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Article

Formaldehyde catalytic oxidation over hydroxyapatite modified with various organic molecules

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ABSTRACT

Hydroxyapatite (HAP) was modified by adding various organic molecules, such as cetyltrimethylammonium bromide, sodium dodecyl sulfate, and sodium citrate, during the precipitation of HAP. Sodium citrate-modified HAP displayed the best activity for formaldehyde oxidation, achieving complete conversion at 240 °C. The influence of the organic modifiers on the structure of HAP was assessed by X-ray diffraction, Fourier transform infrared spectroscopy, N₂ adsorption-desorption, scanning electron microscopy, and thermogravimetry/derivative thermogravimetry. The higher specific surface area and pore volume, and smaller pores, owing to modification with sodium citrate, favored adsorption, mass transfer, and interaction process during formaldehyde oxidation. Furthermore, the higher hydroxyl group content observed in sodium citrate-modified HAP enhanced interactions between formaldehyde and HAP, thus resulting in higher catalytic activity.

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1. Introduction

As one of the most common volatile organic compounds, formaldehyde (HCHO) is generating increasing attention as it poses potential health risks to humans even at low concentrations. Thus, the removal of HCHO has become an important issue [1,2]. Numerous studies have been carried out for the abatement of HCHO; the main techniques being investigated are adsorption, plasma decomposition, biological/botanical filtration, and catalytic oxidation [1]. Among all these techniques, catalytic oxidation is a promising method for HCHO removal because of its efficiency, convenience, and no secondary pollution. Commonly studied catalysts include noble metals (e.g., Pt, Au, Pd, and Ag) [3–6] and transition metal oxide catalysts (e.g., MnO_x and CeO₂) [7–9]. Moreover, transition metal

oxides are usually employed as substrate for loading noble metal catalysts [10–13]. Noble metal-loaded catalysts show relatively better activities towards HCHO oxidation (complete conversion is generally achieved at around 100 °C or below) [5,14]. However, the high cost of noble metal limits the wide practical application of noble metal catalysts. For transition metal oxides, complete HCHO conversion temperatures are generally above 100 °C, and even above 200 °C under some circumstances [7,9,13]. Besides poor performance, the toxicity of some commonly used transition metal oxides (MnO_x) limits the application of such catalyst systems [15,16]. In recent years, many studies on HCHO catalytic oxidation have been conducted to improve the catalytic performance. However, the studied catalytic systems are still focused on noble metal catalysts and transition metal oxides such as MnO_x, Ag/CeO₂, Co₃O₄, and

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Pt/CeO₂ [17–22]. The drawbacks of such catalytic systems are yet to be addressed. Thus, economical, safe, and non-toxic novel materials are required for HCHO catalytic oxidation.

As the main inorganic component of natural bone and teeth, with a wide application in the field of biomedical materials as biological active materials, hydroxyapatite (HAP) is safe and non-toxic [23]. Moreover, unlike noble metals, HAP is a cheaper alternative. In 2010, Xu *et al.* [24] reported HAP as a promising novel, non-precious metal catalyst for HCHO combustion, whereby the hydroxyl groups bonded to the Ca²⁺ channels may act as active sites.

To date, the examination of HAP as a catalytic material for HCHO oxidation remains rare. However, as a novel, non-precious metal catalyst with demonstrated activity towards HCHO oxidation, HAP is worth exploring further. It is well known that the catalyst performance is closely related to its structure. Based on the reported study [1], HCHO adsorption and its interaction with the support are related to the HCHO oxidation process. In that case, larger adsorption areas and abundant interaction between the reaction gas and catalyst will be important for activity enhancement. Organic modifiers have been widely used in morphology- and size-controlled synthesis of nano-sized metals and inorganic materials, as well as for the generation of pores and vacancies in the structure [25–30]. To this effect, in this study, organic modifiers (i.e., cetyltrimethylammonium bromide (CTAB), sodium dodecyl sulfate (SDS), and sodium citrate (SC)) were employed during the synthesis of HAP to modify its structure. Various characterization techniques and subsequent activity tests were conducted to elucidate the structure-performance relationship.

2. Experimental

2.1. Preparation of catalysts

HAP powder was prepared through an aqueous precipitation-hydrothermal method using (NH₄)₂HPO₄ (AR, Kemiou Chemical Reagent Co., Ltd, Tianjin) and Ca(NO₃)₂·4H₂O (AR, Damao Chemical Reagent Factory, Tianjin) as precursors. Ammonia (NH₃) solution (AR, Sinopharm Chemical Reagent Co., Ltd, Shanghai) was used for pH adjustments during the precipitation process. A solution of 0.2 mol/L Ca(NO₃)₂·4H₂O (4.72 g in 100 mL deionized water) containing an organic modifier (5 wt%, CTAB (AR, Sinopharm Chemical Reagent Co., Ltd, Shanghai), SDS (AR, Kemiou Chemical Reagent Co., Ltd, Tianjin), or SC (AR, Reagent No. 1 Factory of Shanghai Chemical Reagent Co., Ltd., Shanghai)) was stirred under a constant temperature of 40 °C. A solution of 0.3 mol/L (NH₄)₂HPO₄ (1.58 g in 40 mL deionized water) was added dropwise to the Ca(NO₃)₂·4H₂O solution. Then, the pH of the suspension was adjusted to 10 with ammonia solution (35%), followed by 8 h of reaction under stirring. Subsequently, the reaction solution was transferred to a Teflon-lined autoclave and heated at 100 °C for 12 h. Finally, the resulting powders were centrifuged and washed multiple times and dried at 100 °C overnight and then calcined at 700 °C for 2 h. The obtained HAP samples were denoted as HAP_{CTAB}, HAP_{SDS}, and HAP_{SC}. Non-modified HAP was also syn-

thesized using the same procedure for comparison studies and denoted as HAP_{BLANK}.

