Spinel $NiAl_2O_4$ Based Catalysts: Past, Present and Future

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Abstract: Nickel aluminate ($NiAl_2O_4$) is a kind of partially antispinel structure oxide. Because of its excellent electronic structure and energy level structure, high thermal stability and high charge transfer and separation efficiency, it has a potential application prospect in catalytic oxidation, photocatalysis, adsorption and other fields. In this paper, the synthesis methods of different $NiAl_2O_4$-based catalysts, their applications in catalytic field and related catalytic mechanisms are reviewed from the appearance of single component $NiAl_2O_4$, ion-doped $NiAl_2O_4$ and multiheterojunction $NiAl_2O_4$ catalysts. The application of $NiAl_2O_4$ photocatalysts in the field of photocatalysis has gradually shifted from the degradation of dyes to the degradation of drugs, so its photocatalytic mechanism and degradation path need to be further studied. This review points out the direction for the future research of $NiAl_2O_4$ based catalysts in the field of catalysis.

Keywords: Nickel aluminate, Catalytic oxidation, Photocatalysis, Catalytic mechanism, Photocatalysts.

1. INTRODUCTION

Catalyst is a kind of substance that can degrade other difficult substances without changing its crystal structure, electronic structure, energy level structure and its own properties [1-5]. Depending on the nature of the catalyst itself, it can be used in adsorption, photocatalysis, piezoelectric catalysis, thermocatalysis, catalytic oxidation, biodegradation and other fields [6-13]. These catalysts may be single-component oxides or multicomponent compounds. Their homogeneous characteristics are relatively stable and do not decompose under acid, base or other conditions [14-20]. They can have both magnetic and photoluminescence properties and other properties, especially excellent magnetic properties can make the photocatalyst with high ability of recycling and reducing secondary pollution of water bodies [21-29].

Spinel aluminate is a kind of common catalyst, because of their special physical and chemical properties such as good thermal stability, low surface acidity, mechanical resistance and water transport, so that they have a wide range of applications in ceramic pigments, magnetic devices, refractories, luminous devices, catalysts and other fields [30-35]. Spinel structure oxides generally have the general structure of AB_2O_4, where A=Mg, Ca, Sr, Ba, Mn, Fe, Cu, et. B=Al, Fe, Cr, *et al*. [36-38]. Single-component aluminates are stable and have high charge carrier migration and separation efficiency, so they have potential applications in pigments, catalysis and light-emitting devices [39-45]. However, due to the large band gap value of aluminate, its application in the field of catalysis is limited. Therefore, surface modification, [46-48] ion doping [49] and heterogeneous structure construction [50-57] are used to enhance its physical and chemical properties.

Nickel aluminate ($NiAl_2O_4$) is a kind of spinel aluminate with partial antispinel structure, which is a special kind of spinel aluminate [58]. This special structure makes $NiAl_2O_4$ lattice easy to produce vacancies, defects and other special structures, but does not affect its high stability, so it has been favored by researchers in the field of catalysis [59-61]. It is worth noting that different synthesis methods tend to affect the physicochemical properties of $NiAl_2O_4$. Therefore, it is of great significance to review the application of $NiAl_2O_4$ and $NiAl_2O_4$ based catalysts in the field of catalysis from the synthesis methods.

In this paper, the synthesis methods of $NiAl_2O_4$, ion-doped $NiAl_2O_4$ and heterojunction $NiAl_2O_4$ based catalysts are reviewed. The effect of synthesis method on the catalytic activity of $NiAl_2O_4$ based catalysis is discussed. Based on different types of $NiAl_2O_4$ based catalysts, its applications in photocatalytic degradation of dyes, pharmaceuticals, catalytic oxidation of methanol, adsorption, and other fields are reviewed in detail. This review will provide technical reference and theoretical guidance for the future research of $NiAl_2O_4$ based catalysts in the field of catalysis.

2. SYNTHESIS OF NICKEL ALUMINATE BASED CATALYST

2.1. Synthesis of Nickel Aluminate Catalyst

When preparing spinel aluminate, different preparation methods will affect the morphology, particle

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size and crystal structure of the synthetic material, and also directly affect its optical properties and catalytic properties. At present, the preparation methods of nickel aluminate are mainly sol-gel method, [62] coprecipitation method, [63] combustion method, [64] hydrothermal method, [65] solvothermal method, [66] acoustochemical method, [67] polymer solution method, [68] solid state reaction method, [69] and so on.

Sol-gel method is a commonly used method to prepare spinel aluminate. Compared with other methods, it can synthesize ultrafine particles with uniform particle size distribution at a lower temperature, [70] but the synthesis time is relatively long. Kunde *et al*. [71] successfully prepared spinel $NiAl_2O_4$ film by combining sol-gel method with ultrasonic induced atomization technology, as shown in Figure **1**. Maddahfar *et al*. [72] synthesized $NiAl_2O_4$ by modified sol-gel method, and studied the effects of different chelating agents (citric acid monohydrate, oxalic acid, salicylic acid and malic acid) on the morphology, particle size and crystal structure of the synthetic materials. The photocatalytic activity of $NiAl_2O_4$ on the photocatalytic degradation of methyl orange (MO) was also studied. The results showed that all the samples were spherical and the best chelating agent was oxalic acid. Zhang *et al*. [73] prepared $NiAl_2O_4$ using citric acid as chelating agent by sol-gel method, and adjusted the size of $NiAl_2O_4$ nanoparticles by adjusting the content of Ni. Jeevanandam *et al*. [62] prepared spinel $NiAl_2O_4$ by sol-gel method, and observed that the calcination temperature would affect the formation and grain size of aluminate nanoparticles. Abdulmajeed *et al*. [74] synthesized spinel $NiAl_2O_4$ by sol-gel method, and measured the obtained samples with different measurement methods. The experiment showed that the calcination temperature would affect the grain size, and the particle size would increase with the increasing of temperature.

