

Study of the efficiency of ZnAl_2O_4 as green nanocatalyst

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Abstract: Waste from chemical reactions is still a hot issue to be discussed today. Green chemistry in its concept offers catalysts as an alternative to reducing waste resulting from chemical reactions. This literature study aims to examine the method of making ZnAl_2O_4 nanocatalysts and doping materials that are more effective in various reactions by considering the advantages and disadvantages of each. The content of the study includes the ZnAl_2O_4 nanocatalyst synthesis method, combination catalyst, and catalytic effectiveness in chemical reactions. Combustion, sol-gel, co-precipitation, hydrothermal, and microwave are the most common methods in the synthesis of ZnAl_2O_4 . The use of precursors, fuel, and precipitating agents are very important factors when using combustion, sol-gel, and co-precipitation methods. Other factors that need to be considered are the raw material ratio, pH, and calcination temperature. The pH of the solution is 6-9 and the calcination temperature of $600^\circ\text{C} - 800^\circ\text{C}$ is the ideal point for producing nanocatalyst. The calcination temperature is lower to $300^\circ\text{C} - 500^\circ\text{C}$ when using hydrothermal and microwave as a synthesis method. ZnAl_2O_4 nanocatalyst has been identified as having good catalytic activity, but not higher than ZnAl_2O_4 combined with other catalysts. The combination of a catalyst with ZnAl_2O_4 spinel in hydrogenation, dehydrogenation, esterification, degradation, and organic synthesis has high catalytic activity with a conversion rate and selectivity of $>70\%$.

Keywords: Green catalyst, synthesis catalyst method, ZnAl_2O_4 , nanocatalyst

Abstrak: Limbah hasil reaksi kimia masih menjadi persoalan yang hangat untuk dibicarakan hingga saat ini. Green chemistry pada konsepnya menawarkan katalis menjadi alternatif dalam mengurangi limbah hasil reaksi kimia. Studi literature ini bertujuan untuk mengkaji metode pembuatan nanokatalis ZnAl_2O_4 serta material doping yang lebih efektif dalam berbagai reaksi dengan mempertimbangkan keuntungan dan kekurangan masing-masing. Combustion, sol-gel, co-precipitation, hidrotermal dan microwave menjadi metode yang paling umum dalam sintesis ZnAl_2O_4 . Penggunaan prekursor, bahan bakar, serta agen pengendap menjadi factor sangat penting Ketika menggunakan metode pembakaran, sol-gel, dan co-presipitasi. Faktor lainnya yang perlu diperhatikan adalah rasio penggunaan bahan, pH, dan suhu kalsinasi. pH larutan pada rentangan 7-9 serta suhu kalsinasi $600-800^\circ\text{C}$ merupakan titik ideal dalam menghasilkan nanokatalis. Suhu kalsinasi menjadi lebih rendah hingga $300-400^\circ\text{C}$ Ketika menggunakan microwave sebagai metode sintesis. ZnAl_2O_4 dalam ukuran nano telah teridentifikasi memiliki aktivitas katalitik yang baik, tetapi tidak lebih tinggi dibandingkan ZnAl_2O_4 yang dikombinasikan dengan katalis lainnya. Kombinasi katalis dengan spinel ZnAl_2O_4 dalam reaksi hidrogenasi, dehidrogenasi, esterifikasi, degradasi, dan sintesis kimia organik memiliki aktivitas katalitik dengan Tingkat konvresi dan selektivitas $>70\%$.

Kata kunci: Katalis ramah lingkungan, metode sintesis katalis, ZnAl_2O_4 , nanokatalis

INTRODUCTION

Chemical reactions have now become an important part of research in producing a new product. In the mechanism, chemical reactions require many chemicals with a long time. As a consequence, the waste generated during the reaction process also increases. The method offered in overcoming this problem is to reduce or replace the use of chemicals that have the potential to cause waste. The use of catalysts can be a solution in reducing waste. The catalyst will be able to accelerate the course of the reaction so that the waste produced also decreases. In addition, the catalyst also facilitates the desired reaction, controls distribution and controls product selectivity (El-araby et al., 2023). Heterogeneous catalysts are one of the alternative catalysts that are environmentally friendly and have high recoverability (Singh & Tandon, 2014).

