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Article

Promotional effect of H_3PO_4 on ceria catalyst for selective catalytic reduction of NO by NH_3

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ABSTRACT

A series of H_3PO_4 -modified CeO_2 samples were prepared by impregnation of CeO_2 with H_3PO_4 solution, and evaluated for the selective catalytic reduction of NO_x by NH_3 . The samples were characterized by X-ray diffraction, N_2 adsorption-desorption, infrared spectroscopy, Raman spectroscopy, X-ray photoelectron spectroscopy, temperature-programmed desorption of NH_3 , and temperature-programmed reduction of H_2 . The results showed that more than 80% NO conversion was achieved in the temperature range 250–550 °C over the H_3PO_4 - CeO_2 catalyst. The enhanced catalytic performance could be ascribed to the increase in acidic strength, especially Brønsted acidity, and reduction in redox properties of the CeO_2 after H_3PO_4 modification.

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1. Introduction

Nitrogen oxides (NO_x), which arise from automobile exhaust gas and the combustion of fossil fuels, are a major source of air pollution. They are responsible for photochemical smog, acid rain, ozone depletion, and greenhouse effects [1,2]. Selective catalytic reduction of NO_x by NH_3 (NH_3 -SCR) is currently regarded as the most promising technology for removing NO_x from the exhaust of vehicles and stationary combustion processes. A typical commercial catalyst for NH_3 -SCR is V_2O_5 - WO_3 (MoO_3)/ TiO_2 [3,4]. However, inevitable problems related to the toxicity of vanadium species, high conversion of SO_2 to SO_3 , and the relatively narrow window temperature for

this catalyst have led to increased interest in developing novel, highly active, stable, environmentally friendly, and vanadium-free NH_3 -SCR catalysts for controlling NO_x emissions.

CeO_2 is a key component in automotive three-way catalysts for the treatment of exhaust gases owing to its large oxygen storage capacity and excellent redox properties [5,6]. However, it is well known that both redox and acidity is necessary in NH_3 -SCR catalysts [7,8]. The redox properties of the catalyst appear to be a key factor in controlling the reactivity of de- NO_x catalysts at low temperatures, while surface acidity plays an important role in the SCR reaction at high temperatures [9–11]. Because ceria is a basic solid [12], it is inevitable that its redox properties and acidity must be adjusted to obtain a wide

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operating temperature window for CeO₂-based NH₃-SCR catalysts for reducing NO_x emissions. For example, Shan et al. [13] reported a novel Ce-W mixed oxide catalyst that exhibited nearly 100% NO_x conversion in a wide temperature range from 250 to 425 °C, in which the W species increased the amount of Brönsted and Lewis acid sites on the catalyst surface. The modification was not only beneficial in improving the low-temperature activity of the catalyst by facilitating “fast SCR” reaction, but also enhanced its activity at high temperature by inhibiting the unselective oxidation of NH₃ [14,15]. Furthermore, modification of CeO₂ with niobate has also been revealed to be an effective method of improving NH₃-SCR activity, ascribed to the resulting significant increase in surface acidity [16]. Si et al. [17,18] showed that sulfate and nickel modifications effectively enhanced the activity and selectivity of ceria-zirconia catalysts for NH₃-SCR. The nickel modification improved the Lewis acidity of the CeO₂-ZrO₂ catalysts, while Brönsted acid sites formed by the sulfate modification facilitated ammonia adsorption instead of ammonia oxidation at high temperatures. Furthermore, Si et al. [19,20] reported that a zirconium phosphate@Ce_{0.75}Zr_{0.25}O₂ catalyst exhibited high NH₃-SCR activity within a wide temperature range of 250–450 °C. Loading zirconium phosphate onto Ce_{0.75}Zr_{0.25}O₂ was found to reduce the strong interaction between phosphate and cerium as well as introduce acid sites onto the surface of the Ce_{0.75}Zr_{0.25}O₂. Very recently, Li et al. [21,22] reported that a Ce-P-O catalyst prepared by a hydrothermal method showed excellent NH₃-SCR activity and K₂O and SO₂/H₂O resistance within a broad temperature range, and thus displayed promise for the de-NO_x process of stationary sources at medium or high temperatures. However, the structure of these Ce-P-O catalysts was not confirmed, and thus the structure-activity relationship remained unclear.

