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In Situ Carbon-Confined MoSe$_2$ Catalyst with Heterojunction for Highly Selective CO$_2$ Hydrogenation to Methanol

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Abstract: The synthesis of methanol from CO$_2$ hydrogenation is an effective measure to deal with global climate change and an important route for the chemical fixation of CO$_2$. In this work, carbon-confined MoSe$_2$ (MoSe$_2$@C) catalysts were prepared by in situ pyrolysis using glucose as a carbon source. The physico-chemical properties and catalytic performance of CO$_2$ hydrogenation to yield methanol were compared with MoSe$_2$ and MoSe$_2$/C. The results of the structure characterization showed MoSe$_2$ displayed few layers and a small particle size. Owing to the synergistic effect of the Mo$_2$C-MoSe$_2$ heterojunction and in situ carbon doping, MoSe$_2$@C with a suitable C/Mo mole ratio in the precursor showed excellent catalytic performance in the synthesis of methanol from CO$_2$ hydrogenation. Under the optimal catalyst MoSe$_2$@C-55, the selectivity of methanol reached 93.7% at a 9.7% conversion of CO$_2$ under optimized reaction conditions, and its catalytic performance was maintained without deactivation during a continuous reaction of 100 h. In situ diffuse infrared Fourier transform spectroscopy studies suggested that formate and CO were the key intermediates in CO$_2$ hydrogenation to methanol.

Keywords: MoSe$_2$@C; CO$_2$; methanol; hydrogenation

1. Introduction

A large amount of CO$_2$ is emitted when extravagant fossil fuels (coal, oil and natural gas) are consumed, which causes a series of climate problems [1,2]. In view of the current situation, in order to reduce CO$_2$ emissions, carbon capture and storage (CCS) and carbon capture and utilization (CCU) are currently the most effective means [3]. However, the high cost and energy consumption of desorption, compression and storage of captured CO$_2$ greatly limit the large-scale application of CCS. CCU can achieve efficient CO$_2$ recovery and bring certain economic benefits, and it is considered a promising technology to reduce CO$_2$ emissions. As a raw material, CO$_2$ can be converted to fuel and value-added chemicals [4,5]. On the one hand, it can reduce the pressure of the fossil resource shortage; on the other hand, it can bring huge economic benefits. Therefore, the chemical utilization of CO$_2$ to produce value-added chemicals has become one of the hot topics for using a non-toxic, inexpensive, abundant and renewable source of carbon [6–9]. Among the CO$_2$ utilization routes, synthesizing methanol has received extensive attention [10,11]. Methanol is water-soluble, non-toxic, harmless and easy to store and transport, and it is known as the simplest 'alcohol', so it has become one of the most important platform compounds in the chemical industry [12]. Methanol can be miscible with water and a variety of organic matter, serving as an alternative clean fuel, liquid organic hydrogen carrier and common organic solvent [12–14]. It can also be used to produce olefins, aromatic hydrocarbons, alkanes and other bulk chemicals [15,16]. At present, the global production of methanol is 110 million metric tons [17].

For the hydrogenation of CO$_2$ to methanol, the utilization of copper-based catalysts has garnered significant interest. The main active substances of copper-based catalysts in over

60% of related reports are Cu-ZnO composite materials [18]. However, two disadvantages hinder the widespread use of copper-based catalysts. One is that the generation of water in the reaction aggravates the sintering of the active phase, resulting in poor stability of the catalyst, and the other is that the selectivity of methanol is limited due to the reverse water gas reaction [19,20]. Compared with copper-based catalysts, noble metal-based catalysts exhibit excellent stability, anti-sintering and anti-poisoning properties and can be used as an effective alternative to copper-based catalysts. Although noble metal catalysts show a high ability to activate hydrogen and promote hydrogenation, the low selectivity of methanol is yielded due to its weak interaction with CO_2 in the reaction process. Meanwhile, its low abundance and high cost also limit its large-scale application in CO_2 hydrogenation to methanol. Recently, metal oxide catalysts such as In_2O_3 and Zn-Zr solid solutions have attracted attention [21]. Due to the formation of oxygen vacancies under reaction conditions of 330 °C and 5 MPa, In_2O_3 provided 100% methanol selectivity in CO_2 hydrogenation, but it could be reduced to In^0 metal, which caused the deactivation during the reaction [22]. Under industrial conditions, the ZnO-ZrO_2 solid solution catalyst demonstrated the capability to facilitate the hydrogenation of CO_2 to methanol [23]. The space–time yield of methanol was as high as 7.75 mol·kg^{-1}·h^{-1} with an 87.0% selectivity of methanol, and excellent stability was shown in the presence of SO_2 and H_2S. However, shortcomings are shown in the harsh reaction conditions, poor activity and high energy consumption. Therefore, it is still a challenge to develop highly effective non-precious metal catalysts for CO_2 hydrogenation to form methanol under relatively mild conditions.

Because of their large surface area and large amounts of coordination-unsaturated surface atoms, two-dimensional layered Mo-based catalysts have attracted widespread attention [24,25]. Due to its similar electronic structure to the noble metal Pt, molybdenum carbide displays excellent catalytic performance for hydrogenation and has been applied in hydrodeoxygenation [26,27] and hydrodenitrogenation [28]. In 1992, molybdenum carbide was used as a catalyst for the hydrogenation of CO_2, resulting in a methanol selectivity of only 17%, with methane and CO being the predominant byproducts [29]. DFT results suggested that enhancing the adsorption of CO_2 on the catalyst surface was beneficial for inhibiting the complete decomposition of CO_2, thus improving the selectivity of methanol [30]. In our previous work, N,S-doped carbon-confined molybdenum carbide catalysts were synthesized by in situ pyrolysis carbonization [31]. The basic sites generated from N and S in the in situ pyrolysis carbonization increased the adsorption amount of CO_2. The selectivity of methanol yielded 90% with a CO_2 conversion of 20%. In this catalyst, nano-sized MoS_2 was also generated in the pyrolysis process, which was a key factor in its excellent catalytic performance. On the one hand, in the presence of MoS_2, CO_2 was adsorbed and dissociated at sulfur vacancies; on the other hand, in-plane sulfur vacancies could inhibit the deep hydrogenation of CO_2 to methane and promote the formation of methanol at low temperatures. More recently, Deng [32] et al. constructed a surface-rich sulfur-vacancy MoS_2 catalyst and applied it for the hydrogenation of CO_2 to form methanol, with the methanol selectivity reaching 94.3% with a CO_2 conversion of 12.5% at 180 °C. $MoSe_2$, as a two-dimensional layered material, has stronger metallicity and lower Gibbs free energy than molybdenum sulfide [33], which is more conducive to the adsorption and activation of hydrogen molecules [34]. More importantly, the adsorption capacity of CO_2 is also better than that of MoS_2 [35]. However, $MoSe_2$ is mainly involved in photocatalysis and electrocatalysis for the hydrogenation of CO_2, and the main reduction products are methane, carbon monoxide and so on [35]. Qu et al. incorporated K into $MoSe_2$ and constructed a K-Mo-Se active phase for catalytic syngas conversion to ethanol. By regulating the K/Mo ratio, the proportion of ethanol in the total alcohol reached 58.7% under optimal reaction conditions [36]. To our best knowledge, there is no report on the use of $MoSe_2$ as a catalyst in the thermocatalytic hydrogenation of CO_2 to produce methanol [37,38]. Therefore, the study of the catalytic behavior of $MoSe_2$ is significant for the development of non-noble metal catalysts for CO_2 hydrogenation to methanol.

