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Synergetic effect between $\text{Ni}_2\text{P}/\gamma\text{-Al}_2\text{O}_3$ and $\text{MoS}_2/\gamma\text{-Al}_2\text{O}_3$ catalysts on their performance in hydrodenitrogenation of quinoline

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Abstract: The synergetic effect between $\text{Ni}_2\text{P}/\text{Al}_2\text{O}_3$ and $\text{MoS}_2/\text{Al}_2\text{O}_3$ catalysts on their performance in the hydrodenitrogenation of quinoline was proved by a simplified experimental design and explained by the remote control model through a migration of hydrogen spillover. The results indicated that the synergism factor of Ni_2P and MoS_2 is slightly higher than that of NiS_x and MoS_2 ; it decreases with the increase of reaction temperature. Since the spillover hydrogen with Ni_2P can increase the amount of hydrogenation active sites of MoS_2 , the hydrogenation rate of 1,2,3,4-tetrahydroquinoline and 5,6,7,8-tetrahydroquinoline to decahydroquinoline over the $\text{Ni}_2\text{P}/\text{Al}_2\text{O}_3$ and $\text{MoS}_2/\text{Al}_2\text{O}_3$ catalyst system is then greatly enhanced; as a result, Ni_2P is a superior promoter for MoS_2 catalyst for hydrodenitrogenation.

Keywords: hydrogen spillover; synergetic effect; hydrodenitrogenation; MoS_2 ; Ni_2P ; quinoline

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Recently, more stringent fuel specifications have been implemented in many countries to minimize air pollution and prevent exhaust treatment catalysts from poisoning. The development of hydrotreating catalysts with superior performance has attracted considerable attention. However, the origin of the synergism of the active components on the catalysts was still not well understood. Many models for synergism have been proposed; among them, the Co (Ni)-Mo-S model proposed by Topsøe et al.^[1] and the remote control model developed by Karroua and Delmon^[2,3] are two of most accepted ones.

In the Co (Ni)-Mo-S model, the effect of promoter on molybdenum sulfide catalysts has been attributed to the amount of promoter atoms that can be accommodated on the edges of MoS_2 layers and also to the electronic transfer that is induced by the promoter atom on Mo atoms located at these sites^[4]. The new "brim site" model proposed by Topsøe is consistent with the known facts in many aspects such as inhibitions, steric and poisoning effects^[5,6]. In the remote control model, the synergism is related to hydrogen spillover (H_{so}), which migrates from a donor phase (such as Co_9S_8 , NiS_x and noble metals) to an acceptor phase (such as MoS_2 and WS_2) that hereby is activated. By using a reactor system of physically separated, layered catalyst beds, Villarroel et al.^[7-11] provided direct proof of the role of a remote control; they demonstrated that Mn, Fe, Co, Ni, Cu, and Zn sulphides were able to generate H_{so} and

thus to promote the Mo sulfide in stacked beds. The investigation of such a synergism was further from hydrodesulfurization (HDS) to hydrodenitrogenation (HDN) reactions^[12,13].

Transition metal phosphides are novel catalytic materials with excellent performance in HDS and HDN. Recently, it was found that the introduction of Ni_2P to MoS_2 catalyst led to markedly higher HDS activity in dibenzothiophene^[14-16], which is related to the high hydrogenation capability of nickel phosphide. In this work, therefore, we endeavor to determine the synergetic effect between Ni_2P and MoS_2 on the HDN of quinoline by a simplified experimental design as well as the role of such a synergism, if present, in the HDN reaction.

1 Experimental

1.1 Catalyst preparation

SiO_2 (Qingdao Ocean Chemical Plant, China) was used as the separator between two physically separated catalyst beds. Ammonium tetrathiomolybdate (ATTM) was prepared following the routes reported in the literature^[17]. Nickel hypophosphite, quinoline, carbon disulfide and decalin were purchased from Sinopharm Chemical Reagent Co., Ltd. of China.

$\gamma\text{-Al}_2\text{O}_3$ with a BET surface area of 265.9 m^2/g and pore volume of 0.65 cm^3/g was used as the catalyst support. $\text{Ni}_2\text{P}/\text{Al}_2\text{O}_3$ catalyst with the Ni_2P content of 4% was prepared by the thermal

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decomposition of nickel hypophosphite. The support was impregnated in the solution of $\text{Ni}(\text{H}_2\text{PO}_2)_2 \cdot 6\text{H}_2\text{O}$; the resultant solid sample was then dried in a vacuum oven at $60\text{ }^\circ\text{C}$ for 2 h and calcined under N_2 atmosphere at $300\text{ }^\circ\text{C}$ for 3 h. The product was washed three times with deionized water to remove any impurities. The $\text{MoS}_2/\text{Al}_2\text{O}_3$ catalyst containing 18.1% of MoO_3 was obtained by the impregnation of the support with a solution of ammonium tetrathiomolybdate (ATTM); the catalyst was dried for 2 h at ambient temperature and subsequently at $60\text{ }^\circ\text{C}$ for 12 h, and then calcined under a flow of nitrogen at $400\text{ }^\circ\text{C}$ for 3 h.

