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Base-free atmospheric O₂-mediated oxidation of 5-Hydroxymethylfurfural to 2,5-Furandicarboxylic acid triggered by Mg-bearing MTW zeolite supported Au nanoparticles

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ABSTRACT

Mg-bearing MTW silicalite zeolite, MgSi-ZSM-12, was straightforwardly synthesized by involving an unusual acidic pre-gelation system and engaged as the task-specific support for loading the Au nanoparticles (NPs). The resulting Au/MgSi-ZSM-12 catalyst showed stably excellent activity for the oxidation of HMF into FDCA in the presence of atmospheric dioxygen (O_2) without externally adding any liquid base, affording a yield of 87 % and turnover number (TON) of 331 based on the surface Au sites. Superior basicity was evidenced by embedding Mg species into the all-silica zeolitic skeleton, which enables strong, weak, and near-zero affinity towards aldehyde, alcohol, and carboxyl groups, respectively, thus, allows rapid and high-uptake adsorption of HMF, but negligible adsorption of FDCA. This unique feature of the Mg-bearing all-silica zeolite support together with its synergy with the active sites of Au NPs is revealed to accelerate the production of FDCA under the base-free mild condition.

1. Introduction

With the depletion of fossil resources and the green-house gas emission resultant environmentally unfriendly effects, growing concerns have been paid on the production of fuels and chemicals from abundant, low-cost and renewable biomass [1-6]. In this field, the conversion of biomass platform molecules provides an important bridge to narrow the gap between the fossil resource and biomass. 5-hydroxymethyl furfural (HMF) obtained from carbohydrates is among the most widely investigated platform compounds to produce diverse synthetic drugs and industrial chemicals [7–11]. Much ink has been spilled about the synthesis of value-added compounds from HMF via oxidation, hydrogenation, and so on [12–16]. Among them, the oxidation of HMF yields a valuable product 2,5-furandicarboxylic acid (FDCA), which is significant for the production of bio-based polymers as the promising alternative of terephthalic acid (TPA) [17-22]. However, construction of a highly effective heterogeneous catalyst for the target oxidation of HMF into FDCA under mild condition still remains challenges.

Generally, oxidation of HMF into FDCA involves the transformation

of mainly three functional groups (hydroxyl, aldehyde and carboxyl group) in a tandem reaction process [23,24]. Both homogeneous and heterogeneous catalysts have been developed by using dioxygen (O_2) as the easily available oxidizing agent. Certain homogeneous systems exhibited high activity under mild condition [25,26]; for example, an FDCA yield of 95 % was obtained over a homogeneous Pt@PVP catalyst at 80 °C and 1 bar O₂ pressure without a liquid base as the additive [25]. As an alternative, heterogeneous catalysts are preferred because of the facile separation, recovering and operation process [27,28]. Nonetheless, the product FDCA is readily adsorbed on the solid surface to deactivate the catalyst, for which a liquid base is usually added into the reaction system to increase the solubility of FDCA. Therefore, externally charging a liquid base additive is a common approach for promoting the activity of a heterogeneous catalyst, wherein the formation of alkoxide and activation of O-H and C-H bonds are accelerated [29,30]. In this regard, harsh conditions such as high temperature and high pressure were required in many cases to proceed the conversion smoothly [31, 32]. If in a more difficult base-free system, high pressure of O₂ was normally demanded for the efficient conversion [1,23]. The surface acid

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and/or base properties were found to significantly affect the activity by determining the varied affinities towards the reactant, intermediate and product in the conversion of HMF into FDCA [33,34]. Solid base materials were reported as capable carries to support noble metal NPs to catalyze the base-free synthesis of FDCA from HMF [35–37]. For instance, N-doped carbon supported Pt catalyst was active in the oxidation of HMF into FDCA with the N species serving as the moderate basic sites, which however was only workable under the pressured O_2 of 10 bar [36]. Several hydrotalcite (HT) supported Au or Pd NPs allowed the oxidation of HMF into FDCA with atmospheric O_2 under base-free condition [38], but the inevitable dissolution of HT occurred during the reaction.

Zeolites are widely applied supports constructed from TO₄ tetrahedra (T = Si or Al), due to the ordered and porous crystal structure plus the high thermal and hydrothermal stability [39-41]. Normally, aluminosilicate forms of zeolites have been used as solid acid catalysts, adsorbents, and ion exchangers [42-44]. In 2013, Au nanoclusters were confined in the supercage of Y zeolite for the oxidation of HMF to FDCA, vet sodium hydroxide was used as the base additive [45]. Recently, Pd NPs encapsulated in BEA zeolite offered the high yield and large turnover number (TON) in this reaction with the adding of liquid base sodium carbonate [46]. Heteroatomic zeolites can extend the intrinsic physical and chemical properties by combining the feature of the embedded heteroatoms [47-51]. Previous literatures indicate that incorporation of alkali earth metal atoms like Mg into zeolite framework enhanced materials' basicity that can effectively catalyze Knoevenagel condensations and CO₂ cycloaddition with epoxides [49,52]. However, none of them has been employed as the supports of noble metals, let alone their application in the base-free selective oxidation of biomass platform molecules.

