Cyanosilylation of benzaldehyde with TMSCN over perovskite-type oxide catalyst prepared by thermal decomposition of heteronuclear cyano complex precursors

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Abstract The perovskite-type oxide catalyst, SmFeO₃, prepared by decomposition method of heteronuclear cyano complex precursor (CN method) was applied to liquid-phase organic reaction, cyanosilylation of benzaldehyde with TMSCN. The maximum catalytic activity per catalyst weight was achieved at 800 °C of calcination temperature in CN method and it was found that the catalytic activity was strongly related to the crystallinity of SmFeO₃ catalyst. The catalytic reaction performed in the presence of pyridine and 2,6-di-*tert*-butylpyridine suggests that the catalytically active sites are the Brønsted acid sites formed on the SmFeO₃ catalyst. The catalytic activity of SmFeO₃ catalyst prepared by CN method was much higher than those of acid catalysts: SiO₂–Al₂O₃ and Amberlyst.

Keywords Perovskite-type oxide · Cyano complex · Cyanosilylation

Introduction

Perovskite-type oxide, ABO₃, is one of the attractive compounds due to its adequate catalytic activity in oxidation processes and its good thermal stability. Numerous efforts of low-temperature wet-chemical method have been undertaken to prepare perovskite-type oxides with high surface areas. For example, sol–gel [1–4], co-precipitation [2, 5, 6], citrate route [1, 5], reverse micelle [7, 8], reverse homogeneous precipitation [9], and polymeric precursor methods [10, 11], and flame hydrolysis of aqueous solution of precursor salts [12] have been developed and designed to prepare nano-sized perovskite-type oxides. Sadaoka and co-workers

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[13–20] reported a new preparation route of perovskite-type oxide via the thermal decomposition of heteronuclear cyano complex, $M[M'(CN)_6] \cdot nH_2O$ (abbreviated as CN method) where M and M' stand for lanthanide and transition metal ions, respectively. Recently, we have prepared SmFe_{0.5}Co_{0.5}O₃ catalyst by CN method and found that this catalyst exhibited the highest CO oxidation activity among a series of SmFe_xCo_{1-x}O₃ catalysts due to high homogeneity in composition [21, 22]. The advantage of the CN method is to prepare perovskite-type oxide catalysts with high crystallinity at relatively low temperature because of the structure similarity between cyano complex and perovskite-type oxide [23–25]. Up to date, several perovskite-type oxides prepared by low-temperature wet-chemical methods have been reported to show the high catalytic activity for catalytic reaction in gas phase, such as the complete oxidation of hydrocarbons [26, 27] and CO [28, 29] and the decomposition of NO [30–33]. However, little is known about the catalytic activity of perovskite-type oxides for organic reactions in the liquid phase.

The cyanosilylation of carbonyl compounds with trimethylsilyl cyanide (TMSCN) is one of the very important transformations that allow the formation of the C–C bond and the protection of a hydroxyl function. Cyanohydrin trimethylsilyl ethers produced by the cyanosilylation can be further transformed into important synthetic intermediates such as α -hydroxy acids, α -amino acids, and β -amino alcohols [34–37], which are widely applied in the chemical industry. Many researchers have reported this transformation using several catalysts [34–43]. The reaction was catalyzed by Brønsted [38] and Lewis acids [39–42] as well as Lewis bases [43]. In the present paper, as a preliminary result of liquid-phase organic reaction, we wish to report the catalytic activity for cyanosilylation of carbonyl compounds with TMSCN over perovskite-type oxide, SmFeO₃, prepared by CN method.

Experimental

Catalyst preparation

SmFeO₃ catalysts were prepared by three different methods: the CN method [15, 23], decomposition method of polymer precursor (abbreviated as the PP method) [10, 23], and the reverse homogenous precipitation method (RHP method) [9, 23].

CN method

The heteronuclear cyano complex, Sm[Fe(CN)₆]·nH₂O, as a precursor of perovskite-type oxide was synthesized at room temperature by mixing aqueous solutions of appropriate amounts of Sm(NO₃)₃ (Wako, 99.5 %) and K₃Fe(CN)₆ (Hayashi, 99.0 %) under continuous stirring, according to the following reaction: Sm(NO₃)₃(aq) + K₃Fe(CN)₆(aq) \rightarrow SmFe(CN)₆·nH₂O(s) + 3KNO₃(aq). The precipitate obtained was collected by suction filtration, washed with deionized water, ethanol, and diethyl ether, and then dried in air at 50 °C. The resulting powder was calcined at 600–1,000 °C for 1 h in air.