2.2. Characterization of catalysts

The crystallinity of the catalysts was established and identified by X-ray diffraction (XRD, Rigaku D/max- γ b X-ray diffractometer, Japan) using Cu K α radiation in the 2 θ range of 10°–80° at room temperature. Fourier transform infrared spectroscopy (FTIR) was carried out on specimens that were prepared into pellets containing the HAP samples and KBr. FTIR spectra were recorded on a Shimadzu IRPrestige-21 spectrophotometer (Japan) in the range of 4000–400 cm⁻¹. A background spectrum of KBr was subtracted from each sample spectrum. Scanning electron microscopy (SEM) analysis was performed on a JEOL JSM-6360 scanning electron microscope (USA) operating at an acceleration voltage of 20–30 kV. N₂ adsorption-desorption measurements were carried out on a Quantachrome Quadrasorb S1 (USA). Prior to analysis, each sample was heated at 200 °C for 4 h under vacuum. Surface areas were calculated using the BET method. The pore size was calculated using the BJH model. Thermogravimetry/derivative thermogravimetry analysis (TG/DTG) was performed on a WCT-1C thermobalance (Beijing) in the temperature range of 20–900 °C.

2.3. Catalytic activity tests

HCHO oxidation activity tests were carried out in a fixed-bed flow reactor under atmospheric pressure. Typically, 0.2 g catalyst was loaded in a quartz tube reactor for activity test. The catalyst was calcined at 400 °C for 1 h in an O₂/Ar flow before the reaction. During the reaction, gaseous HCHO was generated by flowing He over trioxymethylene (99.5%, Acros Organics) in an incubator placed in an ice-water mixture. The feeding stream consisted of 500 ppm HCHO, 20 vol% O₂, and balanced He; the total flow rate throughout the reactor was maintained at 30 mL/min by a mass flow meter. The effluents from the reactor were analyzed by an online gas chromatograph (GC 7890II, Techcomp, China) equipped with a flame ionization detector (FID). To determine the exact concentration of produced CO₂, a nickel catalyst converter was positioned in front of the FID to convert CO₂ quantitatively into methane in the presence of hydrogen. Generally, the reaction data were collected until reaction balance was reached. No other carbon-containing compounds except for CO₂ in the products were detected for all the tested catalysts. Thus, the HCHO conversion was calculated as: HCHO conversion = [CO₂]/[CO₂]* × 100%, where [CO₂]* and [CO₂] represent respective concentrations of CO₂ detected in the effluent when HCHO is completely oxidized and at a given reaction temperature, respectively.

3. Results and discussion

3.1. Catalytic activity for HCHO oxidation

The catalytic activities of HAP_{BLANK} and modified HAP sam-

Fig. 1. HCHO conversion over HAP_{BLANK} and modified HAP samples.

ples towards the oxidation of HCHO are shown in Fig. 1. As noted, the HAP_{SC} sample displayed the best activity with 100% HCHO conversion at 240 °C. In contrast, the remaining three samples exhibited HCHO conversion levels of less than 50% at the same temperature. Moreover, the addition of either CTAB or SDS during sample preparation resulted in catalysts with lower activities when compared with that of the blank sample. Complete conversion was not observed even at 300 °C for the HAP_{CTAB} and HAP_{SDS} samples. Further activity tests were performed on the used HAP_{SC} catalyst to determine the stability of the sample. The results are also shown in Fig. 1. As observed, the activity of HAP_{SC-used} only decreased very slightly when compared with that of HAP_{SC-fresh}, indicating the good stability of the catalyst.

3.2. Catalyst characterization

3.2.1. XRD analysis

XRD patterns of the prepared HAP samples are shown in Fig. 2. Characteristic peaks of HAP (PDF No. 09-0432) [31] were clearly observed in all patterns, indicating successful formation of the HAP structure. Besides the good agreement with the standard HAP pattern, no impurities or distinct differences were observed in the XRD patterns, thereby implying

Fig. 2. XRD patterns of HAP_{BLANK} and modified HAP samples.

Fig. 3. FTIR spectra of HAP_{BLANK} and modified HAP samples.

that the addition of different organic molecules does not instigate any differences in the crystallinity for samples calcined at the same temperature. Moreover, the good agreement of the XRD patterns of the samples (calcined at 700 °C) with characteristic HAP peaks reflects the good thermal stability of the catalysts.