It is well known that, as a typical two-dimensional material, the active sites of $MoSe_2$ are also mainly located at its edges and defect sites. Therefore, reducing the layer number and particle size of $MoSe_2$ is an effective route to enhance its catalytic performance. Confined $MoSe_2$ in carbon materials can effectively prevent the aggregation of $MoSe_2$ and improve its catalytic performance [39–41]. In this work, $MoSe_2$ confined by in situ-formed carbon material ($MoSe_2$@C) was prepared by introducing glucose as a carbon source into the precursors using the pyrolysis method and applied to CO_2 hydrogenation to form methanol in a fixed-bed reactor. The influences of the preparation conditions and the C/Mo ratio in the precursors on the catalytic performance of $MoSe_2$@C were investigated, and the reaction conditions were optimized. Under optimal reaction conditions, a high methanol selectivity of 93.7% was reached. $MoSe_2$@C also showed excellent catalytic stability during performance evaluation and could be used for at least 100 h without deactivation.

2. Results and Discussion

2.1. Catalyst Characterization

2.1.1. Structural Characterizations

Firstly, X-ray powder diffraction was employed to detect the crystal structure of the prepared samples, and the results are shown in Figure 1. The characteristic diffraction peaks of the three samples appeared at 2θ = 13.7°, 31.4°, 37.9°, 47.5°, 55.9°, 66.5° and 69.5°, corresponding to the (002), (100), (103), (105), (110), (108) and (203) crystal planes of $MoSe_2$ (PDF 29-0914) [42], and no other diffraction peaks were found. These results indicate that the $MoSe_2$ crystal phase was prepared. In addition, a slight shift of the (002) crystal plane could be observed, which was attributed to thermal-induced phase segregation [43]. Compared with $MoSe_2$, the intensity of the diffraction peaks was weakened, and the half-peak width of the corresponding diffraction peaks increased in the XRD patterns of the $MoSe_2$/C sample, indicating that the introduction of a carbon carrier could improve the dispersion of $MoSe_2$ and inhibit the growth of $MoSe_2$ particles. Additionally, the characteristic diffraction peaks corresponding to the (002) crystal plane of graphite carbon were also found at 2θ = 26°. Compared with the XRD patterns of $MoSe_2$ and $MoSe_2$/C, the diffraction peak intensity of $MoSe_2$@C-55 was the weakest, the half-peak width was the widest, and the characteristic diffraction peak (2θ = 13.7°) corresponding to the (002) crystal plane of $MoSe_2$ almost disappeared. These results suggested that the grain size of $MoSe_2$ was the smallest and the layer number of $MoSe_2$ was the lowest in $MoSe_2$@C-55 compared with $MoSe_2$ and $MoSe_2$/C [44,45]. As a consequence, introducing glucose to the precursor could suppress the growth of $MoSe_2$ through the confinement of the in situ generation of carbon material in the pyrolysis process. When the C/Mo ratio in the precursor was raised from 15 to 75, $MoSe_2$@C-15, $MoSe_2$@C-35 and $MoSe_2$@C-75 were prepared. Their XRD patterns are shown in Figure S1. The intensity of the diffraction peak corresponding to $MoSe_2$ gradually declined with the enhancement of the carbon content in the precursor, which means that the confinement of the in situ carbon material improved with the increase in carbon content, and the growth of $MoSe_2$ particles was repressed, which was beneficial to the dispersion of $MoSe_2$ in the carbon material.

In order to observe the microstructure and morphology, $MoSe_2$/C and $MoSe_2$@C-55 were characterized by TEM and HRTEM (Figure 2). The image in Figure 2a shows that $MoSe_2$ dispersed on the coconut shell carbon, which resulted in the low intensity of the XRD diffraction peak. However, its distribution was not uniform, and agglomeration was observed, which caused $MoSe_2$ to show larger particles and more layers. In Figure 2b (HRTEM), lattice fringes of 0.28 nm can be observed, which is consistent with the interplanar spacing of the (100) of $MoSe_2$ [46,47]. Observing the image of $MoSe_2$@C-55, as shown in Figure 2c, the agglomeration and accumulation of $MoSe_2$ particles were effectively inhibited when glucose was introduced to the precursor. This took place because the carbon materials formed from the in situ pyrolysis of glucose showed an inhibitory effect on the growth of $MoSe_2$ particles, which ensured the high dispersion of $MoSe_2$. As a result of it, more active sites were exposed, and its catalytic performance improved. As can also be seen