Gahnite or zinc aluminate (ZnAl_2O_4) is a heterogeneous catalyst widely used in electronic reactions, photocatalysts, ceramics, sensors, pigments, and organic synthesis (Akika et al., 2020a; Macedo et al., 2019; Peymanfar & Fazlalizadeh, 2021; Priya et al., 2020). ZnAl_2O_4 catalyst in vanillin synthesis reaction from eugenol (Nofita Birhi et al., 2021), conversion of biomass and petroleum feedstock, and water cracking (El-araby et al., 2023), deliver results with high selectivity in less time. ZnAl_2O_4 is special because it has good photocatalytic activity, hydrophobic behavior, transparency, thermal stability, low acidity, high quantum yields, and mechanical resistance (Akika et al., 2020b; Priya et al., 2020; Tran et al., 2021). Apart from being a catalyst, the effectiveness of ZnAl_2O_4 as a support catalyst has also developed in transformation reactions to green chemistry (Abd-Allah et al., 2022; Birhi et al., 2023; Eskandari Azar et al., 2020). The ability of ZnAl_2O_4 as a support catalyst depends on the type and ratio of precursor, as well as the synthesis method (Chaudhary et al., 2018a; Huang et al., 2020), such as combustion, sol-gel, co-precipitation, hydrothermal, polymer precursor, and microwave.

In addition, particle size is also an important factor in making a green catalyst. Catalysts with a size of 1-100 nm are claimed to be environmentally friendly catalysts (Somwanshi et al., 2020). This is because nanocatalysts can regulate the energy band gap which functions as a balancer of dielectric properties and conductivity of the catalyst. In addition, small particle sizes can increase the surface area of the catalyst, thereby increasing heterojunction interfaces and grain boundaries resulting in the Maxwell-Wagner effect (Peymanfar & Fazlalizadeh, 2020). The catalytic activity of ZnAl_2O_4 nanoparticles as a green catalyst has been proven in syngas conversion (L. Liu et al., 2021), degradation of organic dyes (Chaudhary et al., 2018a), and hydrogen synthesis (Diaz-Torres et al., 2020).

Until now, the synthesis and use of ZnAl_2O_4 as a green catalyst is still a hot topic for research. Therefore, this literature focuses on the study of ZnAl_2O_4 nanocatalyst synthesis methods that have been carried out, material doping, and their effectiveness in every environmentally friendly chemical reaction

METHOD

This study uses the literature review method by collecting, evaluating, and analyzing scientific articles that present this topic in the last 10 years. Article searches are conducted through academic databases such as Google Scholar, ResearchGate, Science Direct, Crossref, and Library Genesis with keywords Green Nanocatalyst, ZnAl₂O₄, ZnAl₂O₄ as nanocatalyst. A collection of research articles on ZnAl₂O₄ obtained, sorted based on the type of particles produced, micro and nanocatalyst. Articles on ZnAl₂O₄ nanocatalyst were then continued in the study, and grouped into 2 main parts. The first part is grouping articles based on nanocatalyst synthesis methods, and the second group focuses on the use of catalysts in chemical reactions with the help of doping materials.

RESULTS AND DISCUSSION

Nanocatalyst ZnAl₂O₄: Synthesis method

The most commonly used catalyst synthesis methods are combustion, sol-gel, co-precipitation, hydrothermal, and microwave. Each method has its own uniqueness, such as the combustion method in the process involves compounds that can function as fuel, sol-gel requires compounds that act as surfactants, and co-precipitation requires precipitation agents. In summary, the nanocatalyst synthesis method can be seen in Table 1.

