analysis of Carbonyl Selenide

3.5.1. Using O$_2$ as an Oxidant

The FT-IR experiment was performed in a high-pressure reactor by reacting 0.1 g of FeSe$_2$ with 8.3 MPa of a mixture gas of CO/O$_2$ (v/v = 80/20) in methanol (30 mL) as solvent at 100 °C. After 4 h reaction, the product was obtained by filtration and dried under vacuum for 12 h. The collected sample was pelletized with KBr and analyzed by the FT-IR spectrometer. The same procedure was also performed with FeSe$_2$/γ-Al$_2$O$_3$ and Se (0) metal.

3.5.2. Using Nitrobenzene (NB) as an Oxidant

A CO chemisorption study was performed using nitrobenzene (NB) as an oxidant instead of using oxygen. For this, 0.1 g of FeSe$_2$ was reacted with 8.3 MPa of CO in a high-pressure reactor with 1 equivalent NB to FeSe$_2$ in MeOH at 100 °C for 4 h. After the reaction, the sample was filtrated and vacuum dried for 12 h. The FT-IR analysis was conducted on the collected sample.

4. Conclusions

In this study, a remarkable yield of MPC was obtained via the reductive carbonylation of NB over a catalyst system consisting of FeCl$_3$, SeO$_2$, and Py, which appeared to be converted into a heterogeneous ferrous diselenide, FeSe$_2$. The FeSe$_2$ was impregnated onto γ-Al$_2$O$_3$ as support to
synthesize a 5 wt% FeSe/γ-Al2O3, which exhibited an impressive enhancement in terms of catalytic performance in the conversion of NB to MPC. The FeSe/γ-Al2O3-catalyzed carbonylation reaction was strongly affected by temperature and reaction time. The substituent at the para position of the aromatic ring has a significant impact on the yields of the corresponding carbamates, that is, the presence of the electron-withdrawing group at the para position tended to reduce the catalytic activity of the carbonylation reaction. Furthermore, the FeSe/γ-Al2O3 could be reused five times without a significant decrease in activity. Based on the FT-IR experiments on FeSe2, it was likely to form asymmetric semi-bridging carbonyl diselenide, FeSe(μ-CO)(1b) during the carbonylation, thus making it possible for the insertion of NB and complete the catalytic cycle, to regenerate 1b. Moreover, a much higher yield of mono- and di-urethanes could be obtained through the FeSe2/γ-Al2O3-catalyzed reductive carbonylation of a dual substrate system comprising nitro- and its corresponding amino-compound. The superiority of this FeSe2/γ-Al2O3 catalyst is its low cost and simple preparation compared to the previously used noble metals such as Pd, Rh, and Ru for the reductive carbonylation of many different kinds of nitroarenes.

Supplementary Materials: The following are available online at www.mdpi.com/2073-4344/10/11/1228/s1, Figure S1: X-ray diffraction spectra (XRD) of standard Ferroselite FeSe2, Figure S2: (a) X-ray diffraction spectra (XRD) of FeSe/γ Al2O3. (b) XRD standard spectra of Al2O3(γ - Aluminium oxide) PDF-number 79-1558-Cubic Fd-3m (227), Figure S3: EDX/EDS spectra of FeSe2 and the atomic ratio calculation of Fe/Se, Figure S4: EDX/EDS spectra of FeSe2/γ-Al2O3 and the atomic ratio calculation, Figure S5: X-ray photoelectron spectroscopy (XPS) survey spectra of FeSe2, Figure S6: X-ray photoelectron spectra (XPS) survey spectra of FeSe2/γ Al2O3, Figure S7: X-ray photoelectron spectroscopy (XPS) spectra of FeSe2 in the region of (a) Fe3p, (b) Se3d, and (c) C1s, Figure S8: X-ray photoelectron spectroscopy (XPS) of FeSe2/ γ-Al2O3 in the region of (a) Fe3p and (b) Se3d, Figure S9: High resolution TEM images of (a) neat FeSe2 prepared with the presence of pyridine, and (b) FeSe2/γ-Al2O3 prepared with the presence of pyridine, Figure S10 Thermogravimetric analysis (TGA) of FeSe2, Figure S11: GC-MS of the filtrate obtained in the reductive carbonylation reaction using FeSe2 as catalyst with molar ratio NB/FeSe2 = 1, Figure S12: GC-MS of the filtrate obtained in the reductive carbonylation reaction using FeSe2 as catalyst with molar ratio NB/FeSe2 = 4, Figure S13: 1H-NMR spectra of Methyl N-phenyl carbamate (MPC) product obtained from the reductive carbonylation rxn. 1H NMR (300 MHz, CDCl3, δ 3.66 (s, 3H, OCH3); 6.59 (s, 1H, NH); 6.95 (t, 1H, ArH); 7.17(m, 2H, ArH); 7.27 (d, 2H, ArH), Figure S14: 13C-NMR of MPC product obtained from the reductive carbonylation reaction of nitrobenzene. 13C NMR (300 MHz, CDCl3, δ 52.5 (OCH3); 118.85 (C=H-); 123.6 (C=H-); 129.1 (C=H-); 137.9 (C=H-); 154.19 (C=H-), Figure S15: GC-MS of Methyl (4-methoxyphenyl) carbamate, Figure S16: GC-MS of Methyl (4-methoxyphenyl) carbamate, Figure S17: GC-MS of Methyl (4-bromophenyl) carbamate, Figure S18: GC-MS of Methyl (4-acetophenyl) carbamate, Figure S19: GC-MS of Dimethyl toluene-2,4-dicarbamate, Figure S20: GC-MS of dimethyl 1,4-phenylenedicarbamate, Figure S21: Scanning electron microscopy (SEM) figures of (a) fresh FeSe2/γ-Al2O3 catalyst, and (b) spent FeSe2/γ-Al2O3, Figure S22: X-ray diffraction spectra of (a) fresh catalyst FeSe2, (b) recovered FeSe2 after 5th recycling in the reductive carbonylation reaction of NB, Figure S23: XPS of the fresh and spent FeSe2/ γ-Al2O3 in the region of (a) Fe 3p; (b) Se 3d, Table S1: Different types of FeSe2/support for the formation of MPC, Table S2: TON value of the reductive carbonylation reaction using FeSe2/γ-Al2O3 as catalyst.

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