PP method

Sm(NO₃)₃ and Fe(NO₃)₃·9H₂O (Wako, 99.0 %) were dissolved in an ethylene glycol solution (Wako, 99.5 %) at the desired metal molar ratio. Acetylacetone (acac) (Wako, 99.0 %) was then added (oxide:acac = 1 mol:8 mol) as a chelating agent and then poly(vinyl alcohol) (PVA) (Wako, 96.0 %) was added as the polymer additive (7.5 wt%) to form the polymer precursor. The prepared polymer precursor was decomposed on a heating plate to obtain the powders. The resulting powder was calcined at 1,000 °C for 1 h in air.

RHP method

Samarium and iron nitrates (0.02 mol for each) were dissolved in 100 ml of deionized water. The mixed nitrate solution was then dropped through a burette at a rate of 0.5–1.0 ml min⁻¹ into aq. NH₃ (300 ml, pH 13) under vigorous stirring. The final pH of the reaction medium was adjusted to be about 11. The suspension was further stirred for 1 h, kept standing for 30 min, and filtrated to collect the solid precursor (hydroxide). The precursor was dried at 110 °C for 12 h, and then calcined at 1,000 °C for 1 h in air.

Characterization of catalysts

The crystalline structure of the product was elucidated using the powder XRD (Rint 2000, Rigaku) with Cu-K α radiation. Sm and Fe contents in samples were measured by X-ray fluorescence spectrometer (RIX2100 (Rigaku), Rh K α radiation source). The specific surface area was determined with BET analysis (Belsorp-mini, BEL Japan) for the adsorption–desorption measurements using N₂ adsorbent at 77 K. The samples used in the present study and their characteristic data are summarized in Table 1.

Sample	Method ^a	Calcination condition (temp./°C)	Surface (area/m ² g ⁻¹)	Crystallite (size/nm) ^b	Atomic composition ^c Sm/Fe
Sm[Fe(CN) ₆]·nH ₂ O	CN	_	-	_	0.98
SmFeO ₃	CN	700	8.7	27	0.98
SmFeO ₃	CN	800	4.0	29	0.98
SmFeO ₃	CN	900	2.7	34	0.99
SmFeO ₃	CN	1,000	1.5	40	0.97
SmFeO ₃	PP	1,000	3.3	37	0.98
SmFeO ₃	RHP	1,000	2.4	34	0.98

Table 1 Characteristic data of catalysts used in the present study

^a Preparation method of precursor

^b The average crystallite size in the (110) direction was evaluated from XRD line broadening using Scherrer's equation

° XRF analysis

Catalytic reaction for cyanosilylation of benzaldehyde with TMSCN

The chemicals, benzaldehyde (Wako, 98.0 %), trimethylsilyl cyanide (TMSCN) (TCI, 98.0 %), and α -(trimethylsilyl)phenylacetonitrile (Sigma Aldrich, 98 %), were used without any purification. The reference materials, SiO₂–Al₂O₃ (JRC-SAH-1) with 28.61 % of Al₂O₃ content, SiO₂–Al₂O₃ (JRC-SAH-2) with 13.75 % of Al₂O₃ content, and Amberlyst 15 DRY, were supplied by the Catalysis Society of Japan. A typical procedure for cyanosilylation of benzaldehyde is as follows; catalyst (25–50 mg), benzaldehyde (0.5 mmol), and dichloromethane (3–12 ml) were successively placed into a Pylex-glass test tube. The reaction was initiated by addition of TMSCN (1.0 mmol) and the reaction mixture was vigorously stirred (800 rpm) at 20–30 °C in air (1 atm). The detailed reaction conditions are shown in the captions of the figures. The conversion of benzaldehyde and the yield of product, α -(trimethylsilyl)phenylacetonitrile, were periodically determined by GC analysis.