3.2.2. FTIR spectroscopy

Figure 3 presents the FTIR spectra of the HAP samples. No organic modifier remained on the surface of HAP after calcination at 700 °C. The presence of PO₄ and OH functional groups was confirmed by various characteristic bands in the FTIR spectra. The peaks at around 1035 and 1091 cm⁻¹ were assigned to asymmetrical stretching modes of PO₄ groups, the asymmetrical bending modes of which were detected at around 565 and 602 cm⁻¹ [32]. The symmetrical stretching vibrations of PO₄ groups were reflected by bands at around 470 and 962 cm⁻¹ [32]. The peaks observed at 631 and 3580 cm⁻¹ were attributed to the bending and stretching modes of OH groups in the hydroxyapatite structure, respectively [33]. Although no residual modifiers were detected in the obtained samples, the peak at 3580 cm⁻¹ that corresponds to OH shows distinct different intensities among the samples. Because the intensity of the peaks is influenced by the amount of samples tested, the OH content of the samples cannot be directly determined by the intensity of the OH characteristic peaks. Therefore, the relative peak intensity of the OH groups to the PO₄ groups was used to estimate the OH content in each sample. The calculated areas of the peak at 3580 cm⁻¹ that was assigned to the stretching mode of OH groups and the peak at 962 cm⁻¹ that was ascribed to the stretching mode of PO₄ groups are shown in Table 1; OH/PO₄ ratios were also calculated based on the calculated areas. HAP_{SC} featured higher OH/PO₄ ratios, indicating that higher amounts of OH groups were formed on the surface of HAP after modification with SC. It has been proposed that OH groups play an important role in the adsorption/activation of HCHO [24]. Therefore, the high content of OH groups in HAP_{SC} was responsible for its significantly improved activity.

The FTIR spectrum of HAP_{SC-used} is also shown in Fig. 3. As observed, the shape of the spectrum of HAP_{SC-used} was not

Table 1

OH and PO₄ peak areas of different samples detected by FTIR and associated relative OH/PO₄ ratios.

Sample	OH peak area (3580 cm ⁻¹)	PO ₄ peak area (962 cm ⁻¹)	OH/PO ₄
HAP _{BLANK}	466	198	2.35
HAP _{CTAB}	617	273	2.26
HAP _{SDS}	580	215	2.69
HAP _{SC}	828	220	3.76
HAP _{SC-used}	637	175	3.64

distinctively different from that of fresh HAP_{SC}, further indicating the good stability of the sample. Moreover, the intensity of the OH groups did not change considerably. For better comparison, the same calculation was adopted to evaluate the OH content in the two samples (Table 1). Based on the calculated results, the OH/PO₄ ratio only decreased slightly from 3.76 to 3.64. Therefore, the content of the OH groups can be considered to be stable before and after the reaction, thereby explaining the similarity in the activities of fresh HAP_{SC} and used HAP_{SC}.

3.2.3. SEM and BET analyses

The SEM images of the four samples (Fig. 4) display the features and structures of the HAP samples. HAP_{BLANK} and HAP_{SC} possessed a uniform sheet stacking structure with a fluffy surface. The addition of sodium citrate during the synthesis process did not change the integrity or uniformity of HAP structure. In contrast, the addition of CTAB (HAP_{CTAB}) and SDS (HAP_{SDS}) destroyed the uniformity of the samples and featured a relatively compact surface.

Differences in the structure can be evaluated from the N₂ adsorption-desorption studies. As shown in Fig. 5(a), all HAP samples featured a type IV adsorption-desorption isotherm with an H3 hysteresis loop according to the IUPAC classification [29,32]. The H3 hysteresis loop indicates the presence of a

Fig. 4. SEM images of HAP_{BLANK} and modified HAP samples.

Fig. 5. N₂ adsorption-desorption isotherms (a) and pore size distribution (b) of HAP_{BLANK} and modified HAP samples.

sheet stacking structure in the samples, which is in accordance with the SEM analysis. In comparison with the isotherms of the three other samples, HAP_{SC} featured a different desorption branch at the higher p/p_0 values that is indicative of the presence of relatively uniform and small pores, owing to the existing resistance during the desorption process. This trend can be observed in Fig. 5(b) that shows the pore size distribution of all four HAP samples; accordingly, the pore size distribution of HAP_{SC} shifts to the lower pore size region.

The textural properties, including the specific surface area, pore volume, and average pore diameter, of the studied samples are listed in Table 2. The specific surface areas of the four samples were in the range of 26–40 m²/g. The average pore size was around 40 nm. As observed, the sample modified with SC, which presented the best catalytic activity, possessed the highest specific surface area (40.36 m²/g) and pore volume (0.3692 m³/g), and the smallest average pore diameter (36.58 nm). In contrast, the SDS-modified HAP sample showed oppo-

Table 2

Textural properties of samples analyzed by N₂ adsorption-desorption method.

Sample	BET surface area (m ² /g)	Pore volume (m ³ /g)	Average diameter (nm)
HAP _{BLANK}	26.42	0.3004	45.48
HAP _{CTAB}	27.52	0.3049	44.32
HAP _{SDS}	23.13	0.2801	48.44
HAP _{SC}	40.36	0.3692	36.58

site trends. The higher specific surface area and pore channel of HAP_{SC} provide additional sites for HCHO adsorption, whereas the smaller pores contribute to longer retention times and favor reactions between HCHO and oxygen on HAP.

