Impact of Titanium in Controlling Silver Particle Size on Enhancement of Catalytic Performance of AgMoO₃/Ti-HMS for Direct Epoxidation of Propylene

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ABSTRACT: In this work, direct gas-phase epoxidation of propylene (DPO) to propylene oxide by molecular oxygen has been studied by using Ag–MoO₃ supported on titanium-containing hexagonal mesoporous silica (Ti-HMSₙ) of different Si/Ti molar ratios. The promotion effect of NaCl on the synthesized catalysts has also been investigated. Among the studied supports, the hexagonal mesoporous silica (HMS) with a Si/Ti ratio of 10 was the most suitable one for production of propylene oxide (PO). The optimal performance of the AgMo/Ti-HMS₁₀ catalyst in DPO exhibited a selectivity to PO of 43.2% with a propylene conversion of 14.1%, at 400 °C, 0.1 MPa, and a space velocity of 12,000 h⁻¹. The catalyst verified good stability over at least 20 h on stream. Only 2.7% PO selectivity with a propylene conversion of 10.1% was achieved over the AgMo/HMS sample. The incorporation of Ti into the HMS frame could optimize the particle size distribution of Ag, producing Ag nanoparticles with an average size of 6.8 nm compared with that of Ag/HMS (24.3 nm). The in situ Raman spectrum of AgMo/Ti-HMS₁₀ heated in a stream of C₃H₆/He at 400 °C showed new bands at 616, 390, and 210 cm⁻¹, characteristic of the Ag₆MoO₁₆ intermediate phase. The obtained results suggested that this formed AgMo/Ti-HMS₁₀ phase could most likely be relevant for selective epoxidation of propylene. However, during the reaction of C₃H₆ with AgMo/HMS, the formation of this intermediate was hardly detected. On the other hand, the hydrogen temperature-programmed reduction measurements indicated improved reducibility of MoO₃ in the AgMo/Ti-HMS₁₀ catalyst, which acknowledged the role of Mo⁶⁺ in gaining electrons from silver to form positively charged Ag. This could reduce the effective charge of the adsorbed oxygen on silver sites and in turn favor the epoxidation path of propylene rather than the combustion route. Also, during the reaction of C₃H₆ with NaAgMo/Ti-HMS₁₀ at 400 °C, two new Raman bands were detected at 277 and 350 cm⁻¹, characteristic of Ag₂MoO₄.

1. INTRODUCTION

Direct gas-phase catalytic epoxidation of propylene (DPO) has received much attention in the last few years as the currently used multiple step processes (viz., chlorohydrin and hydroperoxidation) are extremely energy-consuming and cause some environmental problems. Ag-based catalysts have been extensively studied in DPO in the last years by several researchers. The chemical structure of the industrial catalyst is usually complex involving many elements. For commercialization of DPO process over Ag-based catalysts, additional work seemed to be required. This should assist in the identification of the suitable promoters and moreover in understanding their roles in selective propylene oxide (PO) production. Ag catalysts promoted by MoO₃ and deposited on different materials, such as CaCO₃, CaF₂, SiO₂, TiO₂, ZrO₂, TiO₂–SiO₂, and TiO₂–ZrO₂, were developed by Jin et al. as promising catalysts for DPO to PO in the presence of only molecular oxygen. Ag–MoO₃ supported on ZrO₂ was the more selective one for PO formation at 400 °C, 0.1 MPa, and a space velocity of 7500 h⁻¹. A selectivity to PO of 60.3% was achieved with only propylene conversion approaching 1.0%. Although Ag–MoO₃ supported on TiO₂–SiO₂ was the more stable and active one, at 300 °C, 0.1 MPa, and a space velocity of 7500 h⁻¹, it achieved a selectivity to PO of 2.0% and to CO₂ of 92.7%, with propylene conversion less than 1.0%. The improvement of the supported Ag–MoO₃ catalyst is still demanded to enhance its catalytic performance in DPO. Concerning the role of silver particle sizes on propylene epoxidation, the larger particle sizes of Ag in the mentioned catalytic system were considered to be beneficial to improve the epoxidation performance. However, significant differences between the suggestion of Jin et al. and other views in several related studies were recognized, for example:

- There is a significant difference between the size of the selective silver particles for DPO using Ag supported on an alumina film as reported by Lei group (~3.5 nm)
and that identified by Jin and his co-workers (viz., 300–500 nm) for Ag−MoO3/ZrO2.10

- The study of Lu et al. on Ag/CaCO3 catalyst showed that DPO at 200–220 °C was structure-insensitive with respect to Ag particle size ranging from 50 to 660 nm.14 Later on, in another work by the same group, the Ag particles of sizes between 400 and 700 nm supported on either CaCO3 or α-Al2O3 were found to exhibit the highest propylene selectivity to PO at 260 °C.15

- Zemichael and his co-workers also found that K-promoted Ag/β-Al2O3 catalysts containing silver crystallites of size in 20–40 nm range produced the maximum PO yield.16

- According to Wang et al., Ag particles of 40.1 nm size led to combustion of propylene over 19.9 wt % Ag/TS-1.17 However, Guo et al. indicated that 2 wt % Ag/TS-1 catalyst of 8.0 nm Ag particles size achieves a considerable selectivity to PO (~94%) in C3H6 oxidation in the presence of H2 and O2, but with a very low conversion (1.9%).18

- Recently, Ghosh et al.18 reported that silver nanoparticles (<5 nm) supported on WO3 nanorods successfully catalyzed the DPO.

On the other hand, several studies have found that the selectivity of Au particles in DPO was also extremely sensitive to their size and shape. The reaction of propene with O2 and H2 using Au particles with smaller size, for example, 1.5–2.0 nm, produced mainly propane. The particles larger than 4–5 nm could assist oxidation of propene to CO2 and H2O.19–21 Adapting titanium-containing hexagonal mesoporous silica (Ti-HMS) as a support for Au particles improved their catalytic performance in DPO by O2/H2 mixture. The superior catalytic performance in production of PO in this case was attributed to the homogeneous dispersion and uniformity of titanium species controlling the size of Au particles (~4 nm).22

The present study was undertaken at shed more light on the impact of modification of hexagonal mesoporous silica by titanium on the size of Ag particles and consequently on the silver catalytic performance in the DPO reaction in the presence of promoters (viz., MoO3 and NaCl). For this aim, a series of catalysts with Ag particles of different sizes have been synthesized, having the same composition of Ag, Mo, and NaCl (as promoters) and hexagonal mesoporous silica (HMS) as a support. Controlling of the Ag particles sizes was performed through incorporation of different amounts of Ti into HMS support.22 A trial was also done to control the reducibility of silver and MoO3 by modifying the AgMo/Ti-HMS catalysts with NaCl. The catalytic functionality of the as-synthesized catalyst systems was studied in DPO using solely molecular oxygen at atmospheric pressure in a tubular down flow reactor.23 Detailed investigation of the various physicochemical characteristics of the catalyst samples was displayed through several techniques, for example, N2 physisorption, hydrogen temperature-programmed reduction (H2-TPR), X-ray diffraction (XRD), transmission electron microscopy (TEM), energy-dispersive X-ray (EDX) mapping, Fourier-transform infrared spectroscopy (FT-IR), UV–vis spectroscopy, and potentiometric acid–base titration.24 In addition, in situ laser Raman spectroscopy was used as a powerful technique for investigating the catalytic materials under the reaction conditions.25 The study was extended to characterize the AgMo/Ti-HMS catalysts during the reduction by propylene at 400 °C at different time intervals, followed by reoxidation with oxygen. The objective of involving the Raman spectroscopic features by changing the Ag particle sizes was to confirm the structure–performance relationships and to explore the synergism profile of the catalyst components, namely, Na, Ag, Mo, and Ti.