Table 1. Synthesis method of catalyst

	Raw materials	Fuels	Calcining temperature (°C)	Particle size (nm)	Reference
Combustion	Zn(NO ₃) ₂ , Al(NO ₃) ₃	Mix Glycine-urea	700	10	(Mirbagheri et al., 2020)
	Zn(NO ₃) ₂ .6H ₂ O, Al(NO ₃) ₃ .9H ₂ O	Glycine	1100 (8 hours)	50-200	(Han et al., 2018)
	Zn(NO ₃) ₂ .4H ₂ O, Al(NO ₃) ₃ .9H ₂ O	Urea	800 (4 hours)	25.854	(Priya et al., 2020)
			800 (2 hours)	35	
	Zn(NO ₃) ₂ , Al(NO ₃) ₃	Resinifera latex euphorbia extract	900 (3 hours)	13	(Venkatesh et al., 2021)
	Zn(NO ₃) ₂ , Al(NO ₃) ₃	Cymbopogan citrus extract	800 (2 hours)	1-11	(Nitha & Britto, 2023)
Sol-gel	Raw Materials	Surfactant	Calcining temperature (°C)	Particle size (nm)	Reference
	Al(OPr) ₃ , Zn(OAc) ₂	cationic cetyltrimethylammonium bromide (CTAB)	500 (2 hours)	6	(Chaudhary et al., 2018b)
		anionic sodium lauryl sulfate (SLS)		6	
		-		12	
	Al(NO ₃) ₃ .9H ₂ O, ZnCl ₂	triethanolamine	800 (8 hours)	35	(Mohanty et al., 2021)
	Zn(NO ₃) ₂ .6H ₂ O, Al(NO ₃) ₃ .9H ₂ O	Citric acid	600 (4 hours)	30	(Peymanfar & Fazlalizadeh, 2021)
	Zn(NO ₃) ₃ .9H ₂ O, Al(NO ₃) ₃ .9H ₂ O	Tragacant gel	600 (4 hours)	16	(Eskandari Azar et al., 2020)

Co-precipitation	Raw materials	Agen precipitation	Calcining temperature (°C)	pH	Particle sizes (nm)	References	
	Zn(NO ₃) ₂ .6H ₂ O, Al(NO ₃) ₃ .9H ₂ O	Ammonia	600 (4 hours)	8-9	8	(Farhadi & Panahandehjoo, 2010)	
	Zn(NO ₃) ₂ .6H ₂ O, Al(NO ₃) ₃ .9H ₂ O	Ammonia	600 (4 hours)	10	3.8	(Habibi et al., 2021)	
			800		6.10		
			1000		13.7		
	Zn(NO ₃) ₂ .6H ₂ O, Al(NO ₃) ₃ .9H ₂ O	Ammonia	600 (5 hours)	8-9	13	(Ibrahim et al., 2021)	
Zn(NO ₃) ₂ .6H ₂ O, Al(NO ₃) ₃ .9H ₂ O	Ammonia	700 (4 hours)	9	21-25	(Mohaqeq et al., 2017)		
Hydrothermal		Raw materials	Calcining temperature (°C)	pH	Particle sizes (nm)	References	
	One-liquid	Zn(NO ₃) ₂ .6H ₂ O, Al(NO ₃) ₃ .9H ₂ O	400 (3 hours)	6-7	5-10	(Zhao et al., 2015)	
			700 (8 hours)	7	14	(Dai et al., 2018)	
	Two-liquid	Zn(NO ₃) ₂ .6H ₂ O, Al(NO ₃) ₃ .9H ₂ O	300-900 (9 hours)	-	100	(Dwibedi et al., 2018)	
			Zn(NO ₃) ₂ .6H ₂ O, Al(NO ₃) ₃ .9H ₂ O	200	<9	13	(Ishii et al., 2016)
					>9	40	
Microwave	Raw materials	Reaction time (minutes)	Particle size (nm)		References		
	Zinc nitrates, ferric nitrate	10	12-18		(Bhavani et al., 2017)		
	Aloe vera as a reducing agent	10	50		(Padmapriya & Amudhavalli, 2020)		
	Cetyltrimethylammonium bromide as a surfactant	10	5		(Menon et al., 2017)		

