Catalytic Activities of Transition Metal Phosphides for NO Dissociation and Reduction With CO

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A series of metal phosphides (MoP, WP, CoP, FeP and NiP) were synthesized by H2-temperature-programmed reduction method. Amongst these phosphides, FeP was found to show a considerably higher activity for NO dissociation than other phosphides. Herein, it was firstly used as a catalyst for NO reduction with CO. Although the FeP catalyst showed an excellent activity for NO conversion to N2, there was a competition between NO reduction by CO and FeP oxidation by oxygen originated from NO dissociation. A complete equality of NO conversion and NO reduction degree can be obtained after increasing CO concentration in the system, which demonstrated that a catalytic redox cycle can be established on FeP catalyst, and hence in-situ oxidation of bulk FeP was avoided.

Key words:
Fe2P, NO reduction, NO dissociation, catalytic redox cycle, bulk oxidation

Introduction

Transition metal phosphides are a group of compounds with interesting chemical/physical properties and potential applications in various fields, such as electronics, magnetism, photonics, catalysis, and so on. In particular, metal phosphides (e.g. MoP, NiP, WP, FeP and CoP) have been used as catalysts and extensively studied for hydro-reforming reactions. Among these phosphides, MoP, NiP and WP catalysts have shown significant promise in this regard because of their high activities and resistance to poisoning. Therefore, they have been gradually explored as catalysts in many reactions, including N2 decomposition, carbon dioxide reforming of methane, hydrogen evolution reaction, and hydrogen oxidation reaction. However, compared with phosphides of metals (Ni, Mo and W), FeP has received far less attention due to its poor activity in hydrotreating reactions. Recently, it has been found that a highly dispersed FeP catalyst on activated carbon showed better performance and stability than an iron catalyst. Yet its general catalytic properties have not been explored, and this remains an area of considerable challenge.

In this study, we firstly report that FeP has a much higher catalytic activity for NO dissociation than phosphides of Ni, Mo, W and Co. In view of this unprecedented activity, FeP was selected as the representative of phosphides to investigate the genuine nature of these catalysts for catalytic removal of NO. Although the activity and reaction mechanism of FeP catalyst for NO reduction with H2 had been studied in our previous letter, some important details were still missing about the development of a catalytic cycle in phosphide-catalyzed NO reduction reaction. Currently, the NO/CO reaction was used as a probe reaction to study the catalytic nature of FeP catalyst. The route for keeping the catalyst stable and active was further perfected.

Experimental

Catalyst preparation

Phosphides of metals (Mo, W, Co, Fe and Ni) were prepared in two steps. In the first step, phosphate precursors were prepared by combining stoichiometric quantities of metal salt (NH4)2MoO4·4H2O, (NH4)2W2O7·6H2O, Co(NO3)2·6H2O, Fe(NO3)3·9H2O or Ni(NO3)2·6H2O) and ammonium phosphate (NH4)2HPO4 in sufficient distilled water to form a clear solution. In the case of Ni and Co, several drops of nitric acid were needed to give rise to homogeneous solution. Then the solution was evaporated to dryness and calcined in air at 500 °C for 5 h. In the second step of preparation, the phosphate precursors were converted into phosphides according to H2-temperature-programmed reduction procedure described by Prins and co-workers. Typical-
ly, about 2.0 g of phosphate precursor was placed in a micro-reactor and a flow of H₂ (150 cm³ min⁻¹) was introduced into the system. The temperature was increased from room temperature (RT) to 650 °C at a rate of 1 °C min⁻¹, where it was held for 2 h before quenching to RT in a flow of H₂. Finally, the material was passivated in 1 % O₂/Ar for 12 h before it was exposed to air.

**Catalyst characterization**

XRD examination was performed using an X-ray diffractometer (Rigaku D-Max Rotaflex) with Cu Kα radiation (λ = 1.5404 Å) in the 2θ range from 20 to 90° at a step size of 0.06°. The sample particle size was estimated according to the Scherrer formula. The BET surface areas of passivated samples were measured on an ASAP 2010 instrument. The N₂ gas was used for standard five-point BET surface area measurements. A temperature-programmed surface reaction (TPSR) experiment was performed on a flow reaction system. The catalyst (0.4 g) was pretreated in He flow at 500 °C for 1 h, and then cooled to 150 °C. After thermal stability was reached, the temperature was raised to 500 °C at 15 °C min⁻¹ in 1 % NO/1 % CO/He (50 cm³ min⁻¹). The effluent gases were continuously monitored with a mass spectrometer (MS, HP G1800A) for the analysis of masses (M) = 30 (NO), M = 32 (O₂) and M = 28 (N₂ or CO), and an infrared absorption spectrometer (IRAS, SICK-MAIHAK-S710) for that of N₂O, CO and CO₂.