### 2. RESULTS AND DISCUSSION

#### 2.1. Textural Characteristics

The surface parameters of the catalysts under study, derived from the obtained N2–adsorption–desorption isotherms, are summarized in Table 1. All the titanium-containing HMS samples, including AgMo/Ti-HMS, catalysts, exhibited type IV isotherms in the IUPAC classification, almost characteristic for highly ordered mesoporous materials, with H1-type hysteresis loop indicating a narrow distribution of relatively uniform cylindrical pores26 (Figure S1 in the Supporting Information corresponds to typical large-pore mesoporous materials with cylindrical channels). It is clear from Table 1 that, upon loading Ag and Mo onto the different titanium containing hexagonal mesoporous silica (Ti-HMSn) supports, the Brunauer–Emmett–Teller (BET) surface area and the pore volume decrease, while the pore diameter is slightly increased, as compared to the pure Ti-HMSn supports. This may refer to some incorporation of Ag and/or Mo in the HMS pore system.

| sample | (Si/Ti)a molar | Ag wt (%) | Mo wt (%) | S BET (m2 g−1) | Vp (cm3 g−1) | pore diameterb (nm) | p.z.c |
|--------|----------------|-----------|-----------|---------------|-------------|---------------------|------|
| Ti-HMSn | 5.5 | 627.3 | 0.482 | 3.1 | 9 |
| Ti-HMSn10 | 11.9 | 692.1 | 0.61 | 3.4 | 8.8 |
| Ti-HMSn20 | 21.0 | 871.5 | 0.782 | 3.6 | 5.2 |
| Ti-HMSn40 | 42.3 | 793 | 0.70 | 4.1 | 6.6 |
| AgMo/Ti-HMSn5 | 5.5 | 365.6 | 0.35 | 3.9 | 9.4 |
| AgMo/Ti-HMSn10 | 11.4 | 327.8 | 0.37 | 4.5 | 9.2 |
| AgMo/Ti-HMSn20 | 20.5 | 334.2 | 0.36 | 3.7 | 9.4 |
| AgMo/Ti-HMSn40 | 45.0 | 309.8 | 0.31 | 3.4 | 9.6 |

“Determined by ICP measurements. aCalculated from the desorption branch of nitrogen isotherm by using the Barrett–Joyner–Halenda model.

#### 2.2. XRD Analysis

The XRD patterns of AgMo/Ti-HMSn, Ag/Ti-HMSn, and NaAgMo/Ti-HMSn catalysts are depicted in Figures 1, S2, and S3 (Supporting Information), respectively. For Ag/Ti-HMSn, the diffraction peaks of d spacings 2.34, 2.03, 1.44, and 1.23 Å related to the crystal faces of Ag (1 1 1), (2 0 0), (2 2 0), and (3 1 1) (JCPDS file, 87-0720) were detected (Figure S2). For comparison, the diffraction peaks of d-spacings 2.68, 2.32, 1.64, and 1.402 Å, characteristic of AgO phase (JCPDS file, 03-0796), and those of d-spacings 2.79, 2.68, and 1.418 Å, characteristic of AgO phase (JCPDS file, 43-1038), are represented in Figure S2. It is obviously shown from
Figure 1. XRD patterns of titanium containing hexagonal mesoporous silica (Ti-HMS)-supported silver molybdenum oxides catalysts. Peaks marked by the symbol “O”, “×”, “◊”, and “Δ” assigned to MoO₃, AgO, Ag₂O, and Ag, respectively.

Figure 1 that the same Ag, Ag₂O, and AgO phases can be distinguished in the diffraction patterns of all AgMo/Ti-HMSᵣ catalysts. The XRD patterns of NaAgMo/Ti-HMSᵣ catalysts did not show detectable change in the strength order of different peaks of Ag, Ag₂O, AgO, and MoO₃ phases after doping of AgMo/Ti-HMSᵣ with NaCl. On the other hand, small-angle XRD pattern (Figure S4) of the synthesized Ti-HMS₁₀ shows a single diffraction peak at 2θ = 1.8° due to the (100) reflection, which confirm the presence of HMS of mesoporous structure with short-range hexagonal symmetry.²²

2.3. Surface Acidity. The variation of both ΔΓ₋₋₋ (amount of acid) and ΔΓ₊₊₊ (amount of base) with pH for the different Ti-HMSᵣ supports and their corresponding Ag--MoO₃-supported catalysts as well as the catalysts modified by NaCl is shown in Figures 2 and S5–S7. It is evident that the loading of silver, molybdenum, or sodium chloride over the different Ti-HMSᵣ supports resulted in a shift in the point of zero charge (p.z.c.) to a higher pH values (Table 1). The obtained results suggest that the surfaces of supported Ag--MoO₃ catalysts exhibit weaker acidity than those of the parent Ti-HMSᵣ supports. This may be linked with the interaction of both Ag and MoO₃ species, most likely with the acidic hydroxyl groups of these supports.

2.4. FT-IR Analysis. The incorporation profile of titanium in the silica framework could be confirmed through the FT-IR analysis (Figures S8 and S9). It seems of special interest that both the Ti-HMSᵣ and Ag/Ti-HMSᵣ samples exhibit a band at around 960 cm⁻¹ in their spectra. This band has been widely used to characterize the incorporation of metal ions in the silica framework. The stretching Si–O vibration mode is known to be perturbed by the presence of neighboring metal ions.⁷

2.5. UV--Vis Spectroscopic Analysis. As shown from the UV--vis spectra of the various Ti-HMSᵣ catalysts (Figure S10a), all the samples exhibit the characteristic intraframework tetrahedral-coordinated titanium band at ca. 220 nm.⁹,²³,²⁷,²⁸ However, a very broad band 240–320 nm detected in the spectra (Figure S10b), may characterize the six- or eightfold coordination Ti(IV) species that are most probably generated through the hydration of tetrahedral coordinated species.²⁷–²⁹

In addition, the spectrum of Ti-HMSᵣ shows a shoulder at ca. 330 nm, attributable to bulk titanium oxide.³⁰

The band at ca. 230 nm, characteristic of the intraframework tetrahedral coordinated titanium species, is retained in the spectra of all samples in Figure 3.²³,²⁷,²⁸ On the other hand, the spectra of Ag/HMS and Ag/Ti-HMS₁₀ (Figure 3a,b) show a broad peak centered at 470 nm, which may be linked with the formation of either Ag or Ag₂O aggregates.²⁷,³¹ However, in the case of Ag/Ti-HMS₁₀ (Figure 3c), the absence of this band may point to the effect of increasing Ti content in enhancing even dispersion of Ag species on the Ti-HMS₁₀ surface, effecting the strong Ag--Ti interaction. Moreover, as shown in Figure 3d,e, the observed broad band extending in the 400–600 nm range for both AgMo/Ti-HMS₁₀ and NaAgMo/Ti-HMS₁₀ samples may be referred to the aggregation of silver particles. It can thus be suggested that molybdenum and sodium chloride have negative effects on Ag dispersion, reflecting most probably the strong interaction between these species (Mo and Na) with silver.

