

# Selective Hydrogenation of Acetylene over a MoP Catalyst

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**Abstract:** A MoP catalyst was prepared by high temperature hydrogen reduction. Its properties were investigated by X-ray diffraction and in-situ X-ray photoelectron spectroscopy. It was used for the selective catalytic hydrogenation of acetylene. The results indicated that MoP is formed by hydrogen reduction at 650 °C. The prepared MoP catalyst contained high valence molybdenum and phosphorus species. The catalyst is a bifunctional catalyst, which includes a hydrogenation center and an electron-deficient center. Ethylene selectivity can exceed 73% when the acetylene conversion is higher than 99%.

**Key words:** molybdenum phosphide; acetylene; selective hydrogenation; ethylene

The ethylene obtained from thermal cracking and steam cracking contains small quantities of acetylene (< 2%), which poisons ethylene polymerization catalysts. The selective hydrogenation of acetylene has been extensively investigated over Pd and promoted Pd catalysts. However, since the hydrogenation of acetylene is a series reaction ( $C_2H_2 \rightarrow C_2H_4 \rightarrow C_2H_6$ ), the selectivity for ethylene decreases drastically with increasing acetylene conversion [1–3]. Unpromoted Pd catalysts have high activity for trace acetylene elimination, while they suffer from low ethylene selectivity at high acetylene conversions. Although most selective hydrogenation of acetylene studies to date have involved Pd-based systems, other catalysts have also been considered [4–6]. However, these studies focused on precious metal catalysts rather than a non-noble metal catalyst. Molybdenum phosphide (MoP) is a new hydrogenation catalyst that has attracted the attention of researchers. Many studies have shown that the MoP catalyst has superior catalytic activity for hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) [7–9] but few studies have paid any attention to their reactivity in other hydrogenation reactions such as acetylene selective catalytic hydrogenation.

In this work, MoP was prepared and used for the selective hydrogenation of acetylene. Ammonium heptamolybdate ( $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ ) was mixed with diammonium hydrogen

phosphate  $(NH_4)_2HPO_4$  in distilled water at a Mo/P molar ratio of 1.0. After the evaporation of water and calcination in air at 500 °C for 4 h, the obtained solid was ground to a powder and sieved to 20–40 mesh particles. The obtained particles were placed in a quartz reactor and reduced in a temperature controlled manner from room temperature to 300 °C in 30 min and from 300 to 650 °C over 175 min at a rate of 2 °C/min in flowing  $H_2$  (~100 ml/min). The final temperature was maintained for 2 h followed by cooling to room temperature in  $H_2$ . The sample was then passivated at room temperature for 6–8 h in a stream of 1% $O_2$ -99% $N_2$ .

The X-ray diffraction (XRD) pattern was obtained using a Rigaku D/Max-2500/PC X-ray diffractometer with Cu  $K_\alpha$  radiation. In-situ X-ray photoelectron spectroscopy (XPS) analysis was performed using a KRATOS X-ray source (model VG ESCALAB MK2) with Al  $K_\alpha$  radiation. The chemical state of Mo and P in the MoP catalyst was acquired by XPS analysis.

The hydrogenation of acetylene was evaluated in a continuous flow quartz reactor at ambient pressure. 100 mg of catalyst was pretreated at 600 °C in a 90 ml/min flow of hydrogen for 60 min followed by cooling in  $H_2$  flow to the desired reaction temperature. The feedstock containing 1 vol% acetylene and 10 vol% hydrogen was balanced with Ar at total flow rate of 60 ml/min and this was controlled by mass flowmeters.

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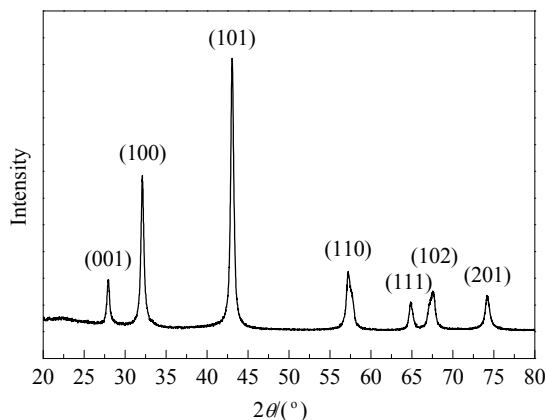


Fig. 1. XRD pattern of the MoP catalyst.

The reactants and products were analyzed using an on-line gas chromatograph (Agilent 6890N) equipped with a FID and a GS-GASPRO column (30 m × 0.320 mm).

The crystal structure of the MoP catalyst prepared in hydrogen at 650 °C for 2 h was examined using XRD and shown in Fig. 1. This figure shows a series of typical peaks at  $2\theta = 27.94^\circ, 32.08^\circ, 43.06^\circ, 57.16^\circ, 57.74^\circ, 64.78^\circ, 67.06^\circ, 67.58^\circ,$  and  $74.12^\circ$ , which can be attributed to the (001), (100), (101), (110), (111), (102), and (201) crystal planes of the MoP phase, respectively. Besides the MoP crystal no other new compounds were detected. The results indicate that the perfect MoP crystal was produced by the reduction of molybdenum phosphate in hydrogen at 650 °C.