1.2 Catalyst characterization

Hydrogen temperature-programmed desorption (H_2 -TPD) was conducted with Quantachrome ChemBET 3000 instrument. Firstly, the promoter (0.1 g) was loaded in a quartz reactor and reduced in a H_2 flow at $500\text{ }^\circ\text{C}$ for 2 h. Subsequently, it was

cooled down to $100\text{ }^\circ\text{C}$ and purged by a flowing He stream for 2 h to remove any excessive and physically adsorbed H_2 . Finally, the treated sample was heated from 100 to $600\text{ }^\circ\text{C}$ at a rate of $10\text{ }^\circ\text{C}/\text{min}$ in a pure He flow. The desorbed hydrogen was detected through a thermal conduction detector (TCD).

1.3 Catalytic activity measurements

As shown in Figure 1, the stacked bed (C) was assembled as follows: the top layer consisted of 2 g $\text{Ni}_2\text{P}/\text{Al}_2\text{O}_3$ and the bottom layer was 2 g $\text{MoS}_2/\text{Al}_2\text{O}_3$; they were separated by a 3-mm-thick SiO_2 layer to prevent the formation of a mixed phase. The remaining space in the reactor was filled with quartz sand. This “stacked bed” was denoted as $\text{Ni}_2\text{P}/\text{MoS}_2$. Similarly, another “stacked bed” (D) represented as $\text{MoS}_2//\text{Ni}_2\text{P}$, with the same amounts of $\text{Ni}_2\text{P}/\text{Al}_2\text{O}_3$ in the bottom layer and $\text{MoS}_2/\text{Al}_2\text{O}_3$ in the top layer.

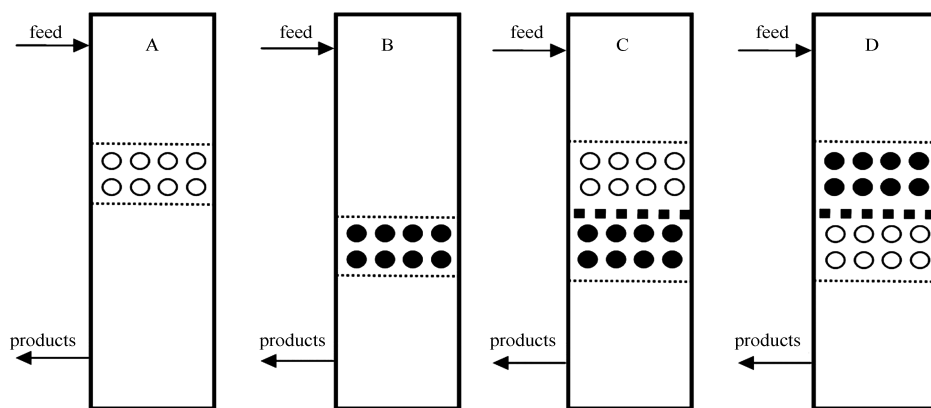


Figure 1 Scheme of different ways for loading catalysts in the reactor

○: $\text{Ni}_2\text{P}/\text{Al}_2\text{O}_3$; ●: $\text{MoS}_2/\text{Al}_2\text{O}_3$; ■: SiO_2

The HDN of quinoline was carried out in a fixed-bed flow reactor. The liquid feed consisted of a solution of quinoline ($1\ 000\ \mu\text{g}/\text{g}$ of nitrogen) and carbon disulfide ($200\ \mu\text{g}/\text{g}$ of sulfur) in decalin was fed to the reactor by a high-pressure pump. The products were collected using a liquid-gas separator at $0\text{ }^\circ\text{C}$. Prior to getting the samples for analysis, these catalysts were stabilized at desired reaction temperature for at least 6 h. The compositions of the products were analyzed by using an Agilent 6820 gas chromatograph equipped with a HP-5 ($30\ \text{m} \times 0.32\ \text{mm} \times 0.5\ \mu\text{m}$) packed column and FID detector.