from the HRTEM image (Figure 2d), a lattice fringe spacing of 0.35 nm was also observed, which belonged to the (004) of $MoSe_2$. In addition, a lattice fringe with a spacing of 0.21 nm was also observed (Figure 2d), which was attributed to the (112) of Mo_2C [48], indicating that Mo_2C particles were generated during the preparation of $MoSe_2$@C-55. Combined with the fact that the corresponding diffraction peaks of Mo_2C were not observed in the XRD pattern, it can be inferred that the content of Mo_2C was low and highly dispersed. In addition, the HRTEM images in Figure 2d show that the presence of Mo_2C interrupted the continuity of $MoSe_2$, causing more edge sites of $MoSe_2$ to expose more active sites [49]. This phenomenon indicated that a $MoSe_2$-Mo_2C heterojunction was generated, which would benefit the synergistic effect of $MoSe_2$ and Mo_2C in the catalytic process and improve its catalytic performance [50]. The results in Figure S2a–d show that increasing the content of glucose in the precursor was favorable to improving the dispersion of $MoSe_2$, resulting in a gradual decrease in the particle size and layer number of $MoSe_2$, which coincided with the characterization results of XRD. The content of glucose in the precursor also affected the exposed crystal planes of $MoSe_2$ and Mo_2C. Setting the C/Mo ratio in the precursor at 15 and 35, lattice fringes of 0.28 nm and 0.23 nm (Figure S2e,f) could be observed in the HRTEM images, which were attributed to the (100) of $MoSe_2$ and the (121) of Mo_2C [46,47]. However, lattice fringes of 0.26 nm and 0.21 nm assigned to the (102) of $MoSe_2$ and the (112) of Mo_2C were observed (Figure S2h) when the C/Mo ratio in the precursor rose to 75 [48]. Owing to the different crystal faces that would display different catalytic performance [49], it can be inferred that there will be a large difference in the catalytic performance of CO_2 hydrogenation to form methanol.
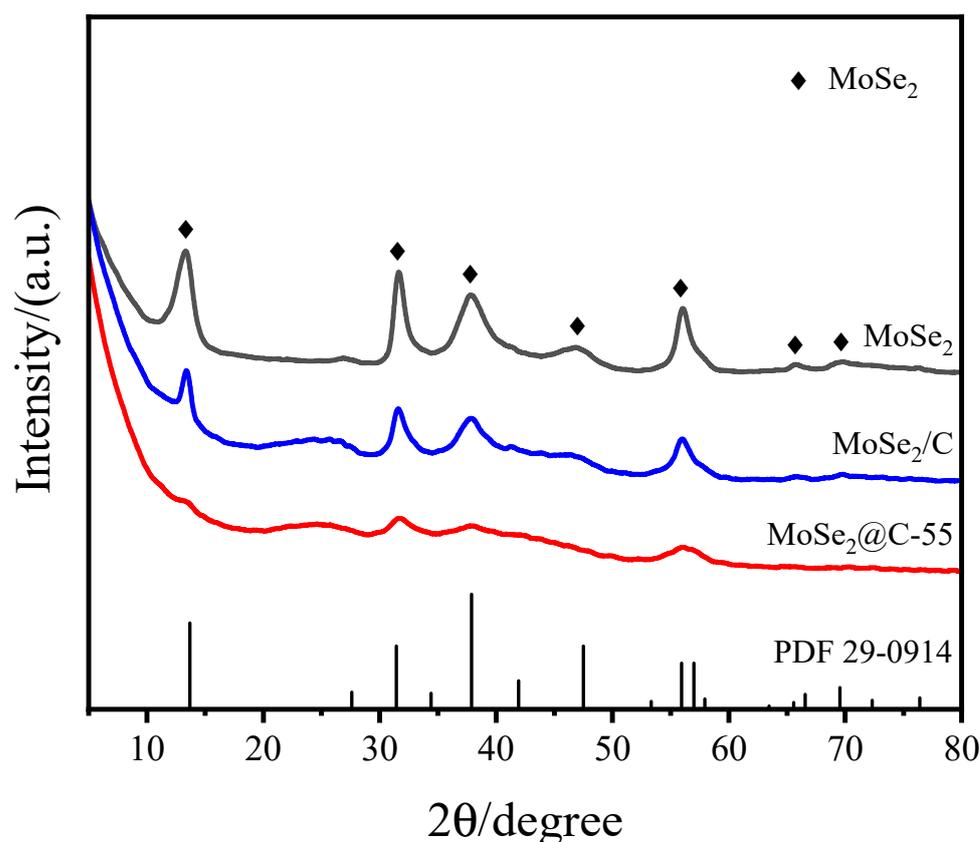

**Figure 1.** XRD patterns of $MoSe_2$, $MoSe_2$/C and $MoSe_2$@C-55 catalysts.
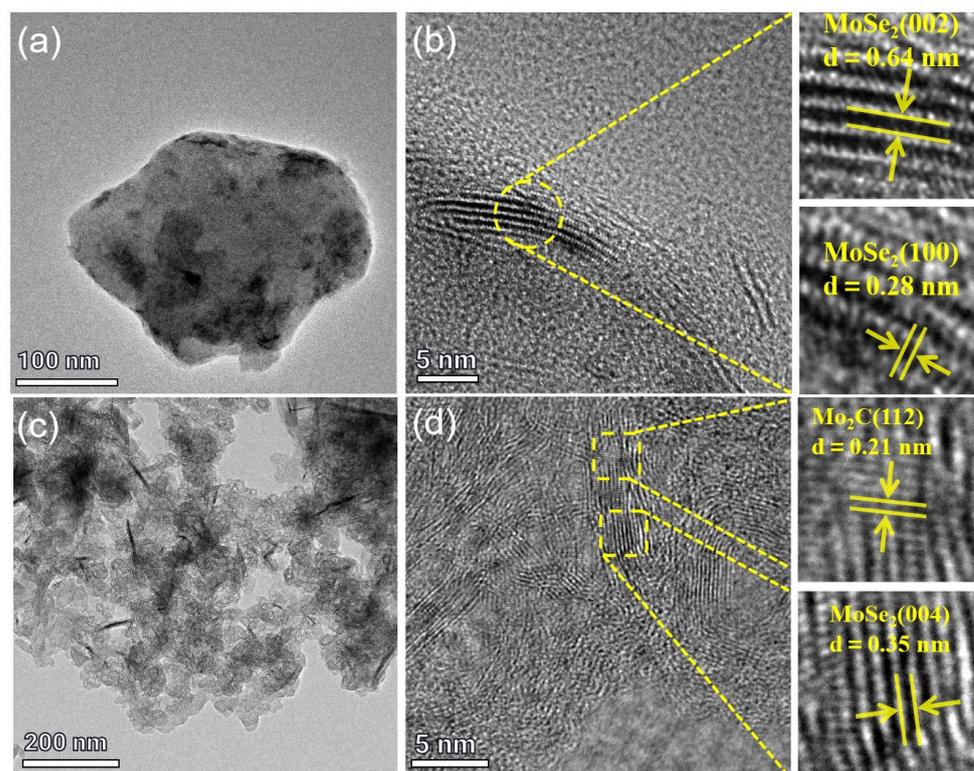
Figure 2. TEM and HRTEM images of MoSe$_2$/C and MoSe$_2$@C-55 catalysts: (**a**,**b**) MoSe$_2$/C; (**c**,**d**) MoSe$_2$@C-55.

