

LITERATURE STUDY OF THE EFFECT ON DOPING COMPONENT ON THE CE-TI OXIDE CATALYST FOR FLUE GAS DENITRATION WITH NH₃-SCR

Rias Becik Sinawang^{1,2} and Cucuk Evi Lusiani¹

¹Department of Chemical Engineering, Politeknik Negeri Malang, Soekarno-Hatta Street No. 9,

Malang 65141, Indonesia

²College of Chemical and Biological Engineering, Shandong University of Science and Technology, 579 Qianwangang Road, Qingdao, China

riasbecik@gmail.com; [lusiani1891@polinema.ac.id]

ABSTRACT

The Ce-Ti oxide catalyst is viewed as an innovation for the reduction of nitrogen oxide (NO_x) and owns outstanding activity in ammonia-selective catalytic reduction (NH₃-SCR) that became the most used denitration reaction in industry. In the flue gas, there will be many substances that inhibit the catalytic activity. Therefore, adding some components to the Ce-Ti oxide catalyst can be a solution. The aim of this literature study is to analyze the effect of doping components (Fe, Zr, Cu, K) on Ce-Ti oxide catalyst in the NH₃-SCR reaction. Several theories and data methods were collected by comparing data based on catalytic activity and characterization of the catalysts. The activity of the catalyst was obtained by calculating the NO_x conversion. The characterization of the catalysts was detected by BET, H₂-TPR, NH₃-TPD, and XPS. The analysis based on the literature study exhibited a catalyst with the best activities, structures, and properties required to successfully reduce NO_x. The results indicate that the effect on doping components of Fe, Zr, and Cu can enhance the characteristics and protect the reduction ability, whilst the doping of K decreases surface acidity and reducibility on Ce-Ti oxide catalyst.

Keywords: catalytic activity, characterization, denitration, flue gas, NH₃-SCR

1. INTRODUCTION

The flue gas coming from the combustion process contains many components that can damage the environment, so a strategy is expected to reduce these poisonous gases. Currently, several studies discuss reducing nitrogen oxide gas. Two major contaminants that are produced from fossil fuel combustion, which are sulfur dioxide (SO₂) and nitrogen oxides (NO_x). In any case, discharges of NO_x have proceeded to rise, and today NO_x pollution is a major issue in industrialized countries [1].

Nitrogen oxides contribute a lot to corrosive downpours, photochemical exhaust clouds, and the consumption of tropospheric ozone [1]. These problems have immediate and round impacts on human well-being and the ecological environment [2]. Ammonia-selective catalytic reduction (NH₃-SCR) as a solution to reduce nitrogen oxide with a catalyst that works effectively. Numerous catalysts have been performed in that process but still have some limitations. V₂O₅-WO₃/TiO₂ catalyst was the most widely used industrial catalyst [3]. However, vanadium-based catalysts have many disadvantages, such as poor activity at

low temperature, low N₂ selectivity at high temperatures, biotoxicity of V₂O₅, low resistance to alkaline and alkaline earth metals from ash [4]. Therefore, it is especially important to develop new environmentally-friendly catalysts with high activity and selectivity for NO_x removal. The CeO₂-TiO₂ catalyst has gained wide attention for its excellent properties. A study on characterization of CeO₂-TiO₂ catalysts by the single step sol-gel method from Gao et al. (2010) showed that the catalyst achieves excellent NH₃-SCR performance due to the high concentration of amorphous or highly dispersed nano-crystalline ceria and a high concentration of amorphous Ce on the surface played a fundamental part in NO_x reduction [5].

It is widely reported that the destruction of reducing property and surface acidity are two important points in deactivating the catalysts of NH₃-SCR. Du et al. (2012) found that the alkali metal atoms (K⁺, Na⁺, Ca⁺) could interact with the oxygen atoms of CeO₂ and TiO₂ to reduce the reducibility and surface acidity of CeTiO_x catalyst, respectively [6]. Another research from Liu et al. (2013) discovered that CuO-doped CeTiO_x catalyst could improve the denitration activity at low temperature, and they ascribed this prompting effect to double redox cycles [7].