HDN conversion (x_{HDN}) was calculated by the following equation to evaluate the HDN activity of the catalysts:

$$x_{\text{HDN}} = (c_{\text{Q0}} - c_{\text{QR}} - c_{\text{NC}}) / c_{\text{Q0}} \times 100\% \quad (1)$$

where c_{Q0} represented the quinoline concentration

in the feed, c_{QR} was the quinoline concentration in the product, and c_{NC} was the total concentration of all the nitrogen-containing intermediates in the product.

For quantitative description of the synergism of the stacked bed, the synergism factor^[11] was defined as a ratio of x_{HDN} (stacked bed) / x_{HDN} (%) (single bed), where x_{HDN} (stacked bed) and x_{HDN} (single bed) were the HDN activities of the stacked bed and the sum of the single $\text{Ni}_2\text{P}/\text{Al}_2\text{O}_3$ and $\text{MoS}_2/\text{Al}_2\text{O}_3$ beds, respectively.

2 Results and discussion

To investigate the synergistic effect between $\text{Ni}_2\text{P}/\text{Al}_2\text{O}_3$ and $\text{MoS}_2/\text{Al}_2\text{O}_3$ catalysts on the performance of these catalysts in the HDN of quinoline, four tests were carried out in a micro-reactor. As listed in Table 1, the HDN activity of the stacked bed catalytic system is compared with the

single bed catalyst at different reaction temperatures. The $\text{Ni}_2\text{P}/\text{Al}_2\text{O}_3$ catalyst gives a very low HDN conversion, which is not strange because of the lower reaction temperature and Ni_2P loading^[18-22]. Meanwhile, the HDN conversion over the $\text{MoS}_2/\text{Al}_2\text{O}_3$ catalyst is 35.2% at 320 °C, indicating a moderate activity of monometallic $\text{MoS}_2/\text{Al}_2\text{O}_3$ catalyst in quinoline HDN.

The HDN conversion attained over the stacked bed that consists of $\text{Ni}_2\text{P}/\text{Al}_2\text{O}_3$ and $\text{MoS}_2/\text{Al}_2\text{O}_3$ separated by 3 mm silica is higher than the sum of HDN conversions achieved over two single beds; for example, the HDN conversions over $\text{Ni}_2\text{P}/\text{MoS}_2$ and $\text{MoS}_2/\text{Al}_2\text{O}_3$ at 320 °C are 46.8% and 35.9%, respectively. As $\text{Ni}_2\text{P}/\text{Al}_2\text{O}_3$ and $\text{MoS}_2/\text{Al}_2\text{O}_3$ beds in the stacked bed are not directly contacted, these results unequivocally demonstrate that there is a synergistic effect between Ni_2P and MoS_2 on the HDN of quinoline, which can be explained by the remote control (RC) model; similarly, Valdevenito et al^[12] also detected a synergistic effect on the HDN of pyridine over $\text{NiS}_x/\text{MoS}_2$. However, if $\text{Ni}_2\text{P}/\text{Al}_2\text{O}_3$ is situated under $\text{MoS}_2/\text{Al}_2\text{O}_3$ (Figure 1D), such a synergy effect cannot be observed; the catalytic performance of $\text{MoS}_2/\text{Al}_2\text{O}_3$ system is similar to that of two single beds. These indicate that the synergy effect only presents itself when the feed flows from the $\text{Ni}_2\text{P}/\text{Al}_2\text{O}_3$ phase to $\text{MoS}_2/\text{Al}_2\text{O}_3$ phase.

Table 1 HDN activity of $\text{Ni}_2\text{P}/\text{Al}_2\text{O}_3$, $\text{MoS}_2/\text{Al}_2\text{O}_3$, $\text{Ni}_2\text{P}/\text{MoS}_2$ and $\text{MoS}_2/\text{Ni}_2\text{P}$ catalysts

Catalyst bed	HDN conversion $x/\%$			
	280 °C	300 °C	320 °C	340 °C
$\text{Ni}_2\text{P}/\text{Al}_2\text{O}_3$	0.1	0.2	0.7	2.1
$\text{MoS}_2/\text{Al}_2\text{O}_3$	4.1	12.6	35.2	53.4
$\text{Ni}_2\text{P}/\text{MoS}_2$	7.8	18.5	46.8	65.4
$\text{MoS}_2/\text{Ni}_2\text{P}$	4.5	12.7	36.1	54.8

note: operating conditions are H_2 pressure of 2.0 MPa, WHSV of 3.0 h^{-1} , and H_2/oil volume ratio of 600/1

Figure 2 shows the synergism factors over the $\text{Ni}_2\text{P}/\text{MoS}_2$ and $\text{NiS}_x/\text{MoS}_2$ stacked beds. The synergism factors are around 1.18 ~ 1.86 and the $\text{Ni}_2\text{P}/\text{MoS}_2$ catalyst system exhibits a slightly higher synergism factor than the $\text{NiS}_x/\text{MoS}_2$ system^[13]. Meanwhile, the synergism factor decreases with the increase of reaction temperature, in accordance with the previous reports^[8].