In this work, we illustrate the direct synthesis of Mg-bearing all-silica ZSM-12 zeolite (shorten as MgSi-ZSM-12), on which the Au NPs were supported to give the catalyst Au/MgSi-ZSM-12. ZSM-12 is an MTW topological zeolite with one-dimensional and straight elliptical 12membered ring channels [52,53], The task-specific MgSi-ZSM-12 solid base support herein was hydrothermally synthesized with an unusual acidic pre-gelation system, in which the Mg and Si sources were co-hydrolyzed and co-condensed in weak acidic environment to strengthen the interaction of Mg ions and silica precursor for the purpose of embodying the Mg species [52]. The resulting Au/MgSi-ZSM-12 showed a stably excellent activity in the synthesis of FDCA from the oxidation of HMF with atmospheric O₂ in the absence of any extra liquid base. To gain insight into the influence of zeolites' framework composition on the activity, the neat all-silica ZSM-12, as well as Mg-/Al-bearing ZSM-12, were synthesized as the control supports to load the Au NPs. Apart from the comprehensive characterizations of the supports and catalysts series, their adsorption behavior of the reactant, intermediates and product were systematically investigated, which unravels the unique role of the intrinsic base properties of the supports in remarkably accelerating the production of FDCA.

2. Experimental

2.1. Materials and methods

All chemicals were used directly without further purification. Magnesium nitrate ($Mg(NO_3)_2 \cdot 6H_2O$, 99 wt%), tetraethylorthosilicate (TEOS, SiO₂ of 28.4 wt%), and sodium hydroxide (NaOH, 96 wt%) were purchased from Sinopharm Chemical Reagent Co., Ltd. Silicon dioxide (SiO₂, 99 wt%), aluminum oxide (Al_2O_3 , 99 wt%) and magnesium oxide (MgO, 99 wt%) were purchased from China National Pharmaceutical Group Corporation. Chloroauric acid (HAuCl₄, Au of 23.5~23.8 wt%) was purchased from Aladdin. 5-hydroxymethyl furfural (HMF, 97 wt%) was purchased from Shanghai LingFeng Chemical Reagent Co. Ltd. Tetraethylammonium hydroxide (TEAOH, 35 wt% aqueous solution)

was purchased from Shanghai RongLi Chemical Reagent Co. Ltd.

2.2. Characterization

Powder X-ray diffraction (PXRD) patterns were collected on a SmartLab diffractometer with Nickel-filtered Cu K α radiation at a 2θ range of $5\sim50^{\circ}$ (40 kV, 100 mA, 0.2° /s). High-resolution PXRD patterns of Si-ZSM-12 and MgSi-ZSM-12 were collected on a SmartLab 9 kW diffractometer with transmission geometry (capillary: 0.7 mm, angle range: 5–90°, step size: 0.015°) and applied in the Rietveld refinement, which was performed by using TOPAS 5.0 Academic suite. Nitrogen sorption isotherms were recorded on a BEL SORP-MINI analyzer. The pore size dispersion curves were calculated by using Barrett-Joyner-Halenda (BJH) and Horvath-Kawazoe (HK) methods. Scanning electron microscope (SEM) images were taken from a Hitachi S-4800 fieldemission scanning electron microscope. Transmission electron microscope (TEM) images were obtained from a Hitachi JEOL JEM-2100 F field-emission transmission electron microscope at 200 kV. Fourier transform infrared spectroscopy (FT-IR) spectra were measured on an Agilent Cary 660 Infrared spectrometer. Ultraviolet visible (UV-vis) diffuse reflection spectra were detected on a SHIMADZU UV-2600 spectrometer by using barium sulfate (BaSO₄) as the internal standard. Inductively coupled plasma emission spectrometry (ICP) was performed on an ICP OPTMA 20,000 V analyzer. X-ray fluorescence (XRF) analysis was performed by Rigaku ZSX Primus II. A PHI 5000 Versa Probe X-ray photoelectron spectrometer was used for the X-ray photoelectron spectroscopy (XPS) analyses. Carbon monoxide (CO) chemisorption (pulse titration) and carbon dioxide temperature programmed desorption (CO2-TPD) measurements were conducted on a JAPAN BELCAT-B Analyzer instrument. Thermogravimetric analysis (TGA) was carried out on an STA 409 instrument in air (10 °C min⁻¹).

2.3. Materials synthesis

Mg-bearing siliceous MTW zeolites (MgSi-ZSM-12) were synthesized in a one-pot hydrothermal route with Si/Mg molar ratio of 50 (20, or 100) in the gel by referring our previous work [52]. Mg- and Al-containing ZSM-12 with the SiO₂/Al₂O₃ molar ratio of 600, named as Mg-ZSM-12(600), was synthesized similarly with the gel composition of 1 SiO₂: 0.02 Mg; 0.00125 Al₂O₃: 0.35 TEAOH: 22.5 H₂O.