In this work, a series of H₃PO₄-modified CeO₂ samples were prepared by impregnation of ceria with phosphoric acid solution and evaluated for NH₃-SCR. We found that H₃PO₄ had a significant promotional effect on the CeO₂ catalyst toward the NH₃-SCR reaction. The bulk and surface structures of this catalyst were characterized using different methods. Furthermore, the structure-activity relationship of the H₃PO₄-modified catalysts was thoroughly investigated.

2. Experimental

2.1. Catalyst preparation

CeO₂ was prepared using the citric acid method previously described in the literature [17]. A certain amount of Ce(NO₃)₃·6H₂O was dissolved in distilled water and then mixed with aqueous citric acid to produce a solution with a citric acid to total metal ions ratio of 1.1:1. The solution was stirred vigorously at room temperature for at least 1 h, and then the water was removed by evaporation. The resulting solid was decomposed to produce the oxide by annealing in air at 200 °C. The obtained oxide was then ground and further calcined at 500 °C for 3 h in a muffle oven.

H₃PO₄-modified CeO₂ samples were prepared by wet

incipient impregnation of the prepared ceria with H₃PO₄ solution. The obtained mixture was first dried at 110 °C overnight and then calcined at 500 °C for 3 h in static air. The resulting catalysts were denoted as xH₃PO₄-yCeO₂, where “x/y” denotes the P/Ce molar ratio.

2.2. Catalyst characterization

Powder X-ray diffraction (XRD) patterns were obtained using a D/Max-II B diffractometer and Cu K_α radiation (λ = 1.5406 Å). The working voltage and current of the X-ray tube were 40 kV and 30 mA, respectively. The samples were scanned within the range 2θ = 10°–80° at a scanning rate of 5°/min.

Infrared spectra were recorded with a Fourier-transform infrared (FT-IR) spectrometer (Bruker Vertex 70 FTIR) using the KBr wafer technique for sample preparation.

Raman spectra were recorded on a Raman 960 FT-Raman spectrometer using a laser with an excitation wavelength of 1064 nm and a resolution of 8 cm⁻¹. All Raman spectra presented in this paper are original and unsmoothed.

X-ray photoelectron spectroscopy (XPS) was conducted on a scanning X-ray microprobe (Thermo ESCALAB 250) using Al K_α radiation (1486.7 eV). The binding energies of Ce 3d, P 3p, and O 1s were calibrated using the C 1s peak (BE = 284.8 eV) as standard.

The specific surface areas of the samples were obtained from N₂ adsorption-desorption analysis at –196 °C using a Micromeritics ASAP 2010. The catalyst samples were degassed at 250 °C overnight prior to the N₂ physisorption.

Pyridine-IR spectra were recorded on a Nicolet 410 FT-IR spectrometer. The samples were heated at 200 °C for 30 min and then cooled to room temperature in vacuum of 10⁻⁴ mmHg. The pre-treated samples were exposed to pyridine as the probe molecule at room temperature, after which the pyridine was evacuated at 100 °C. All the IR measurements were performed at room temperature.

Temperature-programmed desorption of NH₃ (NH₃-TPD) was performed using a quadrupole mass spectrometer to record the signals of NH₃ (m/z = 15 for NH). Prior to the TPD experiments, the samples (50 mg) were pretreated at 500 °C in a flow of pure Ar for 1 h and allowed to cool to room temperature. The samples were then exposed to a flow of 1000 ppm NH₃/Ar at room temperature for 2 h, followed by Ar purge for another 1 h. Finally, the temperature was raised to 800 °C in flowing Ar at a rate of 10 °C/min.

For the H₂ temperature-programmed reduction (H₂-TPR) experiments, the samples (50 mg) were pretreated at 500 °C in a flow of air for 1 h and allowed to cool to room temperature. The temperature was then raised to 900 °C at a rate of 10 °C/min in a flow of 5 vol% H₂/Ar. A thermal conductivity cell was used to detect the consumption of H₂.