2.1.2. XPS Analysis of Catalysts

The surface chemical state of the catalyst was further analyzed by XPS. The XPS survey spectra shown in Figure S3 suggest that the surface elements of the samples were Mo, Se, C and O.

The XPS spectra of the Mo 3d of the three samples (Figure 3a and Table S1) showed that characteristic peaks were observed at 229.1–229.3 eV and 232.1–232.3 eV, which were attributed to Mo^{4+} 3d$_{5/2}$ and 3d$_{3/2}$ in MoSe$_2$ [48,50]. In addition, fitting peaks at 228.6 eV and 231.6 eV were also found in the Mo 3d of MoSe$_2$@C-55, which corresponded to Mo^{2+} 3d$_{5/2}$ and 3d$_{3/2}$, indicating that Mo$_2$C was generated during the preparation of MoSe$_2$@C-55 [51,52], suggesting that a strong interaction between the carbon formed by the in situ carbonization of glucose and the Mo atoms was formed. The specific binding energy data in Table S1 show that the binding energy of Mo^{4+} 3d$_{5/2}$ and 3d$_{3/2}$ in MoSe$_2$@C-55 was 0.2 eV lower than that of MoSe$_2$ and MoSe$_2$/C, which was caused by the electron transfer between MoSe$_2$ and Mo$_2$C [53], and a strong interaction was formed. In addition, peaks at binding energies of 232.5–232.7 eV and 235.4–235.7 eV, corresponding to Mo-O, were observed due to the surface oxidation that took place when MoSe$_2$@C-55 and MoSe$_2$/C were exposed to air [47–52], but the binding energy of MoSe$_2$@C-55 was lower than that of MoSe$_2$/C, which may be due to the protective effect of in situ-formed carbon on the surface of MoSe$_2$@C-55, resulting in a reduction in the oxidation degree. This result demonstrates once again the robust interaction between carbon and Mo in MoSe$_2$@C-55.

The Se 3d XPS spectra are displayed in Figure 3b, and two peaks at 54.7–54.8 eV and 55.7–55.8 eV (Table S2) were assigned to the Se^{2-} 3d$_{5/2}$ and 3d$_{3/2}$ of MoSe$_2$ [42,46]. Moreover, MoSe$_2$/C also showed a characteristic peak at about 59.1 eV, assigned to Se oxide (SeO$_x$) [54]. In addition, as shown in Figure 3c and Table S3, the peaks at 284.8 eV and about 286.1 eV in the C 1s spectrum of all samples indicate the formation of a C-C bond and a C-O bond, respectively [55]. The high-resolution XPS spectra of O 1s are shown in Figure 3d and Table S4. The peaks at 530.4 eV, 531.8 eV and 532.8 eV indicate the formation of lattice

oxygen (O_{lat}), deficient oxygen (O_{def}) and adsorbed oxygen (O_{ads}), respectively [56,57]. The proportion of each oxygen species in all oxygen species is shown in Table S4. The proportion of O_{def} is the highest in the $MoSe_2$@C-55 catalyst. The oxygen vacancies on the surface improved the dissociation of CO_2 and tended to produce the desired methanol [57]. Moreover, only the $MoSe_2$@C-55 sample showed a peak at 282.6 eV, which corresponded to a C-Mo bond [53,54]. The data listed in Figure S5 also show that the binding energy of Mo 3d showed a negative shift with the increase in the C/Mo ratio in the precursor, and the Mo^{2+}/Mo^{4+} ratio on the surface of the catalyst displayed a positive correlation with the carbon content in the precursor (Table S5), suggesting that a higher carbon content in the precursor was beneficial to generating Mo_2C.
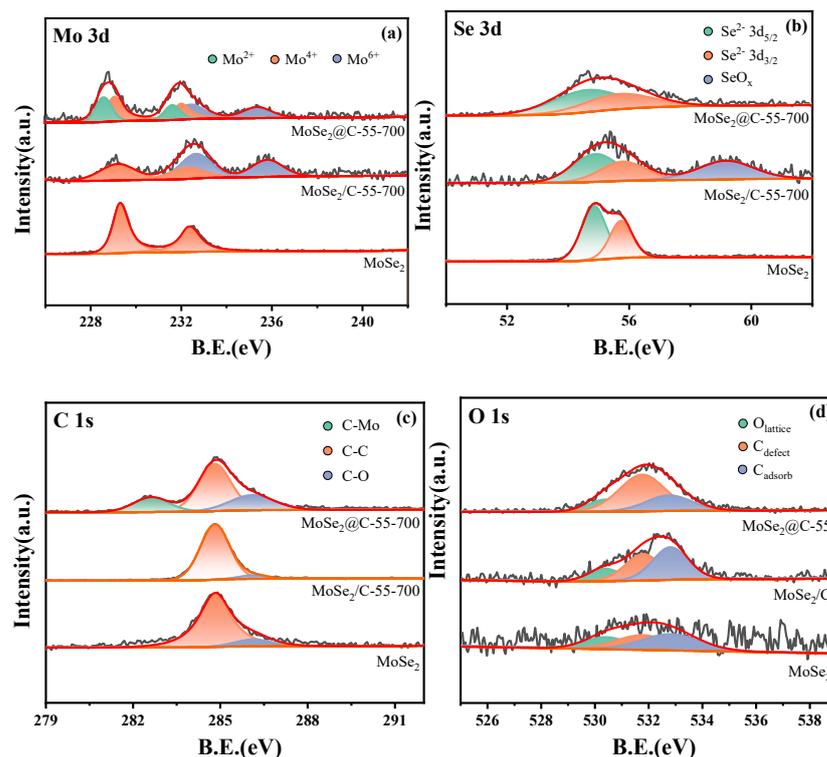

Figure 3. XPS spectra of $MoSe_2$, $MoSe_2$/C and $MoSe_2$@C catalysts: (**a**) Mo 3d; (**b**) Se 3d; (**c**) C 1s; (**d**) O 1s.