Pure silica MTW zeolite, termed as Si-ZSM-12, was synthesized in the absence of Mg species with the similar procedure. After the acid-hydrolysis step, the water was removed through evaporation to produce powder that was additionally dried at 100 °C for 4 h. The powder was mixed with 8 g TEAOH and then the mixture was aged at room temperature for 24 h, with the pH controlled at ~12 by adding NaOH. The gel with the molar composition of 40 SiO₂: 8TEAOH: 320 H₂O was transferred into Teflon-lined stainless-steel autoclave and crystallized at 140 °C for 7 d. The as-synthesized sample Si-ZSM-12-as was obtained with the same procedure as that of MgSi-ZSM-12. Template was removed similarly to offer the sample Si-ZSM-12.

Au NPs supported samples, named as 1%Au/support (the supports covered MgSi-ZSM-12, Mg-ZSM-12(600), Si-ZSM-12, SiO₂, Al₂O₃, and MgO), were prepared through deposition-precipitation (DP) method. 1 mL HAuCl₄ aqueous solution containing 0.01 g HAuCl₄ was mixed with 0.25 g support, and then NH₃·H₂O solution was added to adjust the pH (~9), followed by stirring at 60 °C for 12 h. The solid was isolated by centrifugation, washed with water, dried, and then reduced under 10 % H₂/90 %N₂ flow.

2.4. Synthesis of FDCA from HMF

The transformation of HMF into FDCA was carried out in a 25 mL reaction tube equipped with an oxygen (O_2) balloon. 0.1 mmol HMF was added into the tube containing 4 mL water, followed by the addition of 0.1 g catalyst. The reaction mixture was stirred at 90 °C for preset time.

After the reaction, the liquid phase was separated by centrifugation and diluted with water. High performance liquid chromatography (HPLC, Thermo Scientific UltiMate3000) equipped with Ultraviolet detector and Capillary column (Arcus EP-C18, 5 μ m, 4.6 \times 250 mm) was used to analyze the composition of the collected liquid phase, with a flowing phase of 50 % water and 50 % methyl alcohol (0.5 mL min⁻¹). The collected catalyst was washed with ethyl alcohol, dried at 60 °C and then charged into the next run to measure the reusability in a five-run test.

Conversion of HMF = (mmol HMF converted)/(mmol HMF initial)× 100. Yield of FDCA = (mmol FDCA)/(mmol initial HMF)×100. The errors in conversion and yield were calculated to be within \pm 2%. Turnover number (TON) = (mmol FDCA)/[(mmol Au)×dispersion]. Turnover frequencies (TOF) = (mmol FDCA)/[(mmol Au)×dispersion × reaction time].

2.5. Adsorption of different substrates

Adsorption of 5-hydroxymethylfurfural (HMF), 5-hydroxymethyl-2furancarboxylic acid (HMFCA) and 5-formyl-2-furancarboxylic acid (FFCA) and 5-furandicarboxylic acid (FDCA) on different adsorbents was performed in a 10 mL tube. A mixture of 0.1 g adsorbent, 0.01 mmol adsorbates and 4 mL water was stirred at room temperature for 24 h. After that, the liquid phase was isolated by centrifugation and analyzed by HPLC.

3. Results and discussion

3.1. Construction of Au NPs on MgSi-ZSM-12

Scheme 1 shows the synthetic procedure of Mg-bearing all-silica ZSM-12 zeolite (MgSi-ZSM-12). For comparison, pure silica ZSM-12 (Si-ZSM-12) was synthesized following the modified strategy without involving the Mg source (Scheme S1). The unit cell compositions of Si-ZSM-12-as and MgSi-ZSM-12-as (Table S1) were calculated from the combination of XRF and TG analyses (Fig. S1). High-resolution XRD patterns of Si-ZSM-12-as and MgSi-ZSM-12-as were collected for structure refinement. When the structure parameters of calcined pure-silica ZSM-12 in the International Zeolite Association (IZA) structure database were chosen as the initial point for Le Bail fitting [54], it leads to a large deviation of the fitted patterns from the observed ones (Fig. S2). Furthermore, these unindexed diffraction peaks disappeared after calcination (Fig. S3). Such deviation was also found by employing