**Catalyst activity**

The catalytic activity was measured using a 6.0 mm (o.d.) silica reactor by feeding a gas mixture of 0.1 % NO/0–0.3 % CO/He. Typically, 0.4 g of catalyst was loaded onto a plug of silica wool, and the temperature of the catalytic bed was measured with a thermocouple inserted directly into the bed. The catalyst was pretreated in pure He at 400 °C for 1 h before the reaction. The reactants passed over the catalyst at a flow rate of 20 cm³ min⁻¹, the corresponding W/F was 1.2 g s cm⁻³. The effluent gases were monitored by online GC (HP 5890) using a molecular sieve 5A column (3 m, φ4) with a thermal conductivity detector (for the analysis of O₂, N₂, CO and NO), as well as a mass spectrometer (MS, HP G1800A) and an infrared absorption spectrometer (IRAS, SICK-MAIHAK-S710) (for that of CO₂, N₂O and other possible nitrogen oxides).

**Results and discussion**

XRD patterns of the as-prepared phosphides of metals (Mo, W, Co, Fe and Ni) are shown in Fig. 1.
cycle could be established by introducing a reducing agent into the system so that the oxygen could be removed to avoid bulk oxidation of phosphide catalyst. Generally, redox reaction was dependent on reaction temperature and reaction gas composition. Therefore, the rest of this paper was devoted to investigate the temperature and composition dependence of NO/CO reaction over Fe₂P catalyst, and to give insights into the genuine nature of Fe₂P catalyst for catalytic removal of NO.

Table 2 lists the temperature dependence of NO and CO conversion in NO/CO (1:1 ratio) reaction over Fe₂P catalyst. It can be observed that the Fe₂P catalyst showed a high activity of ca. 100% conversion of NO to N₂ in the temperature range 300–500 °C. Nevertheless, the conversion of CO was lower than that of NO at any temperature. The reaction we were expecting for the NO reduction with CO was stoichiometrically represented as:

\[ 2\text{NO} + 2\text{CO} \rightarrow \text{N}_2 + 2\text{CO}_2 \]  

(1)

Based on the results of TPO and O₂-uptake studies, the oxidation of Fe₂P occurred above 220 °C in an oxidation atmosphere. Therefore, it was deduced that the following oxidation of Fe₂P had occurred:

\[ \text{Fe}_{\text{lattice}} + x\text{O}_{\text{ad}} \rightarrow \text{FeO}_x \]  

(2)

Therefore, the conversion of NO to N₂ was higher than that of CO because of the production of N₂ during the reaction between oxygen (generated from NO dissociation) and Fe₂P catalyst. Obviously, there was a competition between NO reduction by CO (Eq. 1) and Fe₂P oxidation by oxygen species (Eqs. 2 and 3) in the system. The NO reduction with CO was an activated process, and a rise in temperature would enhance the reduction degree of NO. The CO conversion had a maximum (ca. 70%) at 400 °C, indicating that NO reduction degree went through a maximum at this temperature. Above 400 °C, there was a sharp decrease in NO reduction probably due to the large extent of Fe₂P oxidation. It was hence suggested that the addition of CO concentration in NO/CO reaction at 400 °C was most likely to prevent bulk oxidation of Fe₂P catalyst.

Fig. 3 shows the effect of feed composition on the catalytic activity of Fe₂P catalyst in NO/CO reactions. It can be seen that the Fe₂P catalyst showed a stable activity (ca. 100% conversion of NO to N₂) in a gas stream of 0.1% NO/0.1% CO/He at 400 °C, but deactivated quickly after 8 h of on-stream reaction: NO conversion to N₂ decreased from ca. 100% to ca. 65% within a period of 11 h. With the addition of CO in the feed, the Fe₂P catalyst showed a stable activity throughout the test period of 11 h, no matter whether it was in 0.1% NO/0.2% CO/He or 0.1% NO/0.3% CO/He. This result indicated that the lifetime of Fe₂P catalyst can be prolonged when the feed gas was rich in CO. To better analyze the effect of NO:CO compositions on the catalytic activity of Fe₂P catalyst, the NO and CO conversion will be produced by NO dissociation.

\[ \text{NO}_{\text{ad}} \rightarrow \text{N}_{\text{ad}} + \text{O}_{\text{ad}} \]  

(3)

Reactions conditions: NO = 1227 mg m⁻³, CO = 1145 mg m⁻³, W/F = 1.2 g s cm⁻³.

