View Article Online

# **EES Catalysis**

# Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: G. Dong, H. Wang, Q. Jiang, Y. Liao and C. Wang, *EES Catal.*, 2025, DOI: 10.1039/D5EY00123D.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the <u>Ethical guidelines</u> still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



Open Access Article. Published on 30 May 2025. Downloaded on 6/4/2025 8:52:37 AM

# **Broader context**

Due to the wide availability of syngas  $(CO + H_2)$  from various sources (such as coal/biomass gasification, natural gas reforming, and  $CO_2$  hydrogenation), the preparation of chemicals using it as a raw material can reduce the reliance on petroleum and is in accordance with the energy diversification strategy. Among them, the hydrogenation of dimethyl oxalate (DMO) from syngas to ethylene glycol (EG) has been industrialized. However, there are still many challenges in obtaining the intermediate product, methyl glycolate (MG), from DMO hydrogenation to EG, such as low catalyst activity, poor selectivity, and high usage of precious metals. Accordingly, we exploited the confinement effect of mesoporous silica microspheres (MSNS) with center-radial channels mesoporous to fabricate a silver-silicon catalyst, and elaborately discussed the impact of the electronic and crystal structures of silver nanoparticles on the activation of reactants. The characterization results reveal that aminofunctionalization of support enables the silver-silicon catalyst to possess the easily accessible highly dispersed Ag active components, the lattice defects which are conducive to the adsorption, activation and diffusion of H<sub>2</sub>, as well as electron-rich Ag<sup> $\delta$ -</sup> species beneficial for the adsorption and activation of DMO, thereby endowing it with high activity, selectivity, and stability.

Catalvsis Accepted Manusc

## Article Online Amino functionalization of support toward enhanced selective 0123D hydrogenation of dimethyl oxalate to methyl glycolate on silversilicon catalyst

Guilin Dong,<sup>a</sup> Haiyong Wang,<sup>a</sup> Qian Jiang,<sup>a</sup> Yuhe Liao,<sup>a</sup> Chenguang Wang<sup>\*a</sup>

The development of highly efficient catalyst for selective hydrogenation of dimethyl oxalate (DMO) to methyl glycolate (MG) is an important step in the conversion of syngas into high-value chemicals, which is of great significance for reducing dependence on petroleum and facilitating the transformation of energy structure. Herein three Ag nanoparticles with different size distributions were supported on mesoporous silica nanospheres (MSNS) with uniform center-radial mesopore channels (~7nm). The effects of the electronic and crystal structures of Ag nanoparticles on the adsorption and activation of DMO and H<sub>2</sub> were studied. The characterization results reveal that amino-functionalization of support enables the silversilicon catalyst to possess the easily accessible highly dispersed Ag active components, the lattice defects which are conducive to the adsorption, activation and diffusion of H<sub>2</sub>, as well as electron-rich Ag<sup>5-</sup> species beneficial for the adsorption and activation of DMO, thereby endowing it with high activity, selectivity, and stability. In the reaction of DMO to MG, under the conditions of P = 2.0 MPa, T = 220 °C, H<sub>2</sub>/DMO molar ratio = 80, and LHSV = 1.0 h<sup>-1</sup>, the best catalytic state achieved a DMO conversion of 100%, a MG selectivity of 96.6%, a TOF as high as 207, and the MG yield could still remain above 95% after a 250 h lifetime investigation. Our research points out a promising way for the development of high-performance Ag catalysts used in the synthesis gas to MG process.

### 1. Introduction

Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Methyl Glycolate (MG) is an important organic chemical raw material. Due to the two functional groups of hydroxyl and ester, MG has the chemical properties of alcohol and ester, good biocompatibility and degradability, and is widely used in chemical industry, medicine, fragrance, polymer materials and other fields.<sup>1-8</sup> The existing MG mainly uses petroleum and its derivatives as raw materials, and the preparation methods include carbonylation of formaldehyde, coupling of methyl formate and esterification of chloroacetate, which generally requires strong acid or base as catalyst and reaction conditions of high temperature and high pressure, resulting in many side reactions and low yield.<sup>9, 10</sup> Therefore, considering the depletion of global oil resources, the uneven energy reserves of countries and the requirements of green chemical industry worldwide, the development of a mild route of alternative MG synthesis is of great significance to promote its wide application.

Syngas is a kind of raw gas used for chemical synthesis with hydrogen and carbon monoxide as the main components. It comes from a wide range of sources, including fossil fuels (coal, oil, natural gas), renewable biomass, organic waste, and almost all hydrocarbon feedstocks. Since the synthesis of dimethyl oxalate (DMO) from syngas has been industrialized, selective hydrogenation of DMO to MG under mild reaction conditions using an efficient and easily processed heterogeneous catalyst is a more economical and environmentally friendly non-oilbased process route.11-13

CH<sub>3</sub> COOCH<sub>3</sub> CH<sub>2</sub>OH CH2OH 2H<sub>2</sub> 2H Ha OH OH

The hydrogenation process of DMO is a series reaction. With the deepening of the hydrogenation reaction, the products are MG, ethylene glycol (EG), and ethanol (EtOH) in sequence (Scheme 1).14, 15 At present, Cu-based catalyst has been successfully applied in DMO (derived from syngas) catalytic hydrogenation to EG, and has achieved the industrial production of one million tons of EG per year.<sup>16-19</sup> Due to the high activity of Cu-based catalyst for hydrogenation of C=O bond, it is easy to deeply hydrogenate DMO to EG, so it is difficult to obtain large quantities of intermediate MG under the existing process conditions, and the yield of MG is generally less than 80%.<sup>20-22</sup> Therefore, the development of highly selective and stable catalysts for DMO selective hydrogenation to MG, and then the efficient use of syngas to produce ethylene glycol device to achieve product diversification, has become a current research hotspot.

In recent years, more and more research have shown that the catalyst with Ag as the active component, which has lower hydrogenation activity than Cu, shows milder hydrogenation performance in DMO hydrogenation process, and can improve the selectivity and yield of MG.<sup>23, 24</sup> In the existing literature, the Ag-based monometallic catalysts used for DMO hydrogenation to MG have higher Ag content (> 8 wt%), lower catalytic activity (TOF<69), and higher cost.<sup>25-28</sup> The research of Ag-based catalytic system mainly focuses on two directions: First, the use of mesoporous materials instead of traditional silica as the support to increase the dispersion of active components; Second, an additive is introduced into the Ag-based catalyst to adjust the electronic state of Ag. However, mesoporous

	←										
DMO	MG	EG	Et								
Scheme 1 The reaction pathway for the hydrogenation of DMO.											

<sup>&</sup>lt;sup>a.</sup> Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, Guangzhou 510640, PR China.

<sup>\*</sup> Corresponding author. E-mail: wangcg@ms.giec.ac.cn

### ARTICLE

materials, such as SBA-15,<sup>29-31</sup> MCM-41,<sup>27</sup> activated carbon,<sup>32</sup> carbon nanotubes,<sup>25</sup> etc., have long porous channel (micron level), which is not conducive to mass transfer in the pores.<sup>23</sup> The addition of metal auxiliaries Ni and Co can significantly reduce Ag content. However, Ni can decompose DMO to a certain extent, and CoAg catalyst is more sensitive to space speed, and the conversion rate drops rapidly to below 70% when 0.1 h<sup>-1</sup> space speed increases.<sup>10, 29, 31</sup> The introduction of nonmetallic elements N and B can effectively regulate the electronic state of Ag, thus generating more active sites. However, due to low Ag dispersion (<0.254), the Ag content in the catalyst is all higher than 10 wt%.<sup>32, 33</sup>

Previously, we reported that a catalyst loaded with Ag nanoparticles (Ag content < 3 wt%) on mesoporous silica nanospheres (MSNS) showed excellent performance in DMO hydrogenation to MG.<sup>34</sup> Scheme 2 shows the synthesis steps of the catalyst. However, the reason for its high activity was not elaborated. In this study, the effects of electronic and crystal structures of Ag nanoparticles on the adsorption and activation of DMO and H<sub>2</sub> were discussed in detail by comparing silversilicon catalysts prepared by different methods, and the reason why amino functionalization of support enhanced the selective hydrogenation of dimethyl oxalate to methyl glycolate on silversilicon catalysts was explained.



followed by immobilization of Ag nanoparticles onto the aminated MSNS.

### Experimental 2.

### 2.1. Chemicals

Cetyltrimethylammonium chloride (CTAC), triethanolamine (TEA), and 3-aminopropyltrimethoxysilane (APTS) were purchased from J&K Scientific Ltd. Tetraethyl orthosilicate (TEOS), cyclohexane, methylbenzene, ethanol, and silver nitrate (AgNO<sub>3</sub>) were purchased from Sinopharm Chemical Reagent Co., Ltd. All the reagents were used as received without further purification.

