Selective Hydrogenation of Dimethyl Oxalate to Methyl Glycolate over Boron-Modified Ag/SiO$_2$ Catalysts

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ABSTRACT: The addition of boron (B) as a promoter to the Ag/SiO$_2$ catalyst for the selective hydrogenation of dimethyl oxalate (DMO) to methyl glycolate (MG) was investigated. A comparison of the preparation method for incorporation of B found that the addition during the ammonia evaporation deposition—precipitation synthesis of the Ag/SiO$_2$ catalyst (Ag–B/SiO$_2$) was inferior to incipient wetness impregnation introduction of the Ag/SiO$_2$ catalyst (B/Ag/SiO$_2$). Moreover, the effects of B contents (0.5–5 wt %) on the physicochemical properties and catalytic performance of the B/Ag/SiO$_2$ catalysts were investigated by XRF, N$_2$-physisorption, XRD, FTIR, TEM, EDX mapping, H$_2$-TPR, NH$_3$-TPD, XPS, and catalytic testing. The results indicated that both the catalytic activity and stability of the Ag/SiO$_2$ catalyst were noticeably enhanced after the introduction of B. The B/Ag/SiO$_2$ catalyst with 1 wt % B showed the best catalytic performance of 100% DMO conversion and 88.3% MG selectivity, which could be attributed to the highest dispersion of the active metal and the smallest Ag particle size stabilized by the strong interaction between silver and boron species.

1. INTRODUCTION

Recently, catalytic conversion of synthetic gas to produce dimethyl oxalate (DMO) and further hydrogenation of DMO to ethylene glycol (EG) have been successfully scaled up to industrial applications.$^1$ Unfortunately, the production of methyl glycolate (MG), which is a more intermediate product in the hydrogenation of DMO to EG, has not received enough attention. Actually, MG is an important and higher value-added fine chemical in comparison with EG. Because of its α-H, hydroxyl, and ester groups, MG exhibits similar chemical properties to those of alcohol and ester,$^2$–$^6$ and it can be used for the synthesis of numerous fine chemicals, such as polyglycolic acid, pharmaceuticals, and perfumes.$^4$–$^7$ More importantly, these MG-derived products are environmentally friendly and biodegradable. Thus, MG possesses an extensive potential market.

Currently, there are several methods to produce MG; however, some disadvantages of these approaches, such as the limited raw materials, harsh reaction conditions, and low yield of the target product, impede their applications in the industry.$^2$–$^8$ The selective hydrogenation of DMO is a more efficient and greener catalytic procedure for MG synthesis.$^3$–$^7$ However, low activity and poor stability of the catalyst are common problems.$^{13}$–$^{14}$ Therefore, effective catalysts particularly with high reactivity and stability are urgently needed.

Based on the available literatures, the catalysts used in the hydrogenation of DMO reactions are mainly noble metal-free based$^{5,6,15}$–$^{20}$ and silver-based$^{3,11,21}$–$^{26}$ catalysts. Among noble metal-free based catalysts, copper-based catalysts are usually preferred for the synthesis of EG and ethanol.$^{15}$–$^{18}$ Cu/HAP catalysts showed distinct catalytic performance because of the copper phosphate species and abundant surface hydroxy groups.$^{25}$ Abbas et al.$^{28}$ found that Cu nanoparticles wrapped on reduced graphene oxide (RGO) nanosheets possessed a synergistic ratio of Cu$^+$/Cu$^0$ and highly dispersed Cu nanoparticles, which were in favor of catalytic performance in hydrogenation of DMO. Zhao et al. reported that Ni$_3$P/RB-MSN showed better catalytic performance than Ni$_3$P/HMS.
and Ni,P/MCM-41, which was due to the lack of Si−OH in the RB-MSN. As a unilateral hydrogenated product, MG has an inferior yield because of the higher thermodynamic constant of the subsequent hydrogenation of MG to EG. Recently, several silver-based catalysts, such as Ag/SiO$_2$, Ag/MCM-41, Ag/KCC-1, Ag/SBA-15, and Ag/CNT, have been investigated and exhibited superior selectivity for the chemoselective synthesis of MG via hydrogenation of DMO due to the relatively weak hydrogenolysis capability of the silver active sites compared with copper. However, these catalysts have the disadvantages of high raw material cost, complex preparation process, and poor stability, thus impeding their further industrial application.

On the other hand, it has been well demonstrated that the catalytic activity and stability of metal catalysts can be improved by introducing an effective promoter due to the enhanced dispersion of the active metal and interaction between the metal and dopant. Recently, many studies have shown that B$_2$O$_3$ is a promising candidate for its sintering-resistant property and suitable acidity. For instance, He et al. claimed that the catalytic behavior was greatly enhanced with the B$_2$O$_3$-modified Cu−SiO$_2$ catalyst due to the improved copper dispersion. Moreover, boron doping could enhance the metal–support interaction between Cu and SiO$_2$, maintain a suitable Cu$^+$/Cu$^0$ ratio, restrain the growth of Cu particles during DMO hydrogenation, and then improve the catalytic selectivity and stability of Cu/SiO$_2$ catalysts.

