Catalytic oxidation of formaldehyde over silver supported on ZSM-5: The role of Ag and mesopores

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Abstract. Silver nanoparticles (AgNPs) are increasingly drawing a great deal of attention because of their exclusive properties and a huge variety of applications. In recent years, using AgNPs supported on various carriers as heterogeneous catalysts has become promising for treating some toxic gases in the environment, such as HCHO. This study has successfully synthesized AgNPs onto ZSM-5 microporous zeolite and ZSM-5 mesopore-modified zeolite (Meso-ZSM-5) by ion-exchange method using sodium borohydride as a reducing agent. The resulting catalysts were then characterized by N2 adsorption-desorption method. In order to evaluate HCHO adsorption, desorption, and the surface reaction of these catalysts, temperature-programmed desorption (TPD) and temperature-programmed surface reaction (TPSR) were employed. The TPD and TPSR experiments were conducted with different relative humidity. The results showed that Ag/Meso-ZSM-5 exhibited higher catalyst activity in HCHO complete oxidation than Ag/ZSM-5 at high temperatures because of a new larger pore system within the zeolite. Furthermore, TPD and TPSR experiments provided an explanation for the poor performance of the catalysts at low temperatures, which was associated with the high adsorption capacity of the zeolite.

Keywords: Ag nanoparticles, mesoporous zeolite, HCHO catalytic oxidation, TPD experiment, TPSR experiment.

1. Introduction
Formaldehyde is one of the most common indoor gaseous pollutants, which can affect human health and comfort. The main sources of HCHO emission are industrial processes, product use, agriculture and transport. Long-time exposure to HCHO can cause headache, respiratory tract, pneumonia, eye irritation and even cancer. According to World Health Organization, the indoor HCHO concentration must be below 0.1 mg/m³ [1-3]. Several approaches have been used to reduce the amount of HCHO in the air, such as adsorption, bio-filtration, thermal oxidation—Adsorption is the simplest method to remove formaldehyde from the air at a rapid rate and low cost, but limited adsorption capacity is their major problem. Destruction methods are preferable to separation methods as they allow to eliminate formaldehyde completely. Thermal oxidation is one of them, which permits to oxidize formaldehyde to harmless and less harmful products (H2O and CO2) by rising the temperature above the ignition point in O2 flow. However, they require very high operation temperature and choosing the feed composition to avoid explosion [4-6]. Catalytic oxidation is a promising technique to completely convert HCHO into H2O and CO2 at lower operating temperature and lower capital cost. Two types of
catalysts are single/mixed oxides (Cu, Mn, Cr, Fe, Ni) and supported noble metal catalysts. While the main pros of metal oxides are availability and cost, higher activity at low temperature, resistance to deactivation and ability to be regenerated can be achieved with transition metal catalysts. The current challenges lay in developing a new catalyst that is active at low temperature with low cost and good usability [7-11]. Many studies have been taken in recent years and achieved great results, such as Al-rich Beta zeolite supporting Pt (1%) and Pt (0.2%) supported onto pure silica Beta zeolite, which could completely oxidize HCHO at shallow temperature [12, 13]. However, the extortionate cost of noble metals for wide applications is still the main problem. More recently, Ag-based catalysts have been taken into consideration because silver is significantly cheaper than other metals (Pt, Pd and Au) and shows high catalyst activities for HCHO oxidation at low temperatures [14, 15]. For example, 10%Ag/Beta-Si can oxidize HCHO (80 ppm) completely to CO₂ and H₂O at around 70°C, or 8%Ag/TiO₂ can reach 100% conversion of HCHO (110 ppm) at about 95°C [16, 17]. Since the amount of noble metal used as a catalyst is minimal, they need a support to maintain their good performance. Moreover, supports play a vital role in forming, distributing, and accumulating small particles. Zeolite with high surface area, rigid frameworks and shape selectivity have been considered as an ideal support. However, micropores in conventional zeolites have high mass transfer resistance for reactants, intermediates and products to go through their channels and cages. This problem could be addressed by expanding the micropores within zeolites [5, 18-20]. Furthermore, introducing a more extensive pore system into the zeolites can also help reduce coke formation since reactants, intermediates and products can rapidly diffuse through their channels [21, 22]. Several methods have been used to introduce larger pores into zeolites, such as hydrothermal dealumination and other chemical treatments. Among these, desilication is widely applied since they allow to synthesize zeolites with uniform mesopores and little change in the number of acid sites. The Si/Al ratio has a big influence on the structural properties of zeolites modified by alkaline treatment [23-25].