Combustion

The combustion method is one of the simplest methods in catalyst synthesis. This method requires a short time, low cost, homogeneity, requires lower energy but has a high purity product, and can control the stoichiometry of reactions at the molecular level. The combustion reaction begins with the decomposition of the precursor metal with an organic fuel that produces gas. Therefore, the combustion reaction can be controlled by trapping the released gas in a closed system (Mirbagheri et al., 2020). This is because the exothermicity reaction between gases will release enough heat to crystallize the material directly from the precursor molecular compound (Mirbagheri et al., 2020; Nuayi, 2017). The selection and comparison of the ratio of precursors, fuel, temperature, as well as the length of combustion time, need to be considered to produce nano-sized particles. This is because an improper combustion process will result in agglomeration and decrease catalytic activity.

In the synthesis of ZnAl₂O₄, the most commonly used metal precursors are zinc nitrate [Zn(NO₃)₂] and aluminum nitrate [Al(NO₃)₃], which are then reacted with various types of fuel. The fuel used must have precursor metal characteristics such as solubility, material availability, and decomposition temperature. Mirbagheri, et al synthesized ZnAl₂O₄ by mixing fuel between glycine and urea. The results show that the size of ZnAl₂O₄ is in the

range of 10 nm with the presence of ZnO as a result of the slow rate of decomposition. However, the presence of ZnO slowly completely disappears with increasing calcining temperature to 700°C (Mirbagheri et al., 2020). Calcination is an important step because it can improve the crystal structure, reduce the remaining carbon from incomplete combustion, and include dopants in the spinel structure well (Shahmirzaee et al., 2019).

Fuel mixing in ZnAl₂O₄ synthesis gives better results than single fuel. Han, et al in their synthesis only use glycine as fuel. The results provide a fairly noticeable difference compared to those obtained by Mirbagheri, et al. In Han's synthesis, calcining temperatures used reached 1100°C for 8 hours but produced larger ZnAl₂O₄ particles of 50-200 nm (Han et al., 2018). This is because more particles are found to clump together due to the very high calcination temperature. On the other hand, Gahanel (Gahane et al., 2023) and Priya (Priya et al., 2020) used urea as the sole fuel in the synthesis of ZnAl₂O₄ and calcined at 800°C for 4 and 2 hours respectively. The results of the study found that the crystals formed were free from contamination with a size of 25.854 nm and 35 nm. This particle size is still quite large when compared to the use of a mixture of glycine and urea as fuel.

In 2021, Venkatesh et al synthesized ZnAl₂O₄ with a green combustion method that uses plant extracts as fuel. In the process, the fuel used is *Resinifera* latex euphorbia extract and calcined at 900°C for 3 hours. The resulting particle size is quite small, which is 13 nm (Venkatesh et al., 2021). Furthermore, Nitha (Nitha & Britto, 2023) uses *Cymbopogon citrus* extract as part of the green method in the synthesis of ZnAl₂O₄. The size of the catalyst produced is in the range of 1-11 nm, and has good catalytic activity in the synthesis of benzimidazole derivatives.