Combustion method is another common method for preparing spinel aluminate. Compared with other methods, it can quickly and easily synthesize materials with different crystal structures. The performance of synthetic materials using combustion depends on the precursor materials used in the synthesis, the fuel, and the heating conditions. [64, 75-78] The precursor material produces oxygen when it is burned, which makes it easy to produce oxides, so simple oxides and complex oxides can be obtained during the combustion reaction [75, 76]. A novel combustion method has been

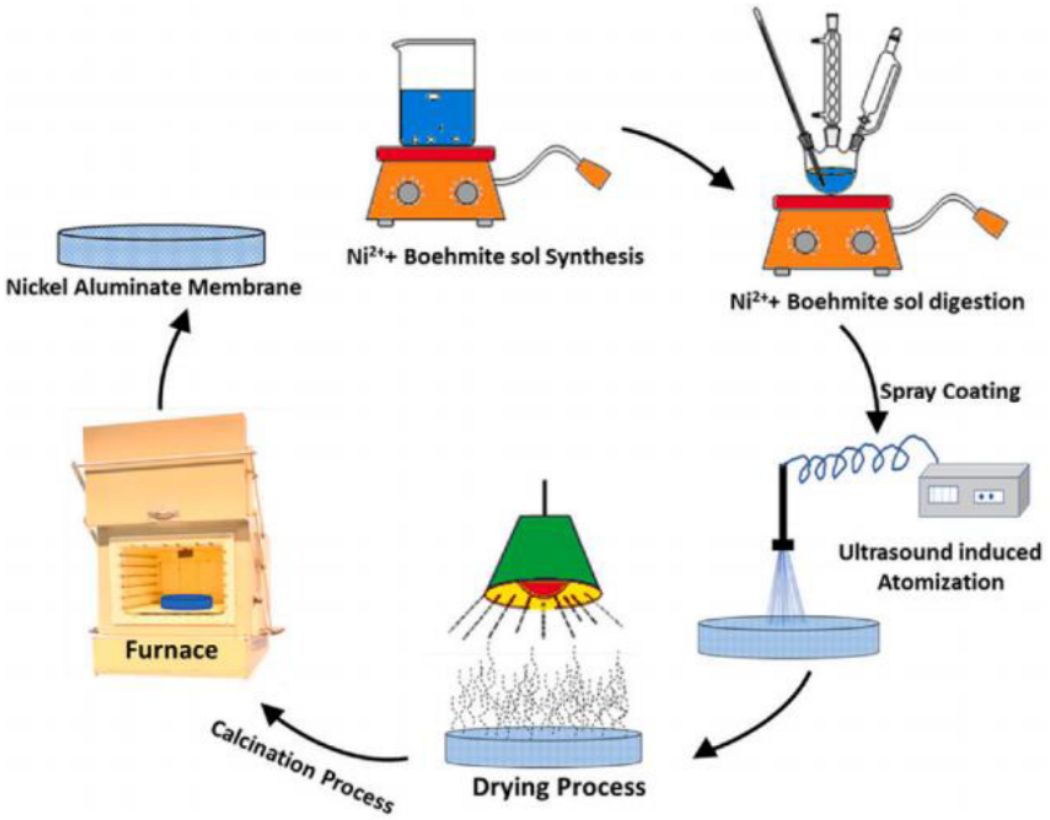

Figure 1: Process flow chart of preparation of nickel aluminate film by sol-gel assisted ultrasonic atomization technology. Adapted from ref. [71]. Copyright © 2021 Elsevier Inc.

proposed in previous studies, whereby oxidant and fuel are burned at low temperatures (<500℃) to produce an exothermic reaction through the gas, producing oxides within minutes [77, 78]. Stella *et al*. [79] synthesized $NiAl_2O_4$ using urea and glycine as fuel. The experimental results showed that when urea was used as fuel, there would be large particles in the synthesized powder, while when glycine was used as fuel, the synthesized powder would be fluffy and foamy. This reason may be that the crystal structure of $NiAl_2O_4$ is affected by the release of gas during the combustion reaction, which is determined by the oxidant and fuel. Elvia Leal *et al*. [64] used the combustion reaction method to use glycine as fuel to study the effect of excessive fuel on the structure of the synthesized $NiAl_2O_4$ powder. The experimental results showed that the main phase of $NiAl_2O_4$ would be produced even with excessive dose, but the larger the dose, the smaller the grain size and the larger the aggregate size.This further shows that fuel can affect the properties and structure of synthetic materials.

In recent years, researchers have developed novel combustion methods based on conventional combustion methods through trial and experiment. Ragupathi *et al*. [80, 81] synthesized $NiAl_2O_4$ from extracts of aloe and sesame as fuel by conventional combustion method (CCM) and microwave combustion method (MCM), and analyzed its shape, particle size, crystal structure, optics and catalytic properties. The experimental results show that the combustion reaction of MCM is much shorter than that of CCM, the heating time is relatively shorter, and the prepared $NiAl_2O_4$ maintains a higher purity. Manikandan *et al*. [82] proved again the characteristics of fast combustion reaction speed and high purity of prepared materials through experiments.Microwave combustion (MCM) provides a novel method for the synthesis of spinel aluminate.

In recent years, the emergence of sol-gel spontaneous combustion provides a new way to synthesize metal oxides. The combination of sol-gel method and combustion method has the characteristics of simple, low cost, rapid heating and short reaction time [83-85]. Thanit Tangcharoen *et al*. [86] synthesized $NiAl_2O_4$ by sol-gel spontaneous combustion method and the morphology, particle size and crystal structure were studied by X-ray diffraction (XRD), X-ray absorption near-side structure (XANES), and extended X-ray absorption fine structure (EXAFX). Tangcharoen *et al*. [87] proved that diethanolamine (DEA) was used as a new fuel to successfully synthesize spinel aluminate by sol-gel spontaneous combustion method, and analyzed its morphology, particle size and crystal structure. The results showed that the aluminate prepared by this method all obtained single-phase spinel structure and different band gap values. Although there are many methods to prepare nickel aluminate, the polyacrylamide gel method has not been used to synthesize nickel aluminate and study its physical and chemical properties.

2.2. Synthesis of Ion-Doped Nickel Aluminate Catalysts

It has been reported that a single ion with bivalent or trivalent properties already possesses conductivity, optics, magnetism and other properties [88]. Metal ions doped aluminate is a simple and effective work to improve the photocatalytic activity of photocatalysts. It can trap electrons and become an effective scavenger, and can prevent electron-hole pair recombination. In recent years, researchers have proposed the method of ion doping nickel aluminate to improve the performance of monomer nickel aluminate on the basis of the good performance of ions. Irshad *et al*. [89] doped silver ions with good electrical conductivity with nickel aluminate by sol-gel method to improve the electrical properties of monomer nickel aluminate. The experimental results show that the electrical conductivity is obviously improved after silver ion doping. At the same time, Irshad *et al*. doped silver ions with $NiAl_2O_4$ by sol-gel method and combined graphite carbon nitride with $NiAl_2O_4$ by ultrasonic-assisted method to synthesize Ag-$NiAl_2O_4$@g-C_3N_4 composite materials, as shown in Figure **2** [59].