2.1.3. Characterization of CO_2 Adsorption Capacity

The adsorptive capacity of a catalyst for CO_2 is an important factor in its catalytic performance in CO_2 hydrogenation. Therefore, CO_2-TPD was carried out, and the desorption curves are displayed in Figure 4. According to the characterization results, all the CO_2 desorption peaks of the prepared $MoSe_2$, $MoSe_2$/C and $MoSe_2$@C-55 catalysts appeared at low temperatures, which corresponded to the presence of weak basic sites on the catalyst surface [58,59]. Compared with $MoSe_2$ and $MoSe_2$/C, $MoSe_2$@C-55 showed the highest desorption temperature of CO_2, which means that the activation degree of CO_2 on the surface of $MoSe_2$@C-55 was the highest, which would be beneficial to the hydrogenation of CO_2. Because the magnitude of the peak area corresponds to the quantity of activated CO_2 present on the catalyst surface, the relative desorbed amount of CO_2 was calculated by calculating the area of these peaks, and the results are also inset in Figure 4. Based on the desorption amounts of CO_2 from $MoSe_2$@C-55 (the relative value is 100%), the desorption amounts of CO_2 from the surface of $MoSe_2$ and $MoSe_2$/C were 45% and 54% (by calculating the area of the CO_2 desorption peak). These results suggest that the order of CO_2 adsorption amounts on the catalyst surface and the ability to activate CO_2 were $MoSe_2$@C-55>$MoSe_2$/C>$MoSe_2$.
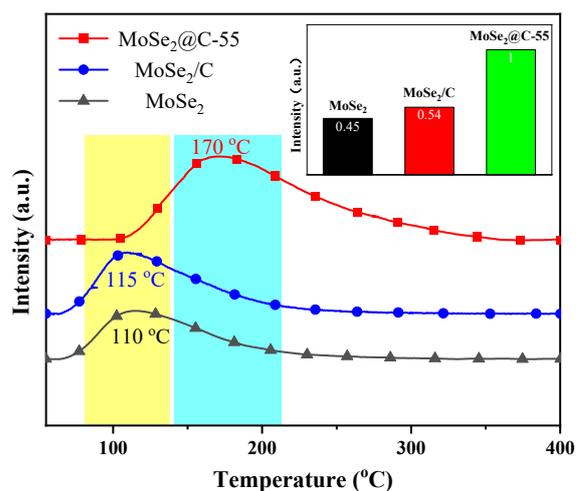
Figure 4. CO_2-TPD profiles of $MoSe_2$, $MoSe_2/C$ and $MoSe_2@C$-55 catalysts.

2.2. Catalytic Performance in CO_2 Hydrogenation to Yield Methanol

In a fixed-bed reactor at 180 °C, 3MPa and a Gas Hourly Space Velocity (GHSV) of 3000 mL·g_{cat}^{-1}·h^{-1}, the catalytic performance of $MoSe_2$, $MoSe_2/C$ and $MoSe_2@C$-55 was evaluated for CO_2 hydrogenation to yield methanol (Table 1). In the presence of the $MoSe_2$ catalyst, the conversion of CO_2 was as low as 2.4%, and only a moderate selectivity (52.5%) of methanol was observed in the hydrogenation process, while CO was yielded with a selectivity of 33.1%. In this process, CO was generated from the reverse water gas shift (RWGS) reaction of CO_2 on the surface of $MoSe_2$, which was an important intermediate for synthesizing methanol. However, the insufficient active sites were exposed and could not achieve further efficient CO conversion, resulting in high CO selectivity [60]. At the same time, the CH_3O^* intermediate generated by CO hydrogenation was more likely to undergo C-O cleavage to generate CH_3^* and OH^* at the active sites, resulting in a high CH_4 selectivity (10.2%) [32]. In addition, a small amount of dimethyl ether was generated by further dehydration of methanol, which was due to the weak acidity generated from the oxidation of the surface of $MoSe_2$ [61]. The selectivity of methanol increased to 89.9% at a CO_2 conversion of 4.3% over the $MoSe_2/C$ catalyst, prepared by using coconut shell carbon as support. This was attributed to an increase in the dispersion of $MoSe_2$ on the support, which was beneficial for exposing more edge sites and surface defects due to the reduction in the particle size and layer number of $MoSe_2$ [32]. The conversion of CO_2 increased to 9.7% by employing $MoSe_2@C$-55 as a catalyst prepared by using glucose as a carbon source with a C/Mo ratio of 55, while the selectivity of methanol further increased to 93.7% and the selectivity of CH_4 decreased to 6.3%, which can be explained by the following reasons: On the one hand, the in situ-formed carbon gave a strong confinement to $MoSe_2$, resulting in a decreasing layer number, which could expose more surface defects conducive to methanol generation. Moreover, the highest amount of deficient oxygen was detected by XPS, and the oxygen vacancies on the surface improved the dissociation of CO_2 and tended to produce the desired methanol [57]. On the other hand, in situ-generated Mo_2C interrupted the continuity of $MoSe_2$, and the $MoSe_2$-Mo_2C heterojunction was formed, which was beneficial for exposing more active sites and activating H_2 (Figure S5). The above factors all led to improved CO_2 conversion and selectivity of methanol in CO_2 hydrogenation. Moreover, the high desorption capacity and the high CO_2 activation ability of $MoSe_2@C$-55 were also important factors for increasing CO_2 conversion. Based on the above research results, the catalytic performances of a series of $MoSe_2@C$-x (x = 15, 35 and 75) catalysts with different C/Mo ratios in the precursors were also evaluated (Table 1). It can be seen that the selectivity of methanol gradually increased with the increase in C/Mo ratios. When $MoSe_2@C$-75 was used as the catalyst, the selectivity of methanol reached a maximum of 94.3%. This was due to the fact that the number of layers of $MoSe_2$ was

reduced as the carbon content in the precursors increased, which was favorable for the exposure of surface defects and conducive to the formation of methanol. The conversion of CO_2 reached its maximum when $MoSe_2@C$-55 was used as the catalyst. This took place because $MoSe_2@C$-55 had a stronger ability to adsorb and activate CO_2 (Figure S6), causing an acceleration of CO_2 conversion.

Table 1. Results of CO_2 hydrogenation to methanol over different catalysts [a].