Sol-gel

Sol-gel is the most common wet-chemistry technique in the manufacture of ceramic, glass materials, and metal oxides. This method offers precise control over the composition and structure of the resulting material (Karoui et al., 2024). In the process, metal alkoxide and metal chloride as precursors will undergo hydrolysis and polycondensation reactions to form colloids. However, the synthesis of ZnAl₂O₄ using this method is somewhat difficult because of the difference in the hydrolysis and condensation rates of two different materials. Different precursors will result in different particle sizes. However, the sol-gel method is one of the efficient methods in producing nanoparticle crystals (Mohanty et al., 2021) if using the right surfactant. Surfactant is an elemental directing agent because it has the ability to control the growth of nanoparticle crystals, and helps achieve nanoparticle morphology. In order to test the role of surfactants on particle size, Chaudhary gave 3 different treatments using 2 types of surfactants, cationic cetyltrimethylammonium bromide (CTAB) and anionic sodium lauryl sulfate (SLS). Samples without surfactant yielded a crystal size of 12 nm. This size is twice as large compared to samples with surfactants that have a size of 6 nm (Chaudhary et al., 2018b).

Furthermore, Mohanty, et al in their research used $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and ZnCl_2 as raw materials, and triethanolamine as precursors. The calcining temperature of 800°C is set for 8 hours. The resulting particle crystal has a size of 35 nm. This size is far from predicted, where based on the Scherer and Williamson-Hall equations the resulting particle should be in the range of 9 nm (Mohanty et al., 2021). However, the resulting crystals are pure ZnAl_2O_4 without other elements. Peymanfar (Peymanfar & Fazlalizadeh, 2021) tried using citric acid as a precursor with aluminum(III) nitrate nanohydrate and zinc(II) nitrate hexahydrate as bases. Synthesis was carried out by sol-gel method with a calcining temperature of 600°C for 4 hours. The results obtained ZnAl_2O_4 particles measuring 30 nm. The difference in particle size clearly proves that surfactants and calcination have an influence in shaping particle size and crystal purity. Tran, et al in the synthesis of ZnAl_2O_4 catalysts tried to use different calcining temperatures for 2 hours with a range of $600^\circ\text{C} - 1400^\circ\text{C}$. The results of imaging using TEM found that the particle size increases with the increase in temperature due to agglomeration. The optimum temperature is seen at 800°C with a much smaller particle size (Tran et al., 2021).

Azar et al in their research offered a green sol-gel method in the synthesis of ZnAl_2O_4 by adding tragacanth gel. In this method, raw material that has been dissolved in deionized water is added with tragacanth gel, and then applied at a temperature of 600°C for 4 hours. The resulting catalyst is at a size of 16 nm. This method has more advantages such as non-toxic, economical, and environmentally friendly (Eskandari Azar et al., 2020).

Co-precipitation

Co-precipitation is one simple method of producing nanoparticles from various inorganic materials. In the process, salts of metal are dissolved in water, and precipitated using precipitating agents. A precipitate in the form of a solid solution containing cations on an atomic scale will be produced. Because the process is simple but can produce on a large scale, several studies agree that this method is one of the best methods in ZnAl_2O_4 synthesis compared to other methods (Habibi et al., 2021). In addition, this method also has the advantage of using much lower temperatures with a high degree of homogenization. Farhadi, et al (Farhadi & Panahandehjoo, 2010) in their research produced ZnAl_2O_4 nanoparticles using ammonia as a precipitating agent. At a calcining temperature of 600°C for 4 hours, Farhadi, et al can produce 8 nm ZnAl_2O_4 . It can be seen that in this method, the temperature used is much lower but still produces nanoparticles

In the same year, Habibi and Ibrahim, et al synthesized ZnAl_2O_4 using the co-precipitation method with ammonia as a precipitating agent. The basic materials used are zinc nitrate and aluminum nitrate which are then calcined at a temperature of 600°C . Habibi, et al (Habibi et al., 2021) produced a much smaller particle size of 3.8 nm while Ibrahim, et al (Ibrahim et al., 2021) of 13 nm. The difference in these two studies is the pH of the solution and the length of calcination time. The calcining process for 4 hours and pH above 10 results in a smaller particle size than the 5-hour calcining time with a pH of 8-9. This proves that in

this method, low time and temperature have managed to obtain a small particle size. Furthermore, Habibi, et al conducted trials by raising the calcining temperature to 800°C and 1000°C, and obtained particle sizes increased to 6.10 nm and 13.70 nm. Furthermore, Mohaqeq (Mohaqeq et al., 2017) in the study synthesized ZnAl_2O_4 with a calcining temperature of 700°C for 4 hours with a pH of 9. The nanoparticles formed are in the range of 21-25 nm. This result is much greater than when using a temperature of 600°C as in the study by Habibi, et al.