In the field of photocatalysis, doping will change the band gap value of semiconductor, and the band gap value may affect the speed of electron-hole pair generation, thus affecting the photocatalytic degradation efficiency of dyes [59]. Elakkiya *et al*. [90] doped $NiAl_2O_4$ with divalent ions (copper, zinc, magnesium) by sol-gel method to degrade methylene blue (MB) and methyl orange (MO), and studied their optical properties. The experimental results show that the degradation efficiency of MB and MO is Mg>Zn> original sample >Cu, and the performance of Mg doping is better. The reason is that the band gap of $Mg_{0.1}Ni_{0.9}Al_2O_4$ is lower than that of $Cu_{0.1}Ni_{0.9}Al_2O_4$, $Zn_{0.1}Ni_{0.9}Al_2O_4$ and $NiAl_2O_4$. This may be because when the band gap value is low, it inhibits the production of electron-hole pairs and therefore dyes

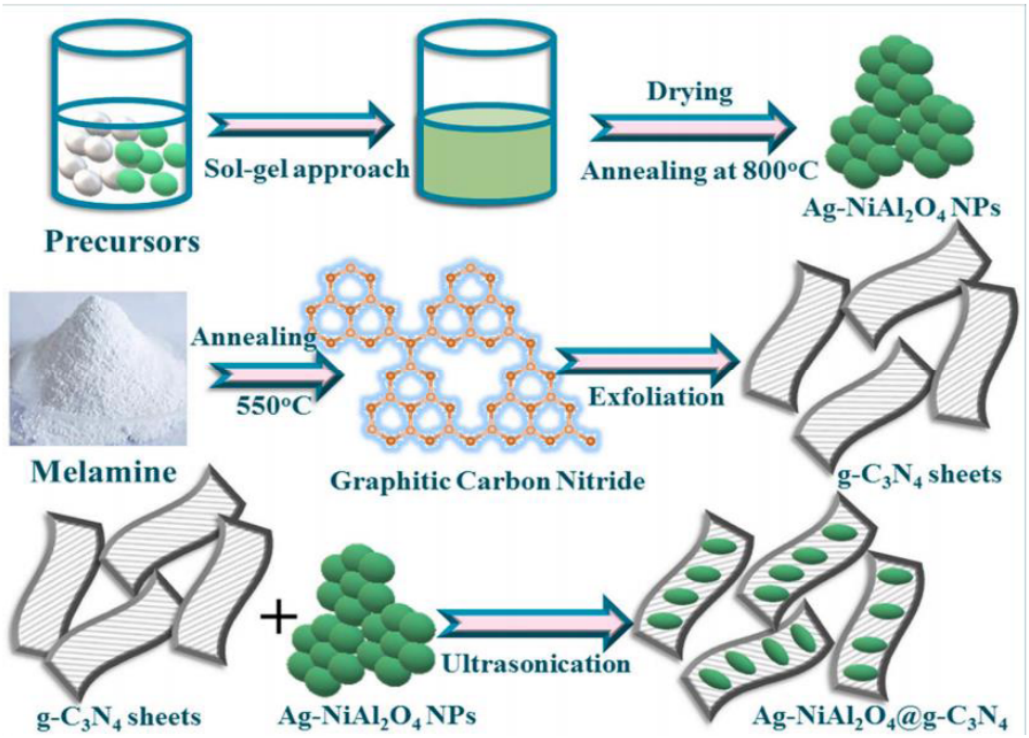

Figure 2: Flow chart of Ag-$NiAl_2O_4$ synthesis by sol-gel method and Ag-$NiAl_2O_4$@g-C_3N_4 synthesis by ultrasonic assisted method. Adapted from ref. [59]. Copyright © 2022 Elsevier B.V.

mineralization faster. Experimental results show that the degradation efficiency of Ag-$NiAl_2O_4$ is much higher than that of single component $NiAl_2O_4$, and the band gap measured by single component $NiAl_2O_4$ is 3.5eV, and the band gap measured by doping is 2.66 eV. Confirming the previous idea, lower band gap values can more easily inhibit the generation of electron-hole pairs, thus improving the photocatalytic efficiency.

Akika *et al*. [91] prepared $Ni_{1-x}Cu_xAl_2O_4$ (x=0.2, 0.4, 0.6, 0.8, 1) nanomaterials by Cu doping $NiAl_2O_4$ by the coprecipitate method and used it for photocatalytic degradation of Congo red (CR). The band gap values of $Ni_{1-x}Cu_xAl_2O_4$ with different doping ratios were measured in the experiment. The results showed that the degradation rate of $Ni_{1-x}Cu_xAl_2O_4$ was much higher than that of the original sample $NiAl_2O_4$. Regulska *et al* [92] doped Er, Tm, Yb with $NiAl_2O_4$ and used it for photocatalytic degradation of oxytetracycin (OTC). The band gap values of $NiAl_2O_4$, Yb-$NiAl_2O_4$, Tm-$NiAl_2O_4$ and Er-$NiAl_2O_4$ measured in the experiment are 3.45, 3.41, 3.27 and 3.12 eV, respectively. The photocatalytic degradation efficiency is Er-$NiAl_2O_4$>Tm-$NiAl_2O_4$>Yb-$NiAl_2O_4$>$NiAl_2O_4$. Therefore, the above conclusion is further confirmed. Effectively changing the band gap value can improve the efficiency of photocatalysis.

2.3. Synthesis of Nickel Aluminate Based Composite Catalysts

In recent years, researchers have compounded $NiAl_2O_4$ based on a single component to improve the performance of the monomer. Dhara *et al*. [93] synthesized thermally stable $NiAl_2O_4/Al_2O_3$ nano-composite powder samples by isomolar mechanochemical reaction, and the synthesis process was shown in Figure **3**. They also studied the microstructure characterization, optical properties, electrical transport and dielectric properties of $NiAl_2O_4/Al_2O_3$. Arunkumar *et al*. [94] synthesized aluminate - activated carbon (MAAC) matrix composites by coprecipitate method.The results show that the photocatalytic efficiency of activated carbon matrix composites is much higher than that of nickel aluminate matrix composites. Kunde *et al*. [95] synthesized nickel aluminate/multi-walled carbon nanotubes $NiAl_2O_4$/MWCNT by an environmentally friendly modified evaporation-induced self-assembly process (m-EISA). Muralidharan *et al*. [96] successfully synthesized $NiAl_2O_4$ and SiO_2 composites ($NiAl_2O_4$:SiO_2) by using in situ sol-gel method. Due to the excellent properties of g-C_3N_4, Ahmad *et al*. [97] synthesized $NiAl_2O_4$ and g-C_3N_4 binary composite by calcination and ultrasonic-assisted method to improve the performance of photodegradation of 2, 4-