### 2.2. Preparation of the MSNS support

The MSNS was synthesized via a biphasic stratification approach using TEOS as the silica source and CTAC as the template agent, according to a method reported in the literature.<sup>35</sup> Typically, 0.4

g of TEA was dropped into a solution of 15 g of CTAC in 120 ml of deionized water and stirred at 60 °C for 21 AP. Then a solution of 7.5 g of TEOS in 25g of cyclohexane was drip added to the above solution, and stirred at 60 °C for 12 h. The precipitate after centrifugation was washed with ethanol and dried at 120°C for 12 h, denoted Sur-MSNS. Then Sur-MSNS was placed in Muffle furnace and calcined at 550 °C for 4 h in static air to remove CTAC, and mesoporous silica nanospheres was obtained, denoted MSNS. 1.5g of MSNS was dispersed in 50g of toluene, then 0.5g of APTS was added, and refluxed at 110 °C for 12 h. The precipitate after centrifugation was washed with ethanol and dried at 120°C for 4 h, and the mesoporous silica microspheres with amino functionalized surface were obtained, denoted NH<sub>2</sub>-MSNS.

### 2.3. Preparation of Ag/NH<sub>2</sub>-MSNS and Ag/MSNS catalysts

Using NH<sub>2</sub>-MSNS as the support, the catalyst with Ag loading of 3 wt% was prepared by in-situ reduction method. This method uses ethanol as the reducing agent and reduces Ag<sup>+</sup> in the precursor AgNO<sub>3</sub> to Ag at 70 °C under normal pressure. Typically, 1.0g of NH<sub>2</sub>-MSNS was ultrasonically dispersed in 90ml of ethanol. Then, 0.049g of AgNO<sub>3</sub> in 24.5ml of ethanol was added to the suspension, stirred at 30 °C for 4 h, then heated to 70 °C, and continued to stir for another 4 h until the suspension colour turns brown. The precipitate after centrifugation was cleaned with ethanol and dried at 60 °C for 12 h under nitrogen atmosphere. Finally, the NH<sub>2</sub>-MSNS supported Ag catalyst was obtained, denoted Ag/NH<sub>2</sub>-MSNS. For comparison, the Ag catalyst prepared by the same method using MSNS as the support was denoted Ag/MSNS.

### 2.4. Preparation of Ag/MSNS\_im catalyst

The impregnation method is the most commonly used method for preparing supported metal catalysts and is also the method that is widely adopted in the current literature for the preparation of silver-silicon catalysts for the hydrogenation of dimethyl oxalate.<sup>1, 25, 36</sup> This method requires high-temperature calcination of metal salts to obtain metal oxides, which are then reduced to metals with hydrogen. For comparison, using MSNS as support, the catalyst with Ag loading of 3 wt% was prepared by equivolumetric solution impregnation method. Typically, the volume of water absorbed by 1.0g of MSNS was determined in advance, and 0.049g of AgNO<sub>3</sub> was dissolved in the measured volume of deionized water, and then a drop of 68 wt% nitric acid solution was added. Then the AgNO<sub>3</sub> solution was added to 1.0 g of MSNS in drops and aged for 24 h at room temperature, sheltered from light. After drying at 110 °C for 12 h, calcining at 450 °C for 4 h in static air, and reduction at 350 °C for 4 h under hydrogen atmosphere, the catalyst with Ag loading of 3 wt% was obtained, denoted Ag/MSNS im.

### 2.5. Catalyst characterizations

The Fourier Transform Infrared Spectroscopy (FTIR) was recorded using the Nicolet 6700 spectrometer from Thermo Fisher. The sample (  $\sim$  1 mg) was fully ground with dry KBr (  $\sim$ 200 mg) until the particle size was less than 2  $\mu$ m and pressed into translucent disks at room temperature. The scanning wavenumber range was 4000  $\sim~$  400 cm<sup>-1</sup>, with a resolution of

ARTICLE

### **Journal Name**

4 cm<sup>-1</sup>, a signal-to-noise ratio of 5500:1, a wavenumber accuracy of 0.01 cm<sup>-1</sup>, and 32 scans were performed. The  $N_2$ physical adsorption of the samples was measured at -196 °C using the ASAP 2020 physical adsorption apparatus of Micromeritics. All the samples were degassed in vacuum at 200 °C for 3 h to remove the impurities physically adsorbed. The specific surface area (S<sub>BET</sub>) was calculated by the Brunauer-Emmett-Teller (BET) method, and the mesopore diameter and mesopore volume were calculated by the Barrett-Joyner-Halenda (BJH) method. The actual Ag loading of the samples was determined by using an Agilent 5110 inductively coupled plasma optical emission spectrometer (ICP-OES). Approximately 50 mg of the sample was accurately weighed into a 50 ml polytetrafluoroethylene beaker, and 6 ml of hydrochloric acid, 2 ml of nitric acid, and 4 ml of hydrofluoric acid were added. The beaker was covered and heated at 90 °C for 1 h. The cover was then removed and the solution was evaporated to near dryness. The sample residue was diluted with 5% HNO<sub>3</sub> solution, and the filtrate was made up to 50 ml in a volumetric flask for measurement.

The morphology and structure of the samples were examined by a JEOL JEM-2100F field emission transmission electron microscope (TEM), with an acceleration voltage of 200 kV and equipped with a Gatan GIF Tridium energy filter. Prior to the test, the catalyst samples were ultrasonically homogeneously dispersed in ethanol, and then dropped onto a 200-mesh carbon-supported copper grid and dried thoroughly. The phase characteristics of the samples were characterized by a D8 Advance X-ray polycrystalline diffractometer (XRD) from Bruker AXS. Cu K $\alpha$  radiation with a wavelength of 0.15418 nm was employed, with an operating voltage of 40 kV and a current of 200 mA. The scanning step size was 0.02°, and the scanning  $2\theta$ range was 10° to 80°. The ultraviolet-visible diffuse reflectance spectra (UV-vis DRS) of the samples were acquired by means of Agilent Cary 5000 ultraviolet-visible-near-infrared the spectrophotometer. Barium sulfate (BaSO<sub>4</sub>), a white standard substance, was adopted as the reference, and the scanning wavelength range was 200 to 800 nm. The surface elemental electronic structure of the samples was analyzed employing the K-Alpha X-ray photoelectron spectrometer (XPS) from Thermo Fisher. The Al K $\alpha$  ray (hv = 1486.6 eV) was utilized as the excitation source, and the binding energy of the contaminated carbon C1s (284.6 eV) was adopted as the external standard for correcting the charging effect of the samples.

The N<sub>2</sub>O chemisorption, H<sub>2</sub> temperature-programmed reduction (H<sub>2</sub>-TPR), and H<sub>2</sub>, DMO, temperature-programmed desorption (H<sub>2</sub>-TPD, DMO-TPD respectively) experiments were carried out in a Micrometrics Autochem II 2920 apparatus with a thermal conductivity detector (TCD). For N<sub>2</sub>O chemisorption, 100 mg of the solid sample was first reduced at 350 °C under a flow of 50 ml·min<sup>-1</sup> of 10% H<sub>2</sub>/Ar for 3 h and then cooled down to 90 °C. Subsequently, the sample was exposed to the pure N<sub>2</sub>O (30 ml·min<sup>-1</sup>) for 1 h to ensure that the surface metallic silver atoms were completely oxidized to Ag<sub>2</sub>O. The sample was

### cooled down to room temperature under AP at hosp here? Next, 10% H<sub>2</sub>/Ar (50 ml·min<sup>-1</sup>) was introduced, and the sample was heated up to 800 °C at rate of 10 °C·min<sup>-1</sup>, during which the hydrogen consumption was monitored using the TCD.<sup>37</sup> In a typical procedure for the TPD tests, 100 mg of sample was reduced at 350 °C for 3 h in a 10% H<sub>2</sub>/Ar atmosphere, followed by purging with He for 2 h at 300 °C to remove physically adsorbed impurities. After cooling the sample down to 50 °C, a flow of the probe molecule ( $H_2$ for $H_2$ -TPD, DMO for DMO-TPD; for the DMO-TPD experiments the vapor of DMO was carried by Ar) was started until saturated adsorption was reached. The probe molecule was then removed by purging with Ar until the baseline of the MS signal was stabilized. After cooling to room temperature, the TPD profile was collected in Ar from room temperature to 800 °C at a ramping rate of 5 °C·min<sup>-1</sup>. The desorbed probe molecule was monitored by using an online mass spectrometer (MS).

purged with a flow of Ar (30 ml·min<sup>-1</sup>) for 30 min and then

In situ FTIR spectra of DMO adsorbed on the catalysts were recorded using a Perkin-Elmer Frontier spectrometer and a transmission FTIR cell. Briefly, 30 mg of dried catalyst was compressed into a self-supporting wafer and carefully loaded into the transmission cell. The catalyst was reduced at 350 °C under 5%  $H_2/N_2$  for 3 h and then evacuated by  $N_2$  for 30 min to remove the chemisorbed hydrogen. After cooling down to 80 °C, DMO was evaporated and flowed through the cell with the aid of a vacuum pump for 1 h. That was followed by evacuation to remove any weakly adsorbed DMO. The FTIR spectra were then recorded at the reaction temperature (i.e., 220 °C) with a spectral resolution of 4 cm<sup>-1</sup> and via the accumulation of 64 scans.