Yin et al. reported that the Cu/HMS catalyst modified by B$_2$O$_3$ exhibited higher conversion and selectivity because of the higher metallic copper surface area and copper dispersion. More recently, Chen et al. demonstrated that a 10%Ag−5% B$_2$O$_3$/SiO$_2$ catalyst prepared by the coimpregnation method displayed an improved catalytic activity and stability compared with the Ag/SiO$_2$ catalyst in the hydrogenation process. However, inhomogeneous agglomeration of active species usually occurs especially at high content for the catalyst prepared by the impregnation method, resulting in large-sized particles and thus low activity and poor stability. In previous work, we found that the addition of 1 wt % B exerted little effect on the DMO conversion and MG selectivity of the 10%Ag/SiO$_2$ catalyst prepared by the one-step ammonia evaporation deposition–precipitation method. The above results indicated that the effect of B addition on the catalytic performance of Ag/SiO$_2$ may depend greatly on the catalyst preparation method and B$_2$O$_3$ content, which has not been investigated so far to the authors’ best knowledge.

In the present work, we report a series of B-modified Ag/SiO$_2$ catalysts with different boron loadings for the selective hydrogenation of DMO to MG. The Ag/SiO$_2$ catalyst was synthesized by a facile ammonia evaporation deposition–precipitation method, which was reported superior to the impregnation method for the preparation of the Cu/SiO$_2$ catalyst. The B promoter was incorporated through two methods, i.e., addition during the ammonia evaporation deposition–precipitation synthesis of the Ag/SiO$_2$ catalyst (Ag−B/SiO$_2$) and incipient wetness impregnation after the synthesis of the Ag/SiO$_2$ catalyst (B/Ag/SiO$_2$). Comprehensive characterization was performed by XRF, N$_2$-physisorption, XRD, FTIR, TEM, EDX mapping, H$_2$-TPR, XPS surface analysis, and NH$_3$-TPD techniques, and the effects of boron loadings on the physicochemical properties of the B/Ag/SiO$_2$ catalysts were investigated. Moreover, the structure–activity relationship of these B/Ag/SiO$_2$ catalysts in DMO hydrogenation was also discussed in detail.

2. RESULTS AND DISCUSSION

2.1. Effect of B Incorporation Order on Catalytic Performance of Ag/SiO$_2$. The effect of incorporation order of B on the catalytic performance of Ag/SiO$_2$ modified with 1% B was investigated, and the results are presented in Figure 1. It can be observed that the DMO conversion of the 1B/Ag/SiO$_2$ catalyst was significantly higher than that of the Ag−1B/SiO$_2$ catalyst (88.3 vs 78.5%). At variance with the DMO conversion, similar MG selectivity was obtained on both catalysts. Thus, the 1B/Ag/SiO$_2$ catalyst exhibited noticeably higher MG yield than the Ag−1B/SiO$_2$ catalyst. It was reported that the introduced B can be removed to a large extent during washing of the precipitate for the B-modified Cu−ZnO−ZrO$_2$ catalyst. And Wittoon et al. found that K species were removed during washing and filtration stages for the preparation of Fe−Co−K−Al mixed oxide catalysts. Thus, we speculate that the inferior activity of the Ag−1B/SiO$_2$ catalyst may be due to the loss of B during the preparation process. To verify the hypothesis, the actual B content of both B-modified catalysts was determined. As expected, the result indicated that the actual B loading of the Ag−1B/SiO$_2$ catalyst (0.57 wt %) was distinctly lower than that of the 1B/Ag/SiO$_2$ catalyst (0.85 wt %). Thus, it can be concluded that the different methods of introducing B had an obvious influence on the actual B content and further affected the catalytic behaviors of the B-modified catalysts. Accordingly, the Ag/SiO$_2$ catalysts modified with different B loadings were prepared by the postincipient wetness impregnation method to investigate the effect of B content on the performance of thexB/Ag/SiO$_2$ catalyst for hydrogenation of DMO to synthesize MG.

2.2. Effect of B Content on the xB/Ag/SiO$_2$ Catalysts. 2.2.1. Characterization of the xB/Ag/SiO$_2$ Catalysts. The composition of the as-prepared xB/Ag/SiO$_2$ catalysts was determined by XRF, and the results are presented in Table 1. As seen, the actual silver loading is in close agreement with the as-added amount. Nevertheless, the actual B loadings were

![Figure 1. Comparison of performance of 1% B-modified Ag/SiO$_2$ catalyst prepared by one-step ammonia evaporation deposition–precipitation and postincipient wetness impregnation.](https://pubs.acs.org/doi/10.1021/acsomega.2c04880)
Cu−SiO phenomenon was also reported previously for the B-modified catalyst. The amount of B was lost during the catalyst preparation; a similar slightly lower than the theoretical values, indicating that a small loop, which is the characteristic of nanostructured materials. The pore size distributions of the adsorption curve of type IV with the H1-type hysteresis (from Figure 2A, all of the samples exhibited a typical continuously with increasing B content, while the showed that the prepared samples are summarized in Table 1. The results slightly of the Ag/SiO catalyst. It can be inferred that the Ag particles aggregated on the support surface due to the weak interaction between silver species and silica support, and the introduction of B could suppress the accumulation of silver species and retard the growth of metallic silver crystallites during the calcination and reduction processes. With the addition of B, the intensity of the diffraction peak of Ag decreased noticeably, and the characteristic peaks of B2O3 emerged at 2θ of 14.6 and 27.8° (PDF # 06-0297) when the doping amount of B was greater than or equal to 3 wt % in the xB/Ag/SiO2 catalyst. Additionally, a broad and diffuse diffraction peak centered at about 22° was observed for all of the catalysts, which was assigned to amorphous SiO2.