para-nitroaniline (pNA) loaded pure silica ZSM-12 (pNA-ZSM-12) as the model (a=24.89 Å, b=5.00 Å, c=24.25 Å, $\beta=107^{\circ}$, space group C12/c1) [55]. Similar phenomenon was observed in the structure refinement of previous pure silica ZSM-12, in which there existed a well-ordered arrangement of tetraethylammonium (TEA) cations in the channel. The size mismatch between guest TEA molecule $(5.5 \times 7.3 \times 7.3 \text{ Å})$ and host zeolite unit cell parameter (24.8 \times 5.0 \times 24.3 Å) resulted in a super-structure along the *b*-axis. In Kasunic's work, many trial structures were constructed to reach the reasonable arrangement of the TEA molecules without any short contact distances between each other, sequentially the space group was lowered from C2/c to Cc with three times larger *b* unit cell (~15.1903 Å) to give the initial structure model [56]. Thus, an improved model was generated in Platon routine with parameter: *a*=25.2177 Å, *b*=15.1903 Å, *c*=24.4754 Å, and β=108.516° in space group Cc was used in the Le Bail fitting, producing good agreement of the calculated pattern with the observed ones (R_{wp}: 4.4 %) (Fig. S4). Accordingly, the reasonable distribution of TEA cations with tt. tt conformation in our work was located by the simulated annealing process, showing that eight TEA cations occluded in the super-structure along *b*-axis, in line with the empirical formula in Table S1. Rietveld refinement was performed with the final model to reach the maximum agreement between calculated patterns and the observed ones (R_{wn}: 10.9 %). The refined crystal structure of Si-ZSM-12-as is deposited in Fig. 1A. Owing to the iso-electronic property of Mg and Si, we evenly distributed Mg at the tetrahedral sites in the structure refinement of MgSi-ZSM-12-as. The final result derived by Rietveld refinement (Rwp: 8.7 %) in Fig. 1B shows almost the same structure for MgSi-ZSM-12-as as that for Si-ZSM-12-as. Specifically, the unique arrangement of TEA in MgSi-ZSM-12-as and Si-ZSM-12-as suggests the same structure-directing function of TEA in the hydrothermal crystallization of the two samples. The unit cell parameters of Si-ZSM-12-as are a = 25.2403(8) Å, b =15.1670(6) Å, c = 24.4801(8) Å, $\beta = 108.449(6)$ ° (Entry 1, Table S1). The longer bond of Mg - O (~2.10 Å) than Si - O (~1.61 Å) results in subtle expanded unit cell size of MgSi-ZSM-12 [a = 25.2365(7) Å, b =15.1691(6) Å, c = 24.4833(8) Å, $\beta = 108.463(3)$ °].

After the high temperature calcination to remove the template TEA, the Au NPs were loaded onto MgSi-ZSM-12 through DP method. XRD patterns of MgSi-ZSM-12 and 1%Au/MgSi-ZSM-12 (Fig. 2A) show that the diffraction peaks from TEA cations mentioned above disappeared. No diffraction peak for Au NPs was found, meaning a high dispersion of Au NPs. As measured by ICP (Table 1), Au content was consistent with the theoretical value. Fig. 2B shows N₂ sorption isotherms of MgSi-ZSM-



Scheme 1. Schematic representation of the synthesis of Au NPs supported on MgSi-ZSM-12.



Fig. 1. Observed (blue), calculated (red), and difference (gray) profiles for the Rietveld refinement of (A) Si-ZSM-12-as and (B) MgSi-ZSM-12-as. The inset is the arrangement pictures of TEA cations within the channels of Si-ZSM-12-as and MgSi-ZSM-12-as viewing along b-axis (blue: Mg and/or Si, red: O) (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).



Fig. 2. (A) PXRD patterns and (B) N2 sorption isotherms of MgSi-ZSM-12 and 1%Au/MgSi-ZSM-12.

Table 1Textural properties of different catalyst.

Entry	Catalyst	Au ^a (wt %)	${S_{BET}}^{b}$ (m ² g ⁻¹)	V_p^{c} (cm ³ g ⁻¹)
1	MgSi-ZSM-12	-	312	0.41
2	1%Au/MgSi-ZSM-12	1.02	278	0.35
3	1%Au/Si-ZSM-12	0.95	289	0.36
4	1%Au/Mg-ZSM-12(600)	0.98	293	0.44
5	1%Au/SiO ₂	0.85	341	0.92
6	1%Au/Al ₂ O ₃	0.89	176	0.26
7	1%Au/MgO	0.92	4	-

^a Au contents measured by ICP.

^b Surface area.

^c Total pore volume. "-" means the pore volume of 1%Au/MgO is negligible.