### 2.6. Catalytic evaluation

The catalytic hydrogenation activity assessment of dimethyl oxalate (DMO) was conducted in a stainless steel fixed-bed reactor with an inner diameter of 8 mm. 0.4 g of the catalyst (40  $\sim$  60 mesh) was loaded into the isothermal section of the fixed-bed reactor, and then reduced for 4 hours at 350 °C in a 100 ml/min H<sub>2</sub> atmosphere to activate the Ag that had been oxidized during storage. At 220 °C and 2 MPa, the DMO in methanol solution (15 wt%) and H<sub>2</sub> with a H<sub>2</sub>/DMO molar ratio of 80 was respectively introduced into the evaporator via a highperformance liquid chromatography constant-flow pump and a mass flow meter. After being fully mixed in a gas mixer, the mixture was fed into the reactor for reaction, with a liquid hourly space velocity (LHSV) ranging from 0.2 to 3.0. The outlet gas flow was sampled at intervals of 30 min employing an automatic six-way valve system and subsequently quantitatively analyzed using an online gas chromatograph (Agilent 7890A), featuring a hydrogen flame ionization detector (FID) and a KB-Wax capillary column (30 m × 0.32 mm × 0.25 μm).

The conversion of DMO and the selectivity toward each product were calculated based on the following equations:

b

ntensity(a.u.)

1200

100 nm

d

700

500

### ARTICLE

а

Transmittance(%)

4000

С

Conversion (%) = 
$$\frac{mol of DMO (in) - mol of DMO (out)}{mol of DMO (in)} \times 100\%$$

Selectivity (%) = 
$$\frac{mol \ of \ MG \ or \ EG \ (out)}{mol \ of \ DMO \ (in) - mol \ of \ DMO \ (out)} \times 100\%$$

Turnover frequencies (TOF) were calculated according to the following equation:<sup>38</sup>

$$\mathrm{TOF} = \frac{W \times V \times C_{DMO}}{D \times N_{Ag}}$$

where W is the DMO concentration in the DMO/methanol solution (mol/L), V is the flow rate of the DMO/methanol solution (L/h),  $C_{\text{DMO}}$  is the DMO conversion,  $N_{\text{Ag}}$  is the total

NH<sub>2</sub>-MSNS

MSNS

Sur-MSNS

2000

Wavenumbers (cm<sup>-1</sup>)

2500

1562

1460 1408

1500

376

1000

2850 2924

3000

3500

100 nm

374

amount of Ag (mol) in the used catalyst and Duis the Ag dispersion obtained from N2O chemisorption33/hdE149212PR measurements. To obtain the TOF values, the reaction was performed at 2.4, 4.5 and 12.0 h<sup>-1</sup> of LHSV for Ag/MSNS\_im, Ag/MSNS and Ag/NH<sub>2</sub>-MSNS, respectively, while the other reaction conditions were kept at the same levels (T = 220  $^\circ\!\mathrm{C}$  , P = 2.0 MPa and  $H_2/DMO$  = 80) to ensure that the conversion of DMO is below 20%.

### 3. Results and discussion

### 3.1. Structure and physical properties of supports

The Fourier transform infrared spectroscopy (FTIR) of Sur-MSNS containing template agent, MSNS removing template agent, and NH<sub>2</sub>-MSNS with surface amination are shown in Fig. 1a.

O1s

C1s Si2s<sup>Si2p</sup>

200

02

N1s

400

378



Fig. 1 (a) FTIR spectra of Sur-MSNS MSNS MH<sub>2</sub>-MSNS. (b) Full range XPS spectra of MSNS NH<sub>2</sub>-MSNS. TEM and inset HR-TEM images of (c) MSNS and (d) NH<sub>2</sub>-MSNS.

The absorption peaks of the three curves at 3424 cm<sup>-1</sup>, 1626 cm<sup>-1</sup> <sup>1</sup>, 1090 cm<sup>-1</sup>, 800 cm<sup>-1</sup> and 468 cm<sup>-1</sup> are respectively attributed to the antisymmetric stretching vibration peak of OH in Si-OH, the H-O-H bending vibration peak of water, the antisymmetric stretching vibration peak of Si-O-Si, the symmetric stretching vibration peak and bending vibration peak of Si-O bond. In addition, at 800 cm<sup>-1</sup> and 690 cm<sup>-1</sup>, there are no double peaks and sharp peaks of Si-O bond symmetric stretching vibration in crystalline SiO<sub>2</sub>. The results show that the catalyst supports are

mainly composed of amorphous SiO<sub>2</sub> covered by Si-OH group. The absorption peaks of Sur-MSNS at 2924 cm<sup>-1</sup> and 2850 cm<sup>-1</sup> are attributed to the antisymmetric and symmetric stretching vibration of CH<sub>2</sub>, respectively, and the absorption peak at 1460 cm<sup>-1</sup> is attributed to the symmetric variable angle vibration of CH<sub>2</sub>. The weak absorption peak at 1408 cm<sup>-1</sup> is attributed to the symmetric variable angle vibration of CH<sub>2</sub> in -CH<sub>2</sub>-N<sup>+</sup>. It can be seen that Sur-MSNS without roasting contain template agent CTAC. The absorption peaks of roasted MSNS almost

### Journal Name

disappeared at 2924 cm<sup>-1</sup>, 2850 cm<sup>-1</sup>, 1460 cm<sup>-1</sup> and 1408 cm<sup>-1</sup>, indicating that the template agent CTAC could be effectively removed by roasting at 550 °C for 4 hours. After surface amination modification, NH<sub>2</sub>-MSNS re-generated absorption peaks at 2924 cm<sup>-1</sup>, 2850 cm<sup>-1</sup> and 1460 cm<sup>-1</sup>, indicating that the surface of MSNS contained CH<sub>2</sub> groups, which came from the organic carbon chain of APTS. At the same time, the weak absorption peaks of NH<sub>2</sub>-MSNS at 1562 cm<sup>-1</sup> and 700 cm<sup>-1</sup> are attributed to the plane shear vibration and the out-of-plane rocking vibration of NH, respectively, indicating that the surface of NH<sub>2</sub>-MSNS contains -NH<sub>2</sub> groups. In addition, the full range XPS spectra of NH<sub>2</sub>-MSNS shows that its surfaces contain N element (Fig. 1b). The above results show that the acetal reaction takes place between the hydroxyl group on the surface of MSNS and the ethoxy group of APTS, and the surface of MSNS is covered by aminopropyl group, and the surface and that on modification of NH<sub>2</sub>-MSNS is obtained.

Transmission electron microscopy (TEM) images of MSNS without template agent and NH<sub>2</sub>-MSNS with surface amination are shown in Fig. 1c and Fig. 1d, respectively. It can be seen that both the MSNS and NH<sub>2</sub>-MSNS have good dispersion, the particle size is uniform, the diameter is about 370nm, the pore channel is a center divergent slit, and the pore size is about 7nm. Compared with MSNS, NH<sub>2</sub>-MSNS has no obvious difference in microstructure. It can be seen that the surface amination of MSNS does not destroy the original microstructure.



### Fig. 2 (a) N<sub>2</sub> adsorption-desorption isotherms, (b) BJH pore size distribution of catalysts and supports.

Sample	Ag content <sup>a</sup> (wt%)	S <sub>BET</sub> <sup>b</sup> (m <sup>2</sup> g <sup>-1</sup> )	V <sub>pore</sub> c (m <sup>3</sup> g <sup>-1</sup> )	D <sub>pore</sub> d (nm)	Ag particle size <sup>e</sup> (nm)	D <sub>Ag</sub> f (%)	S <sub>Ag</sub> <sup>f</sup> (m <sup>2</sup> g <sup>-1</sup> )	TOF (h <sup>-1</sup> )
NH <sub>2</sub> -MSNS	_	323	0.41	6.17	_	_	_	_
Ag/MSNS_im	3.0	425	0.60	6.53	8.5	14.3	2.08	78 <sup>g</sup>
Ag/MSNS	2.5	390	0.54	6.39	6.6	20.8	2.52	135 <sup>t</sup>
Ag/NH <sub>2</sub> -MSNS	2.9	242	0.33	6.12	5.5	31.7	4.46	207

<sup>a</sup> Metal loading was determined by ICP-OES. <sup>b</sup> Specific surface area, calculated by the BET method. <sup>c</sup> BJH Adsorption cumulative volume of pores. <sup>d</sup> BJH Adsorption average pore diameter. <sup>e</sup> Silver particle size was calculated by TEM. <sup>f</sup> Dispersion ( $D_{Ag}$ ) and surface area of Ag ( $S_{Ag}$ ) obtained from N<sub>2</sub>O chemisorption and H<sub>2</sub>-TPR measurements, please refer to Supplementary Information for specific calculation details. <sup>g</sup> Based on a 15.3% DMO conversion under the following reaction condition: T = 220 °C, P = 2.0 MPa, H<sub>2</sub>/DMO = 80 and LHSV = 2.4 h<sup>-1</sup>. <sup>h</sup> Based on a 17.1% DMO conversion under the following reaction condition: T = 220 °C, P = 2.0 MPa, H<sub>2</sub>/DMO = 80 and LHSV = 12.0 h<sup>-1</sup>.