In this paper, we report the catalytic performance of HCHO complete oxidation over Ag/Meso-zeolite compared to that over Ag/zeolite at different temperatures. We also investigated the HCHO adsorption capacity of these materials at various relative humidity. The temperature-programmed desorption (TPD) and temperature-programmed surface reaction (TPSR) were employed in further studies so as to understand the desorption behaviour and surface reaction for formaldehyde oxidation on these catalysts as well as the effect of the support on catalyst activity. The prepared catalysts were characterized by N₂ adsorption/desorption, and experiments related to adsorption and surface reaction of catalysts were carried out in a continuous flow fixed bed reactor.

2. Experimental

2.1. Sample preparation

For synthesis of Ag/Meso-ZSM-5, 100 mL of 0.2M NaOH solution was heated at 65°C. 3.3g of zeolite ZSM-5 (Si/Al = 200) was then added into the heated solution under vigorous stirring. After one hour, the slurry was cooled down immediately using an ice bath. It was then filtered and washed until neutral pH and dried at 80°C overnight. The solid was grinded and labelled Meso-ZSM-5. 2g of Meso-ZSM-5 was suspended in 231.5 mL of 1 × 10⁻³M AgNO₃ solution and stirred for 24 hours at room temperature for complete cation exchange. Then, 23.1 mL of 4 × 10⁻²M NaBH₄ solution was added into the mixture under continuous stirring and left for one hour at room temperature. The obtained suspensions of Ag/ZSM-5 were dried under vacuum at 80°C until the water was removed. The solid was rinsed and filtered with 200 mL of distilled water. After drying at 80°C overnight, the solid product was calcined at 300°C for two hours in the air.

A similar procedure was used for synthesis of Ag/ZSM-5. 2g of NH₄-ZSM-5 was calcined at 450°C for 1 hour in order to completely convert NH₄-ZSM-5 to H-ZSM-5. Then, H-ZSM-5 was suspended in 231.5 mL of 1 × 10⁻³M AgNO₃ solution and stirred for 24 hours at room temperature for complete cation exchange. The following steps were the same as the procedure of Ag/Meso-ZSM-5 preparation.
2.2. Catalyst characterization and catalytic tests

The specific surface area, pore volume, and pore size distribution were investigated by N₂ adsorption-desorption isotherms using Nova 2200e Quantachrome.

The catalytic performance was tested in a fixed bed reactor with 0.1 g of catalyst (granule’s diameter of 1-2 mm). Gaseous formaldehyde was generated by flowing continuously pure N₂ (> 99.99%) over a glass bubbler containing formaldehyde solution, which was put in a water bath. The formaldehyde concentration was controlled by the flow rate of nitrogen and the water bath temperature. Relative humidity (RH) was also generated by consecutive bubbling method. The amount of water vapour was only controlled by the nitrogen flow rate. These gaseous streams were then mixed with the flows of nitrogen and oxygen to form a typical feed consisting of 90 ppm HCHO, 20 vol.% O₂, and N₂ for balance with a total flow rate of 50 mL/min going into the reactor. Before conducting the experiments, the catalysts were pretreated by N₂ stream at 300°C for 1 hour. The HCHO conversion was analyzed by gas chromatography equipped with a flame ionization detector (FID).

2.3. Adsorption/desorption and surface reaction experiments

These experiments were carried out in a fixed bed reactor system. Before the experiments, the catalyst (0.1 g, diameter of 1-2 mm) was activated at 300°C for 1 hour in a flow of N₂ gas. The adsorption of HCHO was carried out under a continuous flow of HCHO/N₂ with 338 ppm of HCHO concentration. Until the adsorption completion indicated by stable peaks in the gas chromatography with the FID, the HCHO-TPD and HCHO-TPSR experiments were carried out. The HCHO-TPD was conducted in a continuous flow of N₂ (F = 50 mL/min), and the HCHO-TPSR was also carried out similarly in a continuous flow of O₂/N₂ (20 vol.% O₂, F = 50 mL/min) with the temperature ramped at 10°C/5 min from room temperature to 400°C. The desorption peaks were recorded at each 10°C.