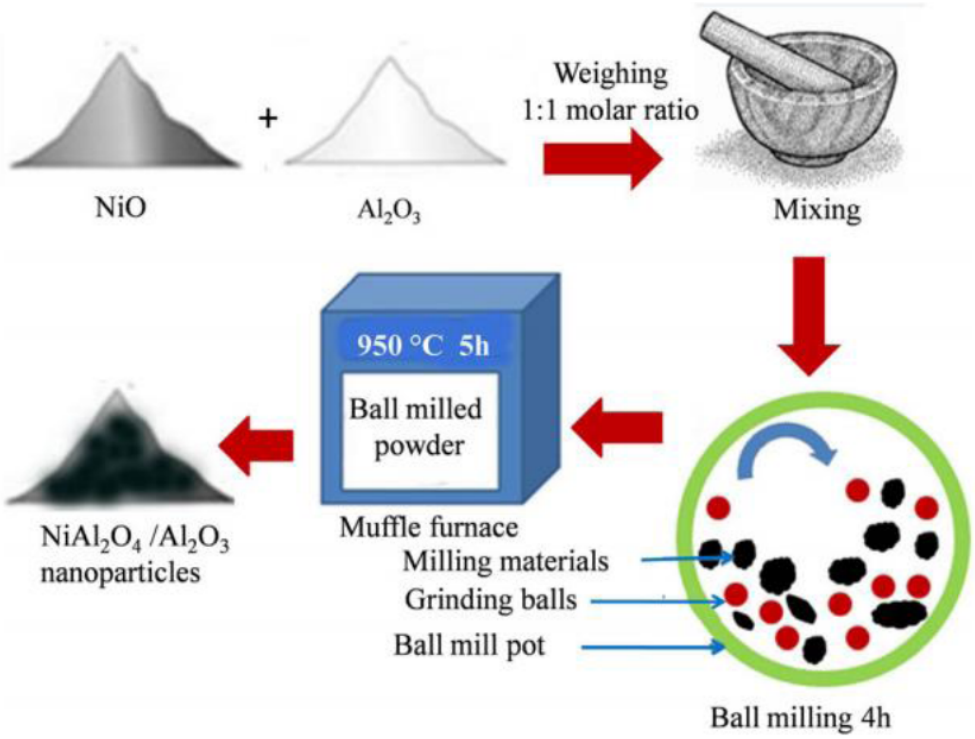

Figure 3: Schematic diagram of the synthesis of $NiAl_2O_4/Al_2O_3$ nanocomposites. Adapted from ref. [93]. Copyright © 1999-2023 John Wiley & Sons, Inc.

dinitrophenol. Regulska *et al*. [98] prepared a composite material of $NiAl_2O_4$ and graphene quantum dots (GQDS) using coprecipitation method.It is used in photocatalytic degradation of rhodamine B, quinoline yellow, eriochrome black T, and methylene blue.

3. APPLICATION OF $NIAL_2O_4$ BASED CATALYSTS IN THE FIELD OF CATALYSIS

$NiAl_2O_4$ belongs to partial antispinel and is a mixed cationic oxide with normal spinel structure. Half of the Al^{3+} ions are distributed in the tetrahedral void and the other half is distributed in the octahedral void. Ni occupies the tetrahedral position and has a stable structure and high catalytic activity at high temperature. Although spinel $NiAl_2O_4$ has a large specific surface area and small particle size, it can easily separate electrons and holes and inhibit the recombination of electron hole pairs under ultraviolet light, so it can be used as a photocatalyst. Due to the continuous emergence of ion-doped $NiAl_2O_4$ photocatalysts and heterojunction $NiAl_2O_4$ based photocatalysts, the catalytic activity of single component $NiAl_2O_4$ has been greatly improved. These catalysts have been widely used in the degradation of drugs, azo dyes, refractory pollutants, catalytic oxidation of benzyl alcohol and methanol, photocatalytic water hydrogen production, etc.

The application of $NiAl_2O_4$ in catalysis began in 1994, when Pena *et al*. [99] used $NiO/NiAl_2O_4$ to study the effect of catalyst pretreatment on the relative rates of the main reaction and coking reaction during acetylene hydrogenation. Subsequently, the research upsurge of $NiAl_2O_4$ in catalytic field was set off [100-103]. However, the research of $NiAl_2O_4$ in the field of photocatalysis is relatively late. It was only reported in 2014 that $NiAl_2O_4$ was used to photocatalyze hydrogen production from water [104, 105]. Since then, $NiAl_2O_4$ has gradually been used to dedegrade dyes [72]. Simultaneously, $NiAl_2O_4$ is also used to adsorb heavy metal ions due to its excellent adsorption performance [106]. In recent years, researchers are trying to use new methods to enhance the photocatalytic activity of $NiAl_2O_4$ to degrade refractory pollutants and drugs.

3.1. Application of $NiAl_2O_4$ Based Catalysts in the Field of Photocatalytic Degradation of Dyes

The application of $NiAl_2O_4$ in dye degradation mainly focuses on the study of photocatalysis. Due to its special electronic structure and energy level structure, $NiAl_2O_4$ can only respond to UV light, so most of the research work focuses on the catalytic activity of UV light. Because the sunlight contains a certain amount of ultraviolet light, so some researchers have used $NiAl_2O_4$ in the field of solar photocatalysis.