2.3. Catalytic activity measurement

SCR activity measurements of the catalysts were performed in a fixed-bed quartz flow reactor. The reaction conditions were

as follows: 500 ppm NO, 500 ppm NH₃, 5% O₂, Ar balance, GHSV = 20000 mL/(g·h). The gas concentrations in the outlet stream were continuously monitored with an online quadrupole mass spectrometer (QIC-20, Hiden, UK). The following ion peaks (*m/z*) were monitored to determine the concentration of products and reactants: 15 (NH₃), 30 (NO), 44 (N₂O), and 46 (NO₂). NO_x conversion was calculated as $X_{\text{NO}_x} = (1 - [\text{NO}_x]_{\text{out}}/[\text{NO}_x]_{\text{in}}) \times 100\%$, and N₂ selectivity was calculated as $S_{\text{N}_2} = 1 - 2[\text{N}_2\text{O}]_{\text{out}}/([\text{NO}_x]_{\text{in}} - [\text{NO}_x]_{\text{out}} + [\text{NH}_3]_{\text{in}} - [\text{NH}_3]_{\text{out}}) \times 100\%$, where $[\text{NO}_x] = [\text{NO}] + [\text{NO}_2]$.

3. Results and discussion

3.1. Catalytic properties

The catalytic performance of the pure and H₃PO₄-modified CeO₂ catalysts for NH₃-SCR of NO in the presence of oxygen are shown in Fig. 1. As expected, the pure CeO₂ showed very poor NO_x conversion throughout the whole temperature range and poor N₂ selectivity at temperatures higher than 400 °C. The poor high-temperature SCR activity of CeO₂ was attributed to the strong redox properties of ceria, which led to the over-oxidation of NH₃ by gaseous oxygen [23–25]. However, the catalytic efficiency was significantly improved after H₃PO₄ modification, and the loading of H₃PO₄ played a pivotal role in broadening the operating temperature window. The window was greatly broadened as the P/Ce molar ratio was increased from 1:10 to 1:1, and more than 80% NO conversion was achieved in the temperature range of 250–550 °C over the

Fig. 1. NO_x conversion and N₂ selectivity over the pure CeO₂ and H₃PO₄-modified CeO₂ samples. Reaction conditions: 500 ppm NO, 500 ppm NH₃, 5% O₂, Ar balance, GHSV = 20000 mL/(g·h).

Fig. 2. XRD patterns of the pure and H₃PO₄-modified CeO₂ samples. (1) CeO₂; (2) H₃PO₄-10CeO₂; (3) H₃PO₄-2CeO₂; (4) H₃PO₄-CeO₂; (5) 1.5H₃PO₄-CeO₂.

H₃PO₄-CeO₂ sample. However, upon higher H₃PO₄ loading, such as for the 1.5H₃PO₄-CeO₂ sample, the low-temperature SCR activity was decreased slightly in comparison with that of H₃PO₄-CeO₂.

3.2. XRD patterns and BET surface area

The XRD patterns of H₃PO₄/CeO₂ samples with various H₃PO₄ loadings are shown in Fig. 2. For all of the samples, the typical diffraction lines of the cubic CeO₂ structure (JCPDS No. 34-0394) were clearly visible. At low P/Ce ratios, no phases except CeO₂ were observed, suggesting that the phosphorus species may have been intercalated into the CeO₂ lattice structure or existed as amorphous phosphate species. However, with increasing H₃PO₄ loading, CeP₂O₇ (JCPDS No. 16-0584) phase appeared in the H₃PO₄-CeO₂ sample, while in the 1.5H₃PO₄-CeO₂ sample, CeP₂O₇ became the main phase, and weak peaks of monazite CePO₄ (JCPDS No. 32-0199), Ce(PO₃)₃, and Ce(PO₃)₄ could also be observed [26–29]. The diffraction peaks of CeO₂ in the H₃PO₄-modified ceria samples were shifted towards lower 2θ values as the H₃PO₄ content increased. This may be ascribed to an increase in lattice parameters caused by part of the phosphorus species entering the fluorite structure of ceria [30,31].