The XRD patterns of the reduced catalysts are shown in Figure 3B, and the average diameter of metallic Ag was calculated by the Scherrer equation. From calculations, the average diameters of metallic Ag on Ag/SiO2, 0.5B/Ag/SiO2, 1B/Ag/SiO2, 3B/Ag/SiO2, and 5B/Ag/SiO2 are 16.9, 14.7, 13.2, 13.6, and 13.7 nm, respectively. It is clear that the crystalline sizes of silver in the xB/Ag/SiO2 catalysts are smaller than that in the Ag/SiO2 catalyst. It can be inferred that the Ag particles aggregated on the support surface due to the weak interaction between silver species and silica support, and the introduction of B could suppress the accumulation of silver species and retard the growth of metallic silver crystallites during the calcination and reduction processes. Specifically, B2O3 doping with a B loading no higher than 1 wt % notably decreased the particle size of Ag from 14.7 to 13.2 nm, whereas further increasing B loading in the range of 1–5 wt % resulted in a gradual increase in the particle size of Ag from 13.2 to 13.7 nm. Evidently, the 1B/Ag/SiO2 catalyst exhibited the smallest particle size among all of the catalysts. The results clearly demonstrated that the introduction of proper amounts of B in

| Catalyst       | Ag loading (wt %) | B loading (wt %) | S_BET (cm²·g⁻¹) | V_p (cm³·g⁻¹) | D_p (nm) |
|----------------|------------------|-----------------|-----------------|--------------|----------|
| Ag/SiO2        | 9.8              | 0.0             | 179.4           | 0.65         | 10.6     |
| 0.5B/Ag/SiO2   | 9.7              | 0.42            | 161.9           | 0.59         | 12.2     |
| 1B/Ag/SiO2     | 9.7              | 0.85            | 152.3           | 0.58         | 12.4     |
| 3B/Ag/SiO2     | 9.7              | 2.8             | 143.6           | 0.54         | 12.4     |
| 5B/Ag/SiO2     | 9.7              | 4.7             | 123.4           | 0.50         | 13.0     |

a Determined by XRF. b BET specific surface area. c Pore volume. d Average pore diameter.

Figure 2 shows the N₂ adsorption–desorption isotherms and BJH pore size distributions of the catalysts. As can be seen from Figure 2A, all of the samples exhibited a typical adsorption curve of type IV with the H1-type hysteresis loop, which is the characteristic of nanostructured materials with uniform mesopores. The pore size distributions of different samples (Figure 2B), derived from desorption data of the isotherm and calculated using the BJH model, show that most of the pores fall into the size range of 2–20 nm and the average pore size is calculated to be about 12 nm.

To investigate the evolution of the crystalline phase structure of the xB/Ag/SiO2 catalysts, the XRD patterns of both calcined and reduced catalysts were collected. As shown in Figure 3A, for all of the catalysts, four peaks appeared at 2θ = 38.1, 44.3, 64.4, and 77.4°, which were assigned to the (111), (200), (220), and (311) lattice planes of metallic silver (PDF # 87-0597). The appearance of the characteristic diffraction peaks of metallic silver in the calcined catalysts can be ascribed to the fact that silver oxide is easily decomposed into metallic silver during the heat treatment at high temperatures. With the addition of B, the intensity of the diffraction peak of Ag decreased noticeably, and the characteristic peaks of B2O3 emerged at 2θ of 14.6 and 27.8° (PDF # 06-0297) when the doping amount of B was greater than or equal to 3 wt % in the xB/Ag/SiO2 catalyst. Additionally, a broad and diffuse diffraction peak centered at about 22° was observed for all of the catalysts, which was assigned to amorphous SiO2.

Figure 2. N₂ adsorption isotherms (A) and BJH pore size distributions (B) of the calcined Ag/SiO2 and xB/Ag/SiO2 catalysts.
the xB/Ag/SiO\textsubscript{2} catalysts could enhance the dispersion of the silver.

The FTIR technique was adopted to further explore the structure information of the calcined samples. As shown in Figure 4, the absorption bands at approximately 1100, 800, and 470 cm\(^{-1}\) on the Ag/SiO\textsubscript{2} catalyst were ascribed to the different vibration modes of the Si–O bonds of the SiO\textsubscript{2} support.\textsuperscript{43,44} In addition, the bands at approximately 1420, 886, and 647 cm\(^{-1}\) appeared with the samples of 3B/Ag/SiO\textsubscript{2} and 5B/Ag/SiO\textsubscript{2}, which were assigned to the B–O stretching vibrations of trigonal (BO\textsubscript{3}) units in different borate groups, the stretching vibrations of B–O bonds in BO\textsubscript{4} units from diborate groups, and the B–O–B bending vibrations, respectively.\textsuperscript{30,45} Furthermore, the intensity of these bands increased noticeably with increasing the boron content. The result is in good accordance with that obtained by XRD (Figure 3A).