Hydrothermal

In general, hydrothermal synthesis is the process of forming crystals in high-pressure hot water in an autoclave (Ishii et al., 2016; Sitohang et al., 2016). In ZnAl_2O_4 synthesis, hydrothermal is an effective option because it can be performed at lower temperatures with less material. This is because this method, the resulting crystals can form at temperatures below 500°C. In addition, hydrothermal synthesis has several advantages such as a simple procedure, stoichiometry, able to control the homogeneity and morphology of particles (Dwibedi et al., 2018). Hydrothermal is divided into 2 synthesis pathways, one-liquid and two-liquid. In the one-liquid path, the precursors used are dissolved simultaneously in distilled water, while in the two-liquid path, each precursor is dissolved in distilled water separately before finally being combined for a second stirring.

Research using the two-liquid pathway by Dwebedi (Dwibedi et al., 2018) obtained a particle size in the range of 100 nm at a calcining temperature of 300°C. The large particle size is certainly far from expected. Ishii, et al then in their research tried to see whether there was an influence of pH in determining the size of the particles produced with a calcining temperature of 200°C. Based on the results of the study, it was found that crystals formed with $\text{pH} < 9$ produced crystals with a size of 13 nm. While crystals with $\text{pH} > 9$ produce crystals of 40 nm using a two-liquid path (Ishii et al., 2016). A different study was conducted by Zhao (Zhao et al., 2015) using a one-liquid pathway. Zinc nitrate hexahydrate and aluminum nitrate nonahydrate are used as precursors with a calcining temperature of 400°C, and crystals with sizes ranging from 5-10 nm are obtained. The particle size is smaller than the two-liquid pathway, because the pH of the sample is conditioned in the range of 6-7. The effect of pH is also proven by Dai (Dai et al., 2018) who use a one-liquid pathway. At neutral pH, ZnAl_2O_4 particles are produced by 14 nm.

Microwave

Microwave irradiation in synthesis reactions is one of the methods being developed lately, because it can synthesize organic and inorganic compounds and is considered an environmentally friendly method compared to other methods (N et al., 2018). This method is a potential technique in the synthesis of spinel nanoparticles, because heat will be directly generated internally within the material itself (Bhavani et al., 2017). The advantages of this method are: faster preheating, improved kinetics, and reaction rate, uniform nucleation,

growth conditions, and the production of nanoparticles with high-purity (Menon et al., 2017, 2020; Padmapriya & Amudhavalli, 2020). Unlike other methods that use furnaces for the calcination process, in this method, direct microwave irradiation is used in calcination. However, this method has several disadvantages such as the high cost of equipment and the limited size of the reactor (Matveyeva et al., 2022).

Research by Bhavani (Bhavani et al., 2017) used zinc nitrates and ferric nitrate as raw materials, with a microwave radiation time of 10 minutes. In a short time, ZnAl_2O_4 nanoparticles are produced with a size of 12-18 nm. On the other hand, Padmapriya (Padmapriya & Amudhavalli, 2020) synthesized ZnAl_2O_4 within the same time period but produced a much larger particle of 50 nm. This can be caused by the presence of aloe vera as a reducing agent mixed in raw material. From several studies, the smallest size was produced by Menon, et al by 5 nm within 10 minutes. This is due to the addition of cetyltrimethylammonium bromide (CTAB) as a surfactant, where the use of organic metal precursors can help the formation of metal oxides through nucleophilic attacks on the carbonyl ligand group.