2.6. TEM--EDX Analysis. The TEM images of Ag/HMS and Ag/Ti-HMSᵣ samples of different Ti contents are depicted in Figure 4. The aggregation of Ag particles with an average size of 24.3 nm on the parent silica (HMS) support of zero titanium content is clearly demonstrated in Figure 4a, while the particle size distribution histogram is represented in Figure 4e.
The addition of titanium to HMS obviously results in a slight decrease of Ag average particle size to 23.0 nm as shown in Figures 4b and S11a, especially for the Ag/Ti-HMS40 sample. By increasing the Ti content, from a Si/Ti molar ratio of 40−10, a further decrease in Ag particle size is noticed. The TEM images (c and d in Figure 4) show almost spherically shaped Ag nanoparticles with average sizes of 6.8 and 7.8 nm in Ag/Ti-HMS10 and AgMo/Ti-HMS10, respectively, as calculated from particle size distribution histograms (Figure S11b) and Figure 4f. The measured average particle size of Ag in the AgMo/Ti-HMS10 sample seems to be an approximate value because of the presence of Mo particles in the sample and further characterization of AgMo/Ti-HMS10 system is necessitated. However, this value was taken into account in our discussion as the weight percentage of Ag in the catalyst was ∼5 times higher than that of Mo, which led us to neglect the Mo particles size effect. It can also be observed that the Ti-HMS10 surface in Figure 4 (images c and d) is largely covered by Ag clusters. Moreover, the wormhole mesoporous structure of the HMS support in Ag/Ti-HMS10 is indicated in the high-magnification image (Figure S12).

The EDX spectra and mapping image collected for AgMo/Ti-HMS10 (Figure S13 and Figure 5) confirm the existence of homogeneously distributed silver and Mo on the top surface of the Ti-HMS10 support, occupying the same location with Ti on the HMS surface. These species seem to be in good contact as illustrated in the EDX mapping morphological image (Figure 5), which shows Ag, Mo, and Ti as having a large contact area on the HMS support with enhanced dual−parallel interactions (mostly between Ag and Ti and between Ag and Mo species).

2.7. Hydrogen Temperature-Programmed Reduction. As shown in the TPR curve of Ag/Ti-HMS10 catalysts (Figure 6a), the reduction peak at $T_r = 210 \degree C$ is characteristic of well-dispersed silver oxide clusters or ions, while that one at $T_r = 843 \degree C$ can be attributed to reduction of Ti-HMS support. For the Mo/Ti-HMS10 catalyst, four reduction peaks are observed (Figure 6b) in the temperature range from 200 to 900 °C, indicating the stepwise reduction of Mo6+ to Mo5−35 The two peaks at 395 and 470 °C can be assigned to the reduction of well dispersed poly-molybdate to MoO2 and reduction of crystalline MoO3 to MoO2, respectively.33,34 The reduction of MoO2 to Mo0 is represented in the third and fourth peaks at 701 and 870 °C. It seems that the fourth reduction peak of Mo4+(MoO2) to Mo0 at 870 °C is overlapped with that one characteristic of the reduction of Ti-HMS support.

In the TPR profile of AgMo/Ti-HMS10 catalyst (Figure 6c), the first peak at 268 °C seems to most likely be attributable to the reduction of Ag2O, which in turn is shifted to a higher temperature by 58°, as probably effected by Ag−Mo interaction. Furthermore, it becomes wider as compared with that of Ag/Ti-HMS10 (Figure 6a). The main two peaks corresponding to the reduction of MoO3 to MoO2 are also shifted to higher temperatures, viz., 409 and 511 °C, being evidently weaker than those peaks observed at 395 and 470 °C for the neat Mo/Ti-HMS10. This may confirm the strong interaction between silver species and MoO3, which can clearly be supported by the acidity results illustrated in Figure 2. On
the other hand, the peak corresponding to reduction of MoO\textsubscript{3} to Mo\textsuperscript{0} (viz., 870 °C) becomes stronger and wider at temperatures ranged between 666 and 892 °C. This may also point to the effect of Ag in enhancing the reduction of Mo\textsuperscript{V} to Mo\textsuperscript{0}. Moreover, the addition of NaCl to AgMo/Ti-HMS\textsubscript{10} appears to induce an increase in the strength of the peak characteristic for reduction of silver oxide, at 248\textdegree, and that one of Mo\textsuperscript{V} to Mo\textsuperscript{0} reduction, at 480 \textdegree (cf., Figure 6d). These findings reveal the positive effect of NaCl on the exposure of more surface Ag oxide species, being accompanied with some complication in the reduction profile of MoO\textsubscript{3}.

2.8. In Situ Raman Spectroscopic Analysis. The in situ laser Raman spectrum of the Ti-HMS\textsubscript{i10} support, collected at ambient temperature, is shown in Figure S14. It consists of a broad strong band at 1070 cm\textsuperscript{-1} and two weak bands at 939 and 512 cm\textsuperscript{-1}, most probably in a parallel manner with that one reported previously for titanium-containing hexagonal mesoporous silicas.\textsuperscript{22} However, a new weak band at 147 cm\textsuperscript{-1}, which corresponds to extra-frame work titanium species, can be observed in the Raman spectrum of Ti-HMS\textsubscript{i10} sample, which corresponds to extra-frame work titanium species, can be observed in the Raman spectrum of Ti-HMS\textsubscript{i10} sample (Figure S14c).\textsuperscript{36} The increase of titanium leads to an increase in the intensity and the breadth of this band (at 147 cm\textsuperscript{-1}) in the spectrum of Ti-HMS\textsubscript{i10} (Figure S14d).

On the other hand, two new bands at 717 and 484 cm\textsuperscript{-1}, characteristic of Ag\textsubscript{2}O species,\textsuperscript{37-39} are detected in the Raman spectrum of Ag/Ti-HMS\textsubscript{i10} (Figure 7b), besides those bands observed for Ti-HMS\textsubscript{i10} support. Also, the spectrum of AgMo/Ti-HMS\textsubscript{i10} (Figure 7c) reveals the presence of a new band at 815 cm\textsuperscript{-1}, which can be assigned to MoO\textsubscript{3}.\textsuperscript{40}

By heating the AgMo/Ti-HMS\textsubscript{i10} sample in a flow of C\textsubscript{3}H\textsubscript{6}/He at 400 \textdegree C, no significant changes could be detected in the Raman features of AgMo/Ti-HMS\textsubscript{i10} through 1.0 h duration. This observation can be attributed to the low concentration of Mo (∼4 wt %) in the catalyst. It is worth mentioning that Raman cannot detect any expected changes in the band features (viz., intensity, broadening, shift, appearance, and disappearance) in the spectrum of AgMo/Ti-HMS\textsubscript{i10} sample, unless these changes are accumulated with time. Therefore, after 1.0 h of exposure of this sample to propylene atmosphere at 400 \textdegree C, the spectrum obtained (Figure 8) declared the appearance of two weak broad bands at 616 and 390 cm\textsuperscript{-1}. Continuous exposure of AgMo/Ti-HMS\textsubscript{i10} pellets to a flow of 10\% C\textsubscript{3}H\textsubscript{6} in He for 2.0 h, at the same temperature (400 \textdegree C), resulted in the appearance of a new additional band at 210 cm\textsuperscript{-1} and disappearance of the two weak bands at 717 and 484 cm\textsuperscript{-1} characteristic of Ag\textsubscript{2}O, and that one of MoO\textsubscript{3} at 815 cm\textsuperscript{-1} (Figure 8). These new bands appeared at 616, 390, and 210 cm\textsuperscript{-1} are most likely assigned to Ag\textsubscript{2}O\textsubscript{3} (Ag/α-MoO\textsubscript{3}).\textsuperscript{31} Moreover, a steady decrease in the intensities of all bands of AgMo/Ti-HMS\textsubscript{i10} sample was observed by increasing the exposure time from 2.0 to 24 h in propylene atmosphere at 400 °C. Cooling the AgMo/Ti-HMS\textsubscript{i10} pellet back to ambient temperature in He atmosphere (Figure 9c) restored the intensities of the band characteristic of Ag\textsubscript{2}O, and that one of MoO\textsubscript{3} at 815 cm\textsuperscript{-1}.

