

Construction of electron-rich active sites in the metallic active phase of iron-based hydrogenation catalysts and their regulation on HDN pathway selectivity

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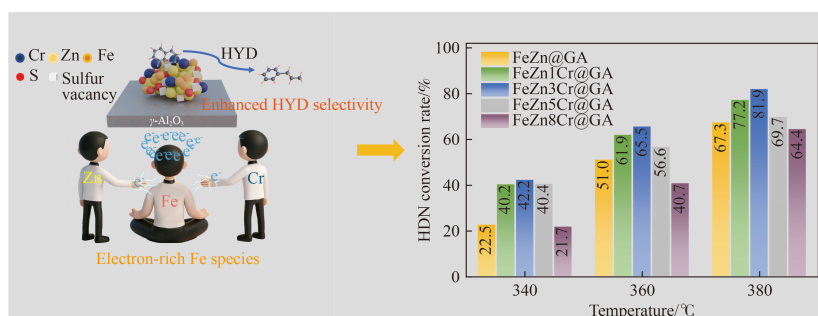
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Abstract: Hydrodenitrogenation

(HDN) process is an effective method for removing nitrogen-containing heteroatom compounds from inferior feedstocks. Its core lies in developing catalysts with both low cost and high performance. In this study, a FeZn-supported catalyst was modified by introducing six

different metal promoters (La, Ti, Ce, Mn, Mg and Cr). It was found that Cr exhibited a pronounced promotional effect on HDN performance. The promoting effect of Cr on the FeZn catalyst's activity originates from its electronic interaction with sulfided Fe species, rather than functioning as an independent active site. Specifically, Cr and Zn species act synergistically as electron donors, transferring electron density to the sulfided Fe species. This thereby modulates the electronic structure of Fe, rendering it in an electron-rich state. The increased electronic density weakens the Fe–S bonds in the active phase, thereby promoting their cleavage. Consequently, it promotes the formation of hydrogenation active sites, known as coordinated unsaturated sulfur vacancies (CUS). After introducing 3% Cr, under conditions of 340–380 °C, 4 MPa pressure, and a high weight hourly space velocity (WHSV) of 8.7 h^{−1}, the catalyst's HDN conversion rate for the basic nitrogen compound quinoline increased by 14.5%–19.7% compared to the unmodified catalyst. The HDN conversion rate reached 81.9% at 380 °C. Furthermore, the introduction of Cr increased the number of medium-strength Lewis acid sites. These acid sites work synergistically with the increased CUS sites, enhancing the overall hydrogenation activity of the catalyst. Cr addition effectively governs the selectivity of the HDN pathway. Consequently, the reaction rate constant for the deep hydrogenation pathway over the FeZn3Cr@GA catalyst reaches 3.2 times higher that of the unmodified FeZn@GA catalyst. In summary, using Fe as the primary active metal component and regulating its electronic structure through promoters represents an effective approach for designing low-cost, high-performance HDN catalysts.

Key words: FeZnCr catalyst; electron-rich Fe species; quinoline; hydrodenitrogenation; C–N bond cleavage



In the fields of oil refining and green energy chemical engineering, the hydrodenitrogenation (HDN) reaction not only effectively reduces the nitrogen content in fuels and decreases the emission of combustion pollutants, but also

enhances the stability and quality of oil^[1–2]. Nitrogen-containing compounds in the fuel (such as pyridine, quinoline, indole, etc.) can be converted into NO_x during combustion, resulting in serious environmental pollution,

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and also cause catalyst poisoning and deactivation during subsequent processing steps^[3–4]. Therefore, the development of highly efficient and stable HDN catalysts is essential for achieving deep denitrogenation of distillate and enabling the production of clean fuels. Currently, the commonly used HDN catalysts are still supported metal sulfide catalysts, typically with γ -Al₂O₃ as the support, Mo/W as the primary active metals and Co/Ni as promoters^[5–6]. However, the limited natural abundance and high extraction cost of these metals, together with their potential environmental toxicity, significantly restrict the sustainable development of conventional Co(Ni)Mo(W) sulfide catalysts^[7–8]. Therefore, the development of resource-abundant and cost-effective alternative HDN catalysts has become an important research direction.

Iron (Fe) has attracted significant attention due to its abundant reserves, excellent economic viability, and environmental friendliness^[9]. Moreover, Fe possesses a crystal structure similar to that of conventional hydrogenation-active metals and features an incompletely filled *d*-electron layer, thereby also exhibiting potential hydrogenation catalytic capability^[10–11]. In our previous studies, FeZn bimetallic supported catalysts, with Fe as the primary active metal and Zn as the promoter, exhibited promising performance in the hydrodesulfurization (HDS) reactions of dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT)^[12]. Experimental results showed that the HDS conversion rate of this catalyst for the aforementioned sulfur-containing compounds approaches that of the MoS₂ catalyst. Moreover, its activity is enhanced by one order of magnitude compared to single-component Fe-based sulfide catalyst. Characterization techniques such as XPS and X-ray absorption near-edge spectroscopy (XANES) revealed that the introduction of Zn promotes electron transfer to the Fe species, forming an electron-rich iron active center. This, in turn, facilitates the formation of a highly active FeZnS mixed phase during the sulfidation process, thereby significantly enhancing the HDS performance. These results convincingly demonstrate the potential of Fe in replacing precious metals or traditional Mo- and W-based hydrogenation catalysts. To further optimize the performance of Fe-based catalysts, our research group has also attempted to modify their electronic structure through methods such as support modification (e.g., introducing Ce^[13], Ti^[14]) or adding promoters (e.g., F^[15], Si^[7]), all of which have effectively enhanced the HDS activity. This demonstrates that the application of Fe-based catalysts in HDS reactions is already relatively mature, laying a solid theoretical and experimental foundation for their extension to HDN reactions.

The selection of promoters in hydrogenation catalysts can influence the formation of the active phase and the electron transfer effect between active metals, thereby further affecting the hydrogenation activity of the catalyst. Among these, chromium (Cr) has been extensively applied as a promoter introduced into hydrogenation catalysts. Research by Ho et al.^[16] demonstrated that Cr outperforms iron in

enhancing HDN performance. This is because the introduction of Cr facilitates the formation of a composite phase structure consisting of nanocrystalline molybdenum disulfide and amorphous Cr₂S₃, while also inhibiting promoter phase segregation. Moreover, the promotional effect of Cr is attributed to the enhancement of the catalyst's hydrogenation activity. Research by Li et al.^[17] on the hydrogenation of sulfur dioxide in the Fe-Si-Cr catalyst system showed that Cr acts as a textural promoter, effectively inhibiting the sintering of iron particles and increasing the catalyst's specific surface area, thereby enhancing its hydrogenation activity. Research by Liu et al.^[18] revealed the crucial role of Cr in In₂O₃-based catalysts: an appropriate amount of Cr (2%) could increase methanol yield by over 50% by generating additional oxygen vacancies. When synergizing with nickel (22%) at a Cr content of 8%, they jointly optimized the hydrogenation steps, stabilized the structure, and increased active sites, ultimately doubling the methanol formation rate. Santana et al.^[19] reported that introducing Cr₂O₃ into Cu/ZnO catalysts increased their CO₂ conversion rate from 2%–10% to 4%–17%. Cr₂O₃ serves dual functions of structural modulation and basicity modification: it enhances interfacial synergy and H₂ dissociation by inhibiting crystal grain growth, increasing specific surface area, and improving Cu dispersion; concurrently, it promotes CO₂ adsorption and conversion by increasing the number of basic sites. This ultimately leads to an efficient increase in methanol selectivity and suppression of side reactions. According to research by Li et al.^[20], the high methanol yield in the hydrogenation of diethyl carbonate to methanol over Cr-Cu/SiO₂ catalyst originates from the ability of Cr to promote the formation of the CuCr₂O₄ phase. This phase can not only inhibit sintering by enhancing the dispersion of Cu, but also optimize the ratio of Cu(0)/Cu(I) to synergistically promote H₂ dissociation and reactant adsorption. Research by Li et al.^[21] demonstrated that when Cr is introduced as a catalyst additive into the W-Mo-Ni/Al₂O₃ catalyst, it can optimize the structure by inhibiting the agglomeration of active components, increase the Brønsted acid centers to enhance the adsorption and activation of reactants, and improve the hydrogen adsorption and desorption ability. Through this synergistic effect, the HDN conversion rate of pyridine is significantly increased to 88.5%, which is much better than that of the catalyst without Cr.