Furthermore, adding active additives to improve the reducibility and surface acidity has caught extensive attention for its high efficiency and flexibility [8]. The addition of Fe³⁺ can efficiently improve the NH₃-SCR activity of Ce-Ti catalyst, which originated from the synergetic effect of Fe and Ce to form reactive intermediates [9]. Moreover, ZrO_2 is widely used as an addictive or co-catalyst for NH₃-SCR for its redox ability, acidity, and excellent dispersing effect by inhibiting particle aggregation. Doping of Zr^{4+} has been proved to efficiently improve the SCR performance and thermal stability of the Ce-based catalyst [10].

According to many substances in the flue gas that inhibit the activity of the catalyst, doping components to the catalyst could be the way to help the catalyst perform optimally. Therefore, the aim of this literature study is to analyze the effect of doping components on Ce-Ti oxide catalyst for flue gas denitration with NH₃-SCR. The evaluation of catalytic activity was performed under NH₃-SCR reaction by calculating the NO_x conversion. The textural features, reductive behaviors, surface acidity, and properties of the catalysts were characterized by BET, H₂-TPR, NH₃-TPD, and XPS.

2. METHODOLOGY

This article is a literature study that is carried out by collecting several theories and data methods. The data are sourced from pre-existing research. The form of this research is qualitative by collecting data on catalytic activity and catalyst characterization, then the analysis comparisons are made and lead to conclusions. These data were concluded to analyze the effect of the doping component on the Ce-Ti oxide catalyst in NH₃-SCR reaction. The data obtained are presented in the form of graphs, and tables are discussed in the next sub-chapter.

2.1. The Procedure of Journal Search

The journal search procedure includes determining the keywords searched for in journal databases such as Science direct, Google scholar, MDPI, and ACS Journal with the same research topic. The selection research results are based on the same variables and

analysis test. The journal search is related to the effect of the doping component on the Ce-Ti oxide catalyst for flue gas denitration with NH₃-SCR. The selection of journals has been prioritized internationally in the last ten years. The data from the journal will be compiled and written as a conclusion.

2.2. The Technique of Data Collection

Data collection is done by comparing data from one journal to the other. Data collection is based on variables:

- The catalytic activity on Ce-Ti catalyst with doping components in NH₃-SCR

- The characterization of the Ce-Ti catalyst with doping components in NH₃-SCR

3. RESULTS AND DISCUSSION

3.1. Catalytic Evaluation on NH₃-SCR Activity

Catalytic performances of the samples for NH₃-SCR of NO_x are shown in Figure 1. NO_x conversion describes percentages of the amount of NO_x that reacted in the reactant. The higher the conversion means the least amount of NO_x [6]. The NO_x conversion of the Ce-Ti catalyst was formed with a mole ratio of 0.5, and it shows the best NH₃-SCR performance [11]. Furthermore, it reaches a maximum NO_x conversion of about 100% within 250 – 350°C. However, the catalytic performance of Ce-Ti catalyst at low-temperature (below 300°C) is still not ideal [12].



Figure 1. NH₃-SCR catalytic activity of the samples within temperature to the value of NO_x conversion [11]–[13]

The Fe/CeTi and Zr/CeTi, both basically retain excellent catalytic activity in the test range. The NO_x conversion of Fe/CeTi and Zr/CeTi is also reduced to some extent [13]. Cu modification can effectively improve the low-temperature activity of Ce-Ti catalysts [12]. It is noteworthy that Cu/CeTi shows better catalytic performance than K/CeTi catalyst over the entire temperature range of the test. The above results show that Cu/CeTi catalysts have good stability in long-term tests. Meanwhile, the catalytic activity of K/CeTi is too low to even reach 20% over the entire temperature interval, and the result

indicates that the potassium resistance of the Ce-Ti catalyst to the NH₃-SCR reaction is very poor [6]. The major by-product of NH₃-SCR is N₂O. However, the N₂O cannot be detected in these samples. It means that NO_x is directly converted to N₂ through those catalysts without the production of N₂O [14].