![Image](https://example.com/image.jpg)

Figure 7. Raman spectra of (a) Ti-HMS\textsubscript{i10} support, (b) Ag/Ti-HMS\textsubscript{i10} and (c) AgMo/Ti-HMS\textsubscript{i10} collected at 25 °C.

![Image](https://example.com/image.jpg)

Figure 8. Raman spectrum (a) of AgMo/Ti-HMS\textsubscript{i10} collected in flow of 22.7\% C\textsubscript{3}H\textsubscript{6}/He at 25 °C and the spectra of the same sample collected in flow of 22.7\% C\textsubscript{3}H\textsubscript{6}/He at 400 °C at different time intervals.

![Image](https://example.com/image.jpg)

Figure 9. Raman spectra of (a) AgMo/Ti-HMS\textsubscript{i10} collected in flow of 22.7\% C\textsubscript{3}H\textsubscript{6}/He at 25 °C, (b) that collected in flow of C\textsubscript{3}H\textsubscript{6}/He at 400 °C for 24 h, (c) collected at 25 °C in flow of He after reduction in flow of propylene at 400 °C for 24 h, and (d) collected at 25 °C after reoxidation with 10\%O\textsubscript{2}/He for 2.0 h at 400 °C.
AgMo/Ti-HMS\textsubscript{10} sample, as suggested by H\textsubscript{2}-TPR and surface acidity results of the present study.

In contrast, the Raman spectra associated with heating of AgMo/HMS showed different features, where heating of this sample in a stream of C\textsubscript{3}H\textsubscript{6} at 400 °C for 18 h (Figure 10c,d) did not distinctly show the bands characteristic of the Ag\textsubscript{10}Mo\textsubscript{10}O\textsubscript{4} phase that was observed in the case of AgMo/Ti-HMS\textsubscript{10} sample. The only change observed is the steady decrease in the intensities of all bands with increasing heating time. Cooling of the sample back to room temperature (Figure 10e) restored the sharper Raman features present in the spectra of AgMo/HMS prior to heating in C\textsubscript{3}H\textsubscript{6} at 400 °C, which may indicate that these detected changes are almost refereed to the temperature treatment.

On the other hand, the Raman spectra of NaAgMo/Ti-HMS\textsubscript{10} collected during the heating in a flow of C\textsubscript{3}H\textsubscript{6}/He at different time intervals at 400 °C are represented in Figure 11. As shown, for instance, in Figure 11b, after 1 h exposure of the sample to propylene atmosphere at 400 °C, the position of the band at 815 cm\textsuperscript{-1} characteristics of MoO\textsubscript{3} has shifted to higher wave number by about 9 cm\textsuperscript{-1}. However, this band disappeared after 24 h of continuous exposure to a stream of C\textsubscript{3}H\textsubscript{6} in He (Figure 11d). Also, it is clear from Figure 11e that the reappearance of this band has occurred after cooling the sample back to ambient temperature. Yet, the cooling or reoxidation of the sample in oxygen atmosphere (Figure 11f) did not restore the band position observed prior to the thermal treatment (Figure 11a). The obtained results may indicate that the noticed small shift in band position arises because of the interaction between MoO\textsubscript{3} and NaCl.\textsuperscript{42} On the other hand, the Raman spectrum associated with heating of NaAgMo/Ti-HMS\textsubscript{10} with C\textsubscript{3}H\textsubscript{6} for 2.0 h at 400 °C (Figure 11) shows the appearance of two weak bands at 277 and 350 cm\textsuperscript{-1}, referred probably to the presence of a well-defined Ag\textsubscript{2}MoO\textsubscript{4} intermediate phase.\textsuperscript{31}

### Table 2. Catalytic Performance of Supported Silver and Molybdenum Oxides on Ti-HMS\textsubscript{n} and That of Catalysts Modified by NaCl\textsuperscript{a}

| catalyst     | C\textsubscript{3} conv. (%) | PO | Acet | AC | CO\textsubscript{2} | other |
|--------------|-----------------------------|----|------|----|---------------------|-------|
| HMS          | 1.2                         | 0  | 0    | 4.3| 94.4                | 1.3   |
| Ag/HMS       | 1.9                         | 0.1| 0.0  | 5.7| 92.4                | 1.8   |
| Mo/HMS       | 0.9                         | 0.0| 0.0  | 4.8| 93.0                | 2.2   |
| AgMo/HMS     | 10.1                        | 2.7| 3.1  | 6.3| 86.1                | 1.7   |
| Ti/HMS\textsubscript{5} | 13.2                      | 0.1| 0.7  | 5.6| 92.2                | 1.4   |
| Ti/HMS\textsubscript{10} | 23.3                      | 0.3| 1.9  | 4.4| 91.7                | 1.7   |
| Ti/HMS\textsubscript{20} | 14.4                      | 0.0| 0.4  | 5.7| 92.3                | 1.6   |
| Ti/HMS\textsubscript{50} | 5.3                       | 0.7| 1.9  | 4.2| 91.4                | 1.8   |
| Mo/Ti-HMS\textsubscript{5} | 8.0                       | 0.0| 13.6 | 3.7| 78.4                | 4.3   |
| Mo/Ti-HMS\textsubscript{10} | 6.1                       | 0.0| 8.9  | 3.3| 84.1                | 3.7   |
| Mo/Ti-HMS\textsubscript{20} | 5.7                       | 0.0| 20.3 | 11.0| 63.2                | 5.5   |
| Mo/Ti-HMS\textsubscript{40} | 4.3                       | 0.0| 17.1 | 9.3| 68.5                | 5.1   |
| Ag/Ti-HMS\textsubscript{5} | 0.9                       | 6.0| 11.5 | 6.9| 75.5                | 0.1   |
| Ag/Ti-HMS\textsubscript{10} | 6.5                       | 2.3| 5.3  | 8.3| 82.8                | 1.3   |
| Ag/Ti-HMS\textsubscript{20} | 2.2                       | 1.6| 2.6  | 6.9| 87.4                | 1.5   |
| Ag/Ti-HMS\textsubscript{50} | 2.3                       | 3.3| 7.7  | 7.0| 81.4                | 0.6   |
| AgMo/Ti-HMS\textsubscript{5} | 23.9                      | 3.9| 12.9 | 5.9| 76.0                | 1.3   |
| AgMo/Ti-HMS\textsubscript{10} | 17.7                      | 23.6| 44.7 | 6.4| 24.3                | 1.0   |
| AgMo/Ti-HMS\textsubscript{20} | 24.3                      | 6.2| 13.7 | 5.6| 72.7                | 1.8   |
| AgMo/Ti-HMS\textsubscript{40} | 18.1                      | 13.3| 17.1 | 8.7| 59.4                | 1.5   |
| NaAgMo/Ti-HMS\textsubscript{5} | 14.3                      | 6.7| 4.3  | 2.9| 88.2                | 0.9   |
| NaAgMo/Ti-HMS\textsubscript{10} | 9.0                        | 30.3| 9.5  | 3.1| 55.8                | 1.3   |
| NaAgMo/Ti-HMS\textsubscript{20} | 12.6                      | 11.2| 4.9  | 2.8| 80.1                | 1.0   |
| NaAgMo/Ti-HMS\textsubscript{50} | 10.2                      | 18.1| 6.8  | 5.2| 63.9                | 1.7   |

\textsuperscript{a}Reaction parameters: C\textsubscript{3}/O\textsubscript{2} = 22.7%/9.0% and additive N\textsubscript{2} total flow rate = 100 mL/min, catalyst weight = 0.1 g, T = 400 °C and after 6 h TOS. PO = propylene oxide, Acet = acetaldehyde, AC = acetone, other = cracking products [C\textsubscript{2}H\textsubscript{6}, C\textsubscript{2}H\textsubscript{4}, C\textsubscript{2}H\textsubscript{6} + their oxygenated species (acrolein)].