Catalyst	Conversion (%)	Selectivity (%)			
		CH_3OH	CH_4	CO	CH_3OCH_3
$MoSe_2$	2.4	52.5	10.2	33.1	4.2
$MoSe_2/C$	4.3	89.9	10.1	-	-
$MoSe_2@C$-55	9.7	93.7	6.3	-	-
$MoSe_2@C$-15	2.8	72.3	27.7	-	-
$MoSe_2@C$-35	3.3	89.5	10.5	-	-
$MoSe_2@C$-75	4.4	94.3	5.7	-	-

[a] Reaction conditions: 180 °C, 3 MPa, GHSV 3000 mL·g_{cat}^{-1}·h^{-1}, H_2:CO_2 = 3.

Compared with the Cu/In_2O_3-, CuZnAl- and MoS_2-based catalysts in the literature, $MoSe_2@C$-55 showed better selectivity for methanol under low reaction temperatures, as shown in Table S7.

In CO_2 hydrogenation, CO_2 conversion and methanol selectivity were sensitive to the reaction temperature. Using $MoSe_2@C$-55 as a catalyst, the effect of the reaction temperature was investigated under conditions of 3 MPa and a GHSV of 3000 mL·g_{cat}^{-1}·h^{-1} (Figure 5a). The results in Figure 5a show that the conversion of CO_2 increased from 7.1% to 13.5% as the reaction temperature rose from 160 °C to 240 °C, suggesting that high temperatures are beneficial for CO_2 to overcome the limitation of its thermodynamic stability, which accelerated the conversion rate of CO_2 [62,63]. Setting the reaction temperature at 180 °C, the selectivity of methanol reached a maximum of 93.7% and gradually decreased as the reaction temperature increased. This took place because the reaction of CO_2 hydrogenation to methanol was an exothermic reaction, and a higher temperature was not conducive to the formation of methanol. Since the reverse water gas reaction is an endothermic reaction [60], high temperatures are beneficial to its occurrence. Therefore, CO was not detected as a byproduct when the reaction temperature was not higher than 220 °C. But 1.5% of CO and 33.6% of CH_4 were generated by raising the reaction temperature to 240 °C. As shown in Figure 5b, the influence of reaction pressure on the hydrogenation of CO_2 was also investigated. The conversion of CO_2 and the selectivity of methanol were all preferential to enhancing reaction pressure. When the reaction pressure was 2 MPa, CO_2 conversion and methanol selectivity were both at a low level (5.6% and 90.6%, respectively). Moreover, the selectivity of methanol improved from 90.6 to 93.7% by changing the reaction pressure from 2 MPa to 3 MPa. When the reaction pressure was further increased, the selectivity of methanol did not change significantly. Finally, the effects of the space–time rate were also investigated (Figure 5c). With the increase in the space–time rate, the residence time of the feed gas on the surface of $MoSe_2@C$-55 was shortened, resulting in a reduction in the conversion of CO_2. When the space velocity was 3000 mL·g_{cat}^{-1}·h^{-1}, the highest methanol selectivity at a moderate CO_2 conversion was obtained. Under optimized reaction conditions, the test of the catalytic stability of the $MoSe_2@C$-55 catalyst was performed, and the results are shown in Figure 5d. It indicated that the $MoSe_2@C$-55 catalyst could be used continuously for at least 100 h without reducing catalytic activity and showing excellent catalytic stability. The selectivity of methanol was maintained at about 93.7% at a CO_2 conversion of approximately 9.7%.
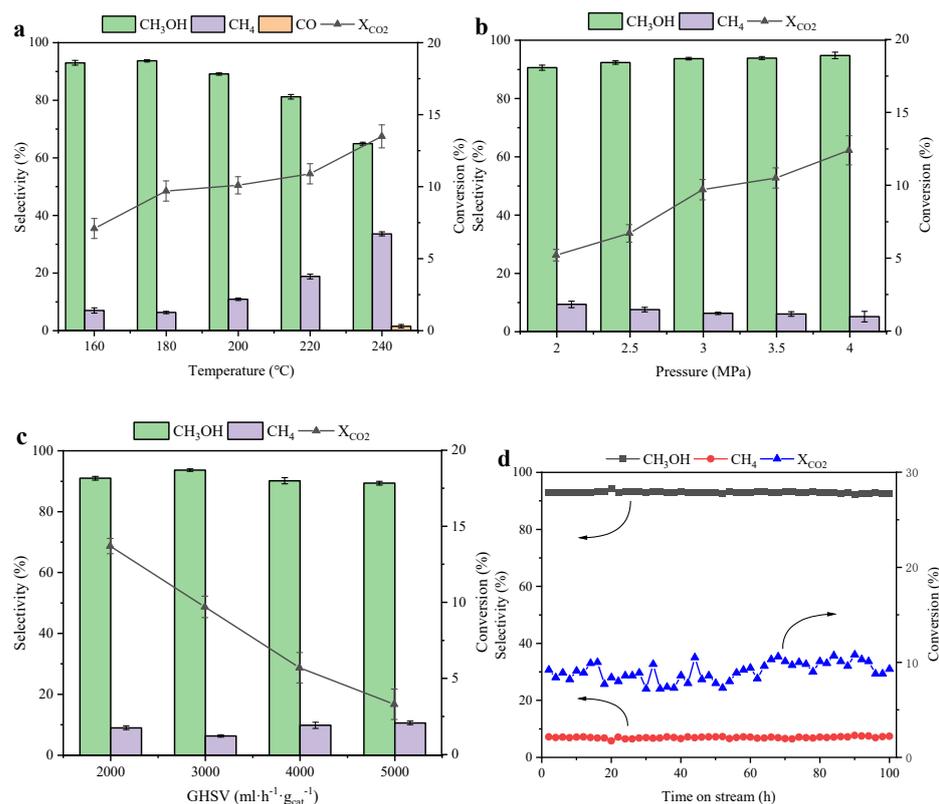
Figure 5. Catalytic performance of hydrogenation of CO_2 over MoSe$_2$@C-55 under different conditions: (**a**) effect of temperature; (**b**) effect of pressure; (**c**) effect of space velocity; (**d**) stability evaluation.