3.3. Effect of organic modifiers and structure-performance relationship

Based on the characterization results discussed above, it can be seen that the addition of organic modifiers did not cause considerable differences in the crystallinity of the resulting samples, and no organic modifiers were retained in the obtained HAP samples. Thus, in the present work, it can be deduced that neither the crystallinity nor the presence of the new groups introduced into HAP contributes to the improved performance of HAP_{SC}. In contrast, the specific surface area and pore structure, which usually influence adsorption and mass transfer during the reaction, are significantly influenced by the addition of various organic modifiers.

The FTIR spectrum of non-calcined HAP_{SC} is shown in Fig. 6; characteristic peaks assigned to the stretching vibrations of carboxyl and C–O groups were detected [30], indicating the presence of citrate on the SC-modified HAP sample. Those peaks were not observed in the calcined HAP_{SC} sample, thereby suggesting that the citrate could be completely decomposed during calcination. The decomposition of citrate could also be confirmed from the thermogravimetry/derivative thermogravimetry (TG/DTG) curve of HAP_{SC} (non-calcined) shown in Fig. 7. The TG curve of the HAP sample modified with SC (before calcination) showed a single and continuous weight loss. However, according to the DTG curve, which reflects the rates of weight loss, three main weight loss stages under 600 °C were observed. The first stage (< 150 °C) corresponds to evaporation of water [34], which accounts for a weight loss of about 2%. The second and third weight loss stages, observed at the higher temperatures (200–600 °C) correspond to the decomposition of the anhydrous citrate and the produced intermediate complex [35]. The total weight loss (< 600 °C) is about 5.7%, which is slightly higher than the amount of SC added to the solution during the synthesis procedure (i.e., 5%), and can be related to the water loss. Further weight loss above 600 °C may be due to carbon loss from the system [34]. The decomposition of sodium citrate attached to HAP can generate structural vacancies and

Fig. 6. FTIR spectrum of non-calcined HAP_{SC}.

Fig. 7. TG/DTG curves of the HAP_{SC} sample before calcination.

contribute to the higher specific surface area and pore volume observed [29]. In addition, the minor weight loss (600–900 °C) partly reflects the good thermal stability of the material.

Based on the characterization results, HAP_{SC} possessed larger specific surface area and pore volume owing to the decomposition of SC during calcination. These features contributed to the improved activity of the resulting catalyst by facilitating the adsorption process during the reaction. Moreover, the smaller pores of HAP_{SC} led to longer retention times of the HCHO molecules in the pores. Also, modification of HAP with SC resulted in increased amounts of hydroxyl groups in the resulting HAP_{SC}; it has been proposed that hydroxyl groups are responsible for the HCHO catalytic oxidation on HAP [24]. Therefore, better adsorption properties, longer retention times, and larger contents of OH groups all lead to better interactions between the reaction gas and active sites of the catalysts, consequently resulting in significantly enhanced performance of HAP_{SC} towards HCHO oxidation.

CTAB and SDS are typically used to regulate the morphology of HAP; pores are generated upon elimination of the modifiers [25,27,28,36]. Upon addition of template CTAB, the positive head of CTAB is assembled onto HAP; a large amount of NH₄⁺ ions are present in the precipitated HAP. During calcination, the organic CTAB templating structures and ammonium salt are decomposed, leading to the generation of pores in the HA skeleton [28]. However, the size of the pores induced by the decomposition of the organic CTAB templating structure is different from that of pores generated by removal of the ammonium salt, thereby explaining the non-uniformity of the resulting sample structure [28]. A similar decomposition process of the sulfate groups was also observed for SDS [27]. It is known from the chemical structure of CTAB, SDS, and SC that at least two types of gases were released during calcination of HAP_{CTAB} (CO₂, NH₃) and HAP_{SDS} (CO₂, SO₂). This caused the poor uniformity of the pores in the samples, as reflected by the wide pore size distributions and the non-uniform structures shown in the SEM images. Moreover, the presence of the longer alkyl chain lengths of CTAB and SDS also instigated the formation of larger pores [37,38]. Therefore, the larger pores and poor uniformity of the structures of HAP_{CTAB} and HAP_{SDS} were due to the structure and composition of CTAB and SDS, as well as the de-

composition properties of the surfactant. In contrast, CO₂ was mostly generated during the calcination of HAP_{SC}, and the smaller SC molecules led to the formation of smaller pores.

4. Conclusions

Modification of HAP with different organic modifiers (CTAB, SDS, and SC) resulted in differences in the specific surface area and pore structure of the final modified HAP samples. Modification with SC significantly improved the activity of HAP towards HCHO oxidation, with complete conversion achieved at 240 °C. HAP_{SC} featured larger specific surface area and pore volume that enhanced the adsorption capacity for HCHO, whereas the smaller pores afforded sufficient time for interaction between the catalyst and reaction gas. Besides the structural differences that influenced adsorption and mass transfer, the content of hydroxyl groups that is responsible for HCHO oxidation was higher in the SC-modified HAP sample. Better adsorption properties, longer retention times, and larger contents of OH groups of HAP_{SC} all lead to better interaction between the reaction gas and active sites of the catalysts, and subsequent significantly enhanced performance of HAP_{SC} towards HCHO oxidation.