Figure 12 represents the variation of propylene conversion in terms of DPO products (acetone, acetaldehyde, PO, and CO\textsubscript{2}) with Si/Ti ratio. It is evident that the pure HMS support is inactive in the conversion of DPO to PO under the studied reaction conditions and (only CO\textsubscript{2} were produced) (Table 2). For Ti-HMS\textsubscript{n} supports, very low selectivity to PO (<1.0%) could be noticed at the different Si/Ti ratios (Figure 12a).
Similarly, Sugiyama et al.\textsuperscript{43} indicated that incorporation of Ti into MCM-41 resulted in no activity for the epoxidation of propylene. Moreover, acetone was detected as the major oxygenate organic product, where the selectivity to acetone remained nearly constant with Si/Ti ratio ranging between 10 and 40 (Figure 12a). Also, no remarkable change could be observed in selectivity to acetone by doping Ti-HMS\textsubscript{n} supports with Ag or Mo and by the presence of NaCl. The selectivity remained almost constant in the range 4−6% at different Si/Ti ratios (Figure 12b−d). It can thus be suggested that Ti-HMS\textsubscript{n} supports are responsible for conversion of propylene to acetone over this type of catalysts. Referring to the report of Liu et al.,\textsuperscript{44} it can be found that propylene can be converted to the carbocation intermediate $\text{CH}_3^+$ over Brønsted acidic sites, which is then converted into acetone. In view of the acidity/basicity results in the present work of Ti-HMS\textsubscript{n} indicating a good Bronsted acidic behavior (Figure S5), one can clearly propose that the conversion of propylene to acetone over Ag/Ti-HMS\textsubscript{n} AgMo/Ti-HMS\textsubscript{n} or NaAgMo/Ti-HMS\textsubscript{n} catalysts is mainly encouraged by Ti-HMS\textsubscript{n} supports.

On the other hand, it is clear that doping of Ti-HMS\textsubscript{n} supports with Ag enhanced their selectivity to PO and reduced the CO\textsubscript{2} production (Table 2). However, the maximum selectively to PO observed over Ag/Ti-HMS\textsubscript{n} was only 6% with a conversion of 0.9% (Figure 12b). In addition, the Ag/Ti-HMS\textsubscript{n} catalysts seemed to exhibit more activity than Ag/Al\textsubscript{2}O\textsubscript{3} in conversion of DPO to PO (Table 2). Zemichael et al. suggested that K-promoted Ag/ CaCO\textsubscript{3} catalysts containing silver crystallites of sizes in the range of 20−40 nm produce the maximum PO yield.\textsuperscript{16} However, the Ag particles in our present work supported either on neat unmodified HMS or on modified HMS by low amount of titanium (Si/Ti = 40), with sizes ranging between 5 and 40 nm exhibited very low selectivity to PO (Figure 13). On the other hand, Lei et al.\textsuperscript{13} have reported that the Ag/Al\textsubscript{2}O\textsubscript{3} catalyst containing smaller size Ag particles (viz., ~3.5 nm) displayed higher PO performance. The TEM and UV−vis results of the present study seemed to run in good agreement with this finding.\textsuperscript{13} As shown in Figure 13, a significant decrease in average particle size of Ag is observed with the increase of Ti content in the HMS (i.e., with a decrease of Si/Ti ratio from 40 to 10). Such a decrease in Ag average particle size is accompanied with a noticeable increase in the catalyst performance in the production of PO. The maximized PO yield can be referred to the strong interaction between Ag nanoparticles and surface-exposed intraframework titanium species, in view of our results of surface acidity and EDX mapping (cf. Figures 2 and 5).

 Modification of HMS with a higher amount of Ti (e.g., Si/Ti ratio = 10), decreased Ag average particle size to ca. 6.8 nm and led to a clear improvement in the PO production. Yet, the turnover frequency (TOF) parameter of 0.065 s\textsuperscript{−1} for the Ag/Ti-HMS\textsubscript{10} catalyst, calculated as based on the total loaded amount of Ag, is still much lower than that one reported by Lei et al., namely, 1.0 s\textsuperscript{−1} for the Ag/alumina.\textsuperscript{13} In terms of particle size distribution profiles, one may attribute the discrepancy in TOFs to the uneven particle size distribution of Ag NPs in the studied catalysts (being ranged between 5 and 40 nm). Nevertheless, the most active sample (Ag/Ti-HMS\textsubscript{10}) had an average size of Ag nanoparticles in the range of 2−12 nm. It can thus be concluded that the propylene epoxidation over Ag-based catalysts supported on HMS or Ti-HMS, at the given operational conditions, is structure-sensitive with respect to the Ag average particle size.

Generally, the role of Ag average particles size seems to be still unclear in the case of neat Ag-supported catalysts, that is, in the absence of a promoter (Mo or Na). As shown in Figure 13, the PO yield is slightly increased from 0.0013 to 0.0695 (mol/mol Ag) by reducing the average particle size from 24.3 to 23.0 nm in the case of Ag/HMS and Ag/Ti-HMS\textsubscript{10} respectively. However, a drastic decrease in Ag average particle size in Ag/Ti-HMS\textsubscript{40} from 23.0 to 6.8 nm in Ag/Ti-HMS\textsubscript{10} could only slightly enhance the PO yield from 0.0695 to 0.1400 (mol/mol Ag). This may reveal that the role of titanium in enhancement of catalytic performance of Ag/Ti-HMS\textsubscript{40} is not restricted in decreasing the Ag average particle sizes. On the other hand, incorporation of a very small amount of Ti into the HMS can create Lewis acid sites.\textsuperscript{15} These acid sites lead to withdrawal of electrons from Ag species, transferring it to the active electron-deficient (Ag\textsuperscript{δ−}) species.\textsuperscript{10} The higher selectivity of Ag/Ti-HMS\textsubscript{10} to PO than that of Ag/HzMS appears thus to be a result of both the smaller particle sizes of AgNPs and the Lewis acid behavior of Ti-incorporated-HMS support. According to this discussion, further study seems to be still needed to solve such confusion.\textsuperscript{43}
In the case of supported AgMo on HMS catalysts, the addition of MoO_3 to Ag/HMS catalysts did not significantly improve the production of PO (Table 2). However, the addition of Mo to Ag/Ti-HMS was much more beneficial for the catalyst in enhancing the % conversion and producing mostly oxygenates (viz., PO and acetaldehyde). The optimal direct propylene functionality to PO at 400 °C was achieved by using AgMo/Ti-HMS_10. The selectivity to PO increased by increasing the Ti content at Si/Ti = 10, followed by a decrease with further increase of Ti content at Si/Ti = 5 in the catalyst (Figure 12c). Liu et al. have reported that some active electrophilic oxygen species, such as [O\(^{-}\)] and [O_2\(^{-}\)], can be formed during the adsorption of O\(_2\) molecule on the catalyst surface. The electrophilic oxygen [O\(_2\)^{-}\)] attacks the C\(=\)C bond of propylene to form unstable peroxy complexes, which in turn causes the break of C\(=\)C to form acetaldehyde as well as formic acid that may be oxidized to CO\(_2\) and H\(_2\)O. However, [O\(^{-}\)] attacks the C\(=\)C bond of propylene to form PO. On the other hand, Jin et al. suggested, from X-ray photoelectron spectroscopy analysis of AgMo/ZrO\(_2\) catalyst, that by transfer of an electron from silver to MoO\(_3\), to form Mo\(^{2+}\). They also suggested that Ag in highly oxidative state was helpful to produce electrophilic oxygen species, which played a positive role in the propylene epoxidation. According to the suggestions of Jin et al. and Liu et al., it appears that the observed higher performance of AgMo/Ti-HMS_10 to PO than that of unmodified AgMo/HMS can be attributed to the coexistence of smaller Ag particles in subnanometer dimension (of 6.8 nm average sizes) in AgMo/Ti-HMS_10 than in AgMo/HMS (of 24.3 nm average sizes) together with MoO\(_3\) particles encouraging their interaction. The interaction product (AgMoO\(_2\)) phase was detected by in situ Raman in AgMo/Ti-HMS_10 but not in AgMo/HMS in the flow of propylene at 400 °C. It seems that Ag_50 species in this AgMoO\(_2\) phase improved the electrophilic property of adsorbed oxygen on AgMo/Ti-HMS_10, therefore enhancing the DPO to PO and acetaldehyde.