The N<sub>2</sub> adsorption-desorption isotherms of the supports and catalysts and their BJH pore size distribution curves are shown in Fig. 2. N<sub>2</sub> adsorption isotherms of NH<sub>2</sub>-MSNS and MSNS are a combination of type II and type IV isotherms, and hysteresis rings belong to type H3 (Fig. 2a). The pore structure of the sample is a wedge slit hole formed by agglomeration of sheet particles, which is consistent with TEM observation results. The shape of isotherms and hysteresis rings is basically the same, which further indicates that the surface amination modification does not damage the particle structure. Among them, the BJH pore size distribution of MSNS is slightly wider (4-10nm), which

may be caused by the narrow inside and wide outside channel structure of the wedge-shaped slit holes (Fig. 2b). Compared with MSNS, the position, area and pore size distribution of NH<sub>2</sub>-MSNS hysteresis ring are all shifted in the negative direction, indicating that the pore volume and pore size of NH<sub>2</sub>-MSNS are reduced to some extent by the introduction of aminopropyl. As shown in Table 1, the specific surface area, pore volume and pore size of MSNS are 665  $m^2 \cdot g^{-1} \sim 0.80 \ m^3 \cdot g^{-1}$  and 6.61 nm, respectively, while for NH<sub>2</sub>-MSNS, they are reduced to 323  $m^2 \cdot g^{-1} \sim 0.41 \ m^3 \cdot g^{-1}$  and 6.17 nm respectively. It is worth noting that the pore size distribution of NH<sub>2</sub>-MSNS is narrower (5-7nm), and

Open Access Article. Published on 30 May 2025. Downloaded on 6/4/2025 8:52:37 AM.

ARTICLE

### **Journal Name**

the possible reason is that the surface modification makes the wide-outside and narrow-inside wedge-shaped slit channels in MSNS tend to be uniform (cylindrical holes) (Fig. 2b).

The above results showed that the surface of MSNS was successfully modified with silane coupling agent APTS, and aminopropyl group was introduced into the surface, and NH<sub>2</sub>-MSNS with amination was obtained. At the same time, MSNS is a good support for catalyst preparation due to its high specific surface area, short pore size and uniform nano pore size.

### 3.2. Structure and physical properties of catalysts

The Ag content of catalyst after ICP-OES test is shown in Table 1. The actual Ag content of Ag/MSNS\_im is essentially consistent with the feeding amount, suggesting that the active component of the catalyst fabricated by the incipient wetness impregnation method suffers almost no loss. Using MSNS as the support, the actual Ag content in the Ag/MSNS prepared by the reduction method is smaller than the feeding amount. This is attributed to the weak adsorption of Ag<sup>+</sup> by the -OH on the surface of MSNS, causing some Ag<sup>+</sup> not to be adsorbed onto the support and thereby resulting in losses. Using NH<sub>2</sub>-MSNS as the support, the actual Ag content of Ag/NH2-MSNS obtained by reduction method is basically consistent with the theoretical content. This is because the introduction of -NH<sub>2</sub> on the surface of modified MSNS enhances the adsorption of Ag<sup>+</sup>, so that Ag<sup>+</sup> is adsorbed on the carrier and reduced, and there is no loss in the liquid phase. The N<sub>2</sub> physical adsorption isotherm and BJH

pore size distribution curves of the catalyst loaded with Ag are shown in Fig. 2. The types of N2 adsorption is the source of the source hysteresis loops of the three catalysts were consistent with those of the support, indicating that the loading and preparation method of Ag particles did not damage the structure of the support. However, the position and area of the hysteresis ring and the pore size distribution are all shifted in the negative direction, which indicates that the introduction of Ag particles has an effect on the physical properties of the support and reduces the pore volume and pore size. As shown in Table 1, the incorporation of Ag leads to a significant reduction in the  $S_{\text{BET}},\,V_{\text{pore}},\,\text{and}\,\,D_{\text{pore}}$  of the catalyst, suggesting that Ag particles have been successfully loaded onto the support. Compared with the MSNS, the pore size distributions of Ag/MSNS and Ag/MSNS\_im narrow down, suggesting that the particle sizes of the Ag particles entering the pore channels of the support are relatively uniform, causing the wedgeshaped slit channels of MSNS, which are narrow on the inside and wide on the outside, to tend to be consistent. Nevertheless, it cannot be excluded that large Ag particles are attached to the surface of the support. It is notable that the D<sub>pore</sub> of the Ag/NH<sub>2</sub>-MSNS catalyst fabricated by the reduction method is essentially consistent with NH<sub>2</sub>-MSNS, and its surface Ag dispersion is the highest (31.7), suggesting that the Ag particle size is relatively uniform and well positioned within the mesopores of the support. The phenomenon that larger particles are located outside the pores is significantly reduced.



Fig. 3 TEM images of (a) Ag/MSNS\_im, (b) Ag/MSNS, (c) Ag/NH<sub>2</sub>-MSNS catalysts, where the corresponding histograms of the Ag particle size distributions are shown in the insets. Typical high-resolution TEM images of (d) Ag/MSNS\_im , (e) Ag/MSNS, (f) Ag/NH<sub>2</sub>-MSNS catalysts.

In order to investigate the morphology characteristics and dispersion of Ag species in catalysts, TEM images and particle size distributions of Ag particles in different catalysts are shown in Fig.  $3a \sim 3c$ . In the Ag/MSNS im, Ag species not only occupy the nanochannels of MSNS in the form of small particles but also attach to the outer surface in the form of aggregated large particles. This implies that the catalyst fabricated by the impregnation method is liable to induce the migration and agglomeration of surface Ag nanoparticles during the calcination and reduction processes (Fig. 3a). Among them, the average diameter of Ag nanoparticles is 8.5 nm, featuring a relatively broad distribution. Furthermore, the particle size distribution is distinct divided into two intervals: a small particle range of 3 to 8 nm and a large particle range of 7 to 17 nm. This indicates that the MSNS nanopores have a limiting effect on the migration of Ag nanoparticles, that is, in the process of calcination and reduction, the Ag species filled in the pores avoid the migration of particles at high temperature due to the limiting effect, while the Ag species attached to the outer surface migrate and agglomerate at high temperature, resulting in the interval distribution of particle size. The pore size of MSNS is 6.61nm (Table 1), and its limiting effect is consistent with the particle size interval distribution of Ag nanoparticles.

In the Ag/MSNS catalyst, except for the small and mediumsized particles filled in the nanochannels of MSNS, the size of the surface aggregated particles is significantly reduced, indicating that the catalyst prepared by reduction method largely avoided the migration and agglomeration of Ag nanoparticles (Fig. 3b). The average diameter of Ag nanoparticles decreased to 6.6nm, the particle size was concentrated between 3 and 10nm, and the interval distribution was not obvious, which further indicated that the agglomeration phenomenon of Ag nanoparticles larger than the MSNS aperture (6.61nm) located on the outer surface was significantly reduced. In order to confirm whether it is the hightemperature calcination process that causes the larger Ag nanoparticles in Ag/MSNS\_im, the Ag/MSNS prepared by the reduction method was calcined at 450 ° C for 4 hours, and its TEM image is shown in Figure S1b. Compared with Ag/MSNS, the particle size of Ag nanoparticles in calcined Ag/MSNS is significantly increased. This indicates that the high-temperature calcination process can indeed increase the particle size of Ag nanoparticles, and the reason for this might stem from the Ostwald ripening process.<sup>39, 40</sup> In the Ag/NH<sub>2</sub>-MSNS, Ag nanoparticles are uniformly loaded in the nanoporous channels of MSNS, and no large agglomerations of Ag particles are found on the outer surface, indicating that the introduction of -NH<sub>2</sub> in MSNS plays a good control role in the growth of Ag nanoparticles during the reduction process, which is due to the complex effect of -NH<sub>2</sub> on Ag species. See the XPS and UV-vis DRS analysis below for more details. In addition, the MSNS nanoporous channels play a good limiting role for Ag nanoparticles, preventing the formation of large particles of Ag during reduction. The average diameter of Ag nanoparticles in Ag/NH<sub>2</sub>-MSNS was 5.4nm, and the distribution was narrow, indicating that the obtained Ag nanoparticles had a relatively

uniform particle size (Fig. 3c). Compared with  $M_{27}^{\text{jew}}$   $M_{27}^{\text{jew}}$ 

HRTEM was used to observe the lattice structures of Ag nanoparticles in different catalysts, as shown in Fig.  $3d \sim 3f$ . Ag nanoparticles in Ag/MSNS\_im catalysts prepared by immersion method showed the characteristic of long-range ordered and periodically rearranged spatial lattice structure. The same domain region covered almost the entire surface of the particles, and there were few grain boundary and lattice defects. The fringe spacing of 0.236nm and 0.204nm are attributed to the lattice spacing of the (111) and (200) faces of the face-centered cubic (fcc) Ag crystal, respectively (Fig. 3d). This indicates that the surface lattice of Ag nanoparticles prepared by impregnation method is relatively complete, which is due to the migration of Ag atoms on the surface caused by the reduction of internal energy in the system during hightemperature calcination and reduction. However, the Ag nanoparticles in the Ag/MSNS and Ag/NH2-MSNS catalysts prepared by reduction method have a greatly reduced degree of ordered particle arrangement, and more crystal domains are distributed on the surface, with a large number of grain boundaries, lattice defects and non-uniform surfaces (Fig. 3e and 3f). The study of Balluffi and Seigle showed that due to the tension across the boundary, a large number of vacancies can be generated at the transverse grain boundaries.<sup>41</sup> The Agbased catalyst prepared by liquid phase reduction method using NH<sub>2</sub>-MSNS as the carrier, due to the complex effect of -NH<sub>2</sub> on Ag species and solvent effect of ethanol, the Ag nanoparticles were stretched by electrostatic force caused by charge separation during the growth process, resulting in atomic dislocation and the resulting grain boundaries and vacancy. The atoms near the dislocation and vacancy have higher energy, increase the valence bond unsaturated, and easily interact with the reactant molecules, showing higher activity.