Figure 5 shows TEM images of the two representative catalysts (calcined Ag/SiO\textsubscript{2} and 1B/Ag/SiO\textsubscript{2}). According to our group’s previous study\textsuperscript{38,46} and the above XRD results (Figure 3), Ag species mainly exist as metallic Ag on calcined catalysts. Both calcined Ag/SiO\textsubscript{2} and 1B/Ag/SiO\textsubscript{2} appear as agglomerates of irregular SiO\textsubscript{2} support (bright areas) and spherical Ag species particles (darker areas). However, the average Ag particle size of 1B/Ag/SiO\textsubscript{2} (5–10 nm) is obviously smaller than that of Ag/SiO\textsubscript{2} (10–20 nm). The dispersion of Ag species was further investigated by EDX mapping (Figure 6). Obviously, Ag species are better dispersed on 1B/Ag/SiO\textsubscript{2} (Figure 6a) than on Ag/SiO\textsubscript{2} (Figure 6b). Besides, the B species on 1B/Ag/SiO\textsubscript{2} is also highly dispersed (Figure S1). The results of TEM and EDX mapping implied that B loading could limit the growth of Ag particles and promote the dispersion of Ag species on the SiO\textsubscript{2} support.

As displayed in Figure 7, all of the samples exhibited one hydrogen consumption peak in the region of 100–300 °C of the TPR profiles. The peak at 137 °C of the Ag/SiO\textsubscript{2} catalyst corresponded to the reduction of silver oxide to metallic silver.\textsuperscript{24} However, the calcined catalysts did not show any characteristic diffraction peaks of silver oxides (Figure 3A), which is probably because the XRD technique cannot detect the thin layer of silver oxides on the catalyst surface.\textsuperscript{38} The xB/Ag/SiO\textsubscript{2} catalysts exhibited a higher reduction temperature and the H\textsubscript{2} consumption peak gradually shifted toward a higher temperature with increasing B amount. This phenomenon may be attributed to the strong chemical interaction between the acidic boric oxide and the basic silver oxide.\textsuperscript{30} With the increase of B content, gaining electrons became harder for the silver species during hydrogen reduction, which was due to the higher electron affinity of boric oxide than that of SiO\textsubscript{2}.\textsuperscript{32} From the H\textsubscript{2}-TPR results, it can be concluded that the amount of B plays a very important role in the distributions of silver species by chemical interaction between boric oxide and Ag species in the xB/Ag/SiO\textsubscript{2} catalysts.
The NH$_3$-TPD profiles are shown in Figure 8. As observed, the profile of the Ag/SiO$_2$ catalyst presented a broad and weak peak centered at 150 °C, indicating that only a small amount of acidic sites existed on the catalyst surface. For the xB/Ag/SiO$_2$...
The NH₃ desorption peak area also increased gradually with the enhancement of B content. Therefore, it can be inferred that boria was mainly responsible for the acidity of the xB/Ag/SiO₂ catalysts.

The chemical states and surface compositions of the reduced catalysts were investigated using an XPS technique. The XPS spectra of Ag 3d for the Ag/SiO₂ and xB/Ag/SiO₂ catalysts are illustrated in Figure 9A. Typically, the two peaks located at binding energies (BEs) of 367.8 and 373.9 eV were mainly ascribed to Ag 3d₅/₂ and Ag 3d₇/₂ peaks of Ag⁰, respectively. As shown in Figure 9B, the B 1s peak centered at about 193.4 eV was attributed to B³⁺, and the absence of a peak at 188.7 eV suggested that no B⁰ existed.

The XPS results are summarized in Table 2. As can be seen, the BE values of Ag 3d₅/₂ of the xB/Ag/SiO₂ catalysts were higher than that of the Ag/SiO₂ catalyst. And the Ag 3d₅/₂ peak shifted to higher BEs from 368.0 to 368.3 eV with the increase of B content, while the B 1s peak moved to lower BEs from 193.4 to 192.7 eV. Therefore, an electron donor–acceptor interaction between silver and boria may occur on the silica surface. The experimental results clarified the presence of strong interaction between Ag and B species wherein the electron transferred from Ag⁰ to B³⁺. Additionally, the surface concentration of Ag over the Ag/SiO₂ and xB/Ag/SiO₂ catalysts (Table 2) shows a volcano-type tendency, in which the highest amount of surface silver was obtained on the 1B/

| catalyst       | binding energy (eV) | surface elemental concentration (at %) |
|----------------|---------------------|----------------------------------------|
|                | Ag 3d₅/₂            | B 1s                                   |
| Ag/SiO₂        | 367.8               | 0.53                                   |
| 0.5B/Ag/SiO₂   | 368.0               | 193.4                                  |
| 1B/Ag/SiO₂     | 368.1               | 193.3                                  |
| 3B/Ag/SiO₂     | 368.2               | 193.2                                  |
| 5B/Ag/SiO₂     | 368.3               | 192.7                                  |

Table 2. XPS Results for the Ag/SiO₂ and xB/Ag/SiO₂ Catalysts

(catalysts, the NH₃ desorption temperature shifted toward a higher temperature with an increase in B loading. In addition,
Ag/SiO₂ catalyst. This result is in good agreement with the dispersion of Ag obtained from XRD measurements (Table 1).

