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Article

Sodium-treated sepiolite-supported transition metal (Cu, Fe, Ni, Mn, or Co) catalysts for HCHO oxidation

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ABSTRACT

Sodium-treated sepiolite (NaSep)-supported transition metal catalysts (TM/NaSep; TM = Cu, Fe, Ni, Mn, and Co) were synthesized via a rotary evaporation method. Physicochemical properties of the as-synthesized samples were characterized by means of various techniques, and their catalytic activities for HCHO (0.2%) oxidation were evaluated. Among the samples, Cu/NaSep exhibited superior performance, and complete HCHO conversion was achieved at 100 °C (GHSV = 240000 mL/(g·h)). Additionally, the sample retained good catalytic activity during a 42 h stability test. A number of factors, including elevated acidity, the abundance of oxygen species, and favorable low-temperature reducibility, were responsible for the excellent catalytic activity of Cu/NaSep. According to the results of the in-situ DRIFTS characterization, the HCHO oxidation mechanism was as follows: (i) HCHO was rapidly decomposed into dioxymethylene (DOM) species on the Cu/NaSep surface; (ii) DOM was then immediately converted to formate species; (iii) the resultant formate species were further oxidized to carbonates; (iv) the carbonate species were eventually converted to CO₂ and H₂O.

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1. Introduction

Formaldehyde (HCHO), a common volatile organic compound (VOC) and an indoor air contaminant, comes from variety of sources, such as building materials, plastic cements, and paints [1]. Long-term exposure to HCHO can cause serious harm to human health. Therefore, the effective removal of HCHO from numerous environments is an urgent necessity. HCHO removal is commonly performed through adsorption [2], plasma treatment [3], or catalytic oxidation [4–7]. Compared

with other methods, catalytic oxidation is currently considered to be the most effective for HCHO removal, wherein HCHO is transformed into harmless CO₂ and H₂O at low temperatures [8,9].

According to the literature, catalysts comprising noble metals (Au, Pt, Pd and Ag) on various supports exhibit good activities towards HCHO removal [10,11]. However, their high cost and poisoning tendency have limited broader application of noble metal-based catalysts. Due to the advantages of cost efficiency and favorable catalytic performance, transition metal

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oxides are commonly used for the oxidative removal of HCHO. For example, Sekine et al. [12] employed MnO_2 to achieve the oxidation of HCHO at room temperature. Tian et al. [13] compared catalytic activities of manganese oxides of varying crystal phases for HCHO oxidation. In general, catalytic activity is dependent on the active components and physical properties of the support used, such as crystal structure, chemical composition, surface area, and thermal stability. Therefore, it is essential to develop suitable supports for transition metal catalysts that will enhance their catalytic performance.

Sepiolite has a higher adsorption capacity and superior physicochemical stability compared to other types of silicate clays; it is a natural clay mineral with specific functional groups and a fibrous appearance. Alternating blocks are found in the direction of the fibers as well as internal tunnels. The block structure is surrounded by two tetrahedral SiO_2 , and the center is composed of MgO [14]. As sepiolite has an abundance hydroxyl groups, no water addition or activation is required. A previous study [15] has employed sepiolite (Sep) for adsorption and catalysis. Song et al. [16] studied the oxidation of CO over Cu-Mn/Ti-Sep catalysts at low temperatures. Ma et al. [17] implemented a 1 wt% Pt/Sep catalyst to completely convert HCHO at room temperature. Zhang et al. [18] studied the decomposition of HCHO over the TiO_2 /Sep catalyst.

Modification of sepiolite with sodium could improve its thermal stability and cation exchange capacity, without altering its original structure. In this study, we utilized Na-treated sepiolite (NaSep) as a support to prepare the TM/NaSep catalysts (TM = Cu, Fe, Ni, Mn, and Co), characterized their physicochemical properties, and evaluated their catalytic activities for the oxidation of HCHO. The synergic action between TM and NaSep was found to improve low-temperature reducibility of the catalyst, contributing to enhanced catalytic performance.

2. Experimental

2.1. Catalyst preparation

The sepiolite raw material was purchased from the Liuyang Sepiolite Mining Industry Company of China. The support was prepared using sodium-leached sepiolite. The modification of sepiolite with sodium is expected to improve the thermal stability and cation exchange capacity of the sample, without altering the original structure of the mineral. The chemical composition of sepiolite and the sodium treatment method are described in the Supplementary material. It is well-known that various raw sepiolites differ slightly in composition. Additionally, following the modification of sepiolite with sodium, its physical properties were determined. In the present study, various transition metals were loaded onto sodium-modified sepiolite and the catalytic activity of the resultant complexes was evaluated for HCHO oxidation.

The Cu/NaSep catalysts (Cu loading = 1.0, 3.0, 5.0, and 7.0 wt%) were prepared using the rotary evaporation method, with NaSep as the support and an aqueous copper nitrate solution (A.R., Merck) as the copper source. To explore the effect of calcination temperature, the 1Cu/NaSep samples were pre-

pared following calcination at a range of temperatures (300, 400, and 500 °C). The samples were dried for 1 day and calcined at 400 °C for 2 h, denoted as x wt% Cu/NaSep, and their catalytic activity for HCHO oxidation are shown in Fig. S1.