2.3. Reaction Mechanism

In order to explore the reaction mechanism of the hydrogenation of CO_2 to generate methanol over the MoSe$_2$@C-55 catalyst, the possible intermediates on the surface of MoSe$_2$@C-55 were detected by in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). Firstly, the catalyst was activated at 400 °C for 1 h in a pure H_2 atmosphere and then refrigerated to 180 °C. Figure 6 shows the experimental results of the CO_2 hydrogenation reaction stage at atmospheric pressure and a reaction temperature of 180 °C.
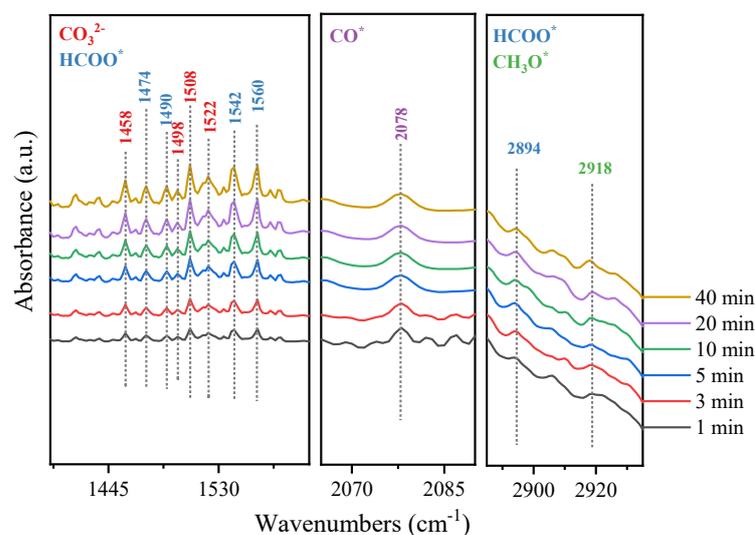
Figure 6. DRIFTS spectra of CO_2 hydrogenation in the presence of MoSe$_2$@C-55.

From the in situ DRIFTS, two peaks were observed at 1458 and 1522 cm^{-1}, corresponding to carbonate species (CO_3^{2-}) [64,65]. In addition, two peaks at 1498 and 1508 cm^{-1} were also observed, corresponding to monodentate and bidentate carbonate species [66], and their intensity gradually increased with the prolongation of the reaction time. As a result of these, CO_2 first adsorbed on the surface of MoSe$_2$@C-55 and then converted into a carbonate (CO_3^{2-}) species. The C-H bond vibration of the formate species at 1490 cm^{-1} [67] and spectral bands at 1560, 1542, 1474 and 2894 cm^{-1} could be observed, corresponding to the symmetric OCO stretching vibration and the stretching vibration of the formate species [68–71]. In addition, the characteristic absorption peak at 2918 cm^{-1} was attributed to the vibration of the C-H bond of the CH$_3$O* species [72]. The above results indicated that there may be a reaction path in the reaction process from CO_2 hydrogenation to HCOO* species and finally to CH$_3$OH. Specifically, the adsorbed CO_2 was converted to carbonate, then HCOO* species were generated from the reaction between carbonate and hydrogen, and CH$_3$O* was formed from the hydrogenation of the HCOO* species. Subsequently, CH$_3$O* → CH$_3$OH* → CH$_3$OH (g) were performed. At the same time, a characteristic peak was observed at 2078 cm^{-1}, attributed to CO* [69], which provided evidence for the dissociation of CO_2 when it was adsorbed on the catalyst surface. However, CO was not detected in the reaction products when the reaction was carried out at 180 °C, suggesting that the hydrogenation of CO occurred. Therefore, there is another reaction path in CO_2 hydrogenation over the MoSe$_2$@C-55 catalyst, where the adsorbed CO_2 is dissociated to CO, which is then directly hydrogenated to CH$_3$O* and finally to CH$_3$OH. The detailed reaction pathway is shown in Scheme 1.
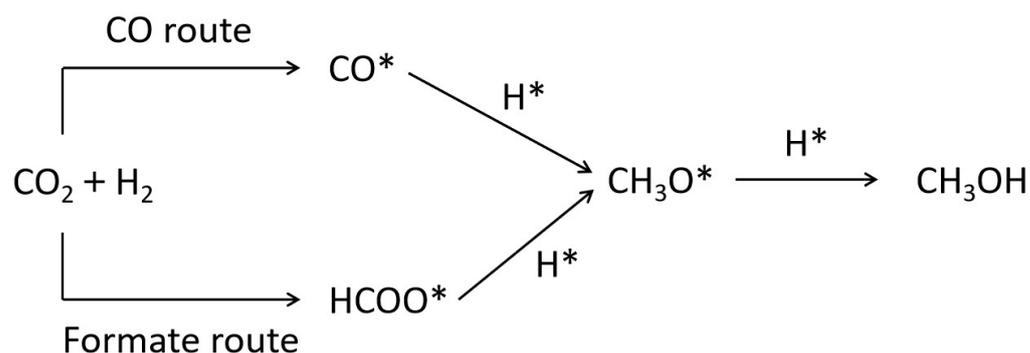
Scheme 1. Supposed reaction path of CO_2 hydrogenation to methanol in the presence of MoSe$_2$@C-55.

3. Experiment

3.1. Materials

Ammonium molybdate ((NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O, AMT) and glucose were obtained from Tianjin Kemiou Chemical Reagents Co., Ltd. (Tianjin, China). Selenium powder was purchased from MackLin Chemical Reagents Co., Ltd. (Shanghai, China), and sodium borohydride was obtained from Tianjin Kemiou Chemical Reagents Co., Ltd. (Tianjin, China). H$_2$ (99.99%), N$_2$ (99.99%), CO_2 (99.99%) and 5% Ar/95% H$_2$ (99.99%) were bought from Qinghua Gas Co., Ltd. (Harbin, China). Without further purification, all reagents were used directly.

3.2. Preparation of Catalysts

3.2.1. Preparing the MoSe$_2$@C-55 Catalyst

Ammonium molybdate (0.4022 g) and glucose (4.1381 g) (n(C)/n(Mo) = 55) were dissolved in deionized water. After removal of the water, the prepared product was dried at 110 °C for 12 h. Subsequently, it was mixed with selenium powder (0.3598 g) and placed in a tubular furnace. In a N$_2$ atmosphere, the temperature was increased to 700 °C at a rate of 5 °C/min for 4 h, and MoSe$_2$ confined in carbon material catalyst (MoSe$_2$@C-55, where 55 is the carbon–molybdenum ratio (C/Mo) in the precursor) was obtained. When

the C/Mo ratio in the precursors changed to 15, 35 and 75, they were named $MoSe_2$@-15, $MoSe_2$@-35 and $MoSe_2$@-75, respectively.