ZnAl_2O_4 as spinel: ZnAl_2O_4 in chemical reaction

ZnAl_2O_4 as a spinel in organic reactions has been widely studied (Table 2). Several studies prove that spinel ZnAl_2O_4 combined with other elements or compounds has high catalytic activity in each chemical reaction. This is because, with the addition of elements or compounds, the active side on the surface of the catalyst will be higher than the use of ZnAl_2O_4 as a single catalyst. Some chemical reactions that combine spinel ZnAl_2O_4 with other elements are hydrogenation, dehydrogenation, photochemistry, synthesis, metathesis, elimination, and substitution reactions.

Table 2. ZnAl_2O_4 as spinel in organic reactions

No	Reaction	Doping material	Effectivity	References
1	Hydrogenation	Cu	High	(Huš et al., 2017)
		SAPO-34		(X. Liu et al., 2020)
		PdZn		(X. H. Zhang et al., 2019)
2	Dehydrogenasi	ZnO		(Matveyeva et al., 2022)
3	Esterification	SO_4^{2-}	98.2%	(Wang et al., 2018)
		SiO_2	99.2%	(Gharibe, 2020)
4	Degradation	Fe	75%-98%	(Tangcharoen et al., 2021)
		Cu		(Akika et al., 2020b)
		Eu		(Venkatesh et al., 2021)
		Bi_2MoO_6	86.36	(Tian et al., 2020)
		CeO_2	93%-99%	(Dhinakaran et al., 2021)
		CuS	95%	(Fahoul et al., 2022)
		ZnO	92%-99%	(Eskandari Azar et al., 2020; Ghribi et al., 2020; Nasr et al., 2016; Shahmirzaee et al., 2019; L. Zhang et al., 2013)
5	Organic synthesis	CoO	100%	(Birhi et al., 2023)
		Co	99.56%	(Manikandan et al., 2016)

Hydrogenation, dehydrogenation, and esterification reactions

Hydrogenation is a chemical process that produces the addition of hydrogen. Research by Ye (Ye et al., 2021) on the catalytic activity of ZnAl_2O_4 as a single catalyst to convert CO into methanol and dimethyl ether gave positive results. As a single catalyst, ZnAl_2O_4 has an active side in the elements Al and Zn. The Al side activates CO and Zn activates H_2 to become an active format bidentate species and hydrogen is adsorbed to produce methanol/dimethyl ether. The combination of ZnAl_2O_4 with several compounds in hydrogenation reactions by several experts including Cu, SAPO-34, and PdZn proved that catalysts with spinel ZnAl_2O_4 have high catalytic activity in the reaction of hydrogenation of CO_2 into methanol and olefins, as well as hydrolysis of glycerol (Huš et al., 2017; X. Liu et al., 2020; X. H. Zhang et al., 2019). In the dehydrogenation reaction, ZnO combined with spinel ZnAl_2O_4 exhibits high conversion and selectivity. The ZnO in the catalyst helps lower acidity and reduce surface zinc oxide reduction which can negatively impact isobutene dehydrogenation reactions.

In the esterification reaction, ZnAl_2O_4 is combined with SO_4^{2-} and SiO_2 . The catalyst was synthesized to obtain nano-sized particles and tested for catalytic activity in the esterification reaction of acetic acid and phthalic anhydride by 2-ethylhexanol. Each catalyst combination provides very high catalytic effectiveness, 98.2%, and 99.2% (Gharibe, 2020). In addition to having high catalytic activity, catalysts can also be reused but do not decrease their catalytic activity.

Degradation

Degradation is a reaction of chemical change or decomposition of a compound into simpler molecules. ZnAl_2O_4 has become a fairly popular spinel in degradation reactions. Elements such as Fe, Cu, and Eu combined with ZnAl_2O_4 show high catalytic activity ranging from 75% - 98% compared to ZnAl_2O_4 as a single catalyst in the degradation of RhB, MO, MR, MB, and Cr(VI) (Akika et al., 2020a; Tangcharoen et al., 2021). In 2019-2021 several catalysts such as Bi_2MoO_6 , CeO_2 , and CuS have been combined with spinel ZnAl_2O_4 . Each catalyst was shown to have a catalytic effectiveness of 86.36% in methylene blue degradation, 93% - 99% in MB, MO, and RhB degradation, and 95% in acid red degradation (Dhinakaran et al., 2021; Nasr et al., 2016; Tian et al., 2020).