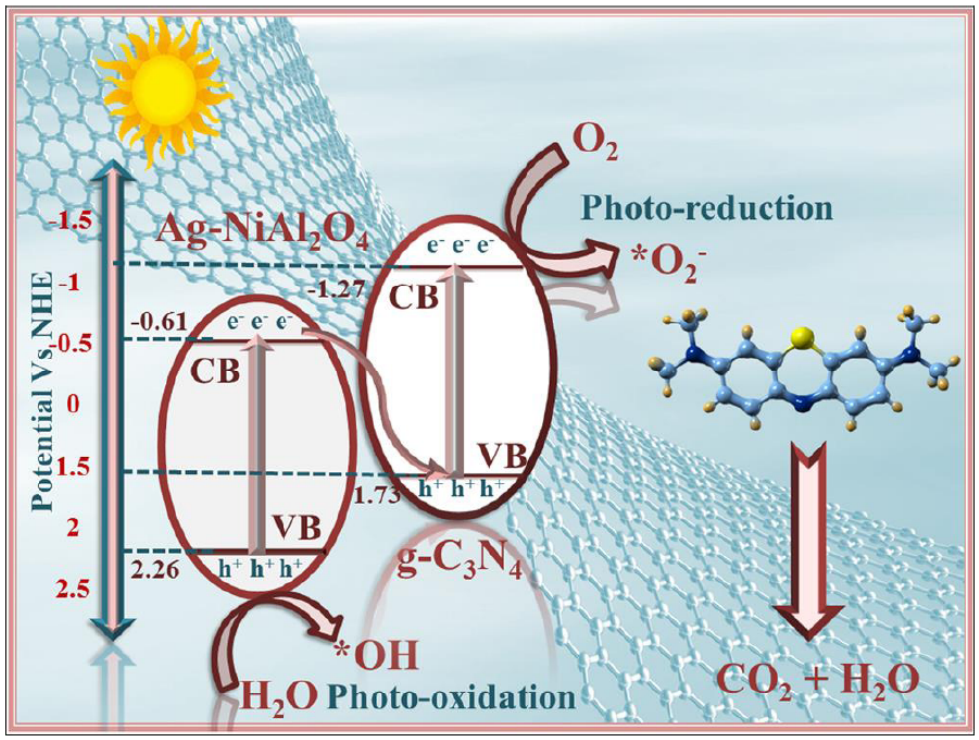

Figure 4: Photocatalytic mechanism of Ag-$NiAl_2O_4$@g-C_3N_4 photocatalysts. Adapted from ref. [59]. Copyright © 2022 Elsevier B.V.

As the research progresses, researchers are working on how to use the visible light in sunlight, which makes up the majority of sunlight, to develop $NiAl_2O_4$ based photocatalysts driven by visible light. The following strategies have been adopted to enhance the photocatalytic activity of $NiAl_2O_4$. In order to solve the problem of large band gap value of $NiAl_2O_4$, the band gap value of $NiAl_2O_4$ can be degraded by ion doping, so as to improve its optical response range, so that $NiAl_2O_4$ can respond to visible light. Noble metal particles are good carriers for electron transport. The modification of noble metal particles on the surface of $NiAl_2O_4$ will help to enhance its photocatalytic activity. The photocatalytic activity of $NiAl_2O_4$ can be greatly improved by combining some excellent visible light responsive semiconductor materials with $NiAl_2O_4$, in addition to introducing interfacial defects to enhance the transfer and separation of electron and hole pairs.

Table **1** shows the comparison of the application of $NiAl_2O_4$ based photocatalyst for the degradation of dyes [34, 59, 72, 87, 90, 91, 94, 107-112]. It can be seen from Table **1** that $NiAl_2O_4$ has high photocatalytic activity in the degradation of organic dyes under ultraviolet light. According to the calculation of specific activity, $NiAl_2O_4$ synthesized by different methods has different photocatalytic activity, and when $NiAl_2O_4$ degrades different dyes, its photocatalytic activity is also different. This was sufficient to confirm that $NiAl_2O_4$ was selective in degrading dyes. When $NiAl_2O_4$ is doped with different ions such as Mg, Zn and Cu, the photocatalytic activity of $ZnAl_2O_4$ is greatly affected by different metal ions. With the increase of ionic radius, the photocatalytic activity of $ZnAl_2O_4$ decreases. The use of ion-doped $NiAl_2O_4$ photocatalysts for degradation of different dyes did not show strong selectivity. The photocatalytic activity of $NiAl_2O_4$ can be enhanced by ion doping, surface modification of noble metal ions and heterojunction construction.

It is interesting that Irshad *et al*. [59] synthesized Ag-$NiAl_2O_4$/g-C_3N_4 composite photocatalysts by sol-gel method with high photocatalytic activity in the degradation of organic dyes. By modifying Ag particles on the surface of $NiAl_2O_4$ and coupling with g-C_3N_4 to form heterojunction, the $NiAl_2O_4$ based photocatalyst has high charge transfer and separation efficiency, which enhances the photocatalytic activity of $NiAl_2O_4$. Figure **4** shows the photocatalytic mechanism of Ag-$NiAl_2O_4$@g-C_3N_4 photocatalysts. Hydroxyl radicals and superoxide radicals dominate the entire photocatalytic reaction, eventually interacting with dyes to produce CO_2 and H_2O.

Table 1: Comparison of the Application of $NiAl_2O_4$ Based Photocatalyst for the Degradation of Dyes. MB- Methylene Blue, MO- Methylene Orange, CV-Crystal Violet, RhB- Rhodamine B, BA- Weak Acid Brilliant blue, CR- Congo Red, MG- Malachite Green, MR-methyl red, D-Degradation Percentage, SA-Specific Activity