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Graphical Abstract

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Formaldehyde catalytic oxidation over hydroxyapatite modified with various organic modifiers

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Better adsorption properties, longer retention times, and larger contents of OH groups of hydroxyapatite modified with sodium citrate (SC) (HAP_{SC}) lead to better interaction between the reaction gas and active sites and higher activity towards HCHO oxidation.

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不同有机分子改性羟基磷灰石用于甲醛催化氧化

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摘要: 分别采用十六烷基三甲基溴化铵(CTAB)、十二烷基硫酸钠(SDS)及柠檬酸钠(SC)对羟基磷灰石(HAP)进行了有机改性。柠檬酸钠改性的羟基磷灰石对甲醛催化氧化表现出最好的催化活性, 在240 °C实现了甲醛完全转化。通过X射线衍射、红外光谱、N₂吸附-脱附、扫描电镜和热重/差重等手段对HAP结构进行了表征。结果表明, SC改性使得HAP比表面积和孔体积增加, 孔径减小, 更有利于吸附及传质, 从而提高了其活性。此外, SC改性的HAP中羟基含量更多, 更有利于甲醛与羟基之间发生相互作用, 这是该样品活性提高的另一个原因。

关键词: 羟基磷灰石改性; 柠檬酸钠; 比表面积; 羟基; 甲醛催化氧化

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1. 前言

作为一种最常见的挥发性有机化合物, 甲醛因其所具有的高毒性而引起了人们越来越多的关注, 即使是低剂量的甲醛, 长期接触也对人体具有潜在危害。因此, 甲醛的消除是亟待解决的问题之一^[1,2]。甲醛消除可采用多种技术, 包括吸附法、等离子体技术、生物过滤法以及催化氧化等^[1]。其中, 催化氧化因简便高效且不存在二次污染等优点而具有良好的发展前景。该过程常用的催化剂为贵金属催化剂(Pt, Au, Pd和Ag等)^[3-6]和过渡金属氧化物(MnO_x和CeO₂等)两类^[7-9]。其中, 过渡金属氧化物也常用作贵金属催化剂的载体^[10-13]。贵金属催化剂在甲醛催化氧化反应中通常表现出较好的催化活性, 甲醛完全转化温度一般在100 °C左右或更低^[5,14]。然而, 贵金属昂贵的价格使得这类催化剂难以得到广泛的应用。过渡金属氧化物用于甲醛催化氧化催化剂时, 在大部分情况下甲醛的完全转化温度在100 °C以上, 有时甚至超过200 °C^[7,9,13]; 此外, 有些过渡金属氧化物(如MnO_x)具有毒性^[15,16], 也不利于广泛应用。近年来, 随着研究的进展, 甲醛氧化所用贵金属催化剂及过渡金属氧化物催化剂如MnO_x, Ag/CeO₂, Co₃O₄和Pt/CeO₂等^[17-22]的性能得到了提高, 但它们的缺点仍未得到解决。因此,

对于甲醛催化氧化, 需要开发经济且安全无毒的新型催化剂来克服贵金属催化剂及过渡金属氧化物的固有缺陷。

羟基磷灰石(HAP)是骨骼与牙齿的主要天然无机成分, 安全无毒, 作为生物活性材料在生物医用材料领域有着广泛的应用^[23]。此外, 作为一种来源广泛的非金属材料, HAP价格低廉。2010年, Xu等^[24]研究表明, HAP对甲醛催化氧化表现出了一定的活性, 是一种具有发展前景的新型非金属材料, 其位于HAP六边形孔道内的羟基可能是甲醛催化氧化反应的活性位。

迄今, HAP用于甲醛催化氧化的研究还十分少见。然而, 由于HAP是一种安全无毒的非金属材料, 且单独用于甲醛催化氧化表现出了良好活性, 因此将它作为催化材料进行较为详细的研究具有重要意义。众所周知, 催化剂催化性能与其结构密切相关。研究发现, 催化氧化过程中甲醛的吸附及其与催化剂之间的相互作用都会影响催化剂的活性^[1], 较大的吸附容量及较充分的相互作用对催化剂活性的提高具有重要作用。另外, 采用有机改性剂可对纳米金属材料及无机材料的形貌、粒径及结构等进行调控^[25]。因此, 本文在HAP合成过程中加入常用有机改性剂(十六烷基三甲基溴化铵(CTAB)、十二烷基硫酸钠(SDS)及柠檬酸钠(SC))对HAP的结构进

行改性, 并通过有机改性剂高温下的分解在HAP结构中产生更多缺陷和空穴^[26–30], 同时对催化剂进行多种表征及活性测试, 并关联多种实验结果得出该类催化剂的构效关系。