The remainder of the transition metal-loaded catalysts (theoretical transition metal loading = 5.0 wt%) were prepared using the above rotary evaporation method, employing the nitrates of Fe, Co, Ni or Mn (A.R., Beijing Chemical Company) as the corresponding metal precursor. The obtained samples were denoted as TM/NaSep.

2.2. Catalyst characterization

The X-ray diffraction (XRD) patterns of the samples were recorded using a Bruker D8-Advance diffractometer in the 2θ range of 5°–80° ($\lambda = 0.15404$ nm at a scan rate of 5°/min). Nitrogen sorption isotherms were obtained at the temperature of liquid nitrogen (–196 °C) on a JW-BK200C apparatus. Specific surface areas were calculated using the Brunauer-Emmett-Teller (BET) equation, and their pore-size distributions were determined using the desorption branch data of the isotherms by the Barrett-Joyner-Halenda (BJH) method.

H_2 temperature-programmed reduction (H_2 -TPR) of the samples was performed on a Builder PCA-1200 analyzer. Prior to the H_2 -TPR experiment, 100 mg of the sample was pretreated in a 5 vol% O_2/N_2 mixture flowing at 30 mL/min at 400 °C for 1 h, and subsequently cooled to RT. The sample was then reduced in a 5 vol% H_2/N_2 mixture flowing at 30 mL/min at a ramp of 10 °C/min from RT to 1000 °C. The reduction peaks were calibrated against data from a powdered CuO reduction (Aldrich, 99.995%).

X-ray photoelectron spectroscopic (XPS) analysis was recorded on a Thermo ESCALAB 250Xi electron spectrometer equipped with an Al K_α X-ray source and a hemispherical electron analyzer operating at constant pass energy (30.0 eV).

Fourier-transform infrared (FTIR) spectra were recorded on a Thermo Scientific Nicolet 6700 FTIR spectrometer. The in situ diffuse reflectance infrared spectroscopic (DRIFTS) experiments were conducted on a Bruker TENSOR II spectrometer characterized by a reaction chamber that could withstand high temperatures (Harrick Praying Mantis). The catalyst sample was packed into the sample cup of the reaction chamber and heated to 400 °C at a total N_2 flow rate of 200 mL/min for 1 h, in order to remove any adsorbed impurities. Each spectrum had a resolution of 4 cm^{-1} , with 32 accumulated scans.

2.3. Catalytic activity evaluation

HCHO oxidation activity was evaluated by mixing 50 mg of catalyst and 50 mg of quartz sand in a fixed-bed quartz tubular reactor. The HCHO concentration was analyzed online on a Techcomp GC-7900 gas chromatograph equipped with a flame ion detector (FID). The conversion of HCHO (X_{HCHO}) was calculated based on the changes in HCHO concentration ($C_{\text{HCHO,inlet}}$ and $C_{\text{HCHO,outlet}}$) in the inlet and outlet gas mixture, according to the formula shown below. Detailed measurement data are listed in the Supplementary material.

$$X_{\text{HCHO}} = \frac{C_{\text{HCHOinlet}} - C_{\text{HCHOoutlet}}}{C_{\text{HCHOinlet}}} \times 100\%$$

3. Results and discussion

3.1. Crystal phase composition

Figure 1 depicts the XRD patterns of the NaSep and TM/NaSep (TM = Cu, Fe, Co, Ni, and Mn) samples. The characteristic diffraction peaks of sepiolite ordinarily appear at $2\theta = 20.6^\circ, 26.6^\circ, 28.0^\circ, 35.2^\circ, 40.4^\circ$, and 50.2° [19]. Evidently, NaSep and TM/NaSep exhibited the crystal phase of sepiolite. The standard XRD patterns of CuO, Fe₂O₃, NiO, and MnO₂ are shown in the Supplementary material, Fig. S2. The Cu/NaSep sample exhibited additional diffraction peaks at $2\theta = 35.5^\circ$ and 38.8° , corresponding to the (002) and (111) planes of the monoclinic CuO phase. In the case of the Fe/NaSep sample, a new diffraction peak was recorded at $2\theta = 35.5^\circ$, which was attributed to the (110) plane of Fe₂O₃. The Ni/NaSep sample exhibited additional diffraction peaks at $2\theta = 44.2^\circ$, which could be assigned to the phase of NiO. Regarding the Mn/NaSep sample, the diffraction peaks at $2\theta = 35.1^\circ$ and 55.1° were ascribed to the phase of MnO₂. In the case of the Co/NaSep sample, no diffraction peaks due to cobalt oxides were observed, indicating extensive dispersion of the cobalt species on the surface of NaSep.

The FT-IR spectra of NaSep and TM/NaSep are illustrated in Fig. S3. The bands at 3680 and 3600 cm⁻¹ were assigned to the stretching vibrations of the sepiolite hydroxyl group [20,21], and the peaks at 3440 and 1625 cm⁻¹ were attributed to the tensile and flexural vibrations of the hydroxyl group, respectively, which arose due to the presence of zeolite and bound water in the sepiolite nanofiber structure [22,23]. The bands at 1030 and 480 cm⁻¹ were due to the tensile vibration of Si–O in the tetrahedral Si–O–Si motif, and the bending vibration of Si–O–Si [24], respectively. The band at 690 cm⁻¹ was attributable to the bending vibration of Mg₃OH [25]. It is noteworthy that all of the characteristic bands remained largely unchanged upon loading of transition metal oxides.