Results and discussion

Figure 1 shows XRD patterns of the samples prepared by the CN, PP, and RHP methods. All the samples were finally calcined at 1,000 °C for 1 h. It is clear that the samples prepared by the CN, PP, and RHP methods provided the XRD patterns indicating the single phase formation of the perovskite-type structure of SmFeO₃ (JCPDS# = 39-1490). Figure 2 shows the amount of product per surface area for cyanosilylation of benzaldehyde with TMSCN over SmFeO3 catalysts prepared by CN, PP, and RHP methods, where the specific surface area of SmFeO₃ prepared by CN, PP, and RHP methods were 1.5, 3.3, and 2.4 m² g⁻¹, respectively, as shown in Table 1. The catalytic activity per specific surface area decreased in the following order: CN > PP > RHP method; $SmFeO_3$ catalyst prepared by CN method exhibited the highest catalytic activity. Therefore, the SmFeO₃ catalysts prepared by the CN method were investigated in more detail. The catalytic activities for cyanosilylation of benzaldehyde with TMSCN over SmFeO₃ catalysts prepared by CN method were investigated as a function of calcination temperature. XRD profiles of the Sm[Fe(CN)₆]·nH₂O precursors calcined at 600-1,000 °C for 1 h were depicted in Fig. 3 together with that of as-prepared Sm[Fe(CN)₆]·nH₂O precursor. The as-prepared Sm[Fe(CN)₆]·nH₂O precursor provided the XRD pattern of the single phase of the heteronuclear metal complex precursor of Sm[Fe(CN)₆]·nH₂O (JCPDS = 39-738) (Fig. 3a). The sample calcined at 600 °C provided no intense XRD peak, suggesting an amorphous phase (Fig. 3b). The samples calcined at 700-1,000 °C provided the XRD pattern indicating the single phase of the perovskite-type structure of SmFeO₃ (JCPDS# = 39-1490) (Fig. 3c-f). The crystallite diameter of SmFeO₃, which was determined by Scherrer's equation, decreased as follows: $1,000 (40 \text{ nm}) > 900 (34) > 800 (29) > 700 \text{ }^{\circ}\text{C} (27)$.

Figure 4a shows the catalytic activities per catalyst weight for this reaction over SmFeO₃ catalysts calcined at several temperatures. The catalytic activity per catalyst weight increased with increasing calcination temperature and reached the maximum value at 800 °C. With further increasing calcination temperature,



Fig. 1 XRD patterns of SmFeO₃ prepared by a CN, b PP, and c RHP methods. These precursors of all methods were calcined at 1,000 °C for 1 h



Fig. 2 Catalytic activity for cyanosilylation over SmFeO₃ catalysts prepared by CN, PP, and RHP methods. *Reaction conditions* benzaldehyde (0.5 mmol), TMSCN (1 mmol), catalyst (50 mg), CH_2Cl_2 (12 ml), 20 °C, and 1 h

catalytic activity slightly decreased. Figure 4b shows the catalytic activities per specific surface area for this cyanosilylation. The specific surface areas of each samples calcined at 600, 700, 800, 900, and 1,000 °C were 41.5, 8.7, 4.0, 2.7, and



Fig. 3 XRD patterns of SmFe-containing samples. A heteronuclear metal cyano complex precursor, $Sm[Fe(CN)_6] \cdot nH_2O(a)$, was calcined at 600 (b), 700 (c), 800 (d), 900 (e), and 1,000 °C (f) for 1 h in air

1.5 m² g⁻¹, respectively (see Table 1); the specific surface area decreased with increasing calcination temperature. The result shown in Fig. 4b leads us to conclude that the catalytic activity per specific surface area monotonously increases with increasing calcination temperature.

We have already reported that for SmFeO₃ catalysts prepared by CN method, an increment of calcination temperature resulted in a decrement of surface area and an increment of crystallite diameter [22-24]. The catalytic activities per specific surface area over SmFeO₃ catalysts prepared by CN method with different calcination temperature were plotted against the crystallite diameter, which was determined by Scherrer's equation. The result is shown in Fig. 5. The catalytic activity per specific surface area seems to be correlated with the crystallite diameter of SmFeO₃ catalysts; the catalytic activity increased with increasing crystallite diameter accompanying with increasing calcination temperature. This result suggests that the crystal growth, that is, the long-term ordering of perovskite-type structure, plays an important role in increasing the catalytic activity for cyanosilylation of benzaldehyde with TMSCN. This is consistent with the result that the catalytic activity per specific surface area decreased in following order: CN > PP > RHP method, shown in Fig. 2, because the crystallite diameter of SmFeO₃ calcined at 1,000 °C decreased in the same order: CN (40 nm) > PP (37) > RHP (34) method.