3. Results and Discussion

Figure 1 presents the N₂ adsorption-desorption isotherms of the HZSM-5 and Meso-ZSM-5 pre and post-doping of Ag nanoparticles. All samples exhibited the type I isotherms which is typical for microporous structures. In addition, the type H4 hysteresis loops in the relative pressure ranging from 0.4 to 1 implied the presence of mesopores in the materials. The hysteresis loop of Meso-ZSM-5 was more extensive than that of ZSM-5, indicating significant mesoporosity formed after zeolite modification. The N₂ adsorption-desorption isotherm of the ZSM-5 was similar to that of Ag/ZSM-5, implying the structure of zeolite was maintained after introducing Ag nanoparticles onto zeolite. This was also true for Meso-ZSM-5 and Ag/Meso-ZSM-5.

![Figure 1. N₂ adsorption-desorption isotherms.](image-url)
Regarding the pore size distribution of initial ZSM-5 zeolite and mesopore-modified ZSM-5, it could be seen that a huge number of mesopores with the size from 3 nm to 15 nm have been introduced into the zeolite after alkaline treatment. However, no single peak could be seen in the mesopores’ size distribution after desilication, which means that the removal of Si from the zeolite framework is not selective. As for the pore size distribution of Meso-ZSM-5 pre and post doping, the material didn’t show a significant change after dispersing Ag. Nevertheless, there was a decrease in the volume of pores ranging from 4 -7 nm, indicating that Ag nanoparticles were deposited in these mesopore cavities.

![Figure 2. Pore size distribution of ZSM-5 zeolite before and after alkaline treatment (a) and pore size distribution of Meso-ZSM-5 pre and post doping Ag (b).](image)

Figure 3 illustrates the pore formation of the zeolite by alkaline treatment. It is evident that the high ratio of silica to aluminum will lead to excessive Si dissolution and thus lead to the broad pore size distribution. Uniform mesopore-modified ZSM-5 is more desirable because it could offer better catalytic properties (selectivity and stability). So it is advised to choose another zeolite with lower Si/Al ratio in desilication treatment to achieve a better support for the catalyst.

![Figure 3. Schematic representation of creating mesopores in the zeolite by desilication [23, 24].](image)

In table 1, it is notable that, after surface modification, the surface area of zeolite was significantly higher than the initial zeolite, which will facilitate the dispersion of Ag nanoparticles onto the zeolite. However, after introducing Ag onto zeolite, the surface area substantially decreased, especially in mesopores. Meanwhile, there was almost no change in the surface area of micropores. This proves that the Ag nanoparticles’ size was as large as the dimension of the mesopores, so they have blocked a part
of these mesopores entirely. This could also be observed in the volume of mesopores and micropores pre and post-doping Ag.

Table 1. Textual properties of HZSM-5 zeolite, Meso-ZSM-5 and Ag supported catalysts.

| Sample          | S_{BET} (m^2/g) | S_{micro} (m^2/g) | S_{meso} (m^2/g) | V_{total} (cm^3/g) | V_{micro} (cm^3/g) | D_{pore} (nm) |
|-----------------|-----------------|------------------|-----------------|-------------------|-------------------|----------------|
| ZSM-5           | 288.3           | 259.4            | 28.9            | 0.1071            | 0.1031            | 1.927          |
| Meso-ZSM-5      | 362.3           | 144.7            | 217.6           | 0.3450            | 0.0595            | 3.810          |
| Ag/Meso-ZSM-5   | 287.1           | 145.1            | 142.0           | 0.2934            | 0.0594            | 4.086          |

Figure 4a illustrates the changes in the amount of HCHO adsorbed on Ag/ZSM-5 and Ag/Meso-ZSM-5 at two different relative humidity conditions according to time, and figure 4b calculates the amount of HCHO stored in the materials. When the relative humidity increased from 18% to 43%, the HCHO adsorption capacity of Ag/ZSM-5 fell significantly from 555.4 μmol-HCHO/g-catalyst to only approximately 140 μmol-HCHO/g-catalyst. This indicated comparative adsorption between water and formaldehyde. Although the ZSM-5 surface is hydrophobic with around 5Å in capillary size, this was easier for water with the molecular diameter of 2.8Å to diffuse into pores as opposed to formaldehyde which is 3.73Å in molecular diameter. However, regarding Ag/Meso-ZSM-5, the adsorption capacity was much lower than that of Ag/ZSM-5 at 18% RH. This is because after NaOH treatment, the ratio of Si/Al decreased considerably. Water molecules preferentially adsorbed on hydrophilic centers (Al^{3+}) more than formaldehyde, which led to the decline in the adsorption capacity. On the other hand, when the concentration of water rose, more water appeared on the surface of the material. These molecules bonded together via hydrogen bonding and formed small water clusters [26]. The clusters could be able to interact with formaldehyde in the gaseous stream, so slightly more HCHO adsorbed on the material.
Figure 4. Graph showing the adsorption capacity of materials over time with different relative humidity (CHCHO = 338 ppm, F = 40 mL/min, T = 32°C) (a) and HCHO adsorption capacity of materials at different relative humidity conditions.