Samples	Dye	Lamp	$C_{Catalyst}$ ($g \cdot L^{-1}$)	C_{Dye} (mmol L^{-1})	t (h)	D (%)	SA (mmol/g/h)	Ref.
$Zn_{0.1}Ni_{0.9}Al_2O_4$	MB	UV light	1.5	0.0312	2	93%	0.0097	90
$Mg_{0.1}Ni_{0.9}Al_2O_4$	MB	UV light	1.5	0.0312	2	97%	0.0101	
$NiAl_2O_4$	MB	UV light	1.5	0.0312	2	91%	0.0095	
$Cu_{0.1}Ni_{0.9}Al_2O_4$	MB	UV light	1.5	0.0312	3	90%	0.0063	
$NiAl_2O_4$	MB	Visible lights	0.2	0.0312	1	47%	0.0733	34
$NiAl_2O_4$	MB	Visible lights	0.3	1×10^{-5}M	2	94%	/	[107]
$NiAl_2O_4$	MB	UV light	0.2	0.0312	1.4	94.2%	0.1049	[87]
$NiAl_2O_4$	MB	Sun light	0.2	0.0156	2.7	58.16%	0.0168	[59]
Ag-$NiAl_2O_4$	MB	Sun light	0.2	0.0156	2.7	71.13%	0.0205	
Ag-$NiAl_2O_4$@g-C_3N_4	MB	Sun light	0.2	0.0156	2.67	85.26%	0.0249	
$NiAl_2O_4$	MB	UV light	0.5	0.0312	1	54%	0.0336	[108]
$NiAl_{1.98}Bi_{0.02}O_4$	MB	UV light	0.5	0.0312	1	89%	0.0554	
$NiAl_{1.98}Ce_{0.02}O_4$	MB	UV light	0.5	0.0312	1	94%	0.0586	
$NiAl_2O_4$	MB	UV light	0.4	0.00625	1.67	99%		[109]
$Zn_{0.1}Ni_{0.9}Al_2O_4$	MO	UV light	1.5	0.0305	3	92%	0.0062	[59]
$Mg_{0.1}Ni_{0.9}Al_2O_4$	MO	UV light	1.5	0.0305	1.5	96%	0.0130	
$NiAl_2O_4$	MO	UV light	1.5	0.0305	3	94%	0.0064	
$Cu_{0.1}Ni_{0.9}Al_2O_4$	MO	UV light	1.5	0.0305	3	84%	0.0057	
$NiAl_2O_4$	MO	Tungstate lamps			4.5	90%		[72]
$NiAl_2O_4$	MO	Mercur lamp		0.1527	1.33	82%		[110]
$NiAl_2O_4$	MO	UV light	0.2	0.0305	1.4	88.4%	0.0962	[87]
$NiAl_2O_4$	MO	UV light	0.5	0.0312	1	31%	0.0193	[108]
$NiAl_{1.98}Bi_{0.02}O_4$	MO	UV light	0.5	0.0312	1	91%	0.0568	
$NiAl_{1.98}Ce_{0.02}O_4$	MO	UV light	0.5	0.0312	1	94%	0.0587	
$NiAl_2O_4$	CV	Sun light	0.2	0.0484	2.7	57.14%	0.0512	[59]
Ag-$NiAl_2O_4$	CV	Sun light	0.2	0.0484	2.7	70.52%	0.0632	
Ag-$NiAl_2O_4$@g-C_3N_4	CV	Sun light	0.2	0.0484	2.67	83.87%	0.0760	
$NiAl_2O_4$	RhB	UV light	0.2	0.0208	1.4	91.7%	0.0681	[87]
$NiAl_2O_4$	RhB	UV light	0.5	0.0312	1	73%	0.0456	[108]
$NiAl_{1.98}Bi_{0.02}O_4$	RhB	UV light	0.5	0.0312	1	87%	0.0543	
$NiAl_{1.98}Ce_{0.02}O_4$	RhB	UV light	0.5	0.0312	1	90%	0.0562	
Ag-$NiAl_2O_4$@g-C_3N_4	BA	Sun light	0.2	0.0409	2.67	68.46%	0.0524	[59]
NiO/$NiAl_2O_4$	CR	UV light	0.33	0.9616	2/3	88.91%/100%	1.2953/0.9713	[111]
$Ni_{0.2}Cu_{0.8}Al_2O_4$	CR	Xenon lamp	1	0.5769	3	90.55%	0.1741	[91]
$Co_{0.85}Ni_{0.15}Al_2O_{4-\delta}$ /AC	MG	Tungsten halogen lamp	0.05	1x10-4M	1.5	100%	/	[94]
$NiAl_2O_4$	MG	Visible lights	0.3	1X10-5M	2	89%	/	[107]
$NiAl_2O_4$	MG	Visible lights	1	0.0027	2	42%	0.0006	[112]
$Ni_{1-x}Co_xAl_2O_{4-\delta}$	MG	Visible lights	1	0.0027	2	20%~39%	0.0003~0.0005	
$NiAl_2O_4$	MR	UV light	0.2	0.0371	1.4	88.9%	0.1178	[87]

3.2. Application of $NiAl_2O_4$ Based Catalysts in the Field of Photocatalytic Degradation of Drugs

In recent years, with the further development of the study of photocatalysis in the field of dyes, the

photocatalysis mechanism and the reaction process of dye degradation are familiar, which makes the study of dyes fall into a trough. Even from the structure of the dye, its structure is so simple that different catalysts are used to degrade the same reaction process, which allowed researchers to quickly understand its reaction mechanism. In order to promote the rapid development of research in the field of photocatalysis, researchers have focused on the degradation of drugs. The molecular structure of drugs such as antibiotics is complex, and the study of its degradation process needs to be combined with many professional characterization equipment and rich research experience of researchers. Therefore, synthesis of new photocatalysts to degrade drugs has become a new research direction in the field of photocatalysis.

The same is true for $NiAl_2O_4$ photocatalyst research, researchers have gradually shifted the focus of research to photocatalytic degradation of drugs. Table **2** shows the comparison of the application of $NiAl_2O_4$ based photocatalyst for the degradation of drugs [34, 92, 113, 114]. Similar to the study on dyes, the researchers also used ion doping and heterostructure to improve the photocatalytic activity of $NiAl_2O_4$ photocatalysts for the photocatalytic degradation of drugs. Since it was in its infancy, $NiAl_2O_4$ based photocatalysts were only used to degrade tetracycline hydrochloride, 2,4-dichlorophenol and oxytetracycline hydrochloride. By doping $NiAl_2O_4$ with rare earth metal ions, it was found that the photocatalytic activity of $NiAl_2O_4$ increased with the increase of ionic radius, which was contrary to the trend of dye degradation. The main reason is that with the increase of the radius of rare earth ion, the outermost electron of rare earth ion is easy to be activated by light energy to produce free electrons, which promotes the separation and transfer of charge carriers, and thus enhances the photocatalytic activity of $NiAl_2O_4$ based photocatalyst.

Figure **5** shows the proposed mechanism of the rare- earth-metals-doped nickel aluminates [92]. The more electrons in the outermost layer of rare earth ions are, the easier they are to be excited by sunlight, which contributes to the transfer and separation in the photocatalytic process, thus promoting the generation of hydroxyl radicals and superoxide radicals. Meanwhile, because $NiAl_2O_4$ is partially antispinel structure, rare earth ion doping will further affect its internal crystal structure, electronic structure and energy level structure, resulting in lattice distortion, produce oxygen vacancy or defect, and enhance the transfer and separation of electron and hole pairs in $NiAl_2O_4$ based photocatalysts. However, the research of $NiAl_2O_4$-based photocatalysts for drug degradation is not mature, especially the photocatalytic mechanism, drug degradation path and reaction process need further exploration in order to understand their internal mechanism.

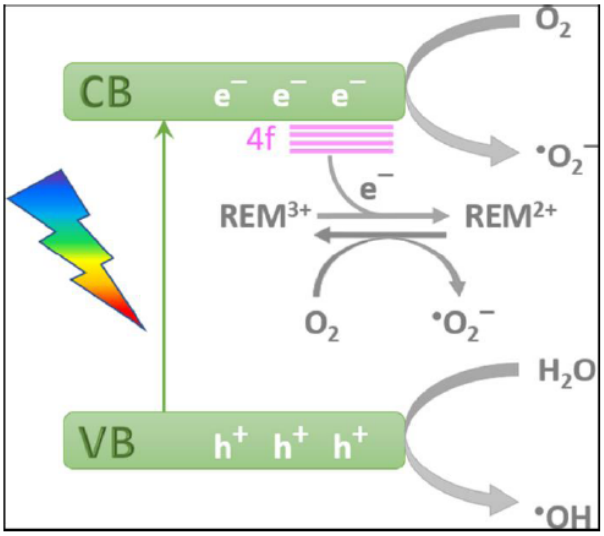

Figure 5: The proposed mechanism of the rare- earth-metals-doped nickel aluminates. Adapted from ref. [92]. Copyright © 2022 Elsevier B.V.