The BET surface areas of the samples are presented in Table 1. The surface area of the catalysts first decreased with increasing P content and then increased at higher P/Ce molar ratio. The lowest surface area appeared at the molar ratio of

Table 1
Physical properties and XPS data of the catalysts

Sample	Binding energy (eV)			Ce ³⁺ /(Ce ⁴⁺ +Ce ³⁺) (%)	S _{BET} ^a (m ² /g)
	Ce 3d _{5/2}	P 2p	O 1s		
CeO ₂	882.4	—	529.3	16.4	35.6
H ₃ PO ₄ -10CeO ₂	882.6	132.7	529.7	25.6	32.8
H ₃ PO ₄ -2CeO ₂	882.5	133.2	529.9	25.3	10.7
H ₃ PO ₄ -CeO ₂	882.8	133.6	530.4	24.1	17.6
1.5H ₃ PO ₄ -CeO ₂	883.0	133.4	530.6	23.0	36.1

^a Specific surface area measured by the Brunauer-Emmett-Teller (BET) method.

1:2. These results indicated that there was no clearly defined relationship between catalytic performance and BET surface area in our study. However, in Li's work [21,22], the authors showed that Ce-P-O(h), prepared by a hydrothermal method, was a novel and efficient catalyst for NH_3 -SCR with NO conversions above 90% within the range of 200–550 °C, a better catalytic performance than our H_3PO_4 -CeO₂ catalyst. Although the two catalysts had the same composition (Ce, P, and O), our H_3PO_4 -CeO₂ catalyst had a much smaller BET surface area (17.6 m²/g) than that reported for the Ce-P-O(h) catalyst (82.4 m²/g). Thus, the larger specific surface area of Ce-P-O(h) catalyst is the likely reason for its excellent performance.

3.3. Raman spectra

The Raman spectra of the H_3PO_4 -modified CeO₂ samples are displayed in Fig. 3. The band at 465 cm⁻¹ in the spectra of all samples was attributed to the symmetric breathing mode of O atoms around each Ce⁴⁺ cation in the cubic CeO₂ phase [32,33]. As the P/Ce ratio was increased from 1/10 to 1.5/1, the intensity of this band at 465 cm⁻¹ decreased monotonously, which meant that the amount of cubic CeO₂ phase continuously decreased. Meanwhile, a new weak band appeared at 1034 cm⁻¹, which could be assigned to the symmetric stretching of PO₃ terminal groups from cerium pyrophosphate [34,35]. Further increasing the P/Ce ratio resulted in an obvious increase in the proportion of the cerium pyrophosphate phase, and pyrophosphate became the main phase in the 1.5 H_3PO_4 -CeO₂ sample, consistent with the XRD result.

3.4. IR spectra

Fig. 4 shows the FT-IR spectra of the pure and H_3PO_4 -modified CeO₂ catalysts. Several new bands at 470, 532, 748, 954, and 1223 cm⁻¹ appeared in the H_3PO_4 -CeO₂ samples as the H_3PO_4 loading was increased. These bands could be attributed to O–P bonds, while the bands at 1223 and 748 cm⁻¹ could be ascribed to $\text{P}_2\text{O}_7^{4-}$ and $\text{P}_4\text{O}_{12}^{4-}$, respectively [36–40]. Additionally, as P/Ce ratio was increased from 1/50 to 1.5/1,

Fig. 3. Raman spectra of the H_3PO_4 -modified CeO₂ samples measured at 100–2000 cm⁻¹.

Fig. 4. IR spectra of the H_3PO_4 -modified CeO₂ samples.

the intensity of the bands at 1223 and 748 cm⁻¹ increased monotonically, consistent with the Raman results.

3.5. XPS spectra

To obtain a better understanding of their surface characteristics and concentration of active species, the CeO₂-based catalysts were investigated using XPS. The electron-binding energies (BE) of the photoelectron peaks pertaining to Ce 3d, P 2p, and O 1s are shown in Table 1. The obtained values agreed well with those previously reported in the literature [14,15,41]. The representative photoelectron peaks of Ce 3d and O 1s for both the pure CeO₂ and H_3PO_4 -modified CeO₂ samples are depicted in Figs. 5 and 6, respectively. As shown in Table 1, the binding energy of the Ce 3d and O 1s core-levels of the H_3PO_4 -modified CeO₂ samples was shifted to higher values with respect to pure CeO₂, indicating the interaction between Ce and P species. As shown in Fig. 5, the Ce 3d spectra of the CeO₂-based samples with different H_3PO_4 loadings were very complicated. By performing peak-fitting deconvolution, the Ce 3d spectra could be separated into eight bands. The sub-bands labeled u' and v'