In addition, Liu et al.^[22] successfully prepared mesoporous LaAlO_x support *via* a solvent evaporation induced self-assembly protocol. Using this support, La was introduced into the NiMo supported catalyst. The results showed that the introduction of La weakened the interaction between Mo-O-Al, promoted the complete sulfidation of Ni and Mo oxides, and changed the distribution morphology of the Ni on the MoS₂ slabs. As a result, it significantly promoted the formation of the highly active “type II” NiMoS active phase, greatly improving the HDS

performance. López-Benítez et al.^[23] revealed that with the introduction of 0.5% Mn into a NiMo hydrosulfurization catalyst, Mn primarily exists as Mn(II) species interact with support. This weakens the support-active phase interaction, thereby increasing the sulfidation degree of the catalyst and also enhancing the intrinsic activity of the NiMoS phase. Vázquez-Garrido et al.^[24] demonstrated that introducing Mg into NiMo-based catalysts renders the support basic. After sulfidation, these catalysts exhibit moderate Lewis acidity and a higher enthalpy of pyridine adsorption. In the absence of quinoline, their HDS activity is lower than that of catalysts supported on pure Al₂O₃, but they possess stronger resistance to quinoline inhibition (i.e., nitrogen poisoning resistance) and favor the direct desulfurization (DDS) pathway to produce biphenyl. In contrast, introducing Ti renders the support acidic. After sulfidation, the catalyst exhibits the lowest Lewis acidity, displays low HDS activity in the absence of quinoline, and is significantly inhibited by quinoline. However, it favors the hydrogenation (HYD) pathway to produce cyclohexylbenzene.

In summary, the introduction of elements such as La, Ti, Ce, Mn, Mg and Cr as promoters in hydrosulfurization catalysts can not only enhance the dispersion of the active phase, improve the textural properties of the catalyst, and inhibit the sintering of active metals, but also, through interactions with the active metals, either induce the formation of new active phases or promote the generation of existing ones. Compared to HDS, studies focusing on the HDN process remain relatively limited. Furthermore, due to the greater difficulty of HDN, its catalysts require higher hydrogenation activity. Introducing promoters with excellent properties into HDN systems to enhance their activity, along with in-depth investigation of their mechanisms, is of significant importance. However, the fundamental mechanism by which promoters regulate the electronic structure of active metals and consequently influence the formation and evolution of active phases remains unclear.

Therefore, building upon previous studies of FeZn-based catalysts for HDS, six metallic promoters (La, Ti, Ce, Mn, Mg and Cr) were introduced to modify the FeZn catalyst. Using quinoline as a model compound, the HDN performance of the catalysts was evaluated to screen for effective promoters. Subsequently, a combination of characterization techniques, including X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS), was used to investigate how the selected promoters modulate the electronic structure of the active metals and influence the formation of the catalyst's active phase, aiming to elucidate the regulatory mechanism of promoter introduction on the selectivity of the HDN reaction pathway for quinoline. Through the aforementioned research, we aim to further reveal effective modification strategies for catalysts, providing new design concepts and a theoretical basis for the development of high-performance, low-cost Fe-based HDN catalysts.

1 Experimental

1.1 Materials and reagents

Ferric nitrate (Fe(NO₃)₃·9H₂O, 98.5%, Macklin Biochemical Co., Ltd., Shanghai), zinc nitrate (Zn(NO₃)₂·6H₂O, ≥99.0%, Sinopharm Chemical Reagent Co., Ltd.), chromium nitrate (Cr(NO₃)₃·9H₂O, 99%, Macklin Biochemical Co., Ltd., Shanghai), zirconium nitrate (Zr(NO₃)₄·5H₂O, 99.99%, Boer Chemical Reagent Co., Ltd., Shanghai), cerium nitrate (Ce(NO₃)₃·6H₂O, 99.99%, Boer Chemical Reagent Co., Ltd., Shanghai), titanium sulfate (Ti(SO₄)₂, ≥96%, Macklin Biochemical Co., Ltd., Shanghai), manganese nitrate solution (Mn(NO₃)₂, AR, 50% in H₂O, Macklin Biochemical Co., Ltd., Shanghai), lanthanum nitrate (La(NO₃)₃·6H₂O, 99%, Aladdin Biochemical Technology Co., Ltd., Shanghai), magnesium nitrate (Mg(NO₃)₂·6H₂O, 99%, Guangfu Fine Chemical Research Institute, Tianjin), quinoline (C₉H₇N, 98.0%, Sun Chemical Technology (Shanghai) Co., Ltd.), carbon disulfide (CS₂, 99.0%, Macklin Biochemical Co., Ltd., Shanghai), *n*-decane (C₁₀H₂₂, 98%, Macklin Biochemical Co., Ltd., Shanghai), pseudo-boehmite (industrial grade, JHN-03, Hejin Juhua Aluminum Industry Co., Ltd., Shanxi), and deionized water (prepared in-laboratory).

1.2 Preparation of support and catalysts

Pseudo-boehmite was dried at 120 °C for 24 h and subsequently calcined at 500 °C for 4 h to obtain the γ-Al₂O₃ support (labeled as GA).

All catalysts in this study were prepared using the incipient wetness impregnation method. Preparation of the FeZn@GA catalyst: measured amounts of ferric nitrate and zinc nitrate were successively dissolved in deionized water to prepare a mixed salt solution. This solution was then slowly dropped onto the GA support. After thorough impregnation and mixing, the sample was dried (first at room temperature for 24 h, and then at 120 °C for 4 h) and subsequently calcined (500°C, 4 h) to obtain the oxidized FeZn@GA catalyst. The designed loadings calculated as the corresponding oxides were as follows: Fe₂O₃ at 12.0% and ZnO at 18.0%.

Preparation of FeZnX@GA catalysts (where X represents the third metal): measured amounts of ferric nitrate, zinc nitrate, and the salt of the third metal were successively dissolved in deionized water. The remaining steps were identical to the preparation method for the FeZn@GA catalyst described above. The designed loadings calculated as the corresponding oxides were as follows: Fe₂O₃ at 12.0% and ZnO at 18.0%. Among these, the catalyst with La content (calculated as La₂O₃) of 5.0% was labeled as FeZn5La@GA, the catalyst with Ti content (calculated as TiO₂) of 5.0% was labeled as FeZn5Ti@GA, the catalyst with Ce content (calculated as CeO₂) of 5.0% was labeled as FeZn5Ce@GA, the catalyst with Mn content (calculated as

MnO₂) of 5.0% was labeled as FeZn5Mn@GA, and the catalyst with an Mg content (calculated as MgO) of 3.0% was labeled as FeZn3Mg@GA. The Cr content (calculated as Cr₂O₃) varied from 1.0% to 8.0%. Catalysts with varying Cr contents were respectively labeled as FeZn1Cr@GA, FeZn3Cr@GA, FeZn5Cr@GA and FeZn8Cr@GA.

Preparation of the Cr@GA catalyst: a measured amount of chromium nitrate was dissolved in deionized water. The remaining steps were identical to the preparation method for the FeZn@GA catalyst described above. The designed Cr loading in this catalyst, calculated as Cr₂O₃, was 3.0%, and the catalyst is labeled as Cr@GA.

Preparation of the mechanically mixed catalyst: following the method for preparing mechanically mixed catalysts reported in Ref. [25], the FeZn@GA and Cr@GA catalysts were mechanically mixed at a mass ratio of 1:1 to obtain the FeZn@GA+Cr@GA catalyst.

1.3 Catalyst characterization

The support and FeZnCr catalysts were characterized using X-ray diffraction (XRD, PANalytical X'Pert Powder, Netherlands), N₂ physisorption (Micromeritics Tristar II 3020, USA), H₂ temperature-programmed reduction (H₂-TPR, Micromeritics Autochem 2920, USA), NH₃ temperature-programmed desorption (NH₃-TPD, Micromeritics Autochem 2920, USA), pyridine-adsorption infrared spectroscopy (Py-FTIR, Thermo Fisher Nicolet IS10, USA), and X-ray photoelectron spectroscopy (XPS, Thermo Fisher K-Alpha, USA). For further details, please refer to our group's published paper^[26].