Table 2: Comparison of the Application of $NiAl_2O_4$ Based Photocatalyst for the Degradation of Drugs. TC-Tetracycline Hydrochloride, OTC-Oxytetracycline Hydrochloride

Samples	Drug	Lamp	$C_{Catalyst}$ ($g \cdot L^{-1}$)	C_{Drug} (mmol L^{-1})	t (h)	D (%)	SA (mmol/g/h)	Ref.
$NiAl_2O_4/g\text{-}C_3N_4$	TC	Sun light	0.3	0.0264	2	90%	0.0396	[113]
$NiAl_2O_4$	TC	UV light	0.5	0.0132	0.5	83%	0.0439	[34]
$NiO–NiAl_2O_4$	2,4-dichlorophenol	UV light	2	0.2454	2	94%	0.0577	[114]
$NiAl_2O_4$	OTC	Sun light	1.5	0.00003	2	27%	0.0000027	[92]
$Yb\text{-}NiAl_2O_4$	OTC	Sun light	1.5	0.00003	2	49%	0.0000049	
$Tm\text{-}NiAl_2O_4$	OTC	Sun light	1.5	0.00003	2	62%	0.0000062	
$Er\text{-}NiAl_2O_4$	OTC	Sun light	1.5	0.00003	2	73%	0.0000073	

3.3. Application of $NiAl_2O_4$ Based Catalysts in the Field of Catalytic Oxidation of Benzyl Alcoho and Methanol

Experimental research on the catalytic oxidation of $NiAl_2O_4$ has been going on for a long time, more than a decade before its use in photocatalytic degradation of dyes and drugs. In the early years, arousing the attention of many scientific researchers, $NiAl_2O_4$ was used in oxidative degradation benzyl alcoho and methanol. Table **3** shows the comparison of the application of $NiAl_2O_4$ based photocatalyst for the catalytic oxidation of benzyl alcoho [30, 115]. By doping Co ions into the lattice of $NiAl_2O_4$ and catalyzing the oxidation of benzyl alcoho, researchers found that it has a high catalytic oxidation performance. Similarly, the crystal structure and microstructure of $NiAl_2O_4$ have great influence on its catalytic oxidation performance. The catalytic oxidation performance of $NiAl_2O_4$ can be improved effectively by fabricating special defective structures with the antispinel structure.

Similar to the study of photocatalysis, the catalytic oxidation performance of single component $NiAl_2O_4$ is relatively low, so special methods should be used to enhance its catalytic oxidation performance. Therefore, $MgO/NiAl_2O_4$ composite oxides with different mass percentages were synthesized to investigate their catalytic oxidation properties. Table **4** shows the comparison of the application of $NiAl_2O_4$ based photocatalyst for the catalytic oxidation of methanol [116-118]. The results confirm that $NiAl_2O_4$-based catalyst methanol has high catalytic oxidation capacity.

Figure **6** shows the redox mechanism of methanol over $Pt/NiAl_2O_4$ and $Pt/\gamma\text{-}Al_2O_3$. Li *et al*. [119] prepared

Table 3: Comparison of the Application of $NiAl_2O_4$ Based Photocatalyst for the Catalytic Oxidation of Benzyl Alcoho

Samples	Organic matter	Ccatalyst ($g \cdot L^{-1}$)	Oxidant	Temperature/Time	Conversion (%)	Selectivity (%)	Ref.
$NiAl_2O_4$	Benzyl alcoho	0.5	Benzyl alcohol (5 mmol) H_2O_2 (5 mmol)	80 °C/8 h	60	100	[80]
$Ni_{0.6}Co_{0.4}Al_2O_4$	Benzyl alcohol	0.5	Benzy lalcohol (5 mmol) acetonitrile (5 mmol) H_2O_2 (5 mmol)	80 °C/5 h	94	100	[115]

Table 4: Comparison of the Application of $NiAl_2O_4$ Based Photocatalyst for the Catalytic Oxidation of Methanol

Samples	Organic matter	Ccatalyst ($g \cdot L^{-1}$)	Oxidant	Temperature/ Time	XCH_4,%	Y_{H2}	Y_{CO}	Y_{CO2}	H_2/CO	CO/CO_2	Ref.
5wt.% MgO/ $NiAl_2O_4$	38,400 cm^3 $CH4\ g^{-1}\ h^{-1}$	0.125	10%CH_4/5% O_2/85%N_2 (O/C = 1)	700 °C/ 20 h	83	0.92	0.75	0.08	2.8	9.6	[116]
5wt.% MgO/ $NiAl_2O_4$	38,400 cm^3 $CH_4\ g^{-1}\ h^{-1}$	0.125	10%CH_4/5% O_2/85%N_2 (O/C = 1)	700°C/ 20h/25 h	63	0.46	0.56	0.07	1.7	7.8	
$NiAl_2O_4$ (0.5)	38400 mL $CH_4\ g^{-1}\ h^{-1}$	0.125	O/C = 1	650 °C/3 h	73	0.67	0.55	0.18	2.4	3	[117]
$NiAl_2O_4$ (0.5)	38400 mL $CH_4\ g^{-1}\ h^{-1}$	0.125	O/C = 1	700 °C/3 h	82	0.77	0.69	0.13	2.2	5.3	
$NiAl_2O_4$	4800 mL $CH_4\ g^{-1}\ h^{-1}$	0.5	10%CH_4/5% O_2/N_2	550 °C	/	1.82	0.52	0,57	3.5		[118]
$NiAl_2O_4$	4800 mL $CH_4\ g^{-1}\ h^{-1}$	0.5	10%CH_4/5% O_2/N_2	650 °C	/	1.77	0.78	0.15	2.29	/	
$NiAl_2O_4$	4800 mL $CH_4\ g^{-1}\ h^{-1}$	0.5	10%CH_4/5% O_2/N_2	750 °C	/	1.74	0.82	0.04	2.11	/	
$NiAl_2O_4$	4800 mL $CH_4\ g^{-1}\ h^{-1}$	0.5	10%CH_4/5% O_2/N_2	850 °C	/	1.72	0.83	0.02	2.08	/	

