Three-dimensional ordered mesoporous Co-Mn oxide: A highly active catalyst for "storage-oxidation" cycling for the removal of HCHO

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Introduction

Catalytic HCHO removal by means of a "storage-oxidation" cycling process has been proposed as a promising approach for indoor HCHO elimination in our previous work [1-6]. In this cycling process, HCHO is partially oxidized at room temperature and stored on the catalyst; the catalyst could be regenerated *in situ* by heating, the stored species being completely oxidized to CO_2 and H_2O. The key issue for such a cycling process is the enhancement of HCHO storage capacity at room temperature in order to prolong the catalyst's useful life for each cycle.

Materials and Methods

Hard-templating (HT) method: The Co-Mn oxide with Co/Mn atomic ratios of 3/1 was prepared by hard-templating method by using KIT-6 as template.

Co-precipitation (CP) method: The Co-Mn oxide with Co/Mn atomic ratio of 3/1 was also prepared by CP method as a comparison.

Results and Discussion

Fig. 1 presents typical TEM images of both samples. CoMn-HT (Fig. 1(A)) is highly uniform with narrow pore size distribution, and is close packed into a highly ordered three-dimensional arrangement. The 3D pore structure replicates that of the KIT-6 template with a space group Ia3d, which is in good agreement with the low-angle XRD results. The pore size of CoMn-HT is estimated to be ca. 3 nm, which is close to the nitrogen adsorption-desorption results. In contrast, it is clear that the CoMn-CP (Fig. 1(B)) sample is composed of nanoparticles.

The CoMn-HT catalyst exhibited a very high HCHO storage capacity even at an extremely high GHSV of 160,000 h^{-1} (Table 1). In contrast, the storage capacity of the CoMn-CP catalyst decreased markedly with increasing GHSV due to the decreased contact time. Table 1 also presents the HCHO storage capacity as a function of RH. It was observed that RH had strong influence on HCHO storage capacity over the CoMn-CP catalyst. The higher RH of the feed gas, the smaller HCHO storage capacity became. However, RH had only a slight influence on the HCHO storage capacity of the CoMn-HT catalyst.

Cycling experiments involving HCHO storage and regeneration were performed over the CoMn-HT catalyst (Fig. 2). During the storage period (80 ppm HCHO/21% O_2/H_2O (RH = 50%)/N_2, GHSV = 36,000 h^{-1}), no HCHO was released until breakthrough occurred, the breakthrough time being ca. 10 h. Since the concentration of HCHO in indoor air is normally below 1 ppm, it is reasonable to believe that the storage phase could be further prolonged to hundreds of hours, indicating the promise of this new method for indoor HCHO elimination. During the oxidation period (21% O_2/H_2O (RH = 50%)/N_2, GHSV = 36,000 h^{-1}, heating rate: 10 ºC/min), the temperature was increased to promote catalytic oxidation of the stored species to CO_2 and H_2O, resulting in the observation of a sharp CO_2 peak at 135 ºC which corresponded to the oxidation of surface species. Moreover, the storage capacity of CoMn-HT remained virtually unchanged for three test cycles. The carbon balance over CoMn-HT was respectively 96.3%, 95.1%, and 95.6% for each cycle. These results demonstrate that CoMn-HT could be totally regenerated without the production of secondary pollutants as evidenced by the absence of CO in the effluent stream and the excellent carbon balances during cycling.

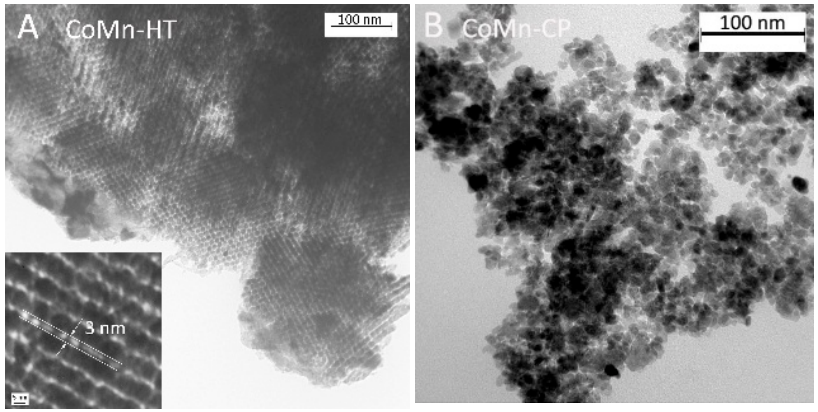

Figure 1 TEM images of (A) CoMn-HT and (B) CoMn-CP.

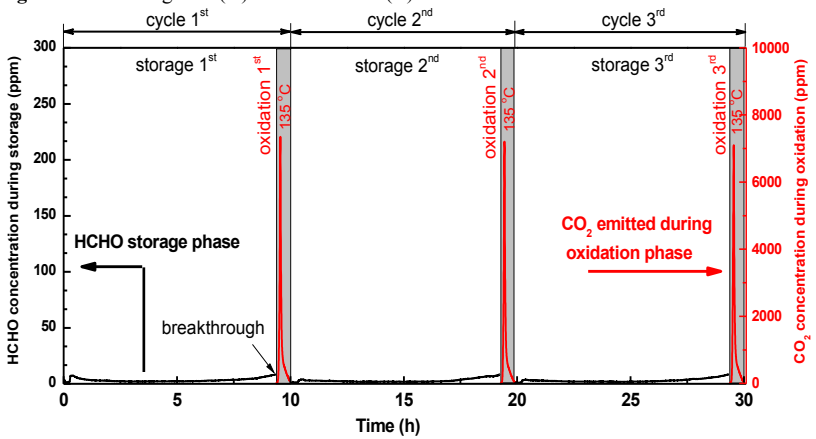

Figure 2 HCHO concentration and CO_2 concentration during three consecutive "storage-oxidation" cycles over CoMn-HT.

Table 1. HCHO storage capacity at different RH and GHSVs.

Catalysts	HCHO storage capacity (mmol/g-cat)					
	Relative humidity [a] (%)			GHSV [b] (h^{-1})		
	0	50	90	36,000	80,000	160,000
CoMn-HT	0.555	0.506	0.453	0.800	0.556	0.405
CoMn-CP	0.536	0.211	0.050	0.428	0.217	0.100

[a] Feed gas: 80 ppm HCHO/21% O_2/N_2, GHSV = 90,000 h^{-1}
[b] Feed gas: 80 ppm HCHO/21% O_2/N_2, RH = 50%

Significance

For the first time 3D ordered mesoporous Co-Mn oxide was successfully prepared by a nanocasting route using mesoporous KIT-6 silica as a hard template and was studied as a catalyst for the removal of HCHO in a "storage-oxidation" cycling process. The excellent catalytic performance of CoMn-HT in HCHO "storage-oxidation" cycling suggests that mesoporous oxide materials are potentially useful for application in the field of VOC removal, especially in the presence of moisture.

References

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