3.2. N₂ adsorption and SEM characterization

Figure S4 displays the N₂ adsorption-desorption isotherms of the samples. All of the sorption isotherms were type I in the range of low relative pressures, due to the existence of a microporous structure [26]. When the relative pressure (p/p_0) was in the range of 0.8–1.0, a type IV adsorption isotherm was

Fig. 1. XRD patterns of (a) NaSep, (b) Cu/NaSep, (c) Fe/NaSep, (d) Co/NaSep, (e) Ni/NaSep, and (f) Mn/NaSep.

observed, with a type H3 hysteresis loop, indicating the presence of slit-like mesopores [27]. BET surface areas of the NaSep and TM/NaSep samples are summarized in Table 1. The surface areas of the TM/NaSep samples (40–63 m²/g) were markedly lower than that of the NaSep support (96 m²/g), which may be due to the partial blocking of the pores by the transition metal oxides. The surface area of the samples decreased in the order of: Fe/NaSep (63 m²/g) > Ni/NaSep (48 m²/g) > Co/NaSep (43 m²/g) > Mn/NaSep (42 m²/g) > Cu/NaSep (40 m²/g).

Figure 2 illustrates the SEM images of the NaSep and TM/NaSep samples. All of the samples displayed a fibrous morphology with a smooth surface, which is typical for a sepiolite structure. Although the surface area of sepiolite decreased upon loading of the transition metal oxides, there were no significant morphological differences between the NaSep and TM/NaSep samples.

3.3. Surface metal oxidation state

XPS was implemented in order to analyze the surface element composition and chemical state. Figure 3 shows the XPS spectra of each sample; their surface element compositions and metal chemical states are listed in Table 2. Figure 3a represents the Cu 2p_{3/2} XPS spectrum of the Cu/NaSep sample. The two asymmetric characteristic peaks could be decomposed into three components: one at a binding energy (BE) of 933.4 eV, the other at 935.7 eV, together with a satellite peak at 943.1 eV. According to the literature [28], the component at 933.4 eV was

Table 1

TM/NaSep and NaSep surface areas, reduction temperatures and H₂ consumption.

Sample	Surface area (m ² /g)	Reduction temperature (°C)			H ₂ consumption (mmol/g _{cat})			
		Peak 1	Peak 2	Peak 3	Peak 1	Peak 2	Peak 3	Total
Cu/NaSep	40	252	293	524	0.157	0.259	0.015	0.431
Fe/NaSep	63	406	556	625	0.157	0.126	0.072	0.355
Co/NaSep	43	466	651	704	0.111	0.044	0.036	0.191
Ni/NaSep	48	342	413	581	0.041	0.123	0.029	0.193
Mn/NaSep	42	374	552	668	0.121	0.179	0.048	0.348
NaSep	96	410	544	633	0.0003	0.091	0.097	0.188

Fig. 2. SEM images of (a) Cu/NaSep, (b) Fe/NaSep, (c) Co/NaSep, (d) Ni/NaSep, (e) Mn/NaSep, and (f) NaSep.

assigned to surface bivalent copper (i.e., isolated Cu^{2+} and CuO) species. The isolated Cu^{2+} and CuO species could be distinguished according to their BEs, as the BE of the isolated Cu^{2+} species was higher than that of the CuO species [16]. The peak in the 943.0–945.9 eV range was a satellite signal, which is a feature of Cu^{2+} presence. Therefore, the component peak at

933.4 eV was attributed to the surface CuO species, the peak at 935.7 eV was assigned to the surface isolated Cu^{2+} species, and the peak at 943.1 eV was ascribed to the satellite of the surface Cu^{2+} species. The atomic ratio of $\text{Cu}^{2+}/\text{CuO}$ was 2.53. The presence of CuO was confirmed by the detection of CuO diffraction peaks in the XRD pattern (Fig. 1b).

Figure 3b illustrates the Fe 2p spectra of the Fe/NaSep sample. The presence of four component peaks was detected at 710.7, 724.0, 713.2, and 725.9 eV in the Fe 2p XPS spectrum. The components at 710.7 and 724.0 eV represented the Fe $2p_{3/2}$ and Fe $2p_{1/2}$ final states of the surface Fe^{2+} species [29], respectively, whereas the peaks at 713.2 and 725.9 eV were attributed to the Fe $2p_{1/2}$ and Fe $2p_{3/2}$ final states of the surface Fe^{3+} species. Therefore, both Fe^{2+} and Fe^{3+} species were present in the sample.

In the Co 2p XPS spectrum of the Co/NaSep sample (Fig. 3c), the oxidation states of Co were Co^{3+} (779.1 eV) and Co^{2+} (781.3 eV) [30]. In addition, the satellite peak at 783.6 eV was indicative of the presence of Co^{2+} species in Co_3O_4 [31]. This suggests that the Co_3O_4 in Co/NaSep was composed of Co^{2+} and Co^{3+} species.