Table 2 – Temperature dependence of NO and CO conversion in 1:1 NO/CO reaction over Fe₂P catalyst

<table>
<thead>
<tr>
<th>Temperature/°C</th>
<th>Reaction time/h</th>
<th>NO conversion to N₂/%</th>
<th>CO conversion/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>10</td>
<td>100</td>
<td>18</td>
</tr>
<tr>
<td>400</td>
<td>32</td>
<td>100</td>
<td>70</td>
</tr>
<tr>
<td>500</td>
<td>32</td>
<td>100</td>
<td>24</td>
</tr>
</tbody>
</table>

Fig. 2 – NO conversion to N₂ at 400 °C over MoP, WP, CoP, FeP and NiP catalysts. Reaction conditions: NO = 1227 mg m⁻³, W/F = 1.2 g s cm⁻³, reaction time = 30 min.

Fig. 3 – Effect of feed composition on catalytic activity of Fe₂P catalyst in NO/CO reactions. Reaction conditions: NO = 1227 mg m⁻³, CO = 1145–3436 mg m⁻³, W/F = 1.2 g s cm⁻³, reaction temperature = 400 °C.
CO conversion as well as NO reduction degree in NO/CO reactions at 400 °C are shown in Table 3. The nitrogen-containing gas products was only N₂, without N₂O and other nitrogen oxides by analysis of MS and IRAS. Thus, the NO reduction degree can be estimated by means of \([\text{[CO]}_{\text{in}} - \text{[CO]}_{\text{out}}]/\text{[NO]}_{\text{in}}\) ratio. As shown in Table 3, the conversion of NO to N₂ was closer in the three reactions. Additionally, reasonable trends can be observed that the consumption of CO increased when the feed composition became gradually richer in CO, and hence the NO reduction degree correspondingly increased. This was because an addition of CO in feed gas could increase the CO concentration on the Fe₃P surface, which helped in the reduction of NO by CO (Eq. 1), in contrast, suppressed Fe₃P oxidation by surface oxygen (Eqs. 2 and 3). Note that a complete equality of NO conversion and NO reduction degree appeared to be achieved when the NO:CO ratio decreased to 1:3. This result indicated that the CO concentration in feed gas with 1:3 NO:CO ratio was sufficient to remove surface oxygen and establish a catalytic cycle on Fe₃P catalyst.

In order to investigate the structural change of Fe₃P catalysts after reaction, the used Fe₃P catalysts (functioned in 0.1 % NO/0.1 % CO/He and 0.1 % NO/0.3 % CO/He, respectively, at 400 °C for 11 h) were characterized by XRD. As shown in Fig. 4, Fe₃P catalyst used in 0.1 % NO/0.1 % CO/He for 11 h showed peaks of Fe₂O₃, Fe₃O₄, and FeP crystallites, and the signals of Fe₃P were untraceable. This was a clear indication that bulk Fe₃P can be oxidized completely by oxygen produced from NO dissociation in 0.1 % NO/0.1 % CO/He reaction. In other words, oxygen from NO dissociation would inevitably incorporate into the bulk of Fe₃P catalyst and hence could be removed completely by CO in the feed gas. Noticeably, the diffraction pattern for the Fe₃P catalyst used in 0.1 % NO/0.3 % CO/He for 11 h was identical to that of the fresh sample. These results indicated that a NO/CO ratio of 1:3 was required to avoid bulk oxidation of Fe₃P catalyst in NO/CO reaction, in good agreement with the results that a catalytic cycle can be established on Fe₃P catalyst in 0.1 % NO/0.3 % CO/He at 400 °C (Table 3).