Furthermore, the PO selectivity was found to decrease significantly with increasing Ti content (at the lowest Si/Ti molar ratio = 5) in the case of AgMo/Ti-HMS_10 catalyst (Figure 12c). Sugiyma et al. also reported that the addition of Ti to Al-Ti-MCM-41 resulted in an enhancement of the formation of CO\(_x\). Referring to our UV–vis results of Ti-HMS\(_5\) support, the observed decrease in the catalytic performance of AgMo/Ti-HMS\(_5\) can be ascribed to the presence of some bulk or extra-framework TiO\(_2\) species (cf, Figure S10). The negative effect of extra-framework TiO\(_2\) species on the performance of titanium silicate in DPO was previously reported by Lu et al. and Wang et al. Moreover, Jin et al. attributed the higher performance of AgMoO\(_3\)/ZrO\(_2\) in DPO to the role of ZrO\(_2\) support (as a P-type semiconductor) in acceptance of electrons from Ag, rendering it to be positively charged species, thus reducing the negative charge of oxygen (O\(_{ads}\)) adsorbed on the silver surface. Such behavior may hinder the acid–base reaction between O\(_{2(ads)}\) (Lewis base) and allylic hydrogen (Lewis acid) of propylene, inhibiting most probably the complete oxidation of propylene and leading to increased selectivity to PO. However, the interaction of extra-framework TiO\(_2\) species (as n-type semiconductor) with Ag seems to play an opposite role to that of ZrO\(_2\) (as p-type semiconductor), that is, enhancing the negative charge of O\(_{ads}\) and directing thereby the reaction toward the deep oxidation of propylene by nucleophilic oxygen, viz., leading to less formation of PO. Based on these findings, it can be concluded that the presence of Ti in an appropriate amount within the hexagonal mesoporous silica controls the Ag particle sizes, leading to an improvement of the interaction between Ag and MoO\(_3\) and thus enhancing the AgMo/Ti-HMS\(_{10}\) catalyst’s selectivity to PO.

2.9.2. Different Factors Affecting the Catalytic Performance in DPO over AgMo/Ti-HMS\(_{10}\). 2.9.2.1. Effect of Reaction Temperature. Figure 14 displays the effect of reaction temperature on the AgMo/Ti-HMS\(_{10}\) performance in DPO process. By increasing the temperature, the propylene conversion increased and selectivity to acetone decreased. On the other hand, the selectivity toward both PO and acetaldehyde increased with increasing the reaction temperature up to 350 °C. However, at higher temperatures, for example, at 400 °C, the selectivity to PO and acetaldehyde decreased. This may be attributed to the formation of a large amount of CO\(_2\) because of either complete oxidation or decomposition of propylene. At 350 °C and space velocity 7500 h\(^{-1}\), the selectivity to PO of 27.9% was achieved with a propylene conversion of 9.0%.

2.9.2.2. Effect of Space Velocity. The effect of the space velocity on the performance of AgMo/Ti-HMS\(_{10}\) in DPO is shown in Figure 15. The propylene conversion decreased with increasing the space velocity, while the selectivity to PO and acetaldehyde increased. With a space velocity of 12,000 h\(^{-1}\) at 400 °C, a selectivity to PO of 43.2% was achieved with a propylene conversion of 14.1%. The reason behind the increase in selectivity to PO with increasing the space velocity is obviously that the higher space velocity shortens the
residence time of PO inside the catalyst bed, thus leading to lower deep oxidation extent of PO to CO2. Under these reaction conditions, the AgMo/Ti-HMS10 catalyst exhibited a good catalytic performance in DPO (Table 3), compared with the Ag-based catalysts reported earlier, especially those Ag catalysts supported on silica and/or titania.

### 2.9.2.3. Effect of Time-on-Stream

Figure 16 displays the time course of DPO over AgMo/Ti-HMS10, where a good stability of the catalyst in DPO was verified during the reaction time-on-stream over at least 20 h.

![Time course of the propylene conversion and PO yield over AgMo/Ti-HMS10 catalysts at 400 °C, space velocity 7500 h⁻¹, and 0.1 MPa.](image)

Figure 16. Time course of the propylene conversion and PO yield over AgMo/Ti-HMS10 catalysts at 400 °C, space velocity 7500 h⁻¹, and 0.1 MPa.

### 2.9.2.4. Effect of NaCl

The results of the effect of NaCl on the catalytic performance of AgMo/Ti-HMS system in production of PO are presented in Table 2. The addition of NaCl has increased the selectivity to PO, but with a significant decrease of propylene conversion. NaAgMo/Ti-HMS10 achieved 30.3% selectivity to PO, with only a low conversion of 9% at 400 °C and a space velocity of 7500 h⁻¹ (Table 2). Recalling the UV–vis and TEM results (Figures 3e and 4d), the low conversion observed for this catalyst can be attributed to the probable aggregation of Ag species affected by addition of NaCl to AgMo/Ti-HMS10. Significant changes were detected in the Raman features and TPR Profile of NaAgMo/Ti-HMS10. In terms of TPR results, an increase in the strength of the characteristic peak for reduction of silver oxide at 248 °C was observed (Figure 6d). This may reveal that more selective silver oxide (Ag₂O) species exist in the NaAgMo/Ti-HMS10 sample. However, the in situ Raman results of NaAgMo/Ti-HMS10 catalyst confirm the formation of Ag₂MoO₄ as an intermediate by heating of the sample in a flow of C₃H₆/He at 400 °C. One may conclude that NaCl promotes the interaction between silver species and molybdenum oxide to form selectively Ag₂O₄, which leads to the formation of Ag₂MoO₄ selective intermediate for DPO to PO over NaAgMo/Ti-HMS10. The higher selectivity of NaAgMo/Ti-HMS10 in DPO can be referred to the role of MoO₃ in the formed (Ag₂MoO₄) intermediate for acceptance of electrons from Ag, rendering it to be positively charged, thus reducing the negative charge of oxygen (Oₐds) adsorbed on the silver surface. Such behavior may hinder the acid–base reaction between O₂(ad) (Lewis base) and allylic hydrogen (Lewis acid) of propylene, which most probably inhibits the complete oxidation of propylene and leads to increase selectivity to PO.⁴⁶⁻⁴⁸

The NaAgMo/Ti-HMS₁₀ catalysts were found to follow the same trend of the variation of propylene selectivity with change of Si/Ti ratio as AgMo/Ti-HMS₂₀, undoped catalysts (Figure 12d). The selectivity to PO increased with increasing Ti content in the catalyst, attaining the maximum effect at Si/Ti = 10 and then decreasing at the ratio equal to 5.0.