### **3.3.** Phase composition and electronic structure of catalyst

In order to study the phase composition and crystal structure of Ag species in the catalyst, the XRD patterns of Ag/NH<sub>2</sub>-MSNS, Ag/MSNS, and Ag/MSNS\_im catalysts are shown in Figure 4.

EES Catalysis Accepted Manusc

Open Access Article. Published on 30 May 2025. Downloaded on 6/4/2025 8:52:37 AM.



The wide peaks of the three catalysts at  $2\theta=23^{\circ}$  are attributed to amorphous SiO<sub>2</sub> (PDF 82-0512). The XRD patterns of Ag/MSNS im show the existence of cubic phase Ag crystals with lattice parameters a=b=c=4.0862 A, and the diffraction peaks at  $2\theta$ =38.2°, 44.3°, 64.5° and 77.6° are attributed to the Ag 3C lattice plane (111), (200), (220) and (311), respectively (PDF 87-0597). The diffraction peak at  $2\theta$ =33.8° is attributed to Ag<sub>6</sub>(Si<sub>2</sub>O<sub>7</sub>) (PDF 85-0281). Due to the large bond energy between Ag and Si atoms, Ag+ is difficult to be reduced, so the catalyst prepared by impregnation method contains an oxidized state of Ag<sup>+</sup>. Compared with impregnation method, the diffraction peaks of Ag/NH<sub>2</sub>-MSNS and Ag/MSNS prepared by reduction method decreased significantly at  $2\theta$ =38.2°, 44.3°, 64.5° and 77.6°. Combined with transmission electron microscopy, Ag nanoparticles are about 6nm (Fig. 3b and 3c), which is much larger than the crystal face distance ((111) 2.3592 A) at 38.2° of the strongest diffraction peak of Ag 3C. The above results show that Ag nanoparticles in Ag/NH<sub>2</sub>-MSNS and Ag/MSNS catalysts are highly dispersed and amorphous, containing a large number of lattice defects and heterogeneous surfaces, which weakens the scattered X-ray interference intensity. In particular, the diffraction peak of Ag 3C lattice surface in Ag/NH<sub>2</sub>-MSNS almost disappeared, indicating that the introduction of -NH<sub>2</sub> in the MSNS further reduces the

**Journal Name** 

particle size of Ag nanoparticles and produces more clattice defects and heterogeneous surfaces, which is consistent with HRTEM analysis. In addition, in the catalysts Ag/NH<sub>2</sub>-MSNS and Ag/MSNS, the diffraction peaks at 20=33.8° disappear, and no diffraction peaks of other Ag species compounds exist, indicating that the reduction method can reduce all Ag precursors during the preparation of the catalyst, and no oxidation state of Ag<sup>+</sup> exists.

In order to further study the electronic structure and surface valence states of Ag nanoparticles in different catalysts, the Xray photoelectron spectroscopy (XPS) of Ag3d is shown in Fig. 5a. The spectral peaks of Ag/MSNS catalysts at the binding energies of 374.2eV and 368.2eV belong to the characteristic peaks of Ag3d<sub>3/2</sub> and Ag3d<sub>5/2</sub> of the elemental state Ag<sup>0</sup>, respectively, and no chemical shift occurs, indicating that the precursor Ag species in the catalyst prepared by the reduction method using MSNS is completely reduced to the elemental state Ag<sup>0</sup> and no other valence species of Ag exist. Ag/MSNS\_im catalyst showed two spectral peaks at the binding energies of 374eV and 368eV, which were negatively shifted by 0.2eV compared to Ag3d<sub>3/2</sub> and Ag3d<sub>5/2</sub> of Ag/MSNS. Further deconvolution of the Ag/MSNS\_im spectrum shows that it is composed of the Ag3d split energy characteristic peaks of the elemental state Ag<sup>0</sup> and the oxidation state Ag<sup>+</sup>, in which the double peaks at 373.7eV and 367.7eV correspond to the characteristic peaks of  $Ag3d_{3/2}$  and  $Ag3d_{5/2}$  of  $Ag^+$  in  $Ag_2O$ respectively.42 Therefore, the precursor Ag species in the catalyst prepared by the impregnation method with MSNS as the support was not completely reduced, and there was an oxidized state of Ag<sup>+</sup>, indicating that there was a strong interaction between the silica support and Ag species. Combined with the XRD pattern, it was found that Ag<sup>+</sup> came from the  $Ag_6(Si_2O_7)$  phase produced during the roasting process. Ag/NH<sub>2</sub>-MSNS catalyst has two spectral peaks at the binding energies of 374.5eV and 368.5eV, which are positively offset by 0.2eV compared with Ag3d<sub>3/2</sub> and Ag3d<sub>5/2</sub> of Ag/MSNS. The spectra of Ag/NH<sub>2</sub>-MSNS were deconvolved, and the double peaks at 374.2eV and 368.2eV were the Ag3d characteristic peaks of Ag<sup>0</sup>. The double peaks at 374.9eV and 368.9eV indicate that there are some Ag species in the catalyst, and the interaction between electron and nuclear charge of the Ag3d orbital is enhanced, thus increasing the binding energy.

This journal is © The Royal Society of Chemistry 20xx



The X-ray photoelectron spectroscopy (XPS) of N1s in the surface amination support NH2-MSNS and the catalyst Ag/NH2-MSNS are shown in Fig. 5b. The peak of NH<sub>2</sub>-MSNS at 398.9eV is attributed to the characteristic peak of N1S in -NH $_{\rm 2}$  ,  $^{43,\;44}$  and the peak at 401eV is attributed to the characteristic peak of N1S in protonated –NH<sub>3</sub><sup>+</sup>.<sup>45, 46</sup> According to the basic principle of Xray photoelectron spectroscopy, when the density of the outer electron cloud decreases, the shielding effect of the outer electron is weakened, and the coulomb effect between the inner electron and the nucleus is enhanced, resulting in an increase in the binding energy of the inner electron. Therefore, the binding energy of N1S in Ag/NH<sub>2</sub>-MSNS catalyst has a positive chemical shift of 0.5eV compared with NH<sub>2</sub>-MSNS, indicating that the outer electron shielding effect of N element in NH<sub>2</sub>-MSNS support loaded with Ag nanoparticles is weakened and it is in a state of electron loss. -NH<sub>2</sub> bonds with Ag via the lone pair of electrons of N, resulting in N $\rightarrow$ Ag electron transfer, and the 399.4eV peak in Ag/NH<sub>2</sub>-MSNS is attributed to the characteristic peak of N1S in the -NH<sub>2</sub>/Ag ligand.<sup>47</sup> At the same time, the peak at 401.5eV was weakened, indicating that the interaction between Ag species and -NH<sub>2</sub> reduced the degree of protonation of -NH<sub>2</sub>. Literature studies have shown that the charge transfer of electron-deprived elements to Ag changes the electron configuration of Ag 4d and 5s,p orbitals (the rehybridization of  $4d \rightarrow 5s,p$ ), resulting in a decrease in the electron cloud density of valence level Ag4d orbitals, a weakening of shielding effect, and an increase in the Ag3d electron binding energy of core level.<sup>48</sup> Therefore, the double peaks at 374.9eV and 368.9eV obtained by deconvolution in the Ag/NH<sub>2</sub>-MSNS catalyst are attributed to the Ag3d<sub>2/3</sub> and Ag3d<sub>5/2</sub> characteristic peaks of the electron-rich state  $Ag^{\delta}$ , which is caused by the electron transfer of  $N \rightarrow Ag$ . In summary, the contact between Ag nanoparticles and  $\ensuremath{\mathsf{-NH}}_2$  in the Ag/NH2-MSNS catalyst generates a -NH<sub>2</sub>/Ag ligand structure through the lone pair electron bonding of N. Electron transfer from N to Ag occurs in this structure, making N in an electron-deprived state and Ag in an electron-rich state (Ag<sup> $\delta$ -</sup>).

This article is licensed under a Creative Commons Attribution-NonCommercial 3.0 Unported Licence

Open Access Article. Published on 30 May 2025. Downloaded on 6/4/2025 8:52:37 AM.