12 and 1%Au/MgSi-ZSM-12. Both exhibited an International Union of Pure and Applied Chemistry (IUPAC) type-I N₂ sorption isotherm, suggesting the formation of typical microchannels. Compared with Si-ZSM-12 (Fig. S5), a small H3 type hysteresis loop was observed in the nitrogen sorption isotherms of these Mg-containing samples, manifesting the formation of certain mesopores, mostly due to the packing of the primary zeolitic crystals. Pore size distribution curves in Figs. S6 and S7 also reveal this variation after the introduction of Mg species. As summarized in Table 1, slight decrease in surface areas and pore volumes was observed after Au loading, however, these Au-containing zeolites demonstrated still high surface areas. SEM image of 1%Au/MgSi-ZSM- 12 (Fig. 3A) illustrates small tablet-like primary crystals with the size ranging from tens to hundreds of nanometers, which aggregated to form secondary particles shaped of the rice grainy and finally highly fused into loosely packed particles in tens of micrometers level. The morphology of 1%Au/MgSi-ZSM-12 resembles its parent support MgSi-ZSM-12 [52], suggesting that the DP loading process could not affect zeolite morphology significantly. By contrast, Si-ZSM-12 was composed of closely packed trigonal prisms with the size of several micrometers (Figure S8). Uniform distribution of Si, O, Mg, Au was observed on the corresponding elemental mapping images (Fig. 3C). TEM image (Fig. 3B) of 1%Au/MgSi-ZSM-12 presents a relatively narrow dispersion of Au NPs with an average particle size of 3.9 nm. Quantitatively, CO chemisorption in Table 2 gives the metal dispersion for 1%Au/MgSi-ZSM-12 of 5.1 % (Entry 2), slightly lower than that for 1% Au/Si-ZSM-12 (8.6 %) (Entry 3).

For these samples, almost the same FT-IR spectra (Figs. S9 and S10) were observed, showing the absorption bands at 1220, 1070 and 796 cm⁻¹ for the external asymmetric stretch vibration, internal asymmetric stretch vibration and external symmetric stretch vibration of tetrahedron, respectively [57]. UV–vis spectra of Au-containing MgSi-ZSM-12 (Figure S11) exhibited a slight absorption between 500 and 600 nm belonging to the typical plasmon band of Au NPs [58], further revealing a good dispersion. XPS analysis was performed to figure out the valence state of Au NPs (Figs. 4A and S12). The survey scan XPS spectrum of Au/MgSi-ZSM-12 shows the signals at 285 eV, 533 eV, 84 eV, and 104 eV for C1s, O1s, Au4f, and Si2p, respectively. The high-resolution Au4f



Fig. 3. SEM images of (A) 1%Au/MgSi-ZSM-12. (B) TEM image of 1%Au/MgSi-ZSM-12. (C) SEM elemental mapping images of Si, O, Mg, and Au of 1%Au/MgSi-ZSM-12.

Table 2
Oxidation of HMF into FDCA ^a .

Entres	Catalyst	Basic site ^b Au dispersion ^c (% (mmol g^{-1})	As dispersion ^C (0/)	Conv. (%)	Yield (%)		TON	TON	TOF	Carbon balance (0()	
Entry			Au dispersion (%)		HMFCA	FFCA	FDCA	ION	ION	TOF	Carbon balance (%)
1	MgSi-ZSM-12	1.45	_	8.0	4.1	1.3	2.0	-	_	-	92.5
2	1%Au/MgSi-ZSM-12	1.24	5.1	>99	9.2	2.0	87	17	331	14	98.3
3	1%Au/Si-ZSM-12	< 0.1	8.6	32	25	4.2	0	0	0	0	91.3
4	1%Au/Mg-ZSM-12(600)	0.89	4.7	62	32.7	5.9	23	4.7	100	4.2	99.3
5	1%Au/SiO ₂	< 0.1	4.1	47	35	7.1	0	0	0	0	89.6
6	1%Au/Al ₂ O ₃	< 0.1	3.4	20	12.6	3.1	4.0	0.9	26.5	1.1	98.5
7	1%Au/MgO	1.3	5.2	94	78	7.9	7.0	1.5	28.8	1.2	98.8
8 ^e	1%Au/Si-ZSM-12	< 0.1	8.6	>99	1.1	0.1	98	20	237	9.9	99.2
9 ^f	1%Au/Si-ZSM-12	< 0.1	8.6	99	18	5.1	76	16	184	7.6	99.2
10 ^g	1%Au/Si-ZSM-12	< 0.1	8.6	98	72	8.6	13	2.7	31.4	1.3	95.5
11 ^h	1%Au/Si-ZSM-12	< 0.1	8.6	20	14	2.8	1.0	0.2	2.30	0.1	89.0

 a Reaction condition: HMF 0.1 mmol, HMF/metal molar ratio = 20:1, water 4 mL, 90 °C, 24 h, O₂ balloon.

^b The density of basic sites measured by CO₂-TPD.

^c Metal dispersion was estimated by CO chemisorption.

^d Turnover number (TON)=(mmol FDCA)/(mmol Au).

^e With the addition of equal molar Mg(OH)₂.

^f With the addition of equal molar MgO.

 g With the addition of equal molar Mg(OH)₂ and filtrated after 8 h.

 $^{\rm h}$ With the addition of equal molar ${\rm Mg}({\rm NO}_3)_2$. "-" means the value is unavailable.