### Table 3. Comparison between Performance of AgMo/Ti-HMS₁₀ Catalyst Understudy in Propylene Epoxidation and That of Both Supported Ag-Based Catalysts with MoO₃ and NaCl Promoters and Recent Catalysts Reported in Literature

| catalyst                                  | P (kPa) | T (°C) | GHSV (mL h⁻¹ g⁻¹) |  | stability TOS (h) | conv. (%) C₃H₆/O₂ | select. PO (%) | ref.       |
|-------------------------------------------|---------|--------|-------------------|---|------------------|------------------|---------------|-----------|
| Ag                                        | 101.3   | 350    | 18,000 h⁻¹        |   | NR               | 32.5/            | 0.35          | 5         |
| MoO₃ (0.255 mmol)/g-SiO₂                   | 506.6   | 300    | 1500 h⁻¹          |   |vx               | 12 h/(PS)        | 17.6/         | 43.6/49   |
| 2%Ag/Ti-1 (H₂O₂)                          | 101.3   | 150    | 4,000 h⁻¹         |   | NR               | 1.9             | 91/           | 17/17     |
| 19.9%Ag/Ti-1 (H₂O₂)                       | 101.3   | 4,000 h⁻¹ | NR               |   | comb.           | 0               | 8/           |           |
| 20%Ag–4%MoO₃                              | 101.3   | 350    | 7500 h⁻¹          |   | NR               | 3.5/0.6         | 57.9/         | 50/50     |
| 20%Ag–4%MoO₃/SiO₂                         | 101.3   | 400    | 7500 h⁻¹          | 6 h (UnSt) at 300 °C | 22.5             | 10.7           | 10/10     |
| 20%Ag–4%MoO₃/TiO₂                          | 101.3   | 400    | 12,000 h⁻¹        | 6 h (St) at 300 °C | /99.4            | 2.0            | 10/10     |
| 20%Ag–4%MoO₃/ZrO₂                          | 101.3   | 400    | 12,000 h⁻¹        | 6 h (PS) at 300 °C | /2.5             | 71.5           | 10/10     |
| 20%Ag–4%MoO₃/CaCO₃                        | 101.3   | 400    | 7500 h⁻¹          | 6 h (St) at 300 °C | /99.9            | 0.0            | 10/10     |
| 20%Ag–(3.75)Mo–(1.25)W/ZrO₂                | 101.3   | 460    | 3000 mL g⁻¹ h⁻¹   | 6 h (St) | ~12/             | 60.0/           | 51/51     |
| 20%Ag–(3.8)%Mo–1.2%W/ZrO₂                  | 101.3   | 460    | 12,000 mL g⁻¹ h⁻¹ | 6 h (St) | ~14/             | 84.0            | 52/52     |
| 20%Ag–4%MoO₃/La₅%–SiO₂                     | 101.3   | 400    | 7500 h⁻¹          | 20 h (St) | 11.4             | 17.0           | 53/53     |
| Au₀.₃Ag₂O₀.₄/Ti-1-B (H₂/O₂)                | 101.3   | 200    | 14,000 cm³ g⁻¹ h⁻¹ | 30 h (St) | 4.5/             | 84/             | 54/54     |
| Ag(56)–Na(1)/SrCO₃                        | 101.3   | 250    | 2.5 × 10⁻³ g·min⁻¹·mL⁻¹ | 0.5 h | 17.4            | 12.5/           | 43/43     |
| Ag nanocube/La₂O₃                         | 101.3   | 270    | 12,000 mL g⁻¹ h⁻¹ | NR  | 11.6             | 51.0            | 55/55     |
| 50%Ag/TiO₂ (rutile amine reduced) (steam promoted) | 101.3   | 260    | 7500 mL g⁻¹ h⁻¹ | 10 h (St) | 33.6/           | 6.1/            | 56/56     |
| Ni₂Ag₀.₃/BA-15                            | 101.3   | 220    | GHSV of 192 h⁻¹    | 10 h (St) | <1.0             | 70.7/           | 57/57     |
| 20%Ag–4%MoO₃/Ti-HMS                        | 101.3   | 400    | 12,000 h⁻¹        | 20 h (St) | 14.1             | 43.2/           | present work/|

⁴⁴⁷ https://dx.doi.org/10.1021/acsomega.9b03645
ACS Omega 2020, 5, 4469–4481

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“NR (nonreported), St (stable), UnSt (unstable), PS (partially stable), figure-NR (figure nonreported).”
3. CONCLUSIONS

In summary, a significant interaction has been observed between Ag particles and titanium-containing hexagonal mesoporous silica supports (Ti-HMS). Incorporating an appropriate amount of titanium in the support was shown to be necessary to attain a maximum interaction level. The interaction between Ag particles and titanium seemed to control the particle sizes of Ag on the Ti-HMS_{10} support, producing Ag nanoparticles (AgNPs) with sizes ranging between 2 and 12 nm. The Ag/Ti-HMS_{10} catalyst exhibited higher selectivity toward direct oxidation of PO by molecular oxygen than Ag/HMS. The higher selectivity of Ag/Ti-HMS_{10} to PO than that of Ag/HMS thus appears to be as a result of both the smaller particle sizes of AgNPs and the Lewis acid behavior of the Ti-incorporated-HMS support; however, further study seems to be still needed to solve such confusion.

The addition of MoO_{3} to Ag/Ti-HMS_{10} has a large positive effect on the selectivity toward PO. The degree of interaction between Ag and MoO_{3} in the AgMo/Ti-HMS_{n} catalysts depends on the sizes of silver particles on Ag/Ti-HMS_{n} systems. The presence of Ag particles of subnanometer sizes on Ti-HMS support surface seemed to increase the possibility of formation of Ag−MoO_{3} interactive selective sites. The involvement of these Ag−MoO_{3} sites in the reaction with propylene could be successfully confirmed by the aid of in situ thermo-Raman spectroscopy. The H_{2}-TPR analysis indicated that the presence of Ag centers in the Ag_{x}MoO_{y} intermediate phases encouraged them to be more positively charged, whereby the adsorbed oxygen atoms became more electrophilic and thus facilitated the reaction with the olefinic carbon of propylene to form PO.

4. EXPERIMENTAL SECTION

4.1. Materials Synthesis. 4.1.1. Synthesis of Ti-HMS. The titanium-containing hexagonal mesoporous silica supports, with Si/Ti molar ratios ranged between 5 and 40, were synthesized by using dodecyl amine as a soft template.\textsuperscript{22} A solution of 0.1 mol of tetraethyl orthosilicate and 0.01−0.025 mol of tetrabutyl orthotitanate in a mixture of ethanol (0.65 mol) and isopropl alcohol (0.1 mol) was first prepared at room temperature. This solution was slowly added under vigorous stirring for 20 min to the other solution consisting of dodecyl amine (0.027 mol), water (3.6 mol), and HCl (0.002 mol). The stirring was continued for 24 h to assist the templating procedure. The solid was then filtered, washed several times with deionized water, and dried under vacuum at 60 °C overnight. The template was removed by calcination in air at 650 °C for 5 h. The final product was denoted as Ti-HMS_{n}, where n is the Si/Ti molar ratio.

4.1.2. Synthesis of Supported Ag Catalysts. The different Ti-HMS_{n} samples (n = 5, 10, 20, and 40) loaded with silver (20 wt %) were prepared by a dry impregnation method.\textsuperscript{10} To an aqueous solution of AgNO_{3} (4.979 g) in distilled water, 12.0 g of the support was slowly added to form a slurry under vigorous stirring, adopting ultrasonication for homogenization at room temperature. After 10 min, the slurry was heated up to 80 °C, dried at 110 °C for 24 h, and then calcined at 400 °C for 4 h to get the finished catalysts (Ag/Ti-HMS_{n}).