Ultraviolet-visible diffuse reflectance spectroscopy (UV-vis DRS) is applicable for determining the charge transfer and dorbital electron transition of transition metal ions and their complexes on the catalyst surface, thereby facilitating the study of its structure, oxidation state, and coordination state.<sup>49</sup> For most D-region metal nanoparticles, their diffuse reflection absorption spectra bands are continuous within the ultravioletvisible light wavelength range.<sup>50</sup> The UV-vis DRS spectra of Ag/NH<sub>2</sub>-MSNS, Ag/MSNS and Ag/MSNS\_im are shown in Fig. 6.

Because the mean free path of the electrons of Ag is relatively long, the three silver catalysts have an obvious wide absorption band in the visible region ( $350 \sim 700$  nm). They are attributed to the surface plasmon resonance (SPR) generated by photon excitation of Ag nanoparticles, whose maximum absorption peak is in the range of 400-500nm, which is also consistent with literature reports.<sup>51-54</sup> According to the size quantum effect theory, when the particle size of nanomaterials is smaller, the band gap is wider, the band density is smaller, and the frequency of electron resonance is larger, which is manifested

### ARTICLE

as the blue shift of SPR spectrum. The maximum SPR absorption bands of Ag nanoparticles in Ag/NH<sub>2</sub>-MSNS, Ag/MSNS and Ag/MSNS\_im were 411nm, 469nm and 494nm, respectively, and showed a redshift in sequence, indicating that Ag nanoparticles gradually increased, which was consistent with TEM test results. The strong terminal absorption peak of the three catalysts at 209nm in the near ultraviolet region is attributed to the electron transfer between  $Si^{4+}$  and  $O^{2-}$  in the support  $\text{SiO}_{2},^{27}$  and the absorption peak at 306nm is attributed to the SPR of the elemental  $Ag_n\ cluster.^{55,\ 56}$  The absorption spectra of Ag/MSNS im in the UV region were generated at 229nm and 280nm. According to the literature,<sup>56, 57</sup> the absorption peak at 229nm is attributed to the electron transfer between isolated Ag<sup>+</sup> and O<sup>2-</sup>, and the absorption peak at 280nm is attributed to the SPR of the oxidation state  $Ag_n^{\delta+}$ cluster. The results show that the catalyst prepared by impregnation method contains Ag<sup>+</sup>, an unreduced oxidation state, which comes from Ag<sub>6</sub>(Si<sub>2</sub>O<sub>7</sub>) phase produced during roasting. The Ag/NH<sub>2</sub>-MSNS and Ag/MSNS catalysts did not have absorption peaks at 229nm and 280nm, indicating that there was no oxidation state of Ag<sup>+</sup>, and the Ag precursor was completely reduced during the preparation process. It is worth noting that Ag/NH<sub>2</sub>-MSNS has an absorption spectrum at 258nm in the ultraviolet region. Combined with XPS analysis of Ag electron valence states of Ag/NH<sub>2</sub>-MSNS, the absorption peak at 258nm is attributed to the electron transfer between Ag and N. Since the electronegativity of N is smaller than that of O, the force between Ag and O is stronger. Therefore, compared with the electron transfer absorption peak between Ag<sup>+</sup> and O<sup>2-</sup> at 229nm, the electron transfer between N and Ag requires lower energy, resulting in redshift phenomenon.

### 3.4. Adsorption and activation of reactants on catalysts

FTIR spectra of the gas-phase DMO molecule and adsorbed ones on the differently catalysts at 220 °C are shown in Fig. 7a. For pure DMO, the absorption peaks at 1805 cm<sup>-1</sup> and 1775 cm<sup>-1</sup> <sup>1</sup> are attributed to  $v_{as}$ (C=O) and  $v_s$ (C=O), respectively, and the

absorption peaks at 1472 cm<sup>-1</sup> are attributed to  $\delta_{as}$  (CH3). The absorption peaks at 1234 cm<sup>-1</sup> and 1184 €A<sup>:1</sup>8#e<sup>3</sup>attribUted to  $v_{as}$ (C-O-C) and  $v_s$ (C-O-C), respectively. For DMO adsorbed on different catalysts, the stretching vibration characteristic peaks of C=O and C-O-C showed a redshift, while the variable angle vibration characteristic peaks of CH<sub>3</sub> were all around 1472 cm<sup>-1</sup> without displacement, indicating that the chemical adsorption of C=O and C-O-C of DMO occurred on the catalyst. The redshift of the characteristic peak of the functional group indicates that the vibration energy of the bond decreases, the bond length becomes longer, and the bond is more likely to break and occur chemical reaction. The order of adsorption and activation of DMO by different catalysts is as follows: Ag/NH<sub>2</sub>-MSNS > Ag/MSNS > Ag/MSNS\_im. The redshift phenomenon of DMO functional group absorption bands can be explained by molecular orbital theory: the outer electrons of the active component Ag of the catalyst enter the antibonding molecular orbital  $(2\pi^*)$  of C=O, thus weakening the bond energy of C=O, reducing the bond vibration energy, reducing the stability of DMO molecules and making chemical reactions easy. According to the XPS and UV-vis DRS analysis above, Ag/MSNS\_im catalyst prepared by impregnation method contains Ag<sup>+</sup> species in oxidation state, which makes it difficult for Ag outer electrons to enter the C=O antibonding orbital, so the absorption bands of C=O and C-O-C have the smallest redshift wavenumber. The active component of Ag/MSNS catalyst prepared by reduction method is Ag<sup>0</sup>, which makes it easier for Ag outer electrons to enter the C=O antibonding orbital, so the absorption band redshift wavenumber of C=O and C-O-C is large. The Ag/NH<sub>2</sub>-MSNS catalyst contains electron-rich Ag<sup>δ-</sup> species, which makes it easiest for Ag outer electrons to enter the C=O antibonding orbital, so the absorption bands of C=O and C-O-C have the largest redshift wavenumber. Therefore, the Ag/NH<sub>2</sub>-MSNS catalyst has the strongest activation capacity for DMO, which is derived from the electron-rich  $Ag^{\delta-}$  species generated by electron transfer from N to Ag.



Catalysis Accepted Manus

Fig.7b shows the TPD profiles for DMO adsorbed on different catalysts, in which a peak at 300 $\sim$ 500 °C associated with DMO desorption is clearly observed. With the increase of Ag dispersion in catalysts, the adsorption capacity of DMO increased gradually. According to the desorption peak area of DMO, it can be seen that Ag/NH<sub>2</sub>-MSNS catalyst has the largest adsorption capacity for DMO, which is due to its high Ag dispersion (31.7%). It is also noted that the desorption temperature of DMO on Ag/NH<sub>2</sub>-MSNS catalyst is the highest (474 °C ), which is due to the enhanced adsorption of DMO by electron-rich  $Ag^{\delta-}$  species, consistent with the FTIR results of DMO adsorption. The above results show that the high dispersion of Ag and the electron-rich  $Ag^{\delta-}$  species in the Ag/NH<sub>2</sub>-MSNS enhance the adsorption and activation of DMO.

In order to study the adsorption and activation of  $H_2$  by catalysts, H<sub>2</sub>-TPD profiles on different catalysts are shown in Fig. 8. The support MSNS and NH2-MSNS have no H2 desorption peak in the temperature range of 25 $\sim$ 650 °C (not marked in the figure). On SiO<sub>2</sub> loaded Cu, Ag and Au nanoparticles, hot electrons generated by energy transfer between external energy and metal surface can achieve H<sub>2</sub> dissociation at room temperature,  $^{\rm 58,\ 59}$  and the peaks above 200 °C of the three catalysts are attributed to the desorption of H atoms adsorbed by dissociation on the surface of Ag particles.<sup>60-62</sup> Pundt pointed out that various defects (such as dislocations, grain boundaries, vacancies, microvoids, impurity atoms, etc.) in metals can form hydrogen traps for hydrogen atom diffusion.<sup>63</sup> Hideaki et al. found that hydrogen traps can attract and trap hydrogen atoms, and hydrogen atoms diffuse much faster in the dislocations and grain boundaries than in the lattice.64,65

This article is licensed under a Creative Commons Attribution-NonCommercial 3.0 Unported Licence

Open Access Article. Published on 30 May 2025. Downloaded on 6/4/2025 8:52:37 AM.



Therefore, in Fig. 8, the peak in the low temperature region is attributed to the desorption of hydrogen atoms in the Ag lattice, while the peak in the high temperature region is attributed to the desorption of hydrogen atoms in the hydrogen trap at the defect of the Ag lattice. Compared with Ag/MSNS im, the desorption peaks of Ag/NH<sub>2</sub>-MSNS and Ag/MSNS in the low temperature region shifted to low temperature by about 30 °C, indicating that Ag nanoparticles in the catalyst prepared by reduction method had more lattice defects, which made the diffusion of hydrogen atoms in the lattice easier, which was consistent with the lattice image analysis of HRTEM. The peak area of H2-TPD on different catalysts represents the adsorption amount of H<sub>2</sub>, and is positively correlated with Ag dispersion. The adsorption capacity of Ag/NH<sub>2</sub>-MSNS on H<sub>2</sub> is the largest, which is due to the high Ag dispersion on its surface.