Fig. 5. Ce 3d XPS spectra of the pure and H_3PO_4 -modified CeO₂ samples. (1) CeO₂; (2) H_3PO_4 -10CeO₂; (3) H_3PO_4 -2CeO₂; (4) H_3PO_4 -CeO₂; (5) 1.5 H_3PO_4 -CeO₂.

represent the $3d^{10}4f^1$ initial electronic state corresponding to Ce^{3+} , while the sub-bands labeled u, u'', u''', v, v'', and v''' represent the $3d^{10}4f^0$ state of Ce^{4+} [14,42]. The Ce^{3+} ratios of the samples, calculated as $\text{Ce}^{3+}/(\text{Ce}^{3+}+\text{Ce}^{4+})$, are shown in Table 1. The Ce^{3+} ratio in H_3PO_4 -modified CeO_2 was significantly higher than that in CeO_2 . Meanwhile, it can be seen that the Ce^{3+} ratio increased remarkably with H_3PO_4 loading until it reached a maximum for the H_3PO_4 -10 CeO_2 sample, after which further increases led to a slightly decreased Ce^{3+} ratio. As indicated by the XRD, IR, and Raman results, besides Ce(IV) pyrophosphate, other phosphates such as the monazite CePO_4 phase appeared in the H_3PO_4 -modified CeO_2 samples as the H_3PO_4 loading was increased, which led to an increased Ce^{3+} ratio. However, the highly stable CePO_4 has been claimed to be responsible for the locking of a considerable fraction of the $\text{Ce}^{3+}/\text{Ce}^{4+}$ redox couple, which may reduce the redox ability of these catalysts [20].

Fig. 6 shows the O 1s XPS spectra of the samples in the range of 524–542 eV. There were three kinds of oxygen species present in the samples. The peak centered at 531.5 eV was assigned to non-bridging oxygen (P–O), the peak centered at 533.0 eV was caused by bridging oxygen (P–O–P), and the peak centered at 529.5 eV is ascribed to lattice Ce–O [43–45]. As shown in Fig. 6, the relative intensities of both the P–O–P and P–O contributions increased and the lattice Ce–O peak intensity significantly decreased with increasing H_3PO_4 content. These results confirm that phosphorus species appeared on the surface of the catalysts after H_3PO_4 modification as expected.

3.6. NH_3 -TPD and pyridine-IR analyses

NH_3 -TPD is a frequently used method for determining the number of acid sites on solid acid catalysts as well as acid strength distribution. Fig. 7 shows NH_3 -TPD profiles of the pure CeO_2 and H_3PO_4 -modified CeO_2 catalysts. Pure CeO_2 showed two broad NH_3 desorption peaks, one at about 120 °C and the other at around 250 °C, which indicate weak acid strength. However, it is noteworthy that the acid site strength changed significantly after H_3PO_4 modification. With increasing H_3PO_4 loading, the weak acid site peak decreased gradually until it

Fig. 6. O 1s XPS spectra of the CeO_2 -based samples with different H_3PO_4 loadings. (1) CeO_2 ; (2) H_3PO_4 -10 CeO_2 ; (3) H_3PO_4 -2 CeO_2 ; (4) H_3PO_4 - CeO_2 ; (5) 1.5 H_3PO_4 - CeO_2 .

Fig. 7. NH_3 -TPD profiles of the pure CeO_2 and H_3PO_4 -modified CeO_2 catalysts. (1) CeO_2 ; (2) H_3PO_4 -10 CeO_2 ; (3) H_3PO_4 -2 CeO_2 ; (4) H_3PO_4 - CeO_2 ; (5) 1.5 H_3PO_4 - CeO_2 .

completely disappeared, while a peak at around 600 °C, assignable to strong acidity, dramatically increased in intensity. As discussed above, the surface area of the catalysts initially decreased with increasing P content and then increased at higher P/Ce molar ratio (Table 1). The lowest surface area was observed for the sample with a P/Ce molar ratio of 1:2. Moreover, the pore paths accessible by NH_3 were partly blocked by the phosphate formed as a result of the P enrichment of the surface of the catalyst. As a result of these two factors, the amount of desorbed NH_3 from 1.5 H_3PO_4 - CeO_2 and H_3PO_4 -2 CeO_2 was much lower than that from H_3PO_4 -10 CeO_2 . However, the H_3PO_4 modification increased the acidic strength of the catalysts, which facilitated the adsorption of NH_3 for the catalysts and simultaneously favored the SCR reaction.