1.4 Catalytic activity evaluation

The HDN performance of the catalysts prepared as described above was evaluated in a fixed-bed reactor using an *n*-decane solution containing quinoline (Q) (2.0×10⁻⁴ N) as the reaction feedstock. The oxidized catalysts were first pre-sulfided (360 °C, 4 MPa H₂, 5 h), during which a 10% CS₂/*n*-decane solution with a flow rate of 3 mL/h was used as the sulfurized oil, while the H₂ flow rate was maintained at 40 mL/min. This sulfidation reaction condition represents the optimized parameter established through prior investigation by our research group. Consequently, all catalysts in this study were subjected to this same sulfidation condition. Subsequently, the HDN of quinoline was carried out at 4 MPa H₂ pressure, an H₂/oil volume ratio of 300, a weight hourly space velocity (WHSV) of 8.7 h⁻¹, and a temperature range of 340–380 °C. For further details regarding the catalyst evaluation device and methodology, please refer to our group's previously published paper^[26].

The nitrogen content in the feedstock oil and reaction products was measured using a sulfur/nitrogen analyzer (RPP-2000SN, Zhonghuan Instrument, China). Prior to the formal determination of nitrogen content in the samples, nitrogen standard solutions with concentrations of 1.0×10⁻⁵, 5.0×10⁻⁵, 1.0×10⁻⁴, 3.0×10⁻⁴ and 5.0×10⁻⁴ were sequentially

injected, and the corresponding signal peak areas for each concentration were recorded. A calibration curve was constructed by plotting the standard solution concentrations on the *x*-axis against their corresponding peak areas on the *y*-axis. When analyzing the reaction samples, the peak areas were integrated, and the nitrogen content was determined using the established calibration curve. The composition of the products was analyzed using an Agilent 7890A gas chromatograph. The HDN conversion rate was calculated according to Equation (1):

$$\text{HDN conversion rate} = \frac{N_f - N_p}{N_f} \quad (1)$$

In Equation (1), *N_f* represents the nitrogen content in the reaction feedstock oil, and *N_p* represents the nitrogen content in the reaction products.

The catalytic activity for HDN of Q was analyzed using a pseudo-first-order reaction rate model. The reaction rate constant (*k_{HDN}*) was calculated by Equation (2)^[27–28]:

$$k_{\text{HDN}} = \frac{F}{m} \ln \left(\frac{1}{1-x} \right) \quad (2)$$

In Equation (2), *x* is the HDN conversion rate of Q, *F* is the feed rate of Q in the feedstock oil (mol/s), *m* is the mass of each catalyst (g), and *k_{HDN}* is the pseudo-first-order reaction rate constant of the catalyst (mol/(g·s)).

It is widely recognized in the field that the HDN reaction of quinoline proceeds *via* two distinct pathways, as illustrated in Figure 1^[29]. In Path 1, quinoline first undergoes hydrogenation on the heterocyclic ring to form 1,2,3,4-tetrahydroquinoline (THQ1). This intermediate then experiences C–N bond cleavage to yield *o*-propylaniline (OPA), and finally denitrogenation to form propylbenzene (PB). Path 2 involves a deeper hydrogenation process: following hydrogenation of either the heterocyclic or benzene ring, quinoline can form either THQ1 or 5,6,7,8-tetrahydroquinoline (THQ5). These intermediates are then fully saturated through further hydrogenation to produce decahydroquinoline (DHQ). Subsequently, DHQ undergoes C–N bond cleavage to yield propylcyclohexylamine (PCHA), which is finally converted *via* a denitrogenation step to propylcyclohexane (PCH) and/or propylcyclohexene (PCHE). PCHE can then either be further hydrogenated to PCH or undergo dehydrogenation to form PB^[30].

Under conventional reaction conditions, the dehydrogenation reaction PCHE→PB is virtually impossible. Therefore, the product selectivities for PB and (PCHE+PCH) respectively represent the selectivity for Path 1 and Path 2. And they can be calculated according to Equations (3) and (4)^[27]:

$$s_1 = \frac{\text{PB}}{\text{THQ1} + \text{THQ5} + \text{OPA} + \text{DHQ} + \text{PB} + \text{PCH} + \text{PCHE} + \text{PVHA}} \quad (3)$$

$$s_2 = \frac{\text{PCH} + \text{PCHE}}{\text{THQ1} + \text{THQ5} + \text{OPA} + \text{DHQ} + \text{PB} + \text{PCH} + \text{PCHE} + \text{PVHA}} \quad (4)$$

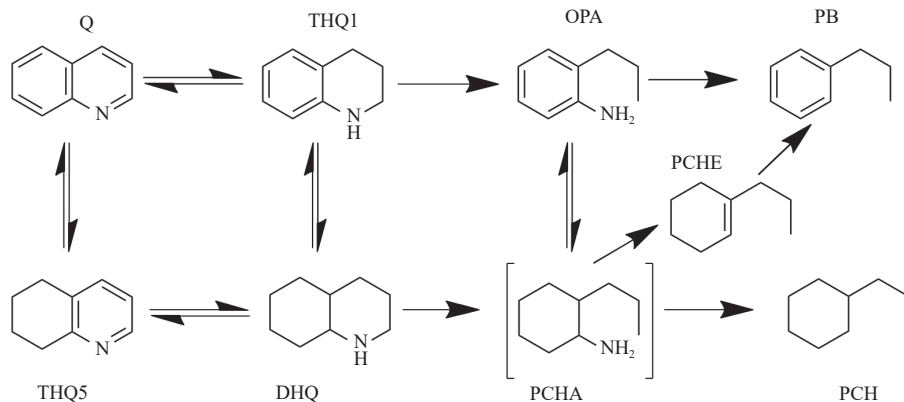


Fig. 1 Quinoline HDN reaction network^[29]
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The reaction rate constants (k_1 and k_2) for these two pathways can be calculated using Equations (5) and (6) respectively:

$$k_1 = k_{\text{HDN}} \times s_1 \quad (5)$$

$$k_2 = k_{\text{HDN}} \times s_2 \quad (6)$$

2 Results and discussion

2.1 HDN evaluation results of FeZn supported catalyst modified with different metals

La, Ti, Ce, Mn, Mg and Cr, six different metals, were respectively introduced into the FeZn supported catalyst for modification. The HDN evaluation results using quinoline as a model compound are shown in Table 1. Only with the introduction of 3% Cr did the HDN conversion rate of the catalyst increase. The introduction of other metals did not significantly alter the catalyst's activity, and even with the addition of 5% La, the HDN rate of the catalyst decreased instead. This may be related to factors such as the method of introducing the promoter metal, the interaction between the promoter metal and the active metal, the catalytic reaction system, and the sulfidation process. This screening result indicates that different metal promoters selectively enhance the HDN process, and their effects differ significantly from those in common HDS reactions. This highlights the unique requirements of the HDN reaction pathway and active sites. Based on this, this study selected Cr as the promoter for the FeZn supported catalyst. Through characterization analysis and investigation of the reaction pathway, the reasons for Cr enhancing the activity of the FeZn catalyst were further revealed.

2.2 Characterization of oxidized catalysts

2.2.1 Physical property

The phase structure characterization of the GA support and the oxidized FeZnCr supported catalyst is shown in

Figure 2. Both the support and the Fe-based catalyst exhibit characteristic diffraction peaks at 2θ angles of 37.7° , 45.6° and 66.7° , which are attributed to the $\gamma\text{-Al}_2\text{O}_3$ support (PDF#29-0063). However, after impregnating FeZn metals onto the support, in addition to the characteristic peaks of $\gamma\text{-Al}_2\text{O}_3$, diffraction peaks attributed to Fe_2O_3 (PDF#89-0596) appear at 2θ angles of 30.5° and 35.4° . Further introduction of Cr into the Fe-based catalyst results in the appearance of a diffraction peak at 58.4° , which is assigned to Cr_2O_3 (PDF#38-1479). No characteristic peaks of ZnO are detected in this series of Fe-based catalysts, indicating high dispersion of Zn species in the FeZnCr catalyst.