### 3.5. Catalytic performance and stability of catalysts

In the reaction of DMO catalytic hydrogenation to MG, the evaluation results of catalyst activity and stability are shown in Fig. 9. Under a certain activity of catalyst, the DMO conversion decreases with the increase of liquid-time space velocity (LHSV) (Fig. 9a). The higher conversion and the higher LHSV, the stronger activation of the catalyst. The sequence of catalytic activity of the three catalysts for DMO conversion is as follows: Ag/NH<sub>2</sub>-MSNS > Ag/MSNS > Ag/MSNS\_im. In particular, when the LHSV is lower than 1.5 h<sup>-1</sup>, the Ag-NH<sub>2</sub>-MSNS catalyst exhibits outstanding catalytic efficacy, with the DMO conversion being higher than 99%. With the increase of LHSV, the MG and EG selectivity tends to be stable around 97% and 3% respectively on the three catalysts (Fig. 9b). However, at low LHSV (< 0.5h<sup>-1</sup>), the MG selectivity order of the three catalysts is Ag-MSNS\_im > Ag-MSNS > Ag-NH<sub>2</sub>-MSNS, which is opposite to that for EG. This is because DMO hydrogenation is a series reaction, the overall higher hydrogenation activity favors deep hydrogenation of MG to EG as the residence time of the mixture increases. Increasing LHSV can effectively inhibit the further conversion of MG. With the increase of LHSV, the variation trend of MG yield is consistent with the DMO conversion (Fig. 9c). The turnover frequency (TOF) sequence of DMO on the three catalysts is as follows: Ag-NH<sub>2</sub>-MSNS (207) > Ag-MSNS (135) > Ag-MSNS im (78) (Table 1).



Open Access Article. Published on 30 May 2025. Downloaded on 6/4/2025 8:52:37 AM.



Fig. 9 (a) DMO conversion, (b) MG and EG selectivity and (c) MG yield from hydrogenation runs with the Ag/NH<sub>2</sub>-MSNS, Ag/MSNS and Ag/MSNS\_im catalysts as a function of LHSV at 220 °C under 2 MPa of H<sub>2</sub>. (d) Kinetic data versus time on stream for DMO hydrogenation on the Ag/NH<sub>2</sub>-MSNS catalyst under the following reaction condition: T = 220 °C, P = 2.0 MPa, H<sub>2</sub>/DMO = 80 and LHSV =  $1.0 h^{-1}$ .

Through the characterization of physical and chemical properties of different catalysts, their catalytic activities for DMO hydrogenation can be explained as follows. Compared with the impregnation method, the catalyst prepared by reduction method has higher dispersion of Ag particles, and the decrease of Ag<sup>+</sup> species in oxidation state enhances the adsorption and activation of DMO. At the same time, there are more lattice defects on its surface, which is more conducive to the activation and diffusion of H<sub>2</sub>, so Ag/MSNS has higher activity. The Ag/NH<sub>2</sub>-MSNS catalyst prepared by reduction method using NH<sub>2</sub>-MSNS as the support, due to the complexation of -NH<sub>2</sub>, Ag nanoparticles have smaller particle size and higher dispersion during the in-situ reduction growth process, and the surface lattice defects further increase, and the activation and diffusion of H<sub>2</sub> are further enhanced. In addition, there is electron transfer between -NH<sub>2</sub> and Ag species on the support surface, and the electron-rich  $Ag^{\delta-}$  is more likely to adsorb DMO and activate the C=O bond. Therefore, the high activity of Ag/NH<sub>2</sub>-MSNS catalyst is due to its highly dispersed Ag active components, a large number of lattice defects, and electron-rich  $Ag^{\delta}$  species. Under the reaction conditions of

P=2.0MPa, T=220 °C ,  $H_2$ /DMO=80 and LHSV=1.0 h<sup>-1</sup>, the DMO conversion and MG selectivity of Ag/NH<sub>2</sub>-MSNS catalyst in the optimal state were 100% and 96.6% respectively.

The stability test results of Ag/NH<sub>2</sub>-MSNS catalyst for DMO hydrogenation are shown in Fig. 9d. After 250h reaction, the selectivity of MG remained basically unchanged, stable at about 96.5%. Compared with almost 100% at the beginning of the reaction, the conversion rate of DMO decreased slightly to 98.5%, and stabilized after 250h, and the MG yield was above 95%. This shows that Ag/NH<sub>2</sub>-MSNS catalyst has excellent catalytic activity, selectivity and stability in the reaction of DMO hydrogenation to prepare MG. The slight reduction in the conversion rate may be due to subtle changes in the surface structure of Ag nanoparticles during the reaction.

### 4. Conclusions

In summary, using mesoporous silica nanospheres (MSNS) with uniform center-radial mesopore channels (  $\sim$  7nm) as the support, -NH<sub>2</sub> was successfully introduced for surface

Journal Name

functionalization, and the Ag/NH<sub>2</sub>-MSNS catalyst with an Ag dispersion of 0.317 and a content of 3 wt% was prepared by the in-situ reduction method. In the reaction of selective hydrogenation of DMO to MG, under the conditions of P = 2.0 MPa, T = 220 °C, H<sub>2</sub>/DMO molar ratio = 80, and LHSV = 1.0 h<sup>-1</sup>, the best catalytic state achieved a DMO conversion of 100%, a MG selectivity of 96.6%, a TOF as high as 207, and the MG yield could still remain above 95% after a 250 h lifetime investigation. Characterization findings indicate that the easily accessible highly dispersed Ag active components, the lattice defects which are conducive to the adsorption, activation and diffusion of H<sub>2</sub>, and the electron-rich Ag<sup>δ-</sup> species that facilitate the adsorption and activation of DMO are the reasons for the catalyst to possess relatively high activity, selectivity and stability.

### Author contributions

Guilin Dong: Conducting a research and investigation process, specifically performing the experiments, or data/evidence collection. Preparation, creation and presentation of the published work, specifically writing the initial draft (including substantive translation).

Haiyong Wang: Development or design of methodology; creation of models. Verification, whether as a part of the activity or separate, of the overall replication/reproducibility of results/experiments and other research outputs.

Qian Jiang: Application of statistical, mathematical, computational, or other formal techniques to analyse or synthesize study data.

Yuhe Liao: Preparation, creation and presentation of the published work by those from the original research group, specifically critical review, commentary or revision – including pre- or post-publication stages.

Chenguang Wang: Ideas; formulation or evolution of overarching research goals and aims. Acquisition of the financial support for the project leading to this publication. Management and coordination responsibility for the research activity planning and execution. Provision of study materials, reagents, materials, patients, laboratory samples, animals, instrumentation, computing resources, or other analysis tools. Oversight and leadership responsibility for the research activity planning and execution, including mentorship external to the core team.

All the authors discussed the results and reviewed the manuscript.

### **Conflicts of interest**

There are no conflicts to declare.

### Data availability

All the experimental data are included in the main text and Supplementary Information.

### Acknowledgements

View Article Online DOI: 10.1039/D5EY00123D

This work was financially supported by the National Natural Science Foundation of China (No. 52276220).