In an attempt to understand the reaction mechanism of Fe₃P catalyst for NO reduction with CO, the TPSR experiment was performed to examine surface reactivity of NO and CO on Fe₃P catalyst. Fig. 5 shows the MS and IRAS profiles as a function of temperature during TPSR. It can be seen that the signals of \(M = 30\) (NO) and \(M = 28\) (N₂ or CO) began to decrease when the temperature was above ~220 °C. This result indicated that NO and CO species adsorption and dissociation, as well as the reaction between the two species had occurred, which was in agreement with the observation of IRAS profile that CO concentration decreased but CO₂ concentration increased above 220 °C, at the same time the production of N₂O peaks occurred at 270 °C. This was a clear indication that NO was mainly converted to N₂O between 220 and 270 °C. However, at temperatures above 270 °C, the concentration of N₂O decreased but that of \(M = 28\) (N₂ or CO) increased, indicating that NO was mainly converted to N₂. Complete NO conversion plateau was obtained at about 300 °C, which was coincident with the signal of \(M = 28\) (N₂ or CO) reaching a maximum. With the temperature increased to 400 °C, the signal of \(M = 28\) (N₂ or CO) and the concentration of CO reached a lower value, but the CO₂ reached the maximum concentration. This demonstrated the highest degree of NO reduction by CO (Eq. 1) at this temperature. However, the change trend of the MS and IRAS profiles above 400 °C showed a decrease in the NO reduction degree. In other words, above 400 °C, the Fe₃P oxidation reaction (Eqs. 2 and 3) was becoming violent. These results agreed well with the data in Table 2.

<table>
<thead>
<tr>
<th>CO:NO</th>
<th>NO conversion to N₂/%</th>
<th>CO conversion/%</th>
<th>NO reduction degree/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>100</td>
<td>62</td>
<td>62</td>
</tr>
<tr>
<td>2:1</td>
<td>97</td>
<td>41</td>
<td>82</td>
</tr>
<tr>
<td>3:1</td>
<td>96</td>
<td>32</td>
<td>96</td>
</tr>
</tbody>
</table>

Reaction conditions: \(\text{NO} = 1227 \text{ mg m}^{-3}\), \(\text{CO} = 1145–3436 \text{ mg m}^{-3}\), \(\text{W/F} = 0.15 \text{ g s cm}^{-2}\), reaction time = 8 h, reaction temperature = 400 °C.

Fig. 4 – XRD patterns of used Fe₃P samples as well as fresh sample for comparison.
Based on the TPSR and XRD results, the surface reactions of NO and CO over Fe$_2$P catalyst can be proposed as follows:

(1) NO dissociation and Fe$_2$P oxidation.

\[
\text{NO (g)} + * \rightleftharpoons \text{NO *} \tag{4}
\]

\[
\text{NO *} + * \rightleftharpoons \text{N} * + \text{O} * \tag{5}
\]

\[
2\text{N} * \rightleftharpoons \text{N}_2 * + *
\]

\[
\text{N}_2 * \rightleftharpoons \text{N}_2(g) + *
\]

\[
\text{NO (g)} + \text{NO *} \rightleftharpoons \text{ON} * \text{NO} \tag{8}
\]

\[
\text{ON} * + \text{NO} * \rightleftharpoons \text{N}_2\text{O} * + \text{O} *
\]

\[
\text{N} * + \text{NO} * \rightleftharpoons \text{N}_2\text{O} * + *
\]

\[
\text{N}_2\text{O} * \rightleftharpoons \text{N}_2\text{O} (g) + *
\]

\[
x\text{O} * + \text{Fe}_2\text{P} \rightarrow \text{FeO}_x + \text{FeP}
\]

In view of the fact that there was no O$_2$ species detected in NO/CO reaction (see Fig. 5a), it was reasonable to deduce that the oxygen produced during NO dissociation was partly released into the gas phase as N$_2$O (g); the rest was captured by Fe$_2$P catalyst. Heavy accumulation of surface oxygen resulted in gradual diffusion of oxygen into the Fe$_2$P lattice, and would cause the ultimate oxidation of the bulk.

(2) NO reduction with CO.

After introducing CO into the system at an appropriate reaction temperature, the poisonous effect of oxygen toward Fe$_2$P can be eliminated by regulating the CO concentration in the feed; the process can be described as follows:

\[
\text{CO (g)} + * \rightleftharpoons \text{CO} *
\]

\[
\text{CO} * + \text{O} * \rightleftharpoons \text{CO}_2 *
\]

\[
\text{CO}_2 * \rightleftharpoons \text{CO}_2 (g) + *
\]

According to the results of activity studies and XRD characterization (Table 3 and Fig. 4), a minimum of 0.3 % of CO in the 0.1 % NO/He feed was required for establishing a catalytic cycle and avoiding bulk oxidation of Fe$_2$P catalyst.

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**References**


