Chemical Engineering Journal 350 (2018) 419–428

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Sodium-promoted Ag/CeO_2 nanospheres for catalytic oxidation of formaldehyde

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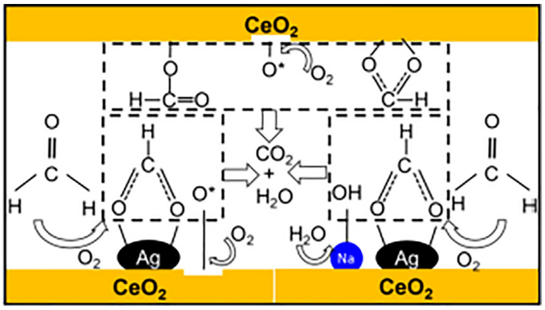
HIGHLIGHTS

- Na-promoted Ag/CeO_2 nanospheres exhibit high intrinsic catalytic activity.
- Strong metal-support interaction affects chemical state of Ag.
- Na compounds prevent hydrogen spillover from Ag to CeO_2 supports during reduction.
- Surface hydroxyl groups become important intermediates with the introduction of Na.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Formaldehyde
Complete catalytic oxidation
Alkali metals
Strong metal-support interaction (SMSI)

ABSTRACT

Ag/CeO_2 nanosphere catalysts were successfully tuned by sodium doping to promote low-temperature catalytic oxidation of formaldehyde (HCHO). It was observed that sodium-promoted Ag/CeO_2 nanosphere catalysts exhibited relatively high intrinsic catalytic activity. Different characterization techniques were performed on the catalysts to elucidate the physicochemical properties that contributed to the improvement of the catalytic performance. Due to electron charge transfer from Ag to CeO_2 nanospheres, Ag species should comprise of Ag_2O as main components along with parts of metallic Ag over CeO_2 nanospheres, while remaining as metallic Ag over conventional CeO_2 bulk particles. The well-dispersed Ag species on CeO_2 nanospheres could activate surface oxygen from CeO_2, and facilitate the surface reduction of CeO_2 nanospheres. The doped sodium might exist in the forms of $NaHCO_3$ and Na_2CO_3 compounds, which could cause that surface hydroxyl (OH^-) concentrations significantly increased on the surface of CeO_2 nanospheres. The presence of sodium compounds could prevent hydrogen spillover from Ag to CeO_2 supports, attesting to the inhibiting role of sodium species in the reduction process. However, with the introduction of sodium into Ag/CeO_2 nanospheres, surface hydroxyl groups would become important reaction species and directly react with adsorbed surface formate species ($HCOO^-$) to form H_2O and CO_2. This reaction route was inconsistent with that over Ag/CeO_2 nanospheres, on which bidentate $HCOO^-$ were the key intermediates during catalytic oxidation of HCHO, and the further oxidation of $HCOO^-$ by activated surface lattice oxygen was the rate-determining step. These results provide guidance for designing highly efficient and economic silver-based catalysts for HCHO catalytic oxidation.

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https://doi.org/10.1016/j.cej.2018.05.179
Received 14 March 2018; Received in revised form 23 May 2018; Accepted 30 May 2018

1. Introduction

Formaldehyde (HCHO), which exists in the indoor atmosphere and the exhaust of diesel or ethanol gasoline vehicles [1–3], represents one of the major air pollutants, and is of concern from a public health perspective. Complete catalytic oxidation technology is recognized as an effective way to eliminate formaldehyde pollutants [4]. At present, precious metals (e.g., Pt [5], Au [6,7], and Pd [8,9]) are the main choice for complete catalytic oxidation of HCHO due to their high catalytic efficiency. These high catalytic properties of HCHO oxidation over supported systems are strongly influenced by the intrinsic properties of the metals (e.g., compositions, chemical states, and particle size, etc.) [8,10], and are also related to the structures of reducible supports due to the strong metal-support interaction (SMSI) [6,7]. Although great progress has been made in the development of precious metal catalysts for catalytic oxidation of HCHO, it is still desirable to improve the catalytic performance and stability for advanced catalytic oxidation techniques at low temperatures. An effective strategy might be a modification of precious metal catalysts by alkali metals to improve the catalytic activity. It has been acknowledged that alkali metals could serve as promoters for the catalytic reaction, and alkali metals could stabilize atomically dispersed Pt species over SiO_2 and provide hydroxyls (OH^-) that would be much more favorable for the water-gas-shift reaction [11]. It was found that doping alkali into Pt/TiO_2 [5] and Pd/TiO_2 [9] catalysts led to much higher catalytic activity for HCHO oxidation. The enhancement effects of alkali metals (e.g., Li^+, Na^+, and K^+) were also found on silver-based catalysts like Ag/Co_3O_4 [12] and Ag/MnO_2 [13] for HCHO oxidation. The main roles of alkali metals are probably to activate H_2O and to catalyze the facile reaction [5,12].