The adsorbed pyridine IR technique was used to determine the acidic properties of the CeO_2 -based catalysts. As shown in Fig. 8, the IR spectra of pyridine adsorbed on CeO_2 exhibited

Fig. 8. IR spectra of pyridine adsorbed on the pure CeO_2 and H_3PO_4 -modified CeO_2 catalysts. (1) CeO_2 ; (2) H_3PO_4 -2 CeO_2 ; (3) H_3PO_4 - CeO_2 ; (4) 1.5 H_3PO_4 - CeO_2 .

bands at 1456, 1485, 1595, 1545, and 1642 cm^{-1} . The bands at 1456 and 1595 cm^{-1} are assignable to Lewis acid sites, while the band at 1490 cm^{-1} is mainly attributed to Lewis and Brönsted acid sites, and the bands at 1545 and 1642 cm^{-1} are caused by Brönsted acid sites [32,46]. Thus, both Lewis and the Brönsted acid centers were found on the surfaces of the CeO_2 catalysts. However, the pyridine-IR profiles exhibited an obvious change after H_3PO_4 modification. The bands attributed to Brönsted acidic sites showed an obvious increase in intensity with the amount of H_3PO_4 modification, while the amount of Lewis acidic sites decreased considerably after H_3PO_4 modification. The enhanced Brönsted acidity is probably connected with POH surface groups on the H_3PO_4 -modified CeO_2 catalysts. Although the nature of the NH_3 adsorption sites was still under debate, Li et al. [47–49] showed that Brönsted acid sites efficiently catalyzed the decomposition of ammonium nitrite (an important intermediate in the SCR cycle), which promoted the NH_3 -SCR reaction. Furthermore, more Brönsted acidic sites might provide more moderate acid sites exhibiting less oxidation activity in comparison with Lewis acid sites, which would be beneficial for avoiding NH_3 consumption at high temperatures [17,25]. Thus, H_3PO_4 modification enhances the high temperature NH_3 -SCR activity of CeO_2 owing to the higher ratio of Brönsted to Lewis acid centers.

3.7. H_2 -TPR analysis

The redox properties of the CeO_2 -based samples were investigated by H_2 -TPR. The H_2 -consumption profiles obtained from the TPR experiments are plotted in Fig. 9. As expected, the reduction profile of pure CeO_2 exhibited two peaks [17,50]. The first peak, centered at around 500 $^\circ\text{C}$, was attributed to the reduction of the uppermost layers of Ce^{4+} , while the second peak, at above 800 $^\circ\text{C}$, originated from bulk reduction. However, the H_2 -TPR profile was significantly affected after H_3PO_4 modification. The position of the CeO_2 reduction peak shifted to higher temperature with increasing H_3PO_4 content, which indicated that the oxidation ability of the catalysts was decreased. This difference in the redox behavior between the H_3PO_4 - CeO_2 catalyst and pure CeO_2 may have arisen from interaction between Ce and P species.

Fig. 9. H_2 -TPR profiles of the CeO_2 and H_3PO_4 -modified CeO_2 catalysts.