Table 1 HDN evaluation results of FeZn-supported catalysts modified by various metals

Catalyst	HDN conversion rate/%		
	340 °C	360 °C	380 °C
FeZn@GA	22.5	51.0	67.3
FeZn5La@GA	17.4	41.9	60.1
FeZn5Ti@GA	31.9	48.5	63.0
FeZn5Ce@GA	28.6	51.5	62.8
FeZn5Mn@GA	30.2	50.8	66.1
FeZn3Mg@GA	28.3	46.4	64.7
FeZn3Cr@GA	42.2	65.5	81.9

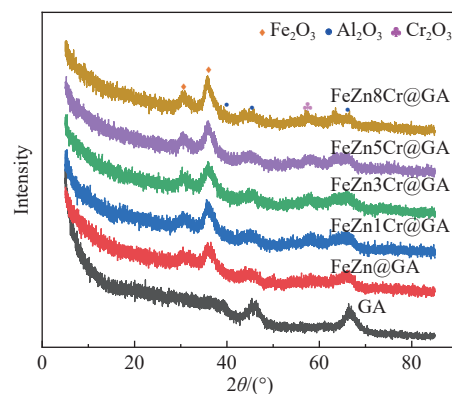


Fig. 2 XRD patterns of the GA support and oxide FeZnCr catalysts

Figure 3 presents the N₂ adsorption-desorption isotherms and pore size distribution of the support and the series of oxidized FeZnCr catalysts. According to the IUPAC classification, both the blank support and the catalysts exhibit Type IV adsorption-desorption isotherms, and both display H3-type hysteresis loops. As shown in Figure 3(b), the pore size distributions of the support and catalysts fall within the range of 2–50 nm, indicating that the catalysts retain the properties of mesoporous materials even after loading the active metal components.

The textural properties of the GA support and the FeZnCr catalyst were calculated, and the results are summarized in Table 2. When FeZn metals were introduced into the GA support, the specific surface area of the catalyst decreased, particularly the external surface area. However, upon further introduction of Cr into the Fe-based catalyst, the specific surface area of the FeZnCr catalyst exhibited an initial increase followed by a decrease, reaching its maximum when 3% Cr was introduced. An increase in the specific surface area of the catalyst is beneficial for the dispersion of active metals. Therefore, the introduction of Cr may help promote the dispersion of active metals in the catalyst. Moreover, after the introduction of FeZn metals, the total pore volume and mesopore volume of the catalyst showed a decreasing trend. With an increase in the amount of Cr introduced, the total pore volume and mesopore volume of the catalyst decreased more significantly. This indicates that FeZnCr species entered the pore structure of the GA support, reducing the pore volume of the catalyst. Nevertheless, the catalyst still maintained a relatively high

specific surface area and a favorable mesoporous structure.

2.2.2 Metal-support Interaction

The interaction between the active metal phase and the support not only affects the dispersion state of the active metals on the support surface but also regulates their reduction process, ultimately influencing the sulfidation degree of the catalyst^[29,31]. Therefore, the metal-support interaction in Cr-modified Fe-based catalysts was measured via H₂-TPR, and the results are shown in Figure 4. Since ZnO is not easily reduced under atmospheric pressure, its reduction process within the tested temperature range is negligible, and only the reduction processes of Fe and Cr oxides are considered^[32–33]. The TPR profile of the FeZn bimetallic catalyst exhibits three distinct characteristic peaks: Peak 1 at 300–400 °C, Peak 2 at 400–500 °C and Peak 3 at 500–600 °C. These correspond to the typical three-step reduction process of Fe₂O₃→Fe₃O₄, Fe₃O₄→FeO and FeO→Fe⁰^[34–35]. After the further introduction of Cr into the catalyst, the reduction peak temperatures of the catalyst shift significantly toward lower temperatures. Peak 1 shifts to the range of 200–300 °C, where it encompasses the reduction processes of Fe₂O₃→Fe₃O₄ and Cr⁶⁺→Cr³⁺, as the further reduction of Cr³⁺ is more difficult^[36]. Therefore, the introduction of Cr enhances the reducibility of Fe oxides and weakens the interaction between Fe oxides and the support, which is conducive to improving the sulfidation degree of the catalyst during the sulfidation process.

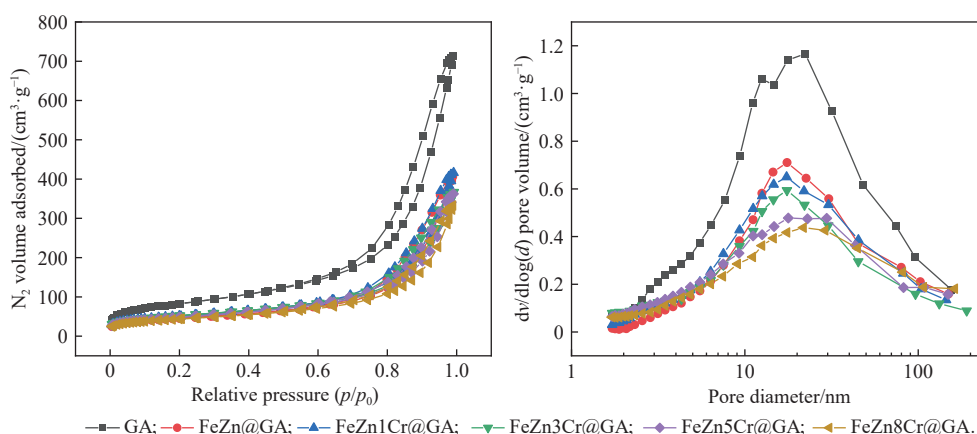


Fig. 3 (a) N₂ physisorption isotherms and (b) pore size distribution curves of the support and oxide FeZnCr catalysts

Table 2 Textural properties of the GA support and the oxide FeZnCr catalysts

Sample	Surface area/(m ² ·g ⁻¹)			Pore volume/(cm ³ ·g ⁻¹)		
	BET ^a	external	micropore ^b	total ^c	mesopore	micropore ^b
GA	296	269	26	1.10	1.09	0.01
FeZn@GA	159	130	29	0.63	0.62	0.01
FeZn1Cr@GA	183	156	28	0.64	0.63	0.01
FeZn3Cr@GA	185	158	27	0.57	0.56	0.01
FeZn5Cr@GA	172	152	20	0.56	0.55	0.01
FeZn8Cr@GA	154	131	23	0.51	0.50	0.01

^a: BET method; ^b: *t*-plot method; ^c: Volume adsorbed at *p*/*p*₀ = 0.99.

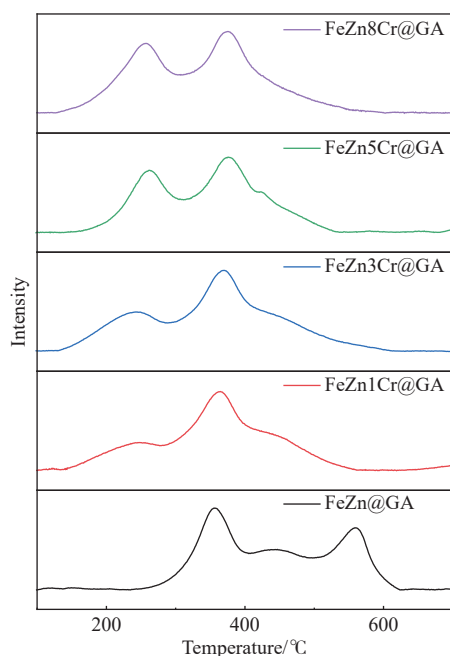


Fig. 4 H₂-TPR profiles of oxide FeZnCr catalysts

2.2.3 Acidity

In HDN catalysts, acidic sites can serve as adsorption centers for nitrogen-containing compounds, thereby promoting the conversion reactions of these compounds under the action of active metal sites^[26,37]. Therefore, the acidic sites of the catalyst have a certain influence on its HDN activity. The acidity of this series of Fe-based catalysts and the support was characterized using NH₃-TPD, and the results are shown in Figure 5. Desorption peaks in the range of 100–250 °C correspond to weak acid sites, those in the range of 250–400 °C correspond to medium strength acid sites, and peaks above 400 °C correspond to strong acid sites^[38–39]. Compared to the GA support, after introducing FeZn active metals, the total acid content of the catalyst decreased, especially the acid content of weak acid sites and medium strength acid sites decreased more significantly. Upon further introduction of Cr, the weak acid content of the catalyst decreased further, while both the

medium strength and strong acid content increased. This indicates that the introduction of Cr altered the acid strength of the catalyst's acid centers, promoting the transformation of weak acid sites into medium strength and strong acid sites. Excessively strong surface acidity can lead to easier coking and carbon deposition on the active components of the catalyst, which is detrimental to its long-term stable use. On the other hand, excessively weak acidity is unfavorable for the conversion of large sulfur- and nitrogen-containing compounds on the catalyst. Therefore, increasing the amount of medium strength acid sites in the catalyst facilitates the adsorption of nitrogen-containing molecules on its surface, which in turn promotes the conversion of such molecules through the synergistic effect between CUS and acid centers^[40–41].