The catalyst most widely combined with spinel ZnAl_2O_4 in degradation reactions is ZnO. Zinc oxide is a semiconductor that is widely used in industrial applications and is considered an alternative catalyst in answering problems related to energy and the environment. ZnO is a semiconductor that is not toxic, but is unable to maintain stability in the long term (Silver et al., 2023; L. Zhang et al., 2013). For this reason, it is necessary to combine with other catalysts such as ZnAl_2O_4 . This has been proven by Zhang, et al where in their research it is said that the combination of ZnO / ZnAl_2O_4 has high photocatalytic

activity up to 99% compared to pure ZnO and ZnAl₂O₄ (Nasr et al., 2016). Other studies have also proven that the use of ZnO/ZnAl₂O₄ catalysts can degrade MO dyes by up to 92%, MB and orange acid 7 by 96%, and degrade water contaminated with metronidazole (Ghribi et al., 2020; Shahmirzaee et al., 2019; Suwanboon et al., 2020).

Organic Synthesis

ZnAl₂O₄ as a single catalyst has been utilized in organic synthesis reactions. Umamahesh (Umamahesh et al., 2015) in their experiments found that a single catalyst ZnAl₂O₄ with a particle size of 6-20 nm at room temperature was able to synthesize 4 components of pseudo pyrimidine chromenoth [2,3-d]. In the following year, we found that ZnAl₂O₄ was shown to have high catalytic activity in the synthesis reaction of vanillin from eugenol (Nofita Birhi et al., 2021). Furthermore, ZnAl₂O₄ is again used in vanillin synthesis but through incorporation with CoO catalysts. Compared to the use of ZnAl₂O₄ as a single catalyst, the CoO/ZnAl₂O₄ combination catalyst has much better catalytic activity with a conversion rate of up to 100% (Birhi et al., 2023). Manikandan (Manikandan et al., 2016) first synthesized benzaldehyde using Co/ZnAl₂O₄ catalysts. The catalyst resulting from green synthesis using aloe vera has a size of 15.72 nm – 26.53 nm with a conversion rate and selectivity reaching 99.56%.

CONCLUSION

ZnAl₂O₄ nanoparticles are heterogeneous catalysts that are environmentally friendly because of their advantages. In the synthesis process, the selection of material ratio, pH, calcination temperature, and synthesis method affect morphology, size, and catalytic activity. The use of green chemistry synthesis methods such as using or mixing raw materials with plant extracts is one alternative in reducing the waste produced. In addition, the use of microwaves also needs to be considered to reduce synthesis time. Unfortunately, the use of microwaves is still a slightly expensive method due to the high cost of the reactor itself. Another alternative that can be done in the synthesis of ZnAl₂O₄ catalysts is to use the combination method.

The combination of ZnAl₂O₄ with other catalysts has been shown to increase catalytic effectiveness better than the use of ZnAl₂O₄ as a single catalyst. In various chemical reactions, combined ZnAl₂O₄ catalysts can be generated and reused without degrading their catalytic effectiveness. The catalyst most widely combined with ZnAl₂O₄ is ZnO. This is because ZnO is a promising catalyst in overcoming energy and environmental supplies, but is less able to maintain its stability. So ZnAl₂O₄ is seen as a suitable spinel to be combined with ZnO. In addition to ZnO, other elements or compounds such as CoO, Cu, Co, Pd, CeO₂, SiO₂, and anions such as SiO₄²⁻ can also be combined with spinel ZnAl₂O₄ and produce high catalytic activity.

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