Fig. 3d shows the Ni 2p XPS spectrum of the Ni/NaSep sample. The peak at 854.8 eV was attributed to the Ni $2p_{1/2}$ split orbital of NiO, whereas the peak at 847.8 eV was assigned to the surface Ni^0 species [32]. The satellite peak at 860.9 eV was indicative of Ni^{2+} presence [33]. The $\text{Ni}^{2+}/\text{Ni}^0$ atomic ratio (2.72) was high, indicating that Ni^{2+} was the dominant surface nickel species, which was consistent with the detection of a NiO phase in the XRD pattern.

The BEs of the Mn $2p_{3/2}$ and Mn $2p_{1/2}$ in the Mn 2p spectrum (Fig. 3e) were 642.0 and 654.0 eV, respectively. The

Fig. 3. (a) Cu 2p, (b) Fe 2p, (c) Co 2p, (d) Ni 2p, (e) Mn 2p, and (f) TM/NaSep O 1s XPS spectra.

Table 2

Surface element compositions obtained by quantitative analysis of the TM/NaSep XPS spectra.

Sample	Metal atomic ratio	$O_{\text{ads}}/(O_{\text{latt}}+O_{\text{OH}})$ atomic ratio
Cu/NaSep	$\text{Cu}^{2+}/\text{CuO}$ (2.53)	0.75
Fe/NaSep	$\text{Fe}^{3+}/\text{Fe}^{2+}$ (1.34)	0.56
Mn/NaSep	$\text{Mn}^{4+}/\text{Mn}^{3+}$ (0.42)	0.45
Ni/NaSep	$\text{Ni}^{2+}/\text{Ni}^0$ (2.72)	0.38
Co/NaSep	$\text{Co}^{3+}/\text{Co}^{2+}$ (0.24)	0.28

components at 640.9, 642.0, and 644.8 eV in the Mn $2p_{3/2}$ spectrum represented the surface Mn^{2+} , Mn^{3+} , and Mn^{4+} species [34,35], respectively. As shown in Table 2, the $\text{Mn}^{4+}/\text{Mn}^{3+}$ atomic ratio was not high (0.42), indicating that the quantities of Mn^{3+} and Mn^{4+} were similar on the surface of the Mn/NaSep sample.

The O 1s XPS spectra of the samples are illustrated in Fig. 3f. The three peaks appearing at 530.8, 531.6 and 532.7 eV, represent surface lattice oxygen (O_{latt}), adsorbed oxygen (O_{ads}) and adsorbed molecular H_2O (O_{OH}) [36], respectively. The $O_{\text{ads}}/(O_{\text{latt}}+O_{\text{OH}})$ atomic ratios are summarized in Table 2, from which it can be seen that the $O_{\text{ads}}/(O_{\text{latt}}+O_{\text{OH}})$ atomic ratio decreases in the order of Cu/NaSep (0.75) > Fe/NaSep (0.56) > Mn/NaSep (0.45) > Ni/NaSep (0.38) > Co/NaSep (0.28). The O_{ads} concentration was closely related to the oxidation of HCHO, with catalytic activity increasing with increasing O_{ads} concentration [37,38]. Therefore, the Cu/NaSep sample exhibited the highest activity among the tested samples.

3.4. Reducibility

The reducibility of a catalyst can be evaluated by the H_2 -TPR technique. Figure 4 represents the H_2 -TPR profiles of the NaSep and TM/NaSep samples; their peak temperatures and H_2 consumption are listed in Table 1. Three reduction peaks were observed for the NaSep sample, at 410, 544, and 633 °C. According to the XRF analysis results, components such as SiO_2 , Al_2O_3 , and MgO accounted for a high proportion of sepiolite, however their reduction is challenging. As the iron oxide content of the NaSep was 2.84 wt%, it is reasonable to attribute the reduction peaks at 410, 544, and 633 °C to the reduction Fe via

$\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$, $\text{Fe}_3\text{O}_4 \rightarrow \text{FeO}$, and $\text{FeO} \rightarrow \text{Fe}^0$ [39], respectively. The H_2 -TPR profile of the Fe/NaSep sample exhibited three reduction peaks at 406, 556, and 625 °C, resembling those of the NaSep sample. This result further confirmed that the reduction peaks of the NaSep sample were caused by the reduction of Fe. In the case of Cu/NaSep, three low-temperature reduction peaks were observed at 252, 293 and 524 °C. The low-temperature reduction peak (252 °C) was due to the reduction of Cu^{2+} to Cu^+ , the peak at 293 °C could be attributed to the reduction of the bulk CuO species [40], and the third peak (524 °C) corresponded to the reduction of Fe^{3+} or Fe^{2+} species. We considered that the interaction between Fe and Cu could improve the catalytic performance. Doping of Cu species gave rise to a shift in the reduction temperature of Fe_3O_4 to FeO to a lower temperature [41,42]. As can be seen from Fig. 4, the reduction temperature of the Cu/NaSep sample was 524 °C, which was lower than that of the Fe/NaSep sample (556 °C), proving that the loading of Cu decreased the reduction temperature of Fe species. Three separate reduction peaks were detected for the Co/NaSep sample, at 466, 651, and 704 °C. The reduction peak at 466 °C was attributed to the reduction of Co^{3+} to Co^{2+} in Co_3O_4 [43], the peak at 704 °C was due to the reduction of Co^{2+} to Co^0 [44], and the peak at 651 °C was ascribed to the reduction of FeO to Fe^0 in sepiolite. The H_2 -TPR profile of the Ni/NaSep sample likewise contained three reduction peaks. The first weak peak at 342 °C was due to the reduction of surface NiO species, the peak at 413 °C was attributed to the reduction of bulk NiO species [45], and the third peak at 581 °C was due to the reduction of small NiO particles [46]. No reduction peaks assignable to the reduction of Fe were observed, which may be due to the coverage of Fe oxides by the supported Ni oxide. The Mn/NaSep sample was reduced at 374, 552, and 668 °C. The reduction of MnO_x could be explained by three successive reduction processes: $\text{MnO}_2 \rightarrow \text{Mn}_2\text{O}_3 \rightarrow \text{Mn}_3\text{O}_4 \rightarrow \text{MnO}$ [47]. The first peak at 374 °C was due to reduction of MnO_2 to Mn_2O_3 , the second one at 552 °C with the largest reduction area was due to reduction of Mn_2O_3 to Mn_3O_4 and Mn_3O_4 to MnO, and the third peak at 668 °C was due to the reduction of FeO to Fe^0 .