2.2.2. Catalytic Performance of the xB/Ag/SiO₂ Catalysts. The results of Ag/SiO₂ and xB/Ag/SiO₂ catalysts for the selective hydrogenation of DMO to MG are listed in Table 3.

Table 3. Catalytic Performance of the Ag/SiO₂ and xB/Ag/SiO₂ Catalysts for DMO Hydrogenation

| catalyst    | conversion (%) | selectivity (%) |
|-------------|----------------|-----------------|
|             | MG  | MF | EG | MG yield (%) |
| Ag/SiO₂     | 77.8| 89.3| 2.2| 8.5 | 69.5 |
| 0.5B/Ag/SiO₂| 79.4| 94.5| 5.5| 0   | 75.0 |
| 1B/Ag/SiO₂  | 100 | 88.3| 2.4| 9.3 | 88.3 |
| 3B/Ag/SiO₂  | 88.0| 87.5| 3.8| 8.7 | 77.0 |
| 5B/Ag/SiO₂  | 89.7| 83.7| 5.3| 11.0| 75.1 |

aReaction conditions: T = 493 K, P = 1.5 MPa, H₂/DMO molar ratio = 150, LHSV = 0.28 h⁻¹.

The products of DMO hydrogenation reaction on the silver-based catalyst include EG and methyl formate (MF) besides the target product of MG. Under the present reaction conditions, the conversion of DMO and the selectivity to MG on the Ag/SiO₂ catalyst are 77.8 and 89.3%, respectively. As B was introduced into the Ag/SiO₂ catalyst, both the catalytic activity and the selectivity of MG were improved. And along with the increase of the B loading, the catalytic performance displayed a volcano-type variation tendency in terms of MG yield. More specifically, the highest yield of MG was observed on the 1B/Ag/SiO₂ catalyst (88.3%); the value was 18.8% higher than that on the unmodified Ag/SiO₂ catalyst.

The TOF was calculated to compare the catalytic performance of different catalysts in DMO hydrogenation, and the DMO conversion was regulated by DMO liquid hourly space velocity (LHSV). As shown in Table 4, both the TOF and DAg values increased first and then decreased with increasing the content of B. 1B/Ag/SiO₂ with the highest TOF value (17.8 h⁻¹) indicated its highest DMO catalytic activity. Besides, the addition of B promoted the dispersion of Ag species on SiO₂, consistent with TEM results (Figure 5). Figure 10 shows that the TOF value decreased gradually with the increase of Ag particle size over five catalysts, suggesting that the DMO hydrogenation is a structure-sensitive reaction.

As well known, there are many factors that can affect the activity of Ag-based catalysts for vapor-phase DMO hydrogenation. On the basis of the above characterization results, the reasons for the effect of B loading on the performance of the xB/Ag/SiO₂ catalysts can be explained as follows: (1) The XPS results show that the surface Ag content increased in the order of Ag/SiO₂ < 0.5B/Ag/SiO₂ < 5B/Ag/SiO₂ < 3B/Ag/SiO₂ < 1B/Ag/SiO₂ (Table 2). This order exactly coincided with that of MG yield of the series of catalysts. In fact, the MG yield increased almost linearly with the surface Ag content of the catalysts, as shown in Figure 11. Thus, the surface metallic

![Figure 10](https://example.com/fig10.png)

**Figure 10.** TOF values as a function of Ag particle sizes of the Ag/SiO₂ and xB/Ag/SiO₂ catalysts.

![Figure 11](https://example.com/fig11.png)

**Figure 11.** Relationship between the MG yield and the surface Ag concentration of the Ag/SiO₂ and xB/Ag/SiO₂ catalysts.

As well as 315x510 catalysts for DMO hydrogenation can be explained as follows: (1) The XPS results show that the surface Ag content increased in the order of Ag/SiO₂ < 0.5B/Ag/SiO₂ < 5B/Ag/SiO₂ < 3B/Ag/SiO₂ < 1B/Ag/SiO₂ (Table 2). This order exactly coincided with that of MG yield of the series of catalysts. In fact, the MG yield increased almost linearly with the surface Ag content of the catalysts, as shown in Figure 11. Thus, the surface metallic

Table 4. TOF of the Ag/SiO₂ and xB/Ag/SiO₂ Catalysts for DMO Hydrogenation

| catalyst    | conversion (%) | selectivity (%) | dAg (nm) | DAg (%) | TOFXRD (h⁻¹) |
|-------------|----------------|-----------------|----------|---------|--------------|
| Ag/SiO₂     | 15.7           |                 | 16.9     | 9.00    | 10.4         |
| 0.5B/Ag/SiO₂| 19.6           |                 | 14.7     | 10.35   | 11.0         |
| 1B/Ag/SiO₂  | 11.7           |                 | 13.2     | 11.25   | 17.8         |
| 3B/Ag/SiO₂  | 9.3            |                 | 13.6     | 11.18   | 14.6         |
| 5B/Ag/SiO₂  | 9              |                 | 13.7     | 11.10   | 14.2         |