As mentioned in the introduction, it has been reported that cyanosilylation proceeds on acid and base catalysts [38–43]. To clarify an active site of SmFeO₃ catalyst, the effect of the addition of pyridine and 2,6-di-*tert*-butylpyridine on the catalytic activity for cyanosilylation was investigated. It is reported that pyridine is strongly adsorbed on both Brønsted and Lewis acid site to inhibit catalytic reaction,



Fig. 4 Catalytic activities **a** per catalyst weight and **b** per specific surface area over SmFeO₃ catalysts calcined at several temperatures (CN method). *Reaction conditions* benzaldehyde (0.5 mmol), TMSCN (1 mmol), catalyst (50 mg), CH₂Cl₂ (12 ml), 20 $^{\circ}$ C, and 1 h

while 2,6-di-*tert*-butylpyridine is adsorbed only on the Brønsted acid site because of steric hindrance [38]. Figure 6 shows catalytic activities for cyanosilylation over SmFeO₃ catalyst prepared by the CN method with calcination at 1,000 °C as a function of the amount of pyridine derivatives. The catalytic activity gradually decreased with increasing the amount of pyridine added. Similarly, the small addition of 2,6-di-*tert*-butylpyridine resulted in the drastic decrease in the catalytic activity slightly increased because 2,6-di-*tert*-butylpyridine may act as a stronger base catalyst than pyridine. From these results, it was concluded that the Brønsted acids formed on SmFeO₃ are catalytically active sites for cyanosilylation of benzaldehyde with TMSCN.

Finally, the catalytic activity of SmFeO₃ (CN method, calcination at 1,000 °C) for cyanosilylation was compared with those of solid acid catalysts: $SiO_2-Al_2O_3$ (JRC-SAH-1 and JRC-SAL-2) and Amberlyst 15 DRY, with Brønsted acid sites.



Fig. 5 Catalytic activities for cyanosilylation as a function of crystallite diameter of SmFeO₃ catalysts. *Reaction conditions* benzaldehyde (0.5 mmol), TMSCN (1 mmol), catalyst (50 mg), CH₂Cl₂ (12 ml), 20 °C, and 1 h



Fig. 6 Catalytic activity for cyanosilylation over SmFeO₃ catalyst prepared by calcination at 1,000 °C as a function of the amount of pyridine derivatives (*black square* pyridine and *black circle* 2,6-di-*tert*-butylpyridine). *Reaction conditions* benzaldehyde (0.5 mmol), TMSCN (1 mmol), catalyst (25 mg), CH₂Cl₂ (6 ml), 20 °C, and 1 h

The result is depicted in Fig. 7. SmFeO₃ catalyst exhibited the highest catalyst activity per catalyst weight among the catalysts shown in Fig. 7, although the specific surface area of SmFeO₃ (1.5 m² g⁻¹) was much lower than those of SiO₂-Al₂O₃ (JRC-SAH-1 (511) and JRC-SAL-2 (560)) and Amberlyst 15 DRY (45). Thus, SmFeO₃ catalyst is one of the potential candidates active for cyanosilylation of benzaldehyde with TMSCN. The reason why SmFeO₃ with low surface area showed high catalytic activity is under investigation.



Fig. 7 Catalytic activities for cyanosilylation over SmFeO₃ (CN method, calcination at 1,000 $^{\circ}$ C), SiO₂–Al₂O₃, and Amberlyst 15 DRY catalysts. *Reaction conditions* benzaldehyde (0.5 mmol), TMSCN (1 mmol), catalyst (50 mg), CH₂Cl₂ (3 ml), 30 $^{\circ}$ C, and 1 h

Conclusions

As a model organic reaction in the liquid phase, the cyanosilylation of benzaldehyde with TMSCN was performed over perovskite-type oxide, SmFeO₃. The catalytic activity per specific surface area over SmFeO₃ catalyst prepared by CN method was higher than those by PP and RHP methods. Among these preparation methods, the CN method was the best for preparing SmFeO₃ catalyst highly active for cyanosilylation. For SmFeO₃ catalyst prepared by CN method, the catalytic activity per catalyst weight increased with increasing calcination temperature of $Sm[Fe(CN)_6]$ complex precursor, reached maximum value at 800 °C, and slightly decreased with further increasing calcination temperature. Taking XRD results into consideration, it was found that the catalytic activity was strongly related to crystallinity of SmFeO₃ catalyst. The cyanosilylation was carried out in the presence of pyridine and 2,6-di-tert-butylpyridine, which act as a catalyst poison for acid catalyst. From this result, the catalytically active sites for cyanosilylation were found to be the Brønsted acid sites formed on SmFeO3 catalyst. It was demonstrated that the catalytic activity of SmFeO₃ catalyst prepared by CN method was much higher than those of acid catalysts: SiO₂-Al₂O₃ and Amberlyst.

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