3.2.2. Preparing the $MoSe_2$/C Catalyst

A total of 0.4022 g ammonium molybdate was impregnated into 1.5036 g coconut shell carbon by the impregnation method and dried at 110 °C overnight. After mixing the dried solid and 0.3598 g selenium powder, the resulting products were roasted in a tube furnace. In a H_2/N_2 atmosphere containing 30% H_2, the temperature was raised to 700 °C at 5 °C/min for 4 h. The $MoSe_2$/C sample was obtained.

3.2.3. Preparing the $MoSe_2$ Catalyst

An aqueous solution containing sodium borohydride (0.3972 g) was added drop by drop to 0.5527 g selenium powder, and the mixture was stirred to form a reddish-brown solution at 70 °C. Then, the reddish-brown mixture was added to an aqueous solution containing ammonium molybdate (0.6180 g). After stirring at ambient temperature for 30 min, the mixture was put into a 50 mL stainless steel autoclave lined with PTFE and crystallized at 220 °C for 24 h, then cooled to ambient temperature. Subsequently, it was centrifuged, washed, dried and put into a tubular furnace. In a N_2 atmosphere, the temperature of the tubular furnace rose to 550 °C at a rate of 5 °C/min, and it was held for 2 h. Then, it was refrigerated to ambient temperature, and the $MoSe_2$ sample was obtained.

3.3. Characterization

X-ray powder diffraction (XRD, Bruker D8, Advance, Salbrücken, Germany) of Cu-Kα radiation diffraction (019B = 1.5406A) was used to characterize the crystal structure of the samples, and transmission electron microscopy (TEM, JEM-2100, Tokyo, Japan) and high-resolution transmission electron microscopy (HRTEM, JEM-2100, Tokyo, Japan) were used to observe their morphology and size. An X-ray photoelectron spectrometer (ESCALAB 250-11 OOV, Thermo Fisher, Waltham, MA, USA) was employed to determine the types and valence of the elements on their surface. CO_2 temperature-programmed desorption (TPD) was carried out on a chemisorption instrument equipped with a thermal conductivity detector (TCD). The process was as follows: After pretreatment at 500 °C for 60 min in Ar (40 mL/min), the sample (0.2 g) was exposed to CO_2 (40 mL/min) for 60 min while it was cooled to 50 °C. Subsequently, the physically adsorbed CO_2 was eliminated in a pure Ar (40 mL/min) atmosphere for 60 min. Then, the desorption of CO_2 was measured from 50 °C to 500 °C at a rate of 10 °C/min in an Ar (40 mL/min) atmosphere. On a Perkin Elmer frontier spectrometer (Waltham, MA, USA), in situ diffuse infrared Fourier transform spectroscopy (DRIFTS) measurements were carried out. Firstly, the sample was pretreated at 400 °C for 60 min with a H_2 flow of 30 mL/min and then chilled to 180 °C. Subsequently, gas feed (H_2 30 mL/min and CO_2 10 mL/min) was introduced after scanning the background spectrum in the range of 400–4000 cm^{-1}, and the samples were scanned four times in the first 10 min and twice in 30 min.

3.4. Catalytic Performance Evaluation

The hydrogenation of CO_2 to yield methanol was performed in a fixed-bed reactor (inner diameter of 6 mm). The schematic diagram of the reaction device is shown in Figure 7. After the catalyst (0.5 g) was pretreated in pure H_2 at 400 °C for 3 h and chilled to 180 °C, the feed gas (H_2/CO_2 ratio of 3/1) was introduced into the reactor under 3.0 MPa. The reaction tail gas was quantitatively analyzed using a gas chromatograph equipped with a hydrogen flame detector (GC-7900, Tianmei, Shanghai, China) and a thermal conductivity detector (GC-7890II, Tianmei, Shanghai, China).
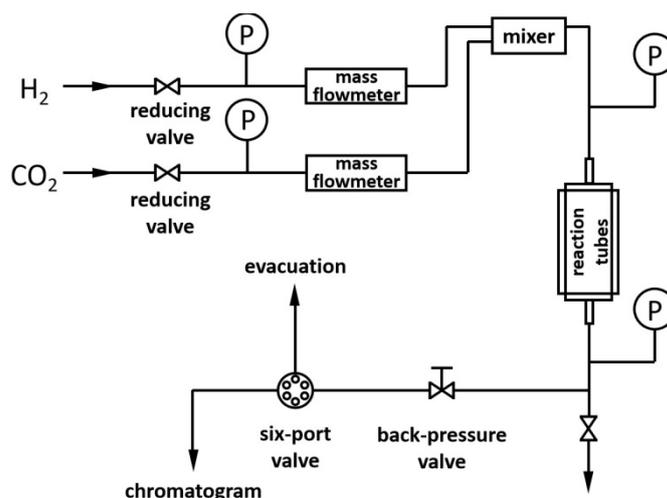
Figure 7. Schematic diagram of the reaction device.

4. Conclusions

$MoSe_2$ catalysts were prepared by different loading methods and applied to carry out the hydrogenation of CO_2 to methanol. The introduction of carbon materials can effectively improve the dispersion of $MoSe_2$. When glucose was introduced into the precursor as a carbon source, small particles and a few layers of $MoSe_2$ were formed in the $MoSe_2$@C-55 catalyst under the confinement of the in situ-formed carbon material, which was beneficial for exposing more active sites.

Due to the strong interaction between $MoSe_2$ and the in situ-formed carbon, the $MoSe_2$-Mo_2C heterojunction was generated, which interrupted the continuity of $MoSe_2$. Under the confinement effect of the in situ-formed carbon material, the layer number and particle size of $MoSe_2$ were reduced in the $MoSe_2$@C-55 catalyst, which was conducive to exposing more active sites.

Over the $MoSe_2$@C-55 catalyst, a higher methanol selectivity of 93.7% and excellent catalytic stability in the continuous reaction within 100 h provide a prospect for the application of the high-efficiency catalyst under the cooperation of the $MoSe_2$-Mo_2C heterojunction and the in situ-formed carbon material. The results of the in situ DRIFTS proved the HCOO* and CO* species were the intermediates for synthesizing methanol from CO_2 in the presence of a $MoSe_2$@C-55 catalyst.

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