Fig. 4. (A) Au 4f XPS spectrum of 1%Au/MgSi-ZSM-12. (B) CO₂-TPD curves of MgSi-ZSM-12 and 1%Au/MgSi-ZSM-12.

spectrum was fitted with two peaks at 83.8 eV ($4f_{5/2}$) and 87.5 eV ($4f_{7/2}$) for the Au⁰ species, revealing that the Au species existed dominantly in the form of metallic state [59]. Notably, the signal at 89.6 eV attributable to Mg2s also occurred explicitly (Fig. 4A) [60]. CO2 TPD profiles for 1%Au/MgSi-ZSM-12 and MgSi-ZSM-12 (Fig. 4B) demonstrate a desorption peak, though broad from 100 to 250 °C, for the moderate basic sites; by contrast, only negligible desorption peak appeared for Si-ZSM-12. The comparison implies that the moderate basicity should have originated from the incorporation of Mg species. The density of basic sites was calculated and listed in Table 2, showing the considerably high density of 1.45 and 1.24 mmol g^{-1} for MgSi-ZSM-12 and 1% Au/MgSi-ZSM-12, respectively.

3.2. Synthesis of FDCA from HMF

MgSi-ZSM-12 supported Au NPs were used as the heterogeneous catalyst for aerobic oxidation of HMF into FDCA by using atmospheric O₂ as the sole oxygen resource under base-free condition (Table 2). The support MgSi-ZSM-12 alone gave a very low HMF conversion of 8% and FDCA yield of 2% (Entry 1). After Au loading, the catalyst 1%Au/MgSi-ZSM-12 could effectively catalyze the synthesis of FDCA with a yield of 87 % and high TON of 331 (average TOF: 14) based on the surface Au species (Entry 2). The influence of Mg and Au contents was investigated. By referring our previous work [52], Mg containing MTW zeolite with the Si/Mg ratio of 100 in the gel was synthesized and used to support Au NPs, giving the catalyst 1.0 %Au/MgSi-ZSM-12-100 with a yield of 18.1 % for FDCA in the oxidation of HMF into FDCA (Entry 1, Table S2). Notably, the higher Mg concentration such as Si/Mg = 25 in the gel caused much weak crystallinity [52]. Therefore, Si/Mg = 50 is the optimized one. Further, different amount of Au NPs was loaded on MgSi-ZSM-12. The catalysis evaluation indicated that low Au content of 0.5 % led to a low FDCA yield, while high Au content of 1.5 % gave a comparable yield to that of 1.0 %Au/MgSi-ZSM-12. These results show that the champion catalyst is 1.0 %Au/MgSi-ZSM-12 with the initial Si/Mg ratio of 50 and Au loading of 1.0 %. For comparison, several control catalysts were prepared and evaluated in parallel. With the Mg-free support Si-ZSM-12, the sample 1%Au/Si-ZSM-12 exhibited a feeble activity without generation of FDCA (Entry 3). With the similarly synthesized Mg and Al co-bearing support of Mg-ZSM-12(600) (Si/Mg = 50, $SiO_2/Al_2O_3 = 600$) (Fig. S13-S16), the resultant counterpart 1% Au/Mg-ZSM-12(600) showed the lowered base sites (0.89 mmol g^{-1}), as well as a drastically decreased FDCA yield (23 %, Entry 4) compared with 1%Au/MgSi-ZSM-12. Besides, inert or weak activity (Entries 5-7) was observed over the Au NPs supported on SiO2, Al2O3 and MgO (Fig. S17-S19). All of these visualize the unique advantageous feature of 1%Au/MgSi-ZSM-12 in catalyzing the base-free oxidation of HMF to FDCA with atmospheric O₂.

In the common cognition, the aerobic oxidation of HMF to FDCA proceeds via two pathways (Scheme 2), in which either 2,5-diformylfuran (DFF) or HMFCA acted as the intermediate in the absence or presence of a liquid base [60,61], respectively. To figure out the oxidation pathway of HMF over 1%Au/MgSi-ZSM-12, time-dependence of the reaction was mapped in Fig. 5A. After the reaction at 90 °C for 4 h, the conversion of HMF reached 95 % with the FDCA yield of 19 %, where HMFCA was accumulated with the yield of 74 %. Prolonging the time promoted the conversion of HMF and production of FDCA. Throughout