To further investigate the changes in acid types in the Cr-modified catalyst, the samples were characterized using Py-FTIR, and the results are shown in Figure 6. In the Py-FTIR spectra, the signal peaks at 1450 and 1540 cm⁻¹ correspond to the adsorption peaks of pyridine on Lewis acid sites and Brønsted acid sites, respectively^[42–43]. As shown in Figure 6, only the characteristic peaks of Lewis acid sites were detected for both the GA support and the catalysts, indicating that the introduction of Cr did not alter the types of acid centers on the surface of the Fe-based catalysts.

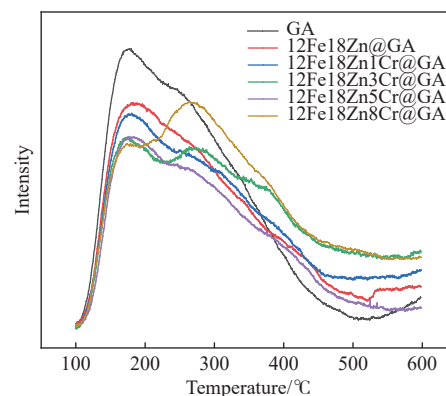


Fig. 5 NH₃-TPD profiles of the GA support and oxide FeZnCr catalysts

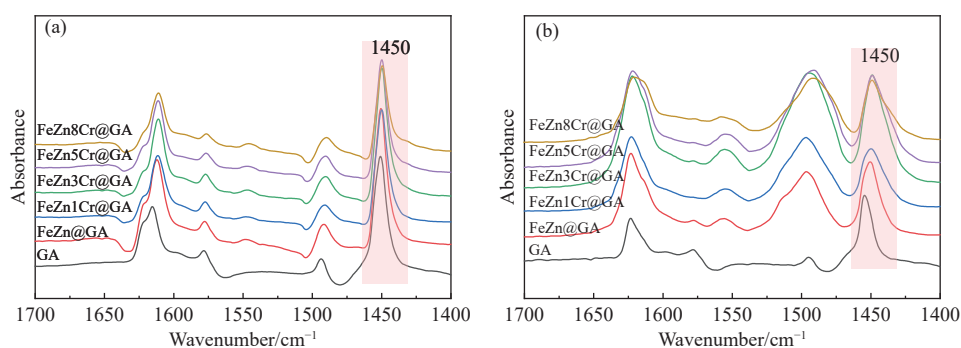


Fig. 6 Py-FTIR spectra of the GA support and oxide FeZnCr catalysts at (a) 150 and (b) 300 °C

The concentrations of acid sites with different strengths were further calculated and summarized in Table 3. The data in Table 3 show that after loading only FeZn active metals onto the GA support, both the strong and weak Lewis acid amounts of the catalyst decreased. Upon further loading of the metal Cr, with an increasing amount of Cr introduced, the total Lewis acid amount and the strong acid amount of the catalyst exhibited a trend of first increasing and then decreasing, while the weak acid amount showed a trend of first decreasing and then increasing. This indicates that the introduction of Cr promotes the transformation between acid centers of different strengths. Research by Li et al.^[44] pointed out that the increase in Lewis acid content in Cr-doped CeTi catalysts can be attributed to the generation of oxygen vacancies and the formation of highly electron-deficient Cr⁶⁺ species. Studies by Otieno et al.^[45] noted that introducing Cr into ZSM-5 zeolite created additional Lewis acid sites, which were described as electron-deficient centers. Therefore, after introducing Cr into the Fe-based catalyst, the changes in the content of different Lewis acid centers indicate that the introduced Cr species occupied weak acid sites, while new medium-strong and strong acid sites were generated. In hydrotreating catalysts, Lewis acidity often favors the hydrogenation reaction. After introducing 3% Cr into the FeZn catalyst, the increase in Lewis acid content will be beneficial for enhancing the hydrogenation reaction process of the catalyst during quinoline HDN^[46–47].

2.3 Characterization of sulfided catalysts

2.3.1 Physical property

XRD characterization was conducted on the sulfided FeZnCr catalyst, and the results are shown in Figure 7. The diffraction peak at $2\theta = 26.6^\circ$ is attributed to quartz sand (SiO₂, PDF-85-0798) used as the proppant. Due to the unavoidable presence of extremely fine sand in the quartz sand used as the proppant, it mixes with the catalyst particles and cannot be completely separated from the catalyst during screening. Therefore, characteristic peaks of quartz sand may appear in the XRD patterns of the sulfided catalyst. However, since the tested catalyst sample does not

contain Si species, the presence of this peak does not affect the identification of the catalyst's active phase. Both the FeZn bimetallic supported catalyst and the Fe-based catalyst after the introduction of Cr exhibit characteristic diffraction peaks at $2\theta = 37.7^\circ$, 45.6° and 66.7° , which are assigned to the γ -Al₂O₃ support (PDF#29-0063). Additionally, diffraction peaks near $2\theta = 28.5^\circ$, 47.4° and 56.2° were detected. Compared with the peaks of ZnS (PDF-89-2156), these peaks are shifted to lower angles by approximately 0.1° . This XRD characteristic closely resembles that of ferroan sphalerite (PDF No. 01-089-4939). Based on previous work published by our research group, these characteristic peaks are attributed to FeZnS species^[12]. Furthermore, compared with the FeZn catalyst, the characteristic diffraction peaks of FeZnS are weakened in the FeZnCr catalyst, indicating that the introduction of Cr improves the dispersion of FeZnS species in the catalyst^[8]. Moreover, when a higher Cr content is introduced, a diffraction peak appears at $2\theta = 30.0^\circ$, which is attributed to the Fe_{1-x}S species (PDF-22-1120). This suggests that the introduction of Cr species affects the dispersion of different types of iron sulfides.

2.3.2 Sulfidation degree

Generally, a higher sulfidation degree (SD) in metal sulfide catalysts indicates the formation of more active phases in the catalyst. Therefore, higher SD values tend to be beneficial for improving HDN activity^[48]. XPS characterization was performed on the sulfided FeZn supported catalyst and the Cr-modified catalyst to calculate the SD values of the catalysts. All XPS spectra were calibrated using the C 1s peak binding energy of 284.8 eV, and a smart background was applied for fitting. Possible species in this series of FeZnCr catalysts include FeS (712.0 eV), Fe(III)-O (711.0 eV), Fe(II)-O (709.5 eV), FeZnS (709.0 eV) and Fe_{1-x}S (707.4 eV) species^[15,49]. Based on the XPS spectral deconvolution method previously developed by our research group for the Fe 2p_{3/2} orbital^[13,26], peak deconvolution fitting was conducted for the Fe 2p_{3/2} orbital of the catalysts. The results are shown in Figure 8, and the relative abundances calculated from the peak areas of each species are summarized in Table 4.