### Notes and references

- 1 J. Qiu, G.-Q. Yang, J. Zuo, X. Liu, Z. Lan, W. Chen, Z.-W. Liu and Y. Yuan, *J. Catal.*, 2024, **435**, 115547.
- H. Wang, T. Lan, G. Zhao, G. Chen and Y. Lu, ACS Catal., 2024, 14, 728-740.
- 3 Y. Wang, H. Yang, B. Li, S. Liu, M. He, Q. Chen and J. Li, Int. J. Mol. Sci., 2022, 23, 11074.
- 4 Y. Sun, H. Wang, J. Shen, H. Liu and Z. Liu, *Catal. Commun.*, 2009, **10**, 678-681.
- 5 Y. Xu, W. Dou, Y. Zhao, G. Huang and X. Ma, *Ind. Eng. Chem. Res.*, 2012, **51**, 11653-11658.
- 6 Q. Xu, Coord. Chem. Rev., 2002, 231, 83-108.
- 7 T. Turek, T. D. L. and N. W. and Cant, *Catal. Rev.*, 1994, **36**, 645-683.
- 8 R. Angamuthu, P. Byers, M. Lutz, A. L. Spek and E. Bouwman, *Science*, 2010, **327**, 313-315.
- 9 Y. Weng, M. Zou, X. Liu, J. Gu, Z. Liu, Y. Fan, Y. Zhang and Y. Liao, *Chem. Commun.*, 2023, **59**, 4340-4343.
- F. Zheng, J. Gong, H. Zhang, W. Shu, X. Wang, S. Qin, C. Zhang and B. Dai, *Chem. Eng. J.*, 2024, **492**, 152350.
- 11 Q. Yang, Y. Fan, C. Liu, J. Zhou, L. Zhao and H. Zhou, *Energy*, 2023, **277**, 127668.
- 12 L. Song, Y. He, C. Zhou, G. Shu, K. Ma and H. Yue, *Chem. Commun.*, 2022, **58**, 11657-11660.
- 13 Y. Sun, K. Fu, J. Wei, Q. Ge, Q. Ma, G. Wang and J. Sun, *ACS Catal.*, 2024, **14**, 18744-18752.
- 14 Z. Li, Y. Li, X. Wang, Y. Tan, W. Yang, H. Zhu, X. Chen, W. Lu and Y. Ding, *Chem. Eng. J.*, 2023, **454**, 140001.
- J. Gong, H. Zhang, W. Shu, F. Zheng, C. Zhang, H. Wang, N. Zhang and B. Dai, *Green Chem.*, 2024, 26, 5966-5976.
- 16 F. S. Rohman, S. H. Syed Sulaiman and N. Aziz, *Int. J. Hydrogen Energy*, 2021, **46**, 30882-30890.
- 17 Y. Fang, H. Sun, B. Ma and C. Zhao, J. Catal., 2022, 407, 44-53.
- 18 J. Zhu, G. Zhao, C. Meng, P. Chen, X.-R. Shi and Y. Lu, *Chem. Eng. J.*, 2021, **426**, 130857.
- 19 J. Xu, Z.-C. Long, Z.-C. Chen, C.-F. Zhu, H.-G. Xu, J.-W. Zheng, E. Janssens, W.-J. Zheng, G.-L. Hou and S.-Y. Xie, *ACS Catal.*, 2024, **14**, 14733-14743.
- 20 Q.-N. Wang, R. Duan, Z. Feng, Y. Zhang, P. Luan, Z. Feng, J. Wang and C. Li, ACS Catal., 2024, 14, 1620-1628.
- 21 L. Wu, M. Guo, X. Xu, J. Ding and Q. Zhong, *J. Environ. Chem. Eng.*, 2024, **12**, 113037.
- 22 C. Liu, L. Zhao, S. Zhu, Y. Shen, J. Yu and Q. Yang, *Energy*, 2023, **282**, 128790.
- 23 Z. Luo, X. Xu, G. Dong, Y. Cao, S. Hu, G. Ye, Y.-A. Zhu, J. Zhou, W. Li and X. Zhou, *Chem. Eng. J.*, 2022, **450**, 138397.
- 24 G. Dong, Z. Luo, Y. Cao, S. Zheng, J. Zhou, W. Li and X. Zhou, *J. Catal.*, 2021, **401**, 252-261.
- 25 J. Zheng, X. Duan, H. Lin, Z. Gu, H. Fang, J. Li and Y. Yuan, Nanoscale, 2016, 8, 5959-5967.
- 26 M. Ouyang, Y. Wang, J. Zhang, Y. Zhao, S. Wang and X. Ma, RSC Adv., 2016, 6, 12788-12791.
- 27 A. Yin, C. Wen, W.-L. Dai and K. Fan, *Appl. Catal.*, *B*, 2011, 108-109, 90-99.
- 28 J. Zheng, H. Lin, X. Zheng, X. Duan and Y. Yuan, *Catal. Commun.*, 2013, **40**, 129-133.

Open Access Article. Published on 30 May 2025. Downloaded on 6/4/2025 8:52:37 AM

- 29 M. M.-J. Li, L. Ye, J. Zheng, H. Fang, A. Kroner, Y. Yuan and S. C. E. Tsang, *Chem. Commun.*, 2016, **52**, 2569-2572.
- 30 J. Zheng, H. Lin, Y.-n. Wang, X. Zheng, X. Duan and Y. Yuan, J. Catal., 2013, 297, 110-118.
- 31 J. Zhou, X. Duan, L. Ye, J. Zheng, M. M.-J. Li, S. C. E. Tsang and Y. Yuan, *Appl. Catal.*, A, 2015, **505**, 344-353.
- 32 M. Hu, Y. Yan, X. Duan, L. Ye, J. Zhou, H. Lin and Y. Yuan, *Catal. Commun.*, 2017, **100**, 148-152.
- 33 H. Chen, J. Tan, J. Cui, X. Yang, H. Zheng, Y. Zhu and Y. Li, Mol. Catal., 2017, 433, 346-353.
- 34 G. Dong, Y. Cao, S. Zheng, J. Zhou, W. Li, F. Zaera and X. Zhou, J. Catal., 2020, **391**, 155-162.
- 35 D. Shen, J. Yang, X. Li, L. Zhou, R. Zhang, W. Li, L. Chen, R. Wang, F. Zhang and D. Zhao, *Nano Lett.*, 2014, 14, 923-932.
- 36 X. Xu, X. Hu, Z. Luo, Y. Cao, Y.-A. Zhu, W. Li, J. Zhou and X. Zhou, *New J. Chem.*, 2023, **47**, 6045-6049.
- 37 C. J. G. Van Der Grift, A. F. H. Wielers, B. P. J. Jogh, J. Van Beunum, M. De Boer, M. Versluijs-Helder and J. W. Geus, J. Catal., 1991, **131**, 178-189.
- 38 M. Boudart, Chem. Rev., 1995, 95, 661-666.
- 39 S. C. Parker and C. T. Campbell, Phys. Rev. B, 2007, 75.
- 40 R. van den Berg, T. E. Parmentier, C. F. Elkjær, C. J. Gommes, J. Sehested, S. Helveg, P. E. de Jongh and K. P. de Jong, *ACS Catal.*, 2015, **5**, 4439-4448.
- 41 R. W. Balluffi and L. L. Seigle, *Acta Mater.*, 1957, **5**, 449-454.
- 42 V. K. Kaushik, J. Electron Spectrosc. Relat. Phenom., 1991, **56**, 273-277.
- 43 B. J. Lindberg and J. Hedman, *Chem. Scr.*, 1975, **7**, 155-166.
- 44 M. Barber, J. A. Connor, L. M. R. Derrick, M. B. Hall and I. H. Hillier, *J. Chem. Soc., Faraday Trans.*, 1973, **69**, 559-562.
- 45 D. S. Everhart and C. N. Reilley, *Surf. Interface Anal.*, 1981, **3**, 258-268.
- 46 T. Yoshida and S. sawada, *Bull. Chem. Soc. Jpn.*, 1974, **47**, 50-53.
- 47 D. M. Thornburg and R. J. Madix, Surf. Sci., 1990, 226, 61-76.
- 48 W. F. Egelhoff, Surf. Sci. Rep., 1987, 6, 253-415.
- 49 P. Morozzi, B. Ballarin, S. Arcozzi, E. Brattich, F. Lucarelli, S. Nava, P. J. Gómez-Cascales, J. A. G. Orza and L. Tositti, *Atmos. Environ.*, 2021, **252**, 118297.
- 50 J. A. Creighton and D. G. Eadon, *J. Chem. Soc., Faraday Trans.*, 1991, **87**, 3881-3891.
- 51 P. Prieto, V. Nistor, K. Nouneh, M. Oyama, M. Abd-Lefdil and R. Díaz, *Appl. Surf. Sci.*, 2012, **258**, 8807-8813.
- 52 Y. Wang, Y. Zheng, C. Z. Huang and Y. Xia, *J. Am. Chem. Soc.*, 2013, **135**, 1941-1951.
- 53 N. G. Bastús, F. Merkoçi, J. Piella and V. Puntes, Chem. Mater., 2014, 26, 2836-2846.
- 54 S. H. Im, Y. T. Lee, B. Wiley and Y. Xia, Angew. Chem., Int. Ed., 2005, 44, 2154-2157.
- 55 K.-i. Shimizu and A. Satsuma, *Phys. Chem. Chem. Phys.*, 2006, **8**, 2677-2695.
- 56 K.-i. Shimizu, J. Shibata, H. Yoshida, A. Satsuma and T. Hattori, Appl. Catal., B, 2001, 30, 151-162.
- 57 K. A. Bethke and H. H. Kung, J. Catal., 1997, **172**, 93-102.
- 58 S. Mukherjee, L. Zhou, A. M. Goodman, N. Large, C. Ayala-Orozco, Y. Zhang, P. Nordlander and N. J. Halas, J. Am. Chem. Soc., 2014, **136**, 64-67.
- 59 Z. Yin, Y. Wang, C. Song, L. Zheng, N. Ma, X. Liu, S. Li, L. Lin, M. Li, Y. Xu, W. Li, G. Hu, Z. Fang and D. Ma, *J. Am. Chem. Soc.*, 2018, **140**, 864-867.
- 60 S. Xia, L. Zheng, W. Ning, L. Wang, P. Chen and Z. Hou, J. Mater. Chem. A, 2013, 1, 11548-11552.

- 61
   H. Wilmer, T. Genger and O. Hinrichsen, J Catal. 2003

   215, 188-198.
   DOI: 10.1039/D5FY00123D
- 62 F. Arena, G. Italiano, K. Barbera, S. Bordiga, G. Bonura, L. Spadaro and F. Frusteri, *Appl. Catal.*, A, 2008, **350**, 16-23.
- 63 A. Pundt and R. Kirchheim, Annu. Rev. Mater. Res., 2006, 36, 555-608.
- 64 H. Iwaoka, T. Ide, M. Arita and Z. Horita, *Int. J. Hydrogen* Energy, 2017, **42**, 24176-24182.
- 65 H. Iwaoka, M. Arita and Z. Horita, Acta Mater., 2016, 107, 168-177.

**14** | J. Name., 2012, **00**, 1-3

# Data Availability Statement

View Article Online DOI: 10.1039/D5EY00123D

All the experimental data are included in the main text and Supplementary

Information.