The sequence of low-temperature reducibility was as follows: Cu/NaSep (252 °C) > Ni/NaSep (342 °C) > Mn/NaSep (374 °C) > Fe/NaSep (406 °C) > Co/NaSep (466 °C). Evidently, the Cu/NaSep sample exhibited the lowest reduction temperature, and hence, superior low-temperature reducibility compared to the other samples.

3.5. Surface acidity

Sepiolite is rich in hydroxyl groups, which allows for the generation of Brönsted acid sites. According to the literature [48,49], adsorption of NH_3 on the Brönsted acid sites ($-\text{OH}$) to form $-\text{NH}_4^+$, and the result of NH_3 -TPD characterization, verified the presence of hydroxyl groups in the sample. Abundant hydroxyl groups would allow for increased adsorption of HCHO on the as-prepared catalysts and improve the catalytic oxidation of HCHO.

Figure 5 shows the NH_3 -TPD profiles of the NaSep and

Fig. 4. TM/NaSep and NaSep H_2 -TPR profiles.

Fig. 5. NH_3 -TPD profiles of the TM/NaSep samples.

TM/NaSep samples. The TPD profiles could be decomposed into desorption stages of 150–220, 220–300, and 300–450 °C, corresponding to the weak, medium, and strong acid sites, respectively. According to the literature, ammonia desorption from the Brønsted acid occurs more readily than desorption of the ammonia coordinated to the Lewis acid sites, during temperature-programmed desorption [50,51]. Therefore, the desorption peak at 150–220 °C was assigned to the desorption of physically adsorbed NH_3 and a portion of NH_4^+ bound to the weak Brønsted acid sites, whereas the peak at 220–300 °C was attributed to desorption of NH_4^+ bound to the strong Brønsted acid sites, and the peak above 300 °C corresponded with the desorption of NH_3 coordinated with the Lewis acid sites.

In the case of the NaSep sample, desorption from the weak Brønsted acid sites of the physically adsorbed NH_3 and a portion of NH_4^+ occurred below 220 °C, and the NH_4^+ bound to the strong Brønsted acid sites were desorbed at 257 °C. As shown in Fig. 5, when the transition metal oxide was loaded onto NaSep, the amount of the adsorbed NH_3 increased, indicating that the transition metal oxide provided additional Brønsted acid sites. The appearance of a Lewis acid site above 300 °C was likewise as a result of transition metal oxide loading. This, in turn, led to significant increases in the amounts of medium and strong acid sites, thus increasing the total acid amount.

As shown in the Table 3, the total acidity amount of NaSep was 18 $\mu\text{mol/g}$. The order of decreasing total acidity was as follows: Cu/NaSep (57 $\mu\text{mol/g}$) > Fe/NaSep (34 $\mu\text{mol/g}$) > Mn/NaSep (30 $\mu\text{mol/g}$) > Ni/NaSep (28 $\mu\text{mol/g}$) > Co/NaSep (26 $\mu\text{mol/g}$). The total acidity of the Cu/NaSep sample was

Table 3

Acidity distribution of the TM/NaSep samples.

Sample	Ammonia uptake ($\mu\text{mol/g}$)			Total
	Weak (150–220 °C)	Medium (220–300 °C)	Strong (300–450 °C)	
Cu/NaSep	32	17	8	57
Fe/NaSep	18	11	5	34
Co/NaSep	15	8	3	26
Ni/NaSep	14	9	5	28
Mn/NaSep	17	10	3	30
NaSep	11	7	—	18

markedly higher compared with that of the other samples. This result might be due to the capability of copper oxide to generate higher amounts of Lewis acid sites than the other transition metal oxides. The results correlated well with the catalytic activity order of these samples for HCHO oxidation.