the whole reaction, slight accumulation of FFCA below 20 % was observed. Nearly complete conversion of HMF was achieved at 8 h and then HMFCA was gradually converted into FFCA and finally FDCA. This phenomenon indicates that the oxidation of the first aldehyde group into carboxyl group is a rapid step while the transformation of the hydroxyl group into aldehyde group in the oxidation of HMFCA into FFCA exhibits as the rate-determining step. This kinetic process is in line with that in the presence of a base as the additive the Au NPs facilitates the oxidation of aldehyde group [62,63]. Therefore, it is rational to reason that the incorporated Mg species serve as a solid base that promotes the conversion of HMF into FDCA. To confirm this speculation, MgO and Mg (OH) $_2$ were employed as the solid base additive in the 1%Au/Si-ZSM-12 catalyzed oxidation of HMF into FDCA. As shown in Table 2, the yield of FDCA reached 98 % and 76 % in the presence of equal molar Mg(OH)₂ and MgO, respectively (Entries 8-9). Normally, the involving of MgO and Mg(OH)₂ in an aqueous solution would inevitably cause the leaching of Mg²⁺ [38]. The detected Mg content in the liquid phase after reaction was 9 ppm, suggesting that 37 % of Mg(OH)₂ had been dissolved. However, the yield dropped to 13 % if the solid part of slurry mixture was filtrated and allowed the reaction with the addition of fresh 1%Au/Si-ZSM-12 (Entry 10, Table 2). This phenomenon excluded the contribution of leached Mg species, which is further confirmed by the inert activity of 1%Au/Si-ZSM-12 in the presence of Mg(NO₃)₂ (Entry 11, Table 2). All these results indicate that the high activity of 1% Au/MgSi-ZSM-12 comes from the synergy of Au NPs and internal solid base property of the support MgSi-ZSM-12.

After the reaction, 1%Au/MgSi-ZSM-12 was recovered by centrifugation and reused. In a five-run test, no apparent deactivation was observed, revealing the stable recycling performance (Fig. 5B). XRD pattern of the spent 1%Au/MgSi-ZSM-12, shorted as 1%Au/MgSi-ZSM-12-r, displays the maintaining of the MTW topological crystal structure (Fig. S20A). Nitrogen sorption isotherm of 1%Au/MgSi-ZSM-12-r is identical to that of the fresh one, suggesting the preservation of the porosity (Fig. S20B). Its TEM image and particle size distribution curve (Fig. S21) shows highly dispersive Au NPs with an average particle size of 4.1 nm, close to the fresh one (3.9 nm). XPS analysis indicates that these Au NPs remained in the metallic stage (Fig. S22). The Au content of 1%Au/MgSi-ZSM-12-r was examined to be 0.96 %, only with a decrease by 0.06 % compared to the fresh one. The Si/Mg molar ratio changed from 32.0 in the fresh 1%Au/MgSi-ZSM-12 to 32.6 in the spent one. All of these demonstrate the stable structure of 1%Au/MgSi-ZSM-12, responsive to the quite steady recyclability. This robust catalytic behavior also excludes the potential formation of Mg(OH)₂ or MgO species in MgSi-ZSM-12. In terms of yield, TON and stability, Table S3 presents a comprehensive comparison of 1%Au/MgSi-ZSM-12 with previous homogeneous and heterogeneous catalysts under different conditions. There were some efficient heterogeneous catalysts exhibiting high yield and TON using atmospheric O2 but with the assistance of base additives (NaOH or K₂CO₃, etc.). Also, there were some catalysts were active in the base-free oxidation of HMF into FDCA but needing the use of high pressure O2. Compared with those catalysts operated under harsh conditions, the present 1%Au/MgSi-ZSM-12 exhibited inferior yield and TON while giving good recyclability. Compared with the several previous catalysts operated under atmospheric O2 in the absence of extra base additive [25,26,33,64,65]. 1%Au/MgSi-ZSM-12 showed comparable yield/TON and superior recycling performance, attributable to the internal stability of zeolitic catalysts. In short, the presently constructed 1%Au/MgSi-ZSM-12 acts as a stable heterogeneous catalyst for the oxidation of HMF into FDCA that turns out to be active under the base-free atmospheric O2-mediated mild condition.

3.3. Understanding of the catalytic behavior

Taking account of the similar dispersion of Au NPs of 1%Au/MgSi-ZSM-12 to the other control catalysts, its high activity seems associating with the specific basic property of the support MgSi-ZSM-12. The inert



Fig. 5. (A) Time-resolved and (B) recyclability for the oxidation of HMF into FDCA over 1%Au/MgSi-ZSM-12; Reaction conditions: HMF 0.1 mmol, HMF/metal molar ratio = 20:1, water 4 mL, 90 °C, O₂ balloon.

or weak activity was observed by using the neutral supports of Si-ZSM-12 and SiO₂, the acid support of Al_2O_3 or the common solid base MgO with weak base property (Fig. S23). This comparison emphasizes the vital role of the basic property of the supports, which is further revealed by the declined activity over 1%Au/Mg-ZSM-12(600).