Table 3 Types and concentrations of acid sites on the GA support and oxide FeZnCr catalysts

Sample	Weak acid sites/($\mu\text{mol} \cdot \text{g}^{-1}$)		Strong acid sites/($\mu\text{mol} \cdot \text{g}^{-1}$)		Total acid sites/($\mu\text{mol} \cdot \text{g}^{-1}$)
	L	B	L	B	
GA	164.9	0	157.9	0	322.8
FeZn@GA	71.9	0	91.0	0	162.9
FeZn1Cr@GA	73.0	0	107.3	0	180.3
FeZn3Cr@GA	17.1	0	180.3	0	197.4
FeZn5Cr@GA	25.5	0	167.9	0	193.4
FeZn8Cr@GA	86.4	0	111.9	0	198.3

The SD values of this series of FeZnCr catalysts were calculated using Equation (7) and the results are listed in Table 4.

$$SD(\%) = \frac{FeS + FeZnS + Fe_{1-x}S}{FeS + FeZnS + Fe_{1-x}S + Fe(III)-O + Fe(II)-O} \times 100\% \quad (7)$$

The results in Table 4 show that the order of SD values for this series of FeZnCr catalysts is FeZn3Cr@GA (67.2%) > FeZn1Cr@GA (65.3%) > FeZn5Cr@GA (63.0%) > FeZn@GA (59.7%) > FeZn8Cr@GA (56.9%). The catalyst's SD value initially increases and then decreases with increasing Cr content, reaching its highest value when 3% Cr is introduced. This indicates that an appropriate amount of Cr introduction favors the sulfidation of active metals, thereby promoting an increase in the quantity of the

active phase. This enhances the accessibility of active sites and contributes to the improvement of catalytic activity.

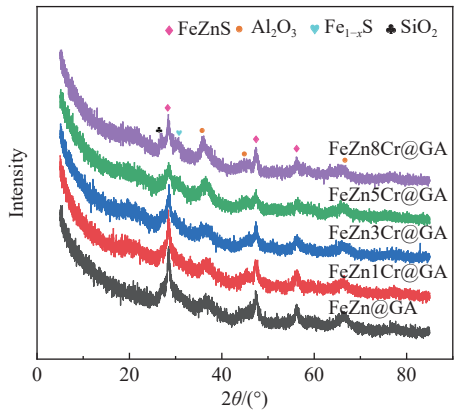


Fig. 7 XRD patterns of sulfided FeZnCr catalysts

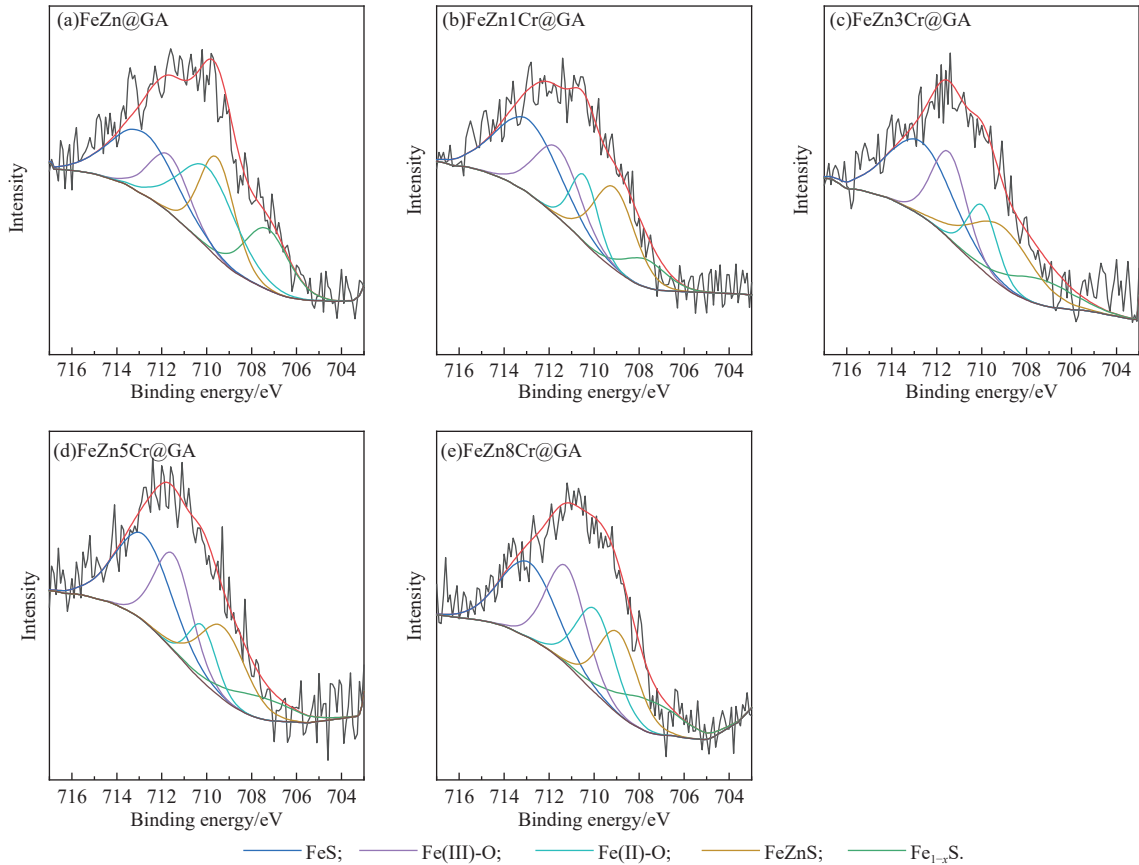


Fig. 8 Peak fitting results of the Fe 2p_{3/2} orbital for the sulfided FeZnCr catalyst

Table 4 XPS peak area percentage of Fe species and SD values in sulfided FeZnCr catalysts

Sample	XPS peak area percentage of Fe species/ar. %					SD/%
	FeS	Fe(III)-O	Fe(II)-O	FeZnS	Fe _{1-x} S	
FnZn@GA	23.4	13.5	26.9	20.5	15.7	59.7
FnZn1Cr@GA	33.1	21.9	12.9	23.8	8.4	65.3
FnZn3Cr@GA	31.7	20.1	12.7	24.6	11.0	67.2
FnZn5Cr@GA	30.1	23.4	13.6	20.5	12.3	63.0
FnZn8Cr@GA	25.1	23.6	19.5	19.3	12.5	56.9

Furthermore, the XPS area fractions of iron sulfide species change with increasing Cr content, suggesting that the introduction of Cr species influences the sulfidation process of active metals and promotes the mutual transformation between different sulfide species. Specifically, the relative content of the FeZnS species reaches its maximum when 3% Cr is introduced, indicating a stronger interaction between sulfided Fe species and Zn species in this catalyst.

2.3.3 Electronic Interactions

The electronic binding energy of the catalysts was analyzed by XPS to investigate the electronic structure after Cr modification. As shown in Figure 9, the Fe 3p orbital exhibits two species: Fe²⁺ and Fe³⁺[50]. The XPS deconvolution results show that the electronic binding energies of Fe²⁺ in this series of catalysts are as follows: FeZn@GA (54.9 eV), FeZn1Cr@GA (54.8 eV), FeZn3Cr@GA (54.5 eV), FeZn5Cr@GA (54.8 eV), FeZn8Cr@GA (54.7 eV). The electronic binding energies of Fe³⁺ in this series of catalysts are as follows: FeZn@GA (57.1 eV), FeZn1Cr@GA (56.9 eV), FeZn3Cr@GA (56.6 eV), FeZn5Cr@GA (56.8 eV), FeZn8Cr@GA (57.0 eV). These binding energy data indicate that compared with the FeZn bimetallic catalyst, the introduction of the third metal Cr shifts the Fe 3p binding energies to lower values. According to the principle of electron shielding effect, an increase in electron cloud density weakens the attraction of the atomic nucleus to electrons, resulting in a corresponding decrease in electronic binding energy. Based on this, the introduction of Cr increases the electron cloud density around Fe, leading to an electron-rich state.

Further analysis of the electronic binding energy of the Cr species 2p orbital was conducted via XPS, with the results shown in Figure 10. The Cr 2p orbital in the catalyst contains two species: Cr³⁺ and Cr⁶⁺. Between the two spin-orbit split peaks of the Cr 2p orbital (2p_{3/2} and 2p_{1/2}), the difference in electronic binding energy is approximately 9.3 eV, and their peak area ratio is fixed at 2:1 (2p_{3/2}:2p_{1/2})^[51–52]. Specifically, the electronic binding energies for the Cr 2p_{3/2} orbital of the Cr³⁺ species in this series of catalysts are: Cr@GA (575.6 eV), FeZn1Cr@GA (575.8 eV), FeZn3Cr@GA (576.2 eV), FeZn5Cr@GA (576.2 eV), FeZn8Cr@GA (576.4 eV). The electronic binding energies for the Cr 2p_{3/2} orbital of the Cr⁶⁺ species in this series of catalysts are: Cr@GA (577.7 eV), FeZn1Cr@GA (578.4 eV), FeZn3Cr@GA (578.6 eV), FeZn5Cr@GA (578.3 eV), FeZn8Cr@GA (577.9 eV).