3.8. Discussion

Phosphorus species, produced by the decomposition of zinc dialkyldithiophosphate present in engine oil, can lead to the poisoning of automotive catalysts because the formed monazite (CePO_4) accumulates on the surface and in the subsurface regions of the three-way catalysts. This deteriorates the oxygen storage and release properties of CeO_2 [32–34]. However, in this work, we found that the addition of H_3PO_4 to CeO_2 catalysts promoted the catalytic efficiency of NH_3 -SCR, and the operating temperature window was greatly broadened. Based on XRD, IR, Raman spectroscopy, and XPS analyses, it was concluded that in the samples with low P/Ce ratio ($<1:2$), the phosphorous species were highly dispersed on the surface of the CeO_2 , while part of the species diffused into the subsurface region and even became incorporated into the CeO_2 lattice. The incorporation of P into the CeO_2 lattice may occur through substitution of anions with PO_4^{3-} or $\text{P}_2\text{O}_7^{4-}$, which would lead to the formation of Ce(III) and excess oxygen in the lattice [32,33,51], consistent with the XPS results shown in Table 1. However, as the P/Ce ratio increased, amorphous pyrophosphates, orthophosphates, and metaphosphate appeared in the samples. With further increases in the H_3PO_4 loading, crystallization of the amorphous CeP_2O_7 occurred on the H_3PO_4 - CeO_2 sample and a mixture of crystalline CeP_2O_7 , CePO_4 , $\text{Ce(PO}_3)_3$, and $\text{Ce(PO}_3)_4$ was formed on the $1.5\text{H}_3\text{PO}_4$ - CeO_2 catalyst, in which CeP_2O_7 as the main phase. Our previous work has demonstrated that rare earth pyrophosphates used as solid acid catalysts show excellent catalytic performance for the Beckmann rearrangement reaction and the vapor-phase dehydration of glycerol [52,53]. Furthermore, we found that polyphosphate possessed much stronger surface acidity than CePO_4 [53]. Therefore, the increase in acidity on the samples with higher H_3PO_4 loading may have been caused by the formed crystalline polyphosphate.

As is well known, both redox and acidic properties are necessary for the SCR reaction [7,8]. Previous studies have showed that the redox properties of a catalyst governs its low-temperature activity, while its surface acidity determined its SCR activity at high temperatures [9–11].

Besides acid properties, redox properties have been claimed to be another important controlling factor for the De-NO_x reaction, especially at high temperatures [1,3]. A high reaction temperature was unfavorable for NH_3 adsorption but promoted H-abstraction of the adsorbed NH_3 . Strong oxidation ability would result in higher catalytic activity for NH_3 oxidation to N_2 or even NO_x , causing decreases in the NH_3 -SCR activity and N_2 selectivity of the catalyst at high temperatures. The present H_3PO_4 modification decrease the oxidation ability of the CeO_2 -based catalysts and inhibited NH_3 oxidation on the catalysts. Therefore, the high-temperature NH_3 -SCR activity and selectivity of the catalysts were improved after H_3PO_4 modification. In summary, the addition of H_3PO_4 to CeO_2 in the present study increased its acidic strength and modified its redox ability, which led to a very broad operation temperature window.

4. Conclusions

The addition of H_3PO_4 to CeO_2 enhanced its activity for NH_3 -SCR remarkably, especially at high temperatures. The modification resulted in an increased acidic strength and reduced redox ability, which were responsible for the very broad operation temperature window of the H_3PO_4 -modified CeO_2 catalysts.

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Graphical Abstract

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Promotional effect of H_3PO_4 on ceria catalyst for selective catalytic reduction of NO by NH_3

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The addition of H_3PO_4 on CeO_2 increased the acidic strength and modified the redox ability, which could lead to a very broad operation temperature window of CeO_2 -based catalyst.

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磷酸对二氧化铈催化剂氨选择性催化还原氮氧化物反应的促进作用

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摘要: 氮氧化物 NO_x (NO 和 NO_2)对大气的污染日益严重, 主要表现为形成酸雨、导致光化学烟雾和产生温室效应等, 严重危害人类健康。氨气选择性催化还原(NH_3 -SCR) NO_x 是目前最有效的固定源 NO_x 消除技术。工业中常用的催化剂主要是 V_2O_5 - WO_3 / TiO_2 , 但其活性组分 V_2O_5 有毒, 且存在氧化能力较强和操作温度窗口过窄等缺点。开发新型环境友好的非钒基 NH_3 -SCR催化剂体系已成为 NO_x 催化净化领域的研究热点。 CeO_2 在稀土市场中占有很大比重且相对廉价, 同时还具有优异的氧化-还原及储氧性能, 因此开发Ce基SCR脱硝催化剂具有非常好的发展前景。