H_2 -TPD profiles of the $\text{NiS}_x/\text{Al}_2\text{O}_3$ and $\text{Ni}_2\text{P}/\text{Al}_2\text{O}_3$ promoters are shown in Figure 3 to recognize the hydrogen species on them. Usually, the hydrogen species desorbed below 320 °C and above 320 °C are ascribed to those adsorbed on the metal sites and the

spilt-over hydrogen, respectively^[23]. There is no hydrogen desorption peak observed below 235 °C, which is different with the result reported by Chen et al^[24], because of their difference in the treatment conditions. Figure 3 indicates that abundant spillover hydrogen species are adsorbed on the $\text{Ni}_2\text{P}/\text{Al}_2\text{O}_3$ catalyst surface, whereas the $\text{NiS}_x/\text{Al}_2\text{O}_3$ catalyst has much less spillover hydrogen species on the surface. It is related to the special structure of Ni_2P in which nickel owns a small positive charge; as a result, more hydrogen was adsorbed over Ni_2P than over NiS_x . This may facilitate the formation of the dissociated hydrogen species, which then migrates from Ni_2P to MoS_2 and removes S atoms from MoS_2 phase as H_2S to create more 3-fold coordinative unsaturated sites (CUS). Since the CUS are considered as the active sites, the presence of Ni_2P is then able to enhance the concentration of hydrogenation sites over the MoS_2 catalyst.

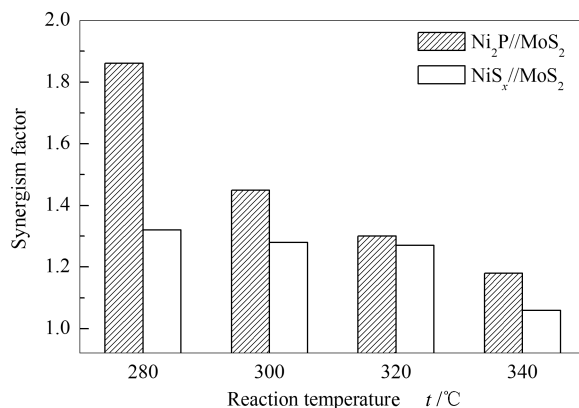


Figure 2 Synergism factors of the stacked beds of $\text{Ni}_2\text{P}/\text{MoS}_2$ and $\text{NiS}_x/\text{MoS}_2$ ^[13]

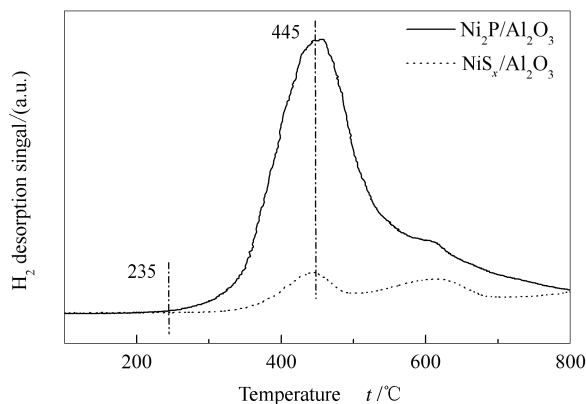


Figure 3 H_2 -TPD profiles of the $\text{Ni}_2\text{P}/\text{Al}_2\text{O}_3$ and $\text{NiS}_x/\text{Al}_2\text{O}_3$ promoters

Quinoline (Q) is usually chosen as the model compound of the HDN reaction, whose reaction mechanism has been studied by several groups^[25,26]. It is generally accepted that HDN of quinoline

proceeds exclusively via the fully saturated intermediates decahydroquinoline (DHQ) and 2-propylcyclohexylamine (PCHA), i. e. Q \rightarrow DHQ \rightarrow PCHA \rightarrow hydrocarbons^[27]. The compositions of liquid products for quinoline HDN at 320 °C are listed in Table 2. PCHA is not detected in the liquid product, indicating that the aliphatic C-N bond cleavage is an easy step for MoS₂ catalyst in this work. The breaking of C-N bond and hydrogenation of the aromatics ring are often supposed to be very slow. However, the concentration of DHQ is only around 5%, much smaller than that of THQ (1,2,3,

4-tetrahydroquinoline (THQ1) and 5, 6, 7, 8-tetrahydroquinoline (THQ5)). So it may be concluded that the breaking of C-N bond in DHQ does not restrict the HDN of quinoline. THQ1 and THQ5 are the main nitrogen-containing intermediates, indicating that the conversion of quinoline to THQ1 and THQ5 is very fast and likely reaches equilibrium during the reaction. It is then reasonable to assume that the hydrogenation of THQ1 and THQ5 to DHQ is the rate-determining step; as a result, any improvement on hydrogenation performance of MoS₂ catalyst may increase the HDN conversion.