The electronic binding energies for the Cr 2p_{1/2} orbital of the Cr³⁺ species in this series of catalysts are: Cr@GA (584.9 eV), FeZn1Cr@GA (585.3 eV), FeZn3Cr@GA (585.7 eV), FeZn5Cr@GA (585.6 eV), FeZn8Cr@GA (586.0 eV). The electronic binding energies for the Cr 2p_{1/2} orbital of the Cr⁶⁺ species in this series of catalysts are: Cr@GA (587.2 eV), FeZn1Cr@GA (587.7 eV), FeZn3Cr@GA (587.9 eV), FeZn5Cr@GA (587.7 eV), FeZn8Cr@GA (587.3 eV).

It can be concluded that, compared to the Cr@GA catalyst, the introduction of FeZn metals shifts the electronic binding energy of the Cr species towards higher values, indicating a decrease in the electron cloud density around the Cr species, placing it in an electron-deficient state.

In our previous research, for the FeZn bimetallic catalyst, the Zn species acted as an electron donor, transferring electrons to the Fe species and placing the Fe species in an electron-rich state^[12]. Therefore, further analysis of the electronic binding energy of the Zn species 2p orbital was conducted via XPS, with the results shown in Figure 11. Since the Zn content is identical across all catalysts and the samples were tested on the same instrument, the peak intensities of the Zn 2p orbital are nearly identical for all samples.

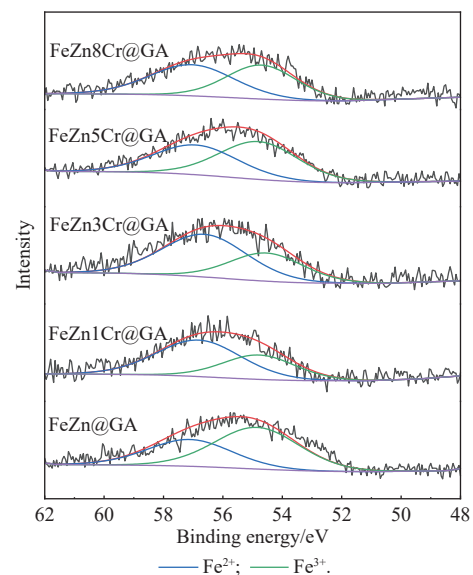


Fig. 9 XPS spectra of the Fe 3p orbital for sulfided FeZnCr catalysts

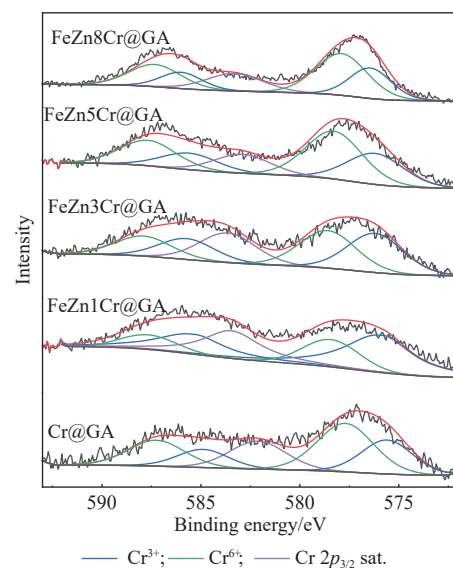


Fig. 10 XPS spectra of the Cr 2p orbital for sulfided FeZnCr catalysts

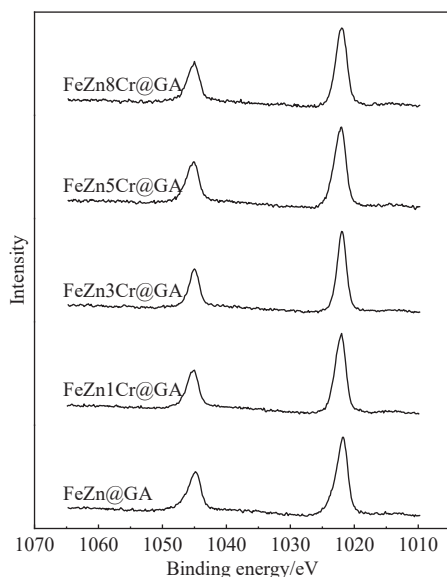


Fig. 11 XPS spectra of the Zn 2p orbital for sulfided FeZnCr catalysts

Furthermore, the electronic binding energies for the Zn species $2p_{3/2}$ orbital in this series of catalysts are as follows: FeZn@GA (1021.8 eV), FeZn1Cr@GA (1022.2 eV), FeZn3Cr@GA (1022.0 eV), FeZn5Cr@GA (1022.3 eV), and FeZn8Cr@GA (1022.0 eV). The electronic binding energies for the Zn species $2p_{1/2}$ orbital in this series of catalysts are: FeZn@GA (1044.9 eV), FeZn1Cr@GA (1045.2 eV), FeZn3Cr@GA (1045.0 eV), FeZn5Cr@GA (1045.3 eV) and FeZn8Cr@GA (1045.1 eV). The introduction of Cr further shifts the Zn binding energy toward higher values, indicating that with Cr incorporated into the catalyst, Zn species remain in an electron-deficient state.

In summary, the synergistic effect among Fe, Zn and Cr in the FeZnCr catalyst can be attributed to electron transfer: both Cr and Zn act as electron donors, collectively providing partial electrons to the sulfided Fe species, thereby inducing an electron-rich state in Fe. The study by Zhang et al.^[53] indicated that N, P co-doped carbon materials can transfer electrons to MoS₂, promoting the electron enrichment of Mo species. DFT calculation results showed that the formation of such electron-rich Mo species weakens the strength of Mo–O/Mo–S bonds, thereby facilitating the formation of more active sites and ultimately enhancing the HDS activity of the catalyst. Similarly, the research by Qin et al.^[54] pointed out that when the electron density of Fe species increases, the involvement of core electrons around the Fe nucleus in Fe–O bond formation decreases, which favors the breaking of Fe–O bonds and makes oxygen removal easier during reduction processes. Furthermore, studies by Li et al.^[12] and Liu et al.^[13–14] also constructed electron-rich Fe species by introducing promoters into Fe-based catalysts. Through DFT calculations, they demonstrated that the electron-donating effect of the promoters on Fe species weakens the Fe–S bond strength in iron sulfides, thereby promoting the

formation of sulfur vacancies. Based on these mechanisms, this study proposes that the introduction of Cr promotes the formation of electron-rich centers in the sulfided Fe species, which is expected to weaken the Fe–S bond and subsequently facilitate the generation of hydrogenation active sites (CUS).

2.4 HDN performance

To further understand the impact of Cr introduction on the HDN activity of Fe-based sulfide catalysts, the HDN performance of this series of Fe-based catalysts was evaluated using quinoline as a model nitrogen-containing compound, and the results are shown in Figure 12. The HDN evaluation results reveal that under fixed reaction conditions of 4 MPa pressure, a weight hourly space velocity (WHSV) of 8.7 h⁻¹, and a hydrogen/oil volume ratio of 300, the HDN conversion rate of the catalysts initially increases and then decreases with increasing Cr content at reaction temperatures of 340, 360 and 380 °C. After the introduction of 3% Cr, the HDN conversion rate reaches its maximum value. Compared to the catalyst without Cr, the HDN conversion rate of the FeZn3Cr@GA catalyst increased by 14.5% to 19.7%. At 380 °C, the HDN conversion rate of the catalyst reached 81.9%. These results indicate that an appropriate amount of Cr enhances the HDN performance of the catalyst, which is consistent with the aforementioned characterization findings.

To further explore the synergistic effect between Cr and Fe-based supported catalysts and exclude the influence of mechanical mixing, HDN evaluation reactions were conducted on the standalone Cr-supported catalyst (Cr@GA) and the mechanically mixed catalyst (FeZn@GA + Cr@GA). The results are shown in Figure 13. The evaluation results show that at 340, 360 and 380 °C, the HDN conversion rates of the Cr@GA catalyst are 4.6%, 6.1% and 8.6% respectively, all of which are relatively low. Additionally, at 340, 360 and 380 °C, the HDN conversion rates of the mechanically mixed catalyst (FeZn@GA+Cr@GA) are 25.0%, 50.4% and 67.7%, respectively. These results are all lower than those of the Cr-modified Fe-based catalyst (FeZn3Cr@GA), which achieved 42.2%, 65.5% and 81.9% under the same conditions.