3.6. Catalytic performance

Figure 6a depicts the catalytic activities of the NaSep and TM/NaSep samples for the oxidation of HCHO. Reaction temperatures required to achieve HCHO conversions of 50% and 100% ($T_{50\%}$ and $T_{100\%}$) were used in order to evaluate the catalytic activity of the samples. The result of the blank test, which contained quartz sand as the only element in the microreactor, indicated that no HCHO conversion was detected below 250 °C. In other words, HCHO and O_2 did not react below 250 °C in the absence of a catalyst. To explore the effect of calcination temperature, we prepared the 1Cu/NaSep-300, 1Cu/NaSep-400, and 1Cu/NaSep-500 by calcining the 1Cu/NaSep sample at 300, 400, and 500 °C, respectively, and their catalytic activities are shown in Fig. S5. Apparently, the 1Cu/NaSep-400 sample exhibited superior performance for HCHO oxidation.

It can be seen from Fig. 6a that HCHO conversion increased with increasing reaction temperature. The catalytic activity of NaSep was the lowest, with $T_{50\%}$ and $T_{100\%}$ being 140 and 260

Fig. 6. (a) HCHO conversion as a function of temperature over the samples and (b) HCHO conversion versus reaction time over the Cu/NaSep sample at 80 °C under the conditions of 0.2% HCHO + 20 vol% O_2 + N_2 (balance) and GHSV = 240000 $\text{mL}/(\text{g}\cdot\text{h})$.

Table 4

Comparison of specific reaction rates (r_{cat}) for HCHO oxidation at 75 °C between the catalysts studied in the present work and those reported in the literature.

Catalyst	r_{cat} (mol/(g _{cat} s))	Ref.
Cu/NaSep	2.89×10^{-6}	This study
Fe/NaSep	2.45×10^{-6}	This study
Mn/NaSep	2.07×10^{-6}	This study
Ni/NaSep	1.47×10^{-6}	This study
Co/NaSep	1.19×10^{-6}	This study
NaSep	4.36×10^{-7}	This study
Cu-Mn/TiO ₂	1.53×10^{-8}	[53]
Cu-Mn/ γ -Al ₂ O ₃	2.30×10^{-8}	[53]
Mn-Cu-Ce mixed oxide	6.81×10^{-8}	[54]

°C, respectively. This was due to the presence of Fe₂O₃ species in NaSep, which exhibited low activity for the oxidation of HCHO. Compared with the NaSep sample, the loading of transition metal oxides decreased the reaction temperature and increased the catalytic activity significantly. The catalytic activity of the Cu/NaSep sample was the highest among the TM/NaSep samples, with $T_{50\%}$ and $T_{100\%}$ being 70 and 100 °C, respectively.

The reaction rate (r_{cat}) can reflect inherent catalytic activity [52]. The r_{cat} is defined as the molar number of HCHO converted per gram of catalyst per second (mol/(g_{cat} s)). The r_{cat} values of HCHO oxidation at 75 °C with the various TM/NaSep samples are summarized in Table 4. The r_{cat} values for HCHO oxidation at 75 °C over TM/NaSep and NaSep (2.89×10^{-6} – 4.36×10^{-7} mol/(g_{cat} s)) were considerably higher than the rates over Cu-Mn/TiO₂ and Cu-Mn/ γ -Al₂O₃ at 75 °C (1.53×10^{-8} mol/(g_{cat} s) and 2.30×10^{-8} mol/(g_{cat} s), respectively) [53]. The reaction rate over the Mn-Cu-Ce mixed oxides at 150 °C (6.81×10^{-8} mol/(g_{cat} s)) was appreciably lower than those exhibited by the samples prepared in this study [54]. The r_{cat} decreased in the order of Cu/NaSep > Fe/NaSep > Mn/NaSep > Ni/NaSep > Co/NaSep > NaSep, which was remarkably consistent with the trend in catalytic activity of the samples.

Figure 6b shows catalytic stability of the Cu/NaSep sample over 42 h of on-stream HCHO oxidation at 80 °C. Evidently, during the 42 h reaction, no significant loss in activity was ob-

served, indicating that the Cu/NaSep sample was catalytically stable under the adopted reaction conditions.

3.7. In situ DRIFTS and catalytic oxidation mechanism

The catalytic HCHO oxidation mechanism of the Cu/NaSep sample was studied using the in situ DRIFTS technique, and the spectra are shown in Fig. 7a. Upon exposure to free-O₂ gas (0.2% HCHO + N₂) at 50 °C, bands at 3510, 2976, 2893, 1725, 1635, 1595, 1460, and 1402 cm⁻¹ were observed. The band at 3510 cm⁻¹ was assigned to the stretching vibration of the hydroxyl group [55,56]; those at 2976, 2893, 1595, and 1402 cm⁻¹ were attributed to the formate species on the surface of the sample; the bands at 2976 and 2893 cm⁻¹ were ascribed to the stretching vibration of the C–H bond; and those at 1595 and 1402 cm⁻¹ were due to the $\nu_{\text{as}}(\text{COO}^-)$ and $\delta(\text{CH})$, respectively [57]. The band at 1635 cm⁻¹ was due to adsorbed water on the catalyst surface [58]. Moreover, the band at 1725 cm⁻¹ was assigned to the vibration of $\nu(\text{C=O})$ in the carbonate species [59,60], and the weak band at 1460 cm⁻¹ was due to dioxymethylene (DOM) [58]. No bands associated with HCHO were recorded, indicating that HCHO was oxidized following its adsorption onto the sample surface. According to the literature [61], when HCHO is catalytically oxidized over noble metals or metal oxides, it progressively transforms into DOM species, followed by immediate decomposition into formate species. As seen in Fig. 7, the amount of DOM species observed was minimal, due to the fact that sepiolite possesses abundant hydroxyl groups, as previously reported [17,62] and corroborated by FT-IR results in the present study. Abundant hydroxyl groups could amplify the adsorption of HCHO on the as-prepared catalysts and thereby improve the activity of HCHO oxidation. In the absence of O₂, HCHO could nonetheless be rapidly oxidized to formate [58], as a result of the reactions between adsorbed HCHO and surface adsorbed oxygen and/or hydroxyl groups:

As the temperature increased, peak intensity for the hydroxyl group decreased, as the hydroxyl group was involved in the oxidation of HCHO, rather than in its desorption from the

Fig. 7. (a) In situ DRIFTS spectra of HCHO adsorption on the Cu/NaSep sample under the condition of 50 °C and 0.2% HCHO + N₂ (balance), and (b) in situ DRIFTS spectra of the Cu/NaSep sample in a flow of 0.2% HCHO + 20 vol% O₂ + N₂ (balance) at 50 °C and at specific times.

catalyst surface.

The in situ DRIFTS spectra of the Cu/NaSep sample for the oxidation of HCHO on the sample surface at 50 °C are shown in Fig. 7b. Peak intensity of the corresponding formate species (1595 and 1402 cm⁻¹) increased significantly, whilst that of the hydroxyl group (3510 cm⁻¹) and carbonate species (1725 cm⁻¹) decreased slightly. HCHO decomposed into formate species when the catalyst surface was oxidized, and the generated formate species further decomposed into carbonates, which were eventually converted to H₂O and CO₂ [57,63,64]. This further confirms that the intermediate product of HCHO oxidation is the formate species. The increase in the intensity of the band assigned to the formates was due to the introduction of oxygen, supplementing the oxygen vacancies on the surface of the sample and increasing the amount of surface active oxygen species, which subsequently increased the production of formate species. While the formate species did not decompose further at 50 °C, it was necessary to explore its transformation at various temperatures as a means of probing the oxidation process of HCHO.

Following the adsorption of HCHO onto the catalyst at 50 °C for 1 h, we analyzed the changes in the species on the catalyst surface in the atmosphere (N₂ + O₂). As can be seen from Fig. S6, the characteristic peaks of the formate species significantly increased in intensity after the introduction of synthetic air. This result further verified that formate was an important intermediate of HCHO oxidation.

In order to investigate the oxidation of intermediates formed during the HCHO oxidation process at varying temperatures, we performed the oxidation of HCHO for 1 h over Cu/NaSep with oxygen at 50, 75 or 100 °C, and the results are shown in Fig. 8. As revealed in the HCHO oxidation at 50 °C (Fig. 7b), the formate and carbonate species were decomposed on the surface of Cu/NaSep. When the temperature reached 75 °C, the intensity of the bands (at 1595 and 1402 cm⁻¹) assignable to the formate species decreased significantly, indicating that the decomposition rate of the formate species increased rapidly. The characteristic band intensity of the hydroxyl group (at 3510 cm⁻¹) likewise began to decrease, suggesting that the hydroxyl group had a crucial role in the oxidation of HCHO. The abundant hydroxyl groups could provide larger numbers of

Fig. 8. In situ DRIFTS spectra of the Cu/NaSep sample after 1 h of HCHO oxidation at 50, 75, and 100 °C.

Fig. 9. Proposed catalytic oxidation mechanism of HCHO on the Cu/NaSep catalyst.

adsorption sites for HCHO and promote the oxidation of formate species. When the temperature reached 100 °C, a near absence of the intermediate products (e.g., the formate and carbonate species) was noted, demonstrating that HCHO was thoroughly oxidized at this temperature, which was in good agreement with the catalytically active temperature of the Cu/NaSep sample.

Following transition metal loading, the redox properties of the NaSep sample were appreciably altered, especially in the case of the Cu/NaSep sample. Specifically, the reduction peak of NaSep shifted to a lower temperature with Cu loading. The Cu/NaSep sample exhibited the highest activity for HCHO oxidation, which was closely related to the highest $O_{\text{ads}}/(O_{\text{latt}}+O_{\text{OH}})$ atomic ratio. According to the literature [65–67], once the catalyst was partially replaced by foreign cations, the proportion of adsorbed oxygen species increased. The loading of Cu significantly increased the $O_{\text{ads}}/(O_{\text{latt}}+O_{\text{OH}})$ molar ratio. The oxygen defect site in the catalyst was conducive to adsorbing gaseous O₂ and generating chemisorbed oxygen species by taking up electrons, resulting in the migration and conversion of adsorbed oxygen and lattice oxygen species. As indicated by H₂-TPR, Cu/NaSep can be reduced at lower temperatures than the other samples, which contributes to the oxidation strength of the catalyst toward HCHO. Therefore, the high $O_{\text{ads}}/(O_{\text{latt}}+O_{\text{OH}})$ ratio, abundance of hydroxyl species (Fig. S3) and its low reduction temperature all contribute to the superior catalytic activity of Cu/NaSep.