So far, silver-based catalysts, with Ag being one of the relatively inexpensive metals, have also exhibited a promising potential application for catalytic oxidation of HCHO [14,15]. It was reported that successful fabrication of single-atom Ag chains inserted into the tunnels of Hollandite manganese oxide nanorods could exhibit excellent activation ability for both lattice oxygen and molecular oxygen in HCHO oxidation at low temperatures [14]. CeO_2 might be considered as one of the ideal catalyst supports, since it can easily undergo the redox cycle of Ce^{IV}-Ce^{III} [16]. In the past decades, different CeO_2 nanostructures, exhibiting large specific surface area and numerous active sites, have been successfully synthesized [17,18], which could easily facilitate the heterogeneous catalytic reactions by tuning electrical interactions between precious metals and CeO_2 supports [19,20]. Among them, CeO_2 nanospheres consist of small nanoparticles that possess higher concentrations of surface oxygen defects, and could also facilitate the dispersion of metals in forms of small clusters. This, in turn, would enhance the reducibility of CeO_2 and improve desorption of surface active oxygen species [15]. The presence of strong interactions in Ag-CeO_2 and the oxygen vacancies in CeO_2 play an important role in surface reactivity and catalytic performance [21]. The interactions in Ag-CeO_2 might depend on the shape and morphology of CeO_2 nanoparticle supports including a high number of oxygen vacancies [21,22]. These abundant oxygen vacancies in Ag/CeO_2 nanospheres are believed to facilitate the catalytic oxidation reaction [15,21,22].

The remarkable enhancement of the catalysts modified by alkali metals motivated us to apply a similar strategy to improve the catalytic oxidation performance of HCHO over silver-based catalysts. The target is to develop lower-cost HCHO oxidation catalysts that are highly efficient at low temperatures. Herein, we present that sodium indeed promotes catalytic oxidation of HCHO over Ag/CeO_2 nanosphere catalysts. Different characterization techniques were employed to gain more detailed insight into the promoting roles of sodium and the morphology effect of the CeO_2 supports. The insights gained provide guidance for designing highly efficient and economic silver-based catalysts for catalytic oxidation.

2. Experimental

2.1. Preparations of catalysts

CeO_2 nanospheres were prepared by hydrothermal methods according to procedures reported in the literature [17]. For comparison purposes, conventional CeO_2 bulk particles were also prepared by direct decomposition of $Ce(NO_3)_3 \cdot 6H_2O$ in static air at 550 °C for 4 h at a ramp rate of 5 °C/min. Ag-Na/CeO_2, Ag/CeO_2, and Na/CeO_2 with 3 wt% Ag and/or 2 wt% Na (weight ratio of Ag/CeO_2 or Na/CeO_2) were prepared by conventional incipient wetness impregnation employing different CeO_2 as the supports. Typically, 1 g CeO_2 powders were dispersed in DI water under vigorously stirring, and then required amounts of $AgNO_3$ and/or Na_2CO_3 aqueous solution was added drop by drop. After mixing, the slurry was vigorously stirred for approximately 10 h. The obtained solid samples were dried in drying oven at 110 °C and then calcined in static air at 300 °C for 4 h at a ramp rate of 5 °C/min. Herein, CeO_2 particles and CeO_2 nanospheres were denoted as CeO_2-P and CeO_2-N, respectively. The chemical compositions of the catalysts were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) with an IRIS Intrepid II XSP apparatus (Thermo Fisher Scientific), and the results are summarized in Table 1.

2.2. Characterizations

Transmission electron microscopy (TEM) was performed on a Hitachi HT7700 instrument with an acceleration voltage of 100 kV. Characterization of the samples by high-resolution transmission electron microscopy (HRTEM) and energy dispersive spectroscopy (EDS)

Table 1
BET surface area, pore volume, average crystallite sizes, Ag cluster sizes, real Ag contents, surface element compositions, and H_2 consumption of different catalysts.

Catalysts	BET surface area (m^2/g)	Pore volume (cm^3/g)	Crystallite sizes of CeO_2 (nm)[a]	Ag cluster size (nm)[b]	Ag contents (wt.%)[c]	Na contents (wt.%)[c]	O_{OH}/O_{total} ratio[d]	H_2 consumption (μmol)[e]
CeO_2-P	60.7	0.197	17	–	–	–	–	109
Ag/CeO_2-P	59.6	0.182	15	–	2.3	–	–	128
Na/CeO_2-P	45.7	0.178	14	–	–	1.6	0.08	105
Ag-Na/CeO_2-P	45.5	0.178	15	–	2.6	1.6	0.14	142
CeO_2-N	148.6	0.380	3	–	–	–	–	105
Ag/CeO_2-N	125.4	0.239	3	2.4	2.6	–	–	132
Na/CeO_2-N	103.9	0.234	3	–	–	1.5	0.04	95
Ag-Na/CeO_2-N	92.0	0.169	2	2.6	2.4	1.7	0.11	139

[a] Determined by the XRD results according to Scherrer equation using FWHM of the (1 1 1) peak of CeO_2.

[b] Determined by STEM-HAADF images.

[c] Determined by ICP-OES technique.

[d] Determined by XPS spectra of O1s core-level, and $O_{total} = O_{surface} + O_{lattice} + O_{OH}$.

[e] Calculated by H_2-TPR peaks below 700 °C.