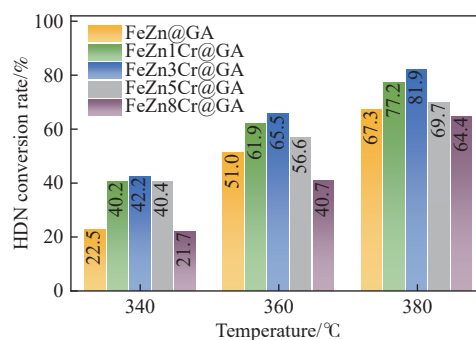


Fig. 12 HDN evaluation results of FeZnCr catalysts

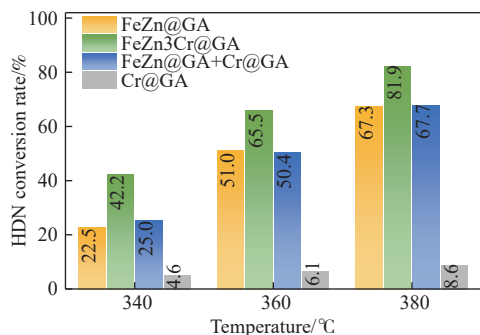


Fig. 13 Effect of mechanical mixing of Cr catalyst and Fe-based catalyst on HDN performance

As a typical nitrogen-containing compound, the HDN reaction of quinoline (Q) proceeds *via* two pathways as shown in Figure 1: Path 1 and Path 2. The selectivity of the HDN reaction of Q over FeZnCr catalysts was further characterized. To accurately study the intrinsic reaction kinetics, mass-transfer limitations at high conversions must be avoided. Therefore, experiments were conducted at 340 °C by adjusting the WHSV to maintain the HDN conversion of all FeZnCr catalysts at approximately 30%. The product distribution, reaction selectivity, and reaction rate constants over the Cr-modified catalysts at 340 °C are

summarized in Table 5. As the Cr content increases, the reaction rate constant initially increases and then decreases, which aligns with the trend observed for the HDN conversion of the Cr-modified catalysts. The FeZn3Cr@GA catalyst exhibits the highest reaction rate constant, which is 1.6 times higher than that of the catalyst without Cr. Further analysis into the influence of Cr introduction on the selectivity of different HDN reaction pathways reveals that for the FeZn3Cr@GA catalyst with the highest HDN conversion rate, its k_1 value is 1.9 times that of the FeZn@GA catalyst, and its k_2 value is 3.2 times that of the FeZn@GA catalyst. This indicates that the introduction of Cr promotes both Path 1 and Path 2 for Q conversion. The s_1/s_2 ratio initially decreases and then increases with increasing Cr content, reaching its minimum value at 3% Cr. This indicates that the introduction of 3% Cr mainly promotes the deep hydrogenation. Nitrogen-containing compounds such as Q typically adsorb *via* the lone pair electrons of the nitrogen atom or the π electrons of the aromatic ring onto CUS sites for hydrogenation reactions^[55–56]. Therefore, the formation of electron-rich Fe species following the introduction of 3% Cr promotes the generation of CUS with hydrogenation activity, thereby enhancing the selectivity for HDN Path 2 of Q.

Table 5 Reaction rate constant and selectivity of HDN over FeZnCr catalyst at 340 °C

Sample	FeZn@GA	FeZn1Cr@GA	FeZn3Cr@GA	FeZn5Cr@GA	FeZn8Cr@GA
THQ1	58.77	51.93	52.18	52.69	61.52
THQ5	5.78	5.17	4.68	4.95	3.74
OPA	21.71	22.47	19.76	20.91	19.79
DHQ	3.78	4.68	4.61	4.79	4.41
PB	2.06	2.76	2.51	3.56	2.27
PCH	7.90	13.00	16.25	13.10	8.26
$k_{\text{HDN}} (\times 10^{-8} \text{ mol}/(\text{g}\cdot\text{s}))$	0.90	1.30	1.42	1.25	0.86
$k_1/(\times 10^{-10} \text{ mol}/(\text{g}\cdot\text{s}))$	1.86	3.60	3.56	4.44	1.95
$k_2/(\times 10^{-9} \text{ mol}/(\text{g}\cdot\text{s}))$	0.71	1.70	2.31	1.63	0.71
s_1	0.02	0.03	0.03	0.04	0.02
s_2	0.08	0.13	0.16	0.13	0.08
s_1/s_2	0.26	0.21	0.15	0.27	0.27

3 Conclusions

By introducing six different metals (La, Ti, Ce, Mn, Mg, Cr) separately into the FeZn supported catalyst, it was found that the incorporation of Cr significantly enhances the HDN activity of the catalyst by regulating the electronic structure of sulfided Fe species. Further characterization results lead to the following conclusions:

The role of Cr species introduction is not to form independent active sites; instead, it acts synergistically with Zn species as an electron donor, transferring electrons to sulfided Fe species and forming electron-rich Fe active centers. The formation of these active centers effectively

weakens the Fe–S bond and promotes its cleavage, thereby inducing the generation of active sulfur vacancies.

The introduction of Cr species improves the interaction between Fe oxides and the support, thereby promoting the reduction process of Fe, facilitating the formation of the active phase during sulfidation, which increases the sulfidation degree.

Cr incorporation also optimizes the distribution of acid sites, promoting the transformation of weak acid sites into medium-strength and strong acid sites, and facilitating the formation of medium-strength Lewis acid sites. These acid sites act synergistically with coordinatively unsaturated sites (CUS) to enhance the hydrogenation activity of the catalyst. In the Fe-based catalyst modified with 3% Cr, the

reaction rate constant of the deep hydrogenation pathway reaches 3.2 times that of the unmodified catalyst.

In summary, this study provides an electronic structure modulation strategy for regulating the hydrogenation activity of the Fe-based catalysts for HDN applications.

Declaration of Competing Interest

The authors declare no conflict of interest.

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铁基加氢催化剂金属活性相富电子活性位构筑及其 对 HDN 路径选择性的调控作用

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摘 要: 加氢脱氮(HDN)工艺是脱除劣质原料油中含氮杂原子化合物的有效手段, 其核心在于开发兼具低成本与高性能优势的催化剂。本研究通过在 FeZn 负载型催化剂中分别引入 La、Ti、Ce、Mn、Mg、Cr 等六种金属进行改性, 发现 Cr 的引入能显著提升催化剂的 HDN 性能。研究揭示了 Cr 对 FeZn 催化剂活性的促进作用源于其与硫化态 Fe 物种之间的电子相互作用, 而非作为独立的活性位点。这种相互作用的关键是 Cr 物种与 Zn 物种共同作为电子供体向硫化态 Fe 物种提供了电子, 调节了 Fe 的电子结构, 使其呈现富电子态。这一电子结构的改变有利于削弱活性相中的 Fe-S 键, 使其更易断裂, 从而促进催化剂中的加氢活性位点、即配位不饱和和硫空位(CUS)的形成。引入 3% Cr 后, 在 340–380 °C、压力 4 MPa、质量空速 8.7 h⁻¹ 的条件下, 催化剂对碱性含氮化合物喹啉的 HDN 率较未改性催化剂提升了 14.5%–19.7%, 在 380 °C 时脱氮率达到 81.9%。此外, Cr 的引入还增加了中等强度的 Lewis 酸中心。这些酸中心与增多的 CUS 位点协同作用, 增强了催化剂的加氢活性。Cr 的引入显著调控了 HDN 路径选择性, FeZn3Cr@GA 催化剂深度加氢路径的反应速率常数达到未改性 FeZn@GA 催化剂的 3.2 倍。以 Fe 为主要活性金属组分, 通过助剂调控其电子结构, 是设计低成本、高性能 HDN 催化剂的一条有效途径。

关键词: FeZnCr 催化剂; 富电子 Fe 物种; 喹啉; 加氢脱氮; C–N 键断裂

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