aReaction conditions: T = 493 K, P = 1.5 MPa, H₂/DMO molar ratio = 150. bOthers include EG and MF. cAverage diameter of metallic Ag on the reduced catalysts calculated by the Scherrer equation. dDispersion of metallic Ag determined by XRD. eTOFXRD was calculated by Ag dispersion. fLHSV = 0.58 h⁻¹. gLHSV = 1.75 h⁻¹.
Ag site density was mainly responsible for the catalytic activity, which can offer a rational explanation for the boron content effect on the catalytic performance of the xB/Ag/SiO\textsubscript{2} catalysts. (2) It has been well illustrated that the dispersion and particle size of metallic Ag have a significant effect on the catalytic performance of the Ag-based catalysts.\textsuperscript{23,30,49} As revealed by XRD measurements, the particle size of silver species decreased in the following order: Ag/SiO\textsubscript{2} > 0.5B/Ag/SiO\textsubscript{2} > 5B/Ag/SiO\textsubscript{2} > 3B/Ag/SiO\textsubscript{2} > 1B/Ag/SiO\textsubscript{2}. This is exactly opposite to the order of MG yield of the catalysts (Table 3). Therefore, the MG yield of the xB/Ag/SiO\textsubscript{2} catalysts increased with the decrease in the particle size of silver species.

It was reported that the acidic sites are propitious to the absorption and activation of acyl groups in the hydrogenation process, thereby improving the selectivity of the target product.\textsuperscript{30} In our case, the acid amount of the xB/Ag/SiO\textsubscript{2} catalysts increased along with the increase of the B content, as revealed by NH\textsubscript{3}-TPD characterization (Figure 8); however, the selectivity of MG did not increase accordingly. This result suggests that the amount of acidic sites is not a critical parameter that determines the MG selectivity of the Ag-based catalyst. This conclusion is inconsistent with that reported by other researchers.\textsuperscript{30}

Stability is an important property that determines the practical applicability of a catalyst. Thus, the stability test was carried out on the Ag/SiO\textsubscript{2} and 1B/Ag/SiO\textsubscript{2} catalysts; the results are shown in Figure 12. For the sample of 1B/Ag/SiO\textsubscript{2}, after \textasciitilde24 h of “running in” stage of the reaction, the conversion of DMO reached constant, with no sign of deactivation observed after 300 h of reaction, while the selectivity of MG initially decreased slightly from 88.8% (at 12 h) to 85.2% (at 96 h) and then remained constant. Contrarily, the Ag/SiO\textsubscript{2} catalyst presented obvious deactivation within 90 h under identical reaction conditions. It can be concluded that the addition of a suitable amount of B greatly enhanced the catalytic stability of the Ag/SiO\textsubscript{2} catalyst. Moreover, the 1B/Ag/SiO\textsubscript{2} catalyst investigated in the present work shows longer stability under a higher liquid hourly space velocity of 0.28 h\textsuperscript{-1}, compared with the corresponding data (264 h, LHSV = 0.2 h\textsuperscript{-1}) of the Ag–5\%B/SiO\textsubscript{2} catalyst reported by Chen et al.\textsuperscript{30}

The difference may result from the different preparation methods for the Ag/SiO\textsubscript{2} catalyst, in which the impregnation method was used in ref 30, while the ammonia evaporation–precipitation method was adopted in the present work.

The increase in the stability of the Ag/SiO\textsubscript{2} catalyst modified by B can be attributed to the strong interaction between silver and boria, which is supposed to stabilize active silver species and suppress sintering of active metal particles during the reaction process.\textsuperscript{23,25} To verify the supposition, the catalysts after a long-term test were studied by XRD characterization, and the results are shown in Figure 13. The size of Ag crystallites calculated by the Scherrer formula over the Ag/SiO\textsubscript{2} catalyst after a 90 h reaction test was 22.4 nm, which was significantly larger than that of the fresh catalyst (16.9 nm). In contrast, the size of Ag crystallites over the 1B/Ag/SiO\textsubscript{2} catalyst after a 300 h reaction test was 13.3 nm, which was almost identical to that of the fresh catalyst (13.2 nm). These results clearly indicate that the addition of a suitable amount of boron can effectively hinder the sintering and growth of Ag particles, thereby improving the long-term stability of the Ag/SiO\textsubscript{2} catalyst.

The comparison of catalytic performance between the best 1B/Ag/SiO\textsubscript{2} catalyst and the recently reported materials has been listed in Table 5. Note that the experimental conditions used in the literature are different from each other. However, we achieved 100% DMO conversion and 88.3% MG selectivity using the 1B/Ag/SiO\textsubscript{2} catalyst with high stability. In comparison, boron-modified Ag/SiO\textsubscript{2} catalysts seem to be promising, even they still need to be optimized.

Figure 12. Long-term performance of the Ag/SiO\textsubscript{2} and 1B/Ag/SiO\textsubscript{2} catalysts. Reaction conditions: 493 K, 1.5 MPa, H\textsubscript{2}/DMO molar ratio = 150, LHSV = 0.28 h\textsuperscript{-1}.