2. 实验部分

2.1. 催化剂制备

采用液相沉淀-水热法制备HAP样品粉末, 制备过程所用HAP前驱物为 $(\text{NH}_4)_2\text{HPO}_4$ (分析纯, 天津市科密欧化学试剂有限公司)和 $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (分析纯, 天津市大茂化学试剂厂), 沉淀过程中的pH值采用氨水(35%, 分析纯, 国药集团化学试剂有限公司)调节。将4.72 g $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ 及0.1 g有机改性剂(CTAB (分析纯, 国药集团化学试剂有限公司), SDS (分析纯, 天津市科密欧化学试剂有限公司)或SC (分析纯, 上海化学试剂厂一厂))加入100 mL去离子水中搅拌使其充分溶解, 得到0.2 mol/L $\text{Ca}(\text{NO}_3)_2$ 溶液, 其中所含有有机改性剂的质量是HAP理论生成量的5%。将含有有机改性剂的 $\text{Ca}(\text{NO}_3)_2$ 溶液置于40 °C水浴锅中搅拌。称取1.58 g $(\text{NH}_4)_2\text{HPO}_4$ 溶解于40 mL去离子水中制得0.3 mol/L溶液。搅拌下将 $(\text{NH}_4)_2\text{HPO}_4$ 滴加到 $\text{Ca}(\text{NO}_3)_2$ 溶液中, 将混合物的pH用氨水调至10, 搅拌下反应8 h。将反应所得混合物移入反应釜中, 100 °C保持12 h。将所得混合物多次离心、洗涤后于100 °C干燥过夜, 700 °C焙烧2 h。所得样品分别标记为 HAP_{CTAB} , HAP_{SDS} 和 HAP_{SC} 。为了对比, 同上制备了未经有机改性剂改性的样品 $\text{HAP}_{\text{BLANK}}$ 。

2.2. 催化剂表征

催化剂结晶度通过X射线衍射(XRD)测试得到, XRD测试在日本理学D/max- γb 型X射线衍射仪上进行, 射线源为 $\text{Cu K}\alpha$, 扫描在室温下进行, 扫描范围 $2\theta = 10^\circ\text{--}80^\circ$ 。傅里叶变换红外光谱(FTIR)在日本Shimadzu IR Prestige-21分光光度计上进行, 将样品与KBr混合压片制备测试样品, 扫描范围 $4000\text{--}400\text{ cm}^{-1}$, KBr的背景光谱从每个样品的光谱中扣除。扫描电子显微镜(SEM)观察在美国JEOL JSM-6360扫描电子显微镜上进行, 加速电压20–30 kV。 N_2 吸脱附测试在美国Quantachrome Quadrasorb S1型物理吸附仪上进行, 测试前将样品于200 °C抽真空预处理4 h, 样品的比表面积和孔径分布分别通过BET方程和BJH方程计算得到。热重分析(TG/DTG)在WCT-1C型热天平(北京)上进行, 温度测试范围为20–900 °C。

2.3. 催化剂活性测试

HCHO催化氧化活性测试在固定床石英反应器中进行, 催化剂用量0.2 g。测试前催化剂在 O_2/Ar 气氛中400 °C预处理1 h。反应过程中的甲醛是将He气通入装有三聚甲醛(99.5%, Acros Organics)的恒温器并将其上方的蒸气带出而产生的。反应气的组成为500 ppm HCHO-20 vol% O_2/He 。反应过程中气体总流量通过质量流量计控制在30 mL/min。反应器出口气体由气相色谱仪(Techcomp, GC 7890II)在线检测, FID检测器。为准确检测出口气体中 CO_2 的浓度, 在FID检测器前设置镍催化剂转换器, 在 H_2 作用下可将 CO_2 定量转换为甲烷。反应数据在反应达到平衡后开始采集。除 CO_2 外未检测到其他含碳副产物, 因此甲醛转化率可通过下式计算: $\text{HCHO conversion} = [\text{CO}_2]/[\text{CO}_2]^* \times 100\%$, 其中 $[\text{CO}_2]^*$ 和 $[\text{CO}_2]$ 分别为甲醛完全转化时和各反应温度下检测到的 CO_2 浓度。

3. 结果与讨论

3.1. 甲醛催化氧化活性

$\text{HAP}_{\text{BLANK}}$ 及有机改性HAP的甲醛催化氧化活性如图1所示。可以看出, SC改性的HAP(HAP_{SC})表现出了最好的催化活性, 在240 °C实现了甲醛完全转化。而其他样品240 °C时甲醛转化率均在50%以下。与 $\text{HAP}_{\text{BLANK}}$ 相比, CTAB与SDS的改性导致HAP活性下降, 在300 °C时甲醛仍未达到完全转化。为了观察催化剂的稳定性, 对进行过活性测试的 HAP_{SC} 样品($\text{HAP}_{\text{SC-used}}$)再次进行活性测试(图1), 与 HAP_{SC} 相比, $\text{HAP}_{\text{SC-used}}$ 的活性并未明显下降, 表明催化剂具有良好的稳定性。