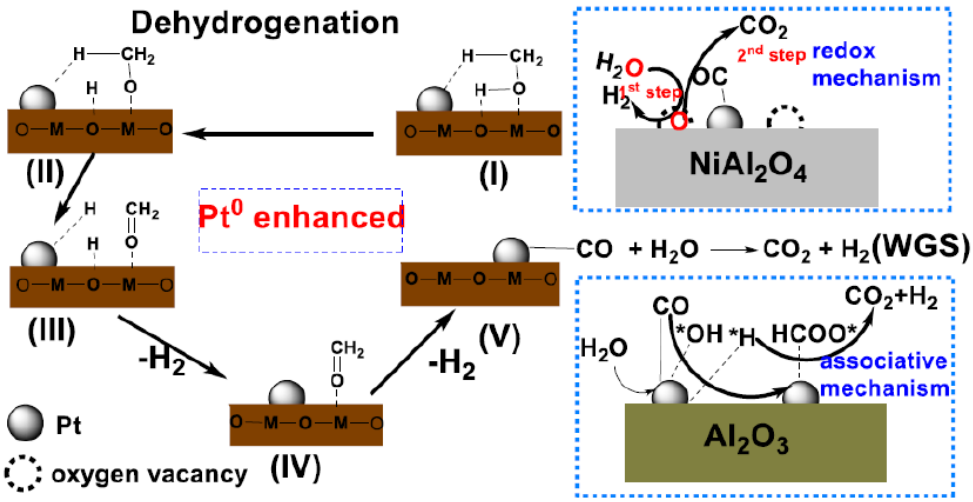

Figure 6: The redox mechanism of methanol over $Pt/NiAl_2O_4$ and $Pt/\gamma\text{-}Al_2O_3$. Adapted from ref. [119]. Copyright © 2019 American Chemical Society.

the $Pt/NiAl_2O_4$ and $Pt/\gamma\text{-}Al_2O_3$ catalysts by co-precipitation method combined with incipient wetness impregnation method. The phase structure, microstructure and catalytic oxidation performance of different catalysts were studied by different characterization methods. For the $Pt/NiAl_2O_4$ catalyst, Pt than $Pt/\gamma\text{-}Al_2O_3$ catalyst has high reducing capacity, methanol can methanol catalytic oxidation, improve $NiAl_2O_4$ catalytic oxidation performance. The catalytic oxidation performance of $NiAl_2O_4$ based catalyst has been concerned by researchers since its discovery, and is still in continuous research.

3.4. Other Applications of $NiAl_2O_4$ Based Catalysts

$NiAl_2O_4$ based catalysts has been widely used in the degradation of dyes, drugs and catalytic oxidation of methanol, and also has potential applications in the photocatalytic reduction of Cr(VI) ions, photocatalytic water hydrogen production and other fields. Bouallouche *et al*. [120] constructed a $NiAl_2O_4$/ZnO heterojunction that allows photocatalytic reduction of Cr(VI) ions under visible light. Of course, in terms of dye adsorption, ternary $CeO_2/NiO/NiAl_2O_4$ nanocomposite was constructed to adsorb Direct Red 23 dye, and the results showed that this adsorbent has high adsorption capacity. [121] Sebai *et al*. [122] using nitrate route, the preparation of the spinel $NiAl_2O_4$ and studied its photocatalytic hydrogen production capacity, the result indicates that it under visible light irradiation conditions with high hydrogen production ability. Due to the special crystal structure, microstructure and energy level structure of $NiAl_2O_4$, its application in the field of catalysis has been paid more and more attention, and some new research fields are also being further studied. Therefore, its research in the new catalytic field will be pursued by more and more researchers and push it towards the climax of the study. Electrocatalysis is a way of clean energy conversion. It is very important to select a reasonable and stable catalyst [123, 124]. Ni has higher alloying efficiency than other metals. Therefore, when conducting electrocatalytic experiments, choosing Ni composite materials can better provide the required properties [125]. Aman *et al*. [126] prepared a composite material of $NiAl_2O_4$ and graphene oxide (GO) as an efficient OER electrocatalyst. On the basis of good electrical conductivity and electron transport ability of carbon-based materials, Aman *et al*. [127] chose $NiAl_2O_4$ to be combined with it to improve the electrochemical and catalytic performance of OER. Regulska *et al*. [128] have combined $NiAl_2O_4$ with graphene quantum dots (GQDs) and conducted electrochemical studies. The results show that for monomer $NiAl_2O_4$, the composite has strong ultracapacitor and electrocatalytic performance.

4. CONCLUSIONS AND PROSPECT

The synthesis of $NiAl_2O_4$ based catalysts and their applications in the degradation of dyes, pharmaceuticals, catalytic oxidation of methanol and other applications are reviewed. The catalytic activity of $NiAl_2O_4$ based catalyst is strongly dependent on the preparation method, crystal structure, energy level structure and microstructure. The research on the catalytic activity of $NiAl_2O_4$ based catalysts is expanding from catalytic oxidation, photocatalytic degradation of dyes, drugs, adsorption and photocatalytic hydrogen production. $NiAl_2O_4$ based catalyst is selective to degradation of dyes, and its

photocatalytic activity varies with the different types of ion doping. Based on the results of the study on the catalytic activity of single-component $NiAl_2O_4$, ion-doped $NiAl_2O_4$ and heterogeneous structures of multi-component $NiAl_2O_4$ heterojunction catalysts, the related catalytic mechanisms are also reviewed in detail.

As a promising catalyst, its research in some aspects is still in the exploratory stage, which can be explored in future studies as follows:

1. The construction of a new $NiAl_2O_4$ based photocatalyst heterojunction and its photocatalytic mechanism were investigated by combining the first principles calculation and experimental study.

2. Based on different intelligent algorithms, an intelligent algorithm optimized neural network model was established to predict the catalytic activity of the synthesized catalyst, and then the optimized prediction model was obtained to predict its catalytic performance.

3. High entropy alloy is a promising photocatalyst. By coupling it with $NiAl_2O_4$ to construct high entropy alloy /$NiAl_2O_4$ heterojunction photocatalyst, using the excellent electron transport ability, cocktail effect and visible light response ability of high entropy alloy, a novel photocatalyst with high efficiency can be obtained.

4. Metal-organic framework materials (MOFs) are a kind of coordination polymers. By combining MOFs with $NiAl_2O_4$ to construct MOFs/$NiAl_2O_4$ heterojunction photocatalysts, MOFs/$NiAl_2O_4$ photocatalysts are expected to be a new reliable photocatalyst due to the design of their own structures and the tunability of photon absorption.

COMPETING INTERESTS

The authors declare that they have no competing interests.

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