Table 2 Liquid product distributions of quinoline HDN over various catalysts at 320 °C

Catalyst	Product contents w/%				
	hydrocarbon	DHQ	OPA	THQ(THQ1+THQ5)	Q
Ni ₂ P/ γ -Al ₂ O ₃	0.7	4.7	17.9	74.7(61.9+12.8)	1.1
MoS ₂ / γ -Al ₂ O ₃	35.2	5.4	7.2	33.5(21.6+11.9)	18.7
Ni ₂ P//MoS ₂	46.8	5.0	5.4	28.0(18.0+10.0)	15.0
MoS ₂ //Ni ₂ P	36.1	5.2	7.4	32.9(21.4+11.5)	18.3

notes: Q: quinoline; OPA: ortho-propylaniline; DHQ: decahydroquinoline; THQ1: 1,2,3,4-tetrahydroquinoline; THQ5: 5,6,7,8-tetrahydroquinoline

The liquid product distribution over Ni₂P//MoS₂ catalyst is similar to that over MoS₂/ γ -Al₂O₃; however, the Ni₂P//MoS₂ catalyst gives much lower concentrations of the intermediate THQ and DHQ but higher concentration of hydrocarbons than MoS₂/ γ -Al₂O₃. The former is ascribed to the enhanced transformation rate of THQ to DHQ by hydrogenation and DHQ to PCHA by the rapid C-N bond breaking, while the latter is accounted for the increased consumption of DHQ through C-N bond cleavage to PCHA and hydrocarbons.

As mentioned before, a great amount of spillover hydrogen species is generated by Ni₂P with the special structure, which jumps to MoS₂ phase and increases the concentration of the hydrogenation active sites. Therefore, the introduction of Ni₂P is able to enhance the hydrogenation rate of THQ to DHQ; meanwhile, MoS₂ catalyst can rapidly transform DHQ and PCHA to hydrocarbons. As a result, the Ni₂P//MoS₂ catalyst system exhibits higher hydrogenation activity than the MoS₂/ γ -Al₂O₃ catalyst; it is similar to the

results obtained from the HDS of DBT^[28], in which H_{so} can modify the active sites by increasing the amount of hydrogenation sites rather than the hydrogenolysis sites of the MoS₂ catalysts.

3 Conclusions

A simplified experimental design proves that there is a synergetic effect between Ni₂P/Al₂O₃ and MoS₂/Al₂O₃ catalysts on their performance in the hydrodenitrogenation of quinoline. The results indicated that the synergism factor of Ni₂P and MoS₂ is higher than that of NiS_x and MoS₂ and it decreases with the increase of reaction temperature.

The synergetic effect can be explained by the remote control model through a migration of hydrogen spillover. Due to the special structure, Ni₂P phase can generate more spillover hydrogen species, which may accelerate the conversion of THQ to DHQ (the rate-determining step of quinoline HDN) by increasing the concentration of hydrogenation sites. As a result, Ni₂P is a superior promoter for MoS₂ catalyst for hydrodenitrogenation.

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Ni₂P 和 MoS₂ 催化剂在喹啉加氢脱氮反应中的协同效应

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摘要: 设计实验证明了 Ni₂P 和 MoS₂ 催化剂在喹啉加氢脱氮反应中存在协同效应, 该协同效应能够用氢溢流遥控模型理论解释。Ni₂P//MoS₂ 的协同因子随反应温度升高而减小, 并且略微大于相同反应条件下 NiS_x//MoS₂ 的协同因子。Ni₂P 产生的溢流氢能够提高 MoS₂ 催化剂上加氢活性位的数量, 促使 Ni₂P//MoS₂ 催化体系增加 1,2,3,4-四氢喹啉和 5,6,7,8-四氢喹啉加氢生成十氢喹啉的速率, 提高其脱氮活性; 因此, Ni₂P 对 MoS₂ 催化剂是很好的助剂。

关键词: 氢溢流; 协同效应; 加氢脱氮; MoS₂; Ni₂P; 喹啉

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