A possible mechanism for catalytic oxidation of HCHO on a Cu/NaSep catalyst is presented in Fig. 9. Initially, HCHO gets adsorbed onto the surface of the sample, followed by oxidation to DOM by oxygen species, which is finally rapidly oxidized to formate species. The results indicate that the efficient and stable catalytic performance of the Cu/NaSep catalyst was principally due to the synergistic action of hydroxyls and adsorbed oxygen. The hydroxyl groups in sepiolite possibly promote the adsorption of HCHO on the sample surface, as well as accelerate formation and decomposition of the formate species [58]. Finally, the formate species are further oxidized to generate the carbonate species, which eventually produce CO₂ and H₂O. Therefore, the total oxidation of HCHO over the sample surface was:

4. Conclusions

The TM/NaSep (Cu, Fe, Mn, Ni, Co) catalysts were prepared by the rotary evaporation method and their catalytic activity for the oxidation of HCHO was evaluated. Cu/NaSep exhibited superior catalytic activity compared to the other samples. The excellent catalytic performance of Cu/NaSep was related to its elevated acidity, the highest $O_{\text{ads}}/(O_{\text{latt}}+O_{\text{OH}})$ ratio and superior low-temperature reducibility. The results of in situ DRIFTS characterization indicate that the HCHO was adsorbed on the catalyst surface via hydroxyl groups and generated the intermediate formate species. A high $O_{\text{ads}}/(O_{\text{latt}}+O_{\text{OH}})$ molar ratio indicates an elevated amount of oxygen vacancies in the catalyst, which facilitates the reaction between formate species and adsorbed oxygen species to ultimately form H_2O and CO_2 .

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Compliance with ethical standards

Conflict of interest the authors declare no competing financial interest.

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Graphical Abstract

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Sodium-treated sepiolite-supported transition metal (Cu, Fe, Ni, Mn, or Co) catalysts for HCHO oxidation

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Among the TM/NaSep (TM = Cu, Fe, Mn, Ni, Co) catalysts, Cu/NaSep exhibited the highest catalytic activity towards the oxidation of HCHO, due to high acidity, favorable reducibility, and the presence of adsorbed oxygen species.

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钠化海泡石负载过渡金属催化剂TM/NaSep (TM = Cu, Fe, Ni, Mn, Co) 催化氧化甲醛性能

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摘要: 甲醛(HCHO)是一种典型的挥发性有机化合物(VOCs)。空气中的甲醛主要来源于建筑材料、塑料、水泥和油漆等, 长时间暴露于含有甲醛的空气中会对人体健康造成严重危害。因此, 消除空气中的甲醛是亟待解决的问题。催化氧化是目前较好的去除甲醛的技术方法之一, 它能有效地在较低温度下将甲醛氧化成CO₂和H₂O。通常, 负载型贵金属(Au, Pt, Pd和Ag)催化剂具有较好的催化氧化甲醛性能, 但高成本和易中毒的特性限制了其应用。负载型过渡金属催化剂具有成本低和催化氧化性能良好等特点, 是当前研究的热点。而催化剂活性通常与所用载体及其物理性质相关, 如晶体结构、化学组成、表面积和热稳定性等。因此, 开发合适的载体, 提高过渡金属催化剂的催化性能具有重要意义。海泡石是具有特定官能团

和纤维状结构的天然粘土矿物, 相比其他类型的硅酸盐粘土, 其具有较高的吸附性能和较好的水热稳定性. 本文通过浸渍法制备了钠化海泡石(NaSep)负载过渡金属催化剂TM/NaSep (TM = Cu, Fe, Ni, Mn, Co), 研究了其物理化学性质, 考察了其催化氧化甲醛(0.2%)性能.

XRD与SEM结果表明, 负载过渡金属不影响海泡石原矿的物理结构. H_2 -TPR, NH_3 -TPD和XPS结果表明, 负载过渡金属对催化剂氧化还原性能、酸性和吸附氧能力影响较大. TM/NaSep总酸度与吸附氧能力($O_{ads}/(O_{latt}+O_{OH})$)按以下顺序递减: Cu/NaSep > Fe/NaSep > Mn/NaSep > Ni/NaSep > Co/NaSep. 这与催化剂催化氧化甲醛活性顺序一致. 在所有样品中, Cu/NaSep表现出最佳的催化氧化甲醛活性, 在100 °C (GHSV = 240000 mL/(g·h))可以完全氧化甲醛. 42 h稳定性测试表明其具有良好的稳定性. 综合研究表明, Cu/NaSep催化剂优良的催化活性与其良好的低温还原性、较高的酸度和吸附氧能力等因素有关. 原位DRIFTS研究Cu/NaSep催化剂催化氧化甲醛机理表明, 首先, 甲醛吸附在催化剂表面, 然后表面的吸附氧物种将其氧化成亚甲二氧基(DOM)并迅速转化为甲酸盐物种. 同时, Cu/NaSep催化剂较高的催化氧化性能还与海泡石载体的羟基与吸附氧的协同作用有关, 海泡石的羟基可以促进甲醛在样品表面吸附, 有利于甲酸盐形成, 甲酸盐再进一步氧化生成碳酸盐, 最终氧化生成 CO_2 和 H_2O .

关键词: 钠化海泡石; 过渡金属负载; 负载型过渡金属催化剂; 挥发性有机化合物; HCHO氧化

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