3. CONCLUSIONS

In summary, we have studied the effects of B contents on the catalytic performance of B\textsubscript{2}O\textsubscript{3}-modified Ag/SiO\textsubscript{2} catalysts for the selective hydrogenation of DMO to the MG reaction. The results indicated that with increasing the content of B, the MG yield increased first, passing through a maximum, and then decreased at higher B contents. The xB/Ag/SiO\textsubscript{2} catalyst with 1 wt % B exhibited the highest catalytic activity for the selective
Table 5. Comparison of Performance of Different Catalysts

| catalyst                        | reaction conditions                  | catalytic performance                           | reference |
|---------------------------------|--------------------------------------|-------------------------------------------------|-----------|
| Na₂SiO₃ modified Cu/SiO₂         | T = 200 °C, P = 2.5 MPa, H₂/DMO = 80 (molar ratio), WHSV = 1.5 h⁻¹ | 83% DMO conversion, 99.8% MG selectivity, and can maintain for 6 h | 3         |
| B-modified carbon aerogel-supported Cu | T = 230 °C, P = 2.4 MPa, H₂/DMO = 180 (molar ratio), LHSV = 1 h⁻¹ | DMO conversion and MG selectivity were 84.6 and 45.2%, respectively. | 20        |
| Naₓ/P/RB-MSN                    | T = 190 °C, P = 2.5 MPa, H₂/DMO = 90 (molar ratio), WHLV = 0.44 g⁻¹ h⁻¹ | 100% DMO conversion, 85.0% MG selectivity, and can maintain for 500 h | 29        |
| Ru(activated carbon)            | T = 90 °C, P = 3 MPa, H₂/DMO = 260 (molar ratio), WHSV = 0.15 h⁻¹ | 97.2% DMO conversion, 94.6% MG selectivity, and can maintain for 1032 h | 50        |
| P-modifiedCo/SiO₂               | T = 240 °C, P = 3 MPa, H₂/DMO = 160 (molar ratio), LHSV = 0.06 h⁻¹ | 94.6% DMO conversion, 88.1% MG selectivity, and can maintain for 300 h | 51        |
| B-modifiedAg/SiO₂ catalysts     | T = 220 °C, P = 1.5 MPa, H₂/DMO = 150 (molar ratio), LHSV = 0.28 h⁻¹ | 100% DMO conversion, 88.3% MG selectivity, and can maintain for 300 h | this work |

hydrogenation of DMO to MG, which could be ascribed to the largest amounts of well-dispersed active metal on the catalyst surface. Additionally, the lifespan of the 1B/Ag/SiO₂ catalyst can be greatly extended to at least 300 h with excellent catalytic behavior at 493 K, 1.5 MPa, and LHSV = 0.28 h⁻¹, which can be attributed to the reduced sintering of Ag for the strong Ag–B interaction. Furthermore, the 1B/Ag/SiO₂ catalyst prepared by post B modification exhibited significantly higher activity than that of the Ag–1B/SiO₂ catalyst prepared by one-step ammonia evaporation deposition–precipitation.

4. EXPERIMENTAL SECTION

4.1. Catalyst Preparation. A commercial silica sol (Qingdao Haiyang Chemicals Company, China) was used as the support in this study. AgNO₃ (AR) and H₂BO₃ (AR) were purchased from Shanghai Titan Scientific Co., Ltd. (China) and used as the starting materials.

The Ag/SiO₂ catalyst with a preset silver loading of 10 wt % was prepared by the ammonia evaporation deposition–precipitation method. A typical procedure is as follows. A certain amount of AgNO₃ was dissolved in deionized water. Then, an ammonia aqueous solution was added and stirred for 30 min at 60 °C to form a silver ammonia complex solution. Next, a certain amount of silica sol was added to the above silver ammonia complex solution and stirred for another 4 h. The initial pH of the suspension was 11–12. The suspension was then heated to 90 °C and held at this temperature to allow the evaporation of ammonia and the decrease of pH and consequently the deposition of silver species on the silica surface. When the pH value of the suspension was decreased to 7–8, the evaporation process was terminated. The resulting precipitate was washed with deionized water three times, and the obtained filter cake was dried at 120 °C overnight to yield a gray powder of Ag/SiO₂ precursor. B-modified Ag/SiO₂ catalysts were prepared by an incipient wetness impregnation method. An aqueous solution of H₂BO₃ was dropped onto the Ag/SiO₂ precursor in a 100 mL crucible. The slurry was ultrasonically aged for 30 min at room temperature, dried overnight at 120 °C, and then calcined in static air at 350 °C at a temperature rate of 1 °C min⁻¹ for 4 h. The obtained catalysts are denoted as xB/Ag/SiO₂ (x = 0.5, 1, 3, and 5), where x represents the nominal weight percent of boron.

The Ag–B/SiO₂ catalyst with 10 wt % Ag and 1 wt % B was also prepared by the ammonia evaporation deposition–precipitation method, according to the procedure described above for the preparation of the Ag/SiO₂ precursor, in which the aqueous solution contains the desired amounts of AgNO₃ and H₂BO₃. Then, the dried powder was calcined in static air at 350 °C for 4 h (heating rate of 1 °C min⁻¹), and the obtained catalyst was designated as Ag–1B/SiO₂.

4.2. Catalyst Characterization. The chemical compositions of the as-prepared samples were determined by X-ray fluorescence (XRF) spectroscopy. Catalyst powders were compressed into a self-supporting wafer prior to analysis.