4.1.3. Synthesis of Supported AgMo Catalysts. The different Ti-HMS_{n} supports loaded with silver (20 wt %) and molybdenum oxide (4 wt %) were furnished by applying the sequential impregnation method. For this aim, the AgNO_{3}—support slurry was impregnated with 5 mL of an aqueous solution of (NH_{4})_{2}MoO_{4}·4H_{2}O (0.78 g), using ultrasonication for homogenization. The rest of the procedure was the same as mentioned above for obtaining the finished AgMo/Ti-HMS_{n} catalyst samples.

4.1.4. Modification of Catalysts by Sodium Chloride. The as-synthesized AgMo/Ti-HMS_{n} catalyst (4.9 g) was mixed with aqueous solutions containing sodium chloride (1.71 mmol) and then dried at 110 °C for 2 h to produce the modified Na (2 wt %) AgMo/Ti-HMS_{n} samples.

4.2. Characterization Techniques. Chemical compositions of catalysts were determined through inductively coupled argon plasma (ICP) analyses using an iCAP 6500 Duo, Thermo Scientific. The changes in acidity were demonstrated via the potentiometric titration method, as expressed in terms of mmol/L g (catalyst sample).\textsuperscript{23} The XRD measurements were performed by adopting the Philips X’Pert MPD (multipurpose X-ray diffractometer) with Cu Kα_{1,2} radiation (λ = 1.5405 Å), measuring the 2θ in the range 10−80°. N_{2} physiosorption measurements were carried out using the surface area analyzer Quanta Chrome Nova 2200. Temperature-programmed reduction (H_{2}-TPR) was performed in Chem-BET 3000, Quantachrome. Freshly calcined catalyst (100 mg) was subjected to heat treatment (20 °C min^{-1} up to 1000 °C) in a flow (85 mL min^{-1}) of a mixture of hydrogen/nitrogen (5/95 vol %). Transmission electron micrographs were obtained using a JEOL JEM-2100 transmission electron microscope operated with an acceleration voltage of 200 kV (in HR configuration with a 50 nm² detector). Images were analyzed using ImageJ 1.41 software. EDX analyses were recorded using a Quanta FEG 250 microscope and equipped with EDX spectrometer (TexSEM Laboratories “TSL” EDAX, AMETEK, Inc, USA). Raman spectroscopic analysis was performed using a Horiba XploRA confocal Raman microscope (Horiba Jobin Yvon). The XploRA was a fully automated Raman microscope based on a 200 mm focal length spectrograph with four fully automated switchable gratings and up to three fully automated internal lasers. It included a confocal microscope, coupling and filtering optics, multichannel air-cooled CCD detector (26.6 nm), and computer package (LabSpec6 spectral software). The XploRA basic configuration was the same as that of a standard Olympus BX41 microscope supplied with XY manual mechanical stage and five positions objective turret equipped with three plan achromatic objectives: 10X, 50X, and 100X. In addition, it included both a white light illuminator with a 12 V/100 W lamp with variable light intensity and Abbe condenser for Koehler illumination by reflection and a white light illuminator with a 6 V/30 W lamp with variable light intensity and Abbe condenser for Koehler illumination by transmission. LabSpec6 spectral software suited for the easy acquisition and analysis of Raman data, namely, control of the hardware and acquisition parameters, autocalibration, customizable methods, FLAT fluorescence subtraction, peak label and fit, image capture, smoothing and spectral subtraction, and so on. The spectral resolution was 2.5 cm^{-1} at 532 nm and 1.8 cm^{-1} at 785 nm. By far, the most popular wavelength used for Raman spectroscopy is 785 nm, as it offers the best balance between avoiding fluorescence, absorption of the laser light (and Raman scattering) by the sample and therefore heating effects, and the limits to detector sensitivity. In situ measurements were performed using an X-LINK CATA thermometric cell working in the range, ambient temperature—1000 °C, with the following specification:
window materials for Raman technique, sample size is 7 mm diameter (between 70 and 100 mg dependent on sample type), standard size 1/16 gas analyzer high pressure connectors, removable ceramic sample holder, water cooling to keep stage body at safe temperature to maintain gases at elevated temperatures, and preventing condensation before analysis. To reduce the heat over the sample with the laser beam during spectra acquisition, the full spectra, hereafter shown for Raman shifts, between 200 and 1200 and 1200 cm⁻¹, were built by accumulating 10 scans during a total time of 100 s. Single crystalline silicon wafer was used to calibrate the Raman shift accumulating 10 scans during a total time of 100 s. Single

Typically, 100 mg of the catalyst, ground and sieved to 212

μm, was used in all experiments. The catalyst was diluted with glass beads to 10 wt % to prevent hot-spot formation, and the reactor was filled with glass beads over and below the catalyst bed to avoid the gas-phase homogeneous oxidation reaction. However, at 400 °C, a space velocity of 7500 or 12000 h⁻¹, and 1 atm in a postcatalytic bed filled space filled with a glass sphere reactor, a conversion of less than 1.0% was observed, and the PO selectivity was zero in the absence of catalyst because of the homogeneous reaction. Therefore, the data were corrected by subtracting the homogeneous reaction data obtained. Feed gases were delivered by Cole Parmer flow meters. All tubing was heated in order to avoid condensation in the system. Both the feed and the product gas were analyzed by on-line gas chromatography (GC), using a Burker GC 450 equipped with three channels. The first channel was equipped with a thermal conductivity detector (TCD) and separation was accomplished by HayeSep Q and molecular sieve 5A for separation of hydrogen. The second channel was also equipped with TCD for analysis of permanent gases (O₂, N₂, CO, and CO₂) and separation was accomplished by HayeSep Q and MolSieve 13X columns connected in series. The third channel was equipped with a flame ionization detector for analysis of propylene and oxygenates (such as PO, acetone, acrolein, and acetaldehyde). The separation was accomplished by a HayeSep Q column. The product gas composition was measured in 20 min intervals, as determined by the duration of the GC analysis, with intermittent increments of the furnace temperature. The initial concentrations of propylene and oxygen were calculated before each catalytic run to verify their constant values with a 98% degree of confidence and the carbon mass balances with error were below 5%. The standard reaction conditions were reaction temperature = 400 °C, 0.1 MPa, and space velocity = 7500 h⁻¹. The feedstock composition consisted of 22.7% propylene, 9.0% oxygen, and the total flow rate was 100 mL/min, balanced with nitrogen. The product selectivity (%) was defined as the product concentration \times 100 divided by the propylene conversion. The propylene conversion (%) was estimated as the concentration of propylene consumed/concentration of propylene in the feed \times 100.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b03645.

Nitrogen adsorption–desorption isotherm of Ti-HMS

XRD patterns of Ag/Ti-HMS, catalysts, XRD patterns of NaAgMo/Ti-HMS catalysts, small-angle XRD pattern of Ti-HMS acidity–basisity curves from potentiometric titration measurement for pure Ti-HMS supports as well as Ag-, Mo-, and Na-doped Ti-HMS supports, FT-IR spectra of Ti-HMS samples and those of Ag and Mo supported on Ti-HMS, diffuse reflectance UV–vis spectra of Ti-HMS samples, histograms of particle size distribution from TEM micrographs of the catalysts: Ag/Ti-HMS10 and Ag/Ti-HMS110, EDX spectra of AgMo/Ti-HMS10, TEM micrograph of Ag/Ti-HMS10 at high magnification, Raman spectra of Ti-HMS3 and Ti-HMS10 supports, Raman spectra of Ti-HMS support collected at 25 °C and in flow of 22.7% C3H6/He at 400 °C at 2.0 h (PDF)

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Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS
The authors acknowledge the financial support of KACST Strategic Technologies research grant 10-PET1103-06. All authors have given approval to the final version of the manuscript.

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