3.2. 催化剂表征

3.2.1. XRD结果

图2为各催化剂的XRD谱。由图可见, 各样品均呈现出明显的HAP特征衍射峰(PDF No. 09-0432)^[31], 说明它们均具有HAP的结构。同时, 这四个样品中均未观察到杂峰, 且各谱图未见明显不同, 表明合成过程中有机改性剂的加入并未引起结晶度的明显变化。此外, 与HAP特征衍射峰良好的契合度表明700 °C高温焙烧并未破坏HAP的结构, 说明HAP的热稳定性良好。

3.2.2. FTIR结果

图3是 $\text{HAP}_{\text{BLANK}}$ 和有机改性HAP的FTIR谱。其中未观察到来自改性剂官能团的特征峰, 说明700 °C焙烧后有机改性剂未在HAP表面形成残留。各样品在1035和1091 cm^{-1} 处出现归属为 PO_4 基团的非对称伸缩振动峰, 在565和602 cm^{-1} 处检测到 PO_4 基团的非对称弯曲振动

峰^[32]. 而 PO_4 基团的对称伸缩振动特征峰出现在470和 962 cm^{-1} ^[32]. OH基团的特征峰包括 631 cm^{-1} 处的弯曲振动和 3580 cm^{-1} 处的伸缩振动^[33]. 尽管FTIR图谱中未显示任何有机改性剂官能团的残留, 但样品特征吸收峰的强度, 尤其是 3580 cm^{-1} 处OH的特征吸收峰表现出较为明显的差异. 由于吸收峰强度受测试样品量的影响, 因此样品中OH的含量并不能通过其特征吸收峰的强度直接比较. 因此, 需要采用OH对 PO_4 的相对强度来比较各样品中OH的含量. 通过计算得到的OH (3580 cm^{-1})和 PO_4 特征吸收峰(962 cm^{-1})的面积如表1所示. 表1还给出了依据峰面积计算得到的OH/ PO_4 . 可以看出, HAP_{SC} 样品具有明显较大的OH/ PO_4 值, 表明SC改性的HAP样品中形成了更多的OH. 研究表明^[24], 在甲醛催化氧化过程中OH对甲醛的吸附与活化具有重要作用. 因此, HAP_{SC} 中较高的OH含量可能是其活性大幅提高的原因之一.

从图3还可以看出, HAP_{SC} 和 $\text{HAP}_{\text{SC-used}}$ 样品的FTIR谱并未表现出明显差异, 同样说明了催化剂在反应前后较好的稳定性. 同时, OH的特征吸收峰强度并未发生明显改变. 从表1可以看出, 反应后 $\text{HAP}_{\text{SC-used}}$ 样品的OH/ PO_4 值从3.76稍降至3.64. 因此, 可以认为反应前后样品中OH的含量是稳定的, 这也解释了 HAP_{SC} 和 $\text{HAP}_{\text{SC-used}}$ 活性相近.

3.2.3. SEM和BET结果

图4是 $\text{HAP}_{\text{BLANK}}$ 及有机改性HAP的SEM照片. 由图可知, $\text{HAP}_{\text{BLANK}}$ 和 HAP_{SC} 为较为均匀的片状堆积结构, 且表面疏松. SC的加入并未破坏HAP样品本身结构的完整性和均一性. 而 HAP_{CTAB} 和 HAP_{SDS} 则具有相对质密的表面结构, 且HAP的均一性受到破坏.

图5为各HAP样品的吸附-脱附等温线和孔径分布图. 根据IUPAC分类, 所有样品吸脱附等温线均为IV型, 回滞环为H3型^[29,32]. H3型回滞环说明样品呈片状粒子堆积, 这与SEM结果一致. 与其他三条等温线相比, HAP_{SC} 的脱附支在高 p/p_0 区域呈现出形状上的差异, 说明 N_2 在 HAP_{SC} 上的脱附过程中遇到了更多的阻力, 进一步表明 HAP_{SC} 具有较小的孔径及较为规则的孔道. 如图5(b)所示, 四个样品均显示出较宽范围的孔径分布, 其中以 HAP_{SC} 的孔径分布最为集中, 且向较小孔径方向移动.

表2列出了 $\text{HAP}_{\text{BLANK}}$ 及有机改性HAP的比表面积、孔体积及孔径. 可见, 四个样品的比表面积在 $26\text{--}40\text{ m}^2/\text{g}$, 平均孔径在40 nm左右. 其中 HAP_{SC} 具有最大的比表面积($40.36\text{ m}^2/\text{g}$)及孔体积($0.3692\text{ m}^3/\text{g}$), 而其平均孔径(36.58 nm)则明显减小. 与 $\text{HAP}_{\text{BLANK}}$ 相比, HAP_{SDS} 样

品的比表面积与孔结构的变化趋势与 HAP_{SC} 相反. HAP_{SC} 较大的比表面积及孔体积能给甲醛提供更大的吸附容量, 且较小的孔径加长了反应气的停留时间, 有利于反应气与催化剂充分接触, 从而有利于 HAP_{SC} 活性的提高.