对于 NH_3 -SCR反应, 催化剂必须同时具有酸性位和氧化还原中心: 酸性位有利于还原剂 NH_3 的吸附与活化, 而氧化还原中心可以促使氧化剂和还原剂之间发生反应。对于低温SCR催化剂, 表面酸性适中即可, 氧化还原性能起决定作用; 而对于中高温SCR催化剂, 不仅要提高其表面酸性以保证足够的 NH_3 吸附量, 同时还要控制其表面氧化性不宜太强, 否则在高温段 NH_3 氧化, N_2 选择性下降, NO 转化率降低。 CeO_2 具有一定碱性以及优异的氧化还原性能, 因此在高温阶段 CeO_2 催化剂上易发生 NH_3 深度氧化, 高温 NH_3 -SCR活性差, 温度窗口窄。为了拓宽 CeO_2 基催化剂的温度窗口, 改善其催化性能, 有必要调整 CeO_2 的氧化还原性能和酸碱性能。

过渡金属磷酸盐或焦磷酸盐具有特殊的表面酸性和氧化还原性, 被广泛应用于多种催化反应。考虑到过渡金属磷酸盐或焦磷酸盐表面同时具有酸性位和氧化还原中心, 因而可用于 NH_3 -SCR反应。最近本课题组通过水热法制备了一种环境友好的Ce-P-O催化剂, 该催化剂在较宽的温度范围(300–550 °C)内表现出较高的催化 NO 转化能力, 同时具有较强的抗碱和耐硫能力, 显示出很好的应用前景。此外, 硫酸盐和镍盐修饰能有效改善铈锆固溶体催化剂的 NH_3 -SCR性能: 镍修饰增强了铈锆固溶体的Lewis酸性, 有利于提高催化剂的低温活性, 而硫酸盐改性提高了催化剂的Brönsted酸性, 因此有利于催化剂高温下吸附 NH_3 , 抑制了 NH_3 的过度氧化。另外, 磷酸盐修饰能提高铈锆固溶体催化剂 NH_3 -SCR反应活性。然而, 有关催化剂结构系统表征鲜见报道, 催化剂的构效关系阐述不够详细。

本文采用浸渍法将不同量的 H_3PO_4 负载于 CeO_2 上制备了 H_3PO_4 修饰的 CeO_2 催化剂, 发现 H_3PO_4 修饰能显著改善 CeO_2 催化剂的 NH_3 -SCR性能。本文对催化剂结构进行了系统表征, 详细探讨了 H_3PO_4 促进作用的原因。

NH_3 -SCR活性测试显示, H_3PO_4 修饰后, 催化剂活性显著提高, 部分抑制了高温时 CeO_2 催化剂上 NH_3 的直接氧化, 提高了SCR反应的选择性, 从而拓宽了温度窗口。X射线衍射、红外光谱和拉曼光谱表征结果发现, 随着 H_3PO_4 负载量增加, 样品中 CeO_2 相逐渐减少, 而新相如 CeP_2O_7 和 $\text{Ce}(\text{PO}_3)_4$ 等逐渐增多, 多磷酸根阴离子可能是表面酸性增强的关键因素。 NH_3 程序升温脱附和吸附吡啶红外光谱结果表明, 随着 H_3PO_4 修饰量的增加, 样品的酸强度逐渐增大, Lewis酸性逐渐减弱至消失, 而Brönsted酸性逐渐增强。增强的Brönsted酸性可能归因于 H_3PO_4 修饰后样品表面不断增加的P-OH基团。相对于Lewis酸, Brönsted酸性位氧化能力更弱, 可以抑制高温下 $\text{NH}_2(\text{ads})$ 继续脱氢, 避免了 NH_3 深度氧化。程序升温还原测试结果表明, H_3PO_4 修饰后, 各还原峰向高温偏移, 偏移量随 H_3PO_4 负载量增加而增加。这说明 H_3PO_4 修饰后 CeO_2 的氧化还原能力降低, 抑制了高温下 NH_3 的过度氧化。因此, H_3PO_4 的修饰使得 CeO_2 催化剂高温 NH_3 -SCR活性和 N_2 选择性大幅提高。综上所述, H_3PO_4 - CeO_2 样品优异的脱硝催化活性可能归因于 H_3PO_4 修饰后催化剂酸性, 尤其是Brönsted酸性的增强以及氧化还原性的降低。

关键词: 氨; 选择性催化还原; 二氧化铈; 磷酸; 氧化还原性能; 酸性

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