Figure 5 and figure 6 show desorption characteristics for HCHO during TPD and TPSR processes on Ag/Meso-ZSM-5 at 43% RH and 18% RH, respectively. It is clear that part of HCHO adsorbed reversibly on the catalyst at room temperature. Despite the fact that the desorption significantly took place from room temperature to 160°C in both cases, there was a difference in the desorption trend in the various presences of moisture. The peak of desorption at RH of 43% was around 50°C, while the desorption at 18% RH happened in a wide range of temperatures, from 40°C to 240°C. An answer could be the desorption of water vapor at high temperatures, which means that the interaction between water and Ag/Meso-ZSM-5 is stronger than that between the material and formaldehyde. It is remarkable that there was no change between the TPD curve and TPSR curve in both situations. This means that the catalyst showed almost no activity at low temperatures.

Figure 5 shows data about the amount of HCHO desorbed from the zeolite surface. The adsorption and desorption amount has a great impact on catalyst activity. The catalyst will have better performance if the desorption is considerable at low temperatures. It will recover new sites for HCHO to be adsorbed on the catalyst [19]. However, if we look at Ag/Meso-ZSM-5, the desorption was still intense until 160°C, so there are a lot active sites covered by HCHO at high temperatures.
A lot of researches showed a strong association between catalyst activity and the formation of DOM (intermediate species), which we can see in figure 8 [5, 7, 27]. More specifically, the more and faster the number of DOM species is generated, the better the catalytic performance. Most formaldehyde molecules adsorb onto the zeolite since the amount of Ag doping on the catalyst is relatively small. No difference in the TPD and TPSR curves points out that the support is inner in the formaldehyde oxidation. Ag nanoparticles are the only active sites for the reaction, which formaldehyde molecules adsorb on and converse into CO$_2$ and H$_2$O in the presence of O$_2$. In addition, high adsorption capacity of the carrier could influence catalytic performance because a majority of formaldehyde species adsorbed physically on the catalyst, which can prevent formaldehyde from approaching active centers.

Figure 9 shows HCHO complete conversion as a function of temperature over Ag/ZSM-5 and Ag/Meso-ZSM-5 at 65% relative humidity. There was no catalyst activity until the temperature above 120°C in both Ag/Meso-ZSM-5 and Ag/ZSM-5, which suited the discussion in desorption character. Furthermore, Ag/Meso-ZSM-5 showed a better catalyst than Ag/ZSM-5 at the same condition. Especially at 200°C, the HCHO conversion to CO$_2$ over Ag/Meso-ZSM-5 achieved 70% in comparison with 20% of conversion Ag/ZSM-5 exhibited. It could be assumed that the diffusion has been improved after surface modification, which permits organic reactants and products to diffuse easily throughout the nanochannels of the zeolite. The overall rate of reaction includes both the reaction rate on the exterior and interior surface. The external surface reaction rate simply depends on the reaction rate constant and the concentration of reactants. Meanwhile, the reaction rate at the interior surface relies on not only these factors but also pore diffusion. At high reaction temperature, the reaction process is relatively fast to the diffusion processes. In this case, the rate of reaction is
dominated by diffusion [28]. Introducing extra mesopores into conventional zeolite helped to reduce diffusion limitation and thus enhanced catalyst efficiency at high temperatures.

![Figure 9. HCHO complete oxidation over Ag/Meso-ZSM-5 and Ag/ZSM-5 (RH = 65%).](image)

4. Conclusion
In short, we have already prepared silver nanoparticles supported onto ZSM-5 and Meso-ZSM-5 and investigated their performance in HCHO complete oxidation. Both Ag/ZSM-5 and Ag/Meso-ZSM-5 have not exhibited high catalytic performances at low temperatures. However, at high temperatures, Ag/Meso-ZSM-5 showed better HCHO oxidation than Ag/ZSM-5. In addition, this work has studied HCHO adsorption-desorption properties and surface reaction of Ag/Meso-ZSM-5. There is clear that Ag nanoparticles are the only active sites of the catalyst, and the high adsorption capacity of the zeolite caused the poor catalytic performance. Introduction of an additional mesopores system enhanced catalyst activity due to reducing diffusion resistance.

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