3.3. 有机改性剂的影响及催化剂构效关系

根据上述表征结果可知, 合成过程中有机改性剂的加入并未导致最终样品结晶度的差异, 且在最终样品中没有有机改性剂的残留. 由此可推断, 在本实验中, 并非结晶度的不同或组合到HAP上的来自有机改性剂的新基团导致了样品间活性的差异. 合成过程中不同有机改性剂的加入导致比表面积及孔结构较大的改变, 而比表面积及孔结构通常会影响催化反应过程中的吸附与传质过程, 从而影响催化剂的活性.

图6是未焙烧 HAP_{SC} 的FTIR谱. 在谱图中观察到了羧基及C—O的特征伸缩振动吸收峰^[30], 说明在未焙烧 HAP_{SC} 样品中SC的存在. 但经 $700\text{ }^\circ\text{C}$ 焙烧后, 这些特征吸收峰消失, 表明在焙烧过程中SC能完全分解. 同时, SC的分解可通过未焙烧 HAP_{SC} 的TG/DTG曲线(图7)得到证实. HAP_{SC} 的TG曲线表现出了持续的质量损失, 而从反应样品质量损失速率的DTG曲线来看, 未焙烧的 HAP_{SC} 在 $600\text{ }^\circ\text{C}$ 以下有三个质量损失阶段. 第一阶段发生在 $150\text{ }^\circ\text{C}$ 以下, 来自水的蒸发^[34], 这一阶段的质量损失为2%. 随着温度升高, 在 $200\text{--}600\text{ }^\circ\text{C}$ 间出现了第二及第三次质量损失, 这两阶段分别对应于柠檬酸根及其分解中间产物的再次分解^[35]. $600\text{ }^\circ\text{C}$ 以下的总质量损失为5.7%, 比合成过程中加入的SC的质量(5% HAP 理论质量)稍大, 是由于水分损失造成的. 高于 $600\text{ }^\circ\text{C}$ 持续的慢速质量损失可能是来自系统中的碳损失^[34]. 焙烧过程中SC的分解能在HAP结构中产生空穴, 从而使其具有较大的比表面积及孔体积^[29]. 此外, 样品加热到 $900\text{ }^\circ\text{C}$ 高温时的质量损失依然很少, 这也反映出材料较好的热稳定性.

以上表征结果显示, HAP_{SC} 在焙烧过程中发生了SC的分解, 从而导致其较大的比表面积及孔体积, 有利于反应中的吸附过程, 使得催化剂活性提高. 同时, HAP_{SC} 较小的孔径使得反应气在与催化剂的接触过程中有更多的停留时间. 不同样品的FTIR结果表明, SC改性提高了样品中的羟基含量, 而羟基在甲醛催化氧化过程中有着重要作用^[24]. 因此, HAP_{SC} 较好的吸附性能、较长的停留时间以及较高含量的羟基都有利于反应过程中反应气与催化剂活性位的充分相互作用, 从而提高 HAP_{SC} 对

甲醛的催化氧化活性.

CTAB和SDS常被用作模板剂在合成过程中调控材料的形貌, 并通过模板剂的去除在结构中产生更多孔道^[25,27,28,36]. 当CTAB加入到反应溶液中时, 其带正电荷的一端即能附着于HAP上, 同时在合成的HAP中会存在大量的 NH_4^+ . 在焙烧过程中, CTAB有机部分的分解及铵盐的分解能够在HAP结构中留下孔道^[28]. 然而, 由于CTAB有机组成部分及铵盐的分解产生的孔大小不一, 从而导致样品结构的均一性较差^[28]. SDS对HAP的改性及SDS的分解过程与CTAB相似^[27]. 从CTAB, SDS和SC的结构可知, 高温焙烧时, CTAB和SDS的分解过程中至少会产生两种气体(CTAB产生 CO_2 和 NH_3 , SDS产生 CO_2 和 SO_2). 不同大小气体分子的产生会导致孔的均一性较差. HAP_{CTAB} 和 HAP_{SDS} 较宽的孔径分布及SEM图都证实了这一点. 此外, CTAB和SDS较长的烷基链也导致 HAP_{CTAB} 和 HAP_{SDS} 样品较大的平均孔径^[37,38]. 因此, HAP_{CTAB} 和 HAP_{SDS} 较大的平均孔径及较差的均一性是

由CTAB和SDS的结构组成及分解特点决定的. 而对于 HAP_{SC} , 高温下SC分解产生的大部分为 CO_2 , 且其较小的分子也形成了较小的平均孔径.

4. 结论

不同有机改性剂(CTAB, SDS和SC)对HAP的改性导致了不同样品比表面积及孔结构较为明显的差异, 且SC的改性显著提高了HAP对甲醛催化氧化的催化性能, 在 240°C 实现了甲醛完全转化. HAP_{SC} 具有较大的比表面积、孔体积以及较小的孔径. 较大的比表面积和孔体积能够提高HAP对甲醛的吸附性能, 同时较小的孔径可保证反应过程中反应气在催化剂中足够的停留时间. 此外, 在 HAP_{SC} 的结构中还存在更多的羟基, 对甲醛催化氧化起到了重要的作用. HAP_{SC} 较好的吸附性能、较长的停留时间以及较多含量的羟基都有利于反应过程中反应气与催化剂活性位的充分相互作用, 从而提高了 HAP_{SC} 对甲醛的催化氧化活性.