Figure 2 shows in-situ XPS spectra of the MoP catalyst pretreated at 500 °C for 60 min in pure hydrogen. The Mo  $3d_{5/2}$  peak positions for the catalyst is located at electron binding energies of about 228.0, 229.1, and 232.2 eV, and these are with the same as those of  $\text{Mo}^{3+}$ ,  $\text{Mo}^{\delta+}$ , and  $\text{Mo}^{6+}$  in a multiphase environment. These results are in agreement with previously reported results [10]. Additionally, the P  $2p_{3/2}$  peaks were at 129.2 and 133.4 eV, which is with the same as that for the  $\text{P}^{3-}$  and  $\text{P}^{5+}$  species, and this is also in agreement with a previous report [11].

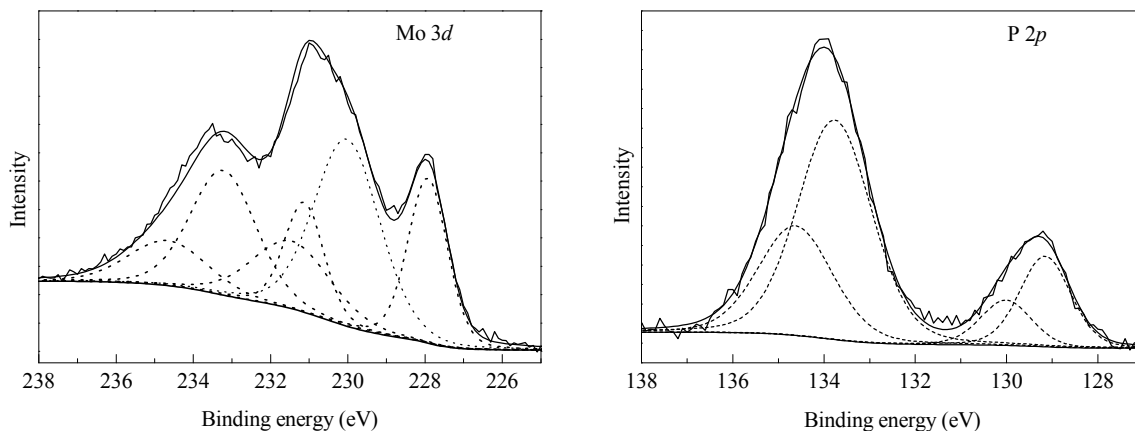


Fig. 2. XPS spectra of the MoP catalyst.

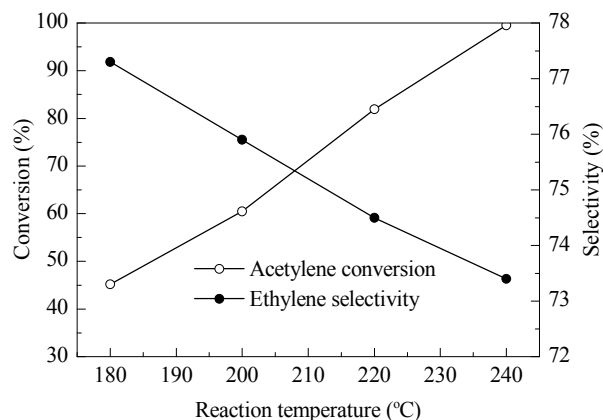


Fig. 3. Influence of reaction temperature on the hydrogenation activity of the MoP catalyst. Reaction conditions: atmosphere,  $\text{H}_2/\text{C}_2\text{H}_2 = 10$ ,  $\text{SV} = 36000 \text{ ml}/(\text{g}\cdot\text{h})$ .

The  $\text{P}^{3-}/\text{P}$  and  $\text{Mo}^{3+}/\text{Mo}$  ratios are 0.22 and 0.24, respectively, on the surface of the MoP catalyst and this is based on XPS peak areas. The results show that the  $\text{Mo}^{3+}$  and  $\text{P}^{3-}$  species (MoP) can be formed by hydrogen reduction. However, some high valence state molybdenum and phosphorus compounds still exist in the MoP catalyst.

The catalytic hydrogenation reaction was investigated at  $\text{H}_2/\text{C}_2\text{H}_2 = 10$ , a space velocity of 36000 ml/(g·h), and different reaction temperatures for the prepared MoP catalyst. The results are shown in Fig. 3. As shown in Fig. 3, the MoP catalyst has good catalytic hydrogenation activity toward acetylene and the conversion reaches 45.2% at 180 °C. The main hydrogenation product is ethylene and the selectivity exceeds 77.3%. Acetylene conversion and ethylene selectivity is 99.5% and 73.4% at a reaction temperature of 240 °C, respectively.

XRD and XPS results indicated that the molybdenum phosphate precursor material can be reduced by hydrogen to form the MoP phase at 650 °C over 2 h. The characteristic IR band is attributed to linearly adsorbed CO on the Mo atoms of the MoP surface and is similar to the IR bands at 2040–2060  $\text{cm}^{-1}$ , which corresponds to CO adsorbed on noble metals such as platinum, palladium, and rhodium [12]. The results imply

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