BET specific surface areas (S_{BET}), pore volumes (Vₚ), and average pore diameters (Dₚ) of the catalysts were measured by N₂ adsorption–desorption isotherms at −196 °C using a Micromeritics ASAP 2020 HD88 adsorption apparatus after degassing the samples under vacuum at 200 °C for 6 h. S_{BET} was calculated using a value of 0.162 nm² for the cross-sectional area of the nitrogen molecule. The total pore volume was derived from the adsorbed N₂ volume at a relative pressure of approximately 0.99, and the Barrett–Joyner–Halenda (BJH) method was used to calculate the pore size distributions according to the desorption branch of the isotherms.

Powder X-ray diffraction (XRD) patterns of the samples were acquired on a PANalytical X’Pert instrument using Ni-filtered Cu Kα radiation at 40 kV and 40 mA. 20 angles ranged from 10 to 80° with a speed of 4° per minute. Each XRD pattern was identified by matching the results with reference patterns that were included in the ICPSD database. The full width at half-maximum of Ag(111) reflection was measured to calculate the crystallite sizes using the Scherrer equation.

The infrared (IR) spectra were recorded on a Nicolet iZ10 (Thermo Fisher Scientific, American) FTIR spectrophotometer in the range of 400–4000 cm⁻¹. The powder samples were mixed with KBr (2 wt %) and pressed into translucent disks at room temperature.

Transmission electron microscopy (TEM), scanning TEM, and energy-dispersive X-ray spectroscopy mapping (EDX mapping) were conducted on a JEOL JEM 2100F transmission electron microscope working at 200 kV.

Temperature-programmed reduction (TPR) measurements were performed in a linear quartz microreactor. One-hundred milligrams of the sample was purged with N₂ at 200 °C for 2 h to remove adsorbed water and other contaminants. After being cooled down to 30 °C, the catalyst was exposed to 10% H₂/N₂ (30 cm³·min⁻¹) and heated up to 650 °C at a heating rate of 10 °C min⁻¹. H₂ consumption was monitored by a thermal conductivity detector (TCD).

NH₃-TPD was performed in a continuous flow apparatus equipped with a temperature programmer. One-hundred milligrams of the sample (40–60 mesh) was loaded into a microreactor (linear quartz tube), pretreated at 300 °C in flowing 10% H₂/N₂ for 1 h, and then cooled to 50 °C and fed with NH₃ for 40 min. Afterward, the sample was swept with N₂ at 100 °C for 1 h to purge out the physically adsorbed NH₃,
NH3 desorption was conducted in flowing N2 (30 ml/min) by heating up from 100 to 600 °C at 10 °C/min. A gas chromatograph (GC) equipped with a thermal conductivity detector (TCD) was used to continuously monitor the desorbing gas.

X-ray photoelectron spectroscopy (XPS) was performed on an Escalab 250 Xi spectrometer with MgKα radiation (1486.6 eV). The samples were pretreated in situ in a reaction chamber and then transferred to an analysis chamber under vacuum. The binding energy (BE) was calibrated by setting the C 1s peak (BE = 284.6 eV) as a reference. The surface atomic concentrations were quantified by sensitivity factors of the XPS instrument.

4.3. Catalytic Performance Measurement. DMO hydrogenation was carried out using a fixed-bed, stainless-steel tubular reactor. The catalyst (0.5 g; 40–60 mesh) packed between two layers of quartz sand was pretreated in H2 stream (50 cm3/min) at 300 °C (heating rate of 1 °C/min) for 4 h and then cooled to the reaction temperature. The reactant (13 wt % DMO/methanol solution) and pure H2 are fed into the reactor through a series 2PB constant-flux pump (Beijing Xingda Science & Technology Development Co., Ltd., China) with 1.5 MPa system pressure. A Qiyang GC-9860 gas chromatograph equipped with an HP-INNOWAX capillary column (30 m × 0.25 mm × 0.25 μm) and a flame ionization detector (FID) was used for product analysis. The DMO conversion (C_{DMO}) and product selectivity (S_i) were defined as below

\[
C_{DMO} = \left(1 - \frac{A_{fDMO}}{A_{dDMO}} \sum A_{f_i} \right) \times 100\% \tag{1}
\]

\[
S_i = \left(\frac{A_{f_i}}{\sum A_{f_i}} \right) \times 100\% \tag{2}
\]

where \(A_{f_i}\) represents the peak area of the individual component \(i\) in the product stream, and \(f_i\) represents the molar correction factor.

The turnover frequency (TOF) was calculated by the below formula

\[
\text{TOF} = \frac{C_{DMO} \times X_{DMO} \times V}{D \times N_\text{Ag}} \tag{3}
\]

where \(C_{DMO}\) is the DMO concentration in the reactant solution; \(X_{DMO}\) is the DMO conversion; \(V\) is the flow rate of the reactant solution; \(D\) is the Ag dispersion; and \(N_\text{Ag}\) is the total amount of Ag.

**ASSOCIATED CONTENT**

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/DOI/10.1021/acsomega.2c04880.

Additional characterization data and reaction testing data of relevant samples can be found in the Supporting Information (PDF).

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**Notes**

The authors declare no competing financial interest.

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