Normally, the acid and/or base properties of solid catalysts significantly affect their surficial affinity toward reactant, intermediate and product, and thus would make a crucial contribution in a heterogeneous catalytic process [33,34]. Having this in mind, we investigated the adsorption behavior to unravel the affinity of HMF, HMFCA, FFCA, and FDCA towards different supports. At the beginning, we compared the adsorption of HMF, HMFCA, FFCA, and FDCA on MgSi-ZSM-12 at 90 °C (the reaction temperature in the oxidation of HMF into FDCA) and the room temperature of 25 °C (Fig. S24), observing quite similar adsorption amount. Based on these and the convenience for experimental operation, the adsorption study was carried out at 25 °C. The kinetic adsorption curves of HMF and FDCA on MgSi-ZSM-12 (Fig. 6A and B) display a high uptake of HMF and rapid adsorption rate; by contrast, negligible adsorption amount of FDCA was detected even elongating the adsorption time up to 24 h. This favorable adsorption towards the reactant HMF, together with near-zero affinity towards the product FDCA, is particularly important for the smoothly adhesive access of HMF catalytic active sites and then the generated FDCA product with better leaving ability. The low adsorption of HMFCA and moderate adsorption of FFCA were found on MgSi-ZSM-12, indicating the affinity towards different groups is in the sequence of aldehyde > alcohol > carboxyl. The inferior adsorption of HMFCA can be attributable to the repulsive force towards carboxyl groups, responding to the apparent

accumulation of this intermediate reflected by kinetic curves. On the contrary, acidic Al₂O₃ adsorbed more FDCA than HMF, and basic MgO effectively adsorbed all of them. Further, SiO2 and Si-ZSM-12 of neutral supports and Mg-ZSM-12(600) with both inferior basic sites and certain Al-derived acidic sites also showed unfavorable adsorption performance; weak adsorption was demonstrated for all those organic compounds. Consequently, the adsorption behaviors for the versatile control supports hamper the HMF adsorption and FDCA leaving, and thus resulting in much lowered activity. Oxidation of HMF into FDCA was further carried out in the presence of FDCA with the amounts of 0.01 and 0.02 mmol, respectively, by using the catalysts of 1%Au/MgSi-ZSM-12, 1%Au/Mg-ZSM-12(600) and 1%Au/Si-ZSM-12+MgO. As shown in Fig. S25, declining yield was observable with the increasing dosage of FDCA, revealing the inhibition effect of the product. A more significant effect was found over 1%Au/Mg-ZSM-12(600) than 1%Au/Mg-Si-ZSM-12, corresponding to the higher adsorption amount over the former than the latter (Fig. 6A). The weakest influence over 1% Au/Si-ZSM-12+MgO is assignable to preferential adsorption of acidic FDCA on basic sites of MgO rather than the relavely neutral 1% Au/Si-ZSM-12, preserving the active Au species on 1%Au/Si-ZSM-12 to a large degree. The above analysis on the adsorption behavior allows drawing that, it by virtue of the superior basicity of the heteroatomic zeolite MgSi-ZSM-12 that the favorable reactant adsorption and product desorption are achieved, for which the thus supported Au NPs can smoothly and effectively catalyze the atmospheric O2-mediated oxidation of HMF into FDCA under the base-free mild condition.



Fig. 6. (A) Adsorption amount of HMF, HMFCA, FFCA, and FDCA on different solid. Adsorption condition: adsorbate 0.01 mmol, adsorbent 0.1 g, water 4 mL, 25 °C, 24 h. (B) Time-resolved adsorption of HMF and FDCA on MgSi-ZSM-12. To show the Time-resolved adsorption amount more significant, we increased the adsorption concentration. Adsorption condition: adsorbate 0.01 mmol, adsorbent 0.05 g, water 1 mL, 25 °C.

4. Conclusions

MgSi-ZSM-12 heteroatomic zeolite was directly synthesized in a hydrothermal route, showing same structure-directing effect of the TEA template as that of the all-silica Si-ZSM-12 itself. After Mg incorporation, The basicity of MgSi-ZSM-12 was greatly strengthened due to the in situ embedding of Mg species. With this solid base MgSi-ZSM-12 as the support, the resultant Au NPs sized \sim 3.9 nm effectively catalyzed the oxidation of HMF into FDCA with atmospheric O2 under base-free condition. The catalyst was conveniently recovered and reused without apparent deactivation. We clarify that MgSi-ZSM-12 has sufficient affinity to aldehyde group, weak interaction to alcohol group and repulsive force to carboxyl. Owing to this unique character, the catalyst reached desirably preferential adsorption of HMF and facile desorption of FDCA, responsive to the excellent catalytic performance. This work highlights the potentially promising application of alkaline-earth metalbearing heteroatomic zeolites as the multi-functional supports of noble metal NPs in biomass conversion field.

CRediT authorship contribution statement

Lei Chen: Investigation, Formal analysis, Writing - original draft. Wenxia Zhuang: Data curation, Formal analysis, Writing - review & editing. Jingmin Lan: Writing - review & editing, Formal analysis. Xiaoling Liu: Writing - review & editing, Formal analysis. Shi Jiang: Writing - review & editing, Formal analysis. Lei Wang: Writing - review & editing, Formal analysis. Yu Zhou: Conceptualization, Investigation, Methodology, Supervision, Writing - review & editing. Jun Wang: Conceptualization, Supervision, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.apcata.2021.118106.

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