3.2. Characterization (Textural Features, Reductive Behaviors, and Surface Acidity and Properties) of the Catalysts in NH₃-SCR

The textural features of the samples are exhibited in Table 1. The specific surface area, pore diameter, and pore volume of the catalysts were calculated by the BET (Brunauer-Emmett-Teller) method that calculates based on the adsorption layer thickness [14].

Sample	Surface area (m ² ·g ⁻¹)	Pore volume (cm ³ ·g ⁻¹)	Pore diameter (nm)
Ce-Ti [11]	141	0.14	4.04
Fe/CeTi [13]	200	0.36	7.2
Zr/CeTi [13]	193	0.37	7.7
Cu/CeTi [12]	70	0.23	13.4
K/CeTi [12]	67	0.25	14.5

Table 1. The textural data of the catalyst samples using the BET method

As shown in Table 1, catalysts with larger specific surface areas and larger pore volumes provide more active sites for adsorption of reactants and intermediates, as well as improving the spread of reactant and product molecules, and further enhancing the activity of catalysts [15]. It is also showing the values with the smallest pore diameter of the Ce-Ti catalyst. The introduction of small amounts of cerium species inhibited the formation of nanoparticles, but the further introduction of cerium increased the pore diameter due to the formation of secondary particle piled pore due to the agglomeration of nanoparticle building blocks [11].

On the other hand, Fe/CeTi retains maximum specific surface area, further promoting Fe dispersion and grain growth. Doping of Fe, Zr, and Cu can partially inhibit crystallization and further increase the specific surface area compared to K/CeTi [13]. The surface of the doped K catalyst is smaller than the others, indicating that K species are predominantly present on the pore structure and the surface of the catalyst, which can have a certain adverse effect on catalytic activity. However, the BET specific surface area and total pore volume of the catalyst decrease after Cu modification, but the average pore diameter increases. This can cause some of the loaded Cu particles to cover the surface and block it in the pores of the catalyst [12].

The reductive behaviors of the catalyst are generally accepted to be important for NH_3 -SCR, which can be tested with H_2 -temperature programmed reduction (H_2 -TPR), and the results are summarized in Table 2.

Comulo	Peak temp	H ₂ consumption (µmol·g ⁻¹)			
Sample	T ₁	T ₁ T ₂		S ₂	S ₁ + S ₂
Ce-Ti [12]	463	598	107	7	114
Fe/CeTi [13]	401	551	143	25	168
Zr/CeTi [13]	519	617	97	24	121
Cu/CeTi [12]	186	234	88	103	191
K/CeTi [12]	539	630	73	10	83

Table 2. The reductive behaviors of the catalysts tested using H₂-TPR

Table 2 present of Ce-Ti catalyst has the broad temperature peaks that are shown near 463, and 598°C belong to the reduction of Ce-O-Ti structure due to surface and bulk. The reduction of peak temperature of the Ce-Ti catalyst is much lower than those of pure TiO₂ and CeO₂ due to the interaction between Ce and Ti caused by the incorporation of Ce⁴⁺ into the lattice of TiO₂ [16].

In contrast to the Ce-Ti catalyst, the K/CeTi has a reduction peak that moves towards high temperature orientation, and the H₂ consumption of the K/CeTi reaches 83 μ mol·g⁻¹ lower than the 114 μ mol·g⁻¹ of Ce-Ti. This indicates that K-doping adversely affects the reducing properties of the catalyst [12]. The strong bond between K and Ce weakens the Ce-Ti catalyst [17]. Otherwise, the H₂ consumption of Fe/CeTi, Zr/CeTi, and Cu/CeTi have higher values. It means that doping of Fe, Zr, and Cu plays an important role in improving the reducing ability [13]. Moreover, the H₂ consumption of Cu/CeTi has the highest value means that the Ce-Ti component in this catalyst is hard to be fully reduced [12].

An important role in NH₃-SCR reaction is the amount and strength of surface acid over Ce-Ti based catalysts [18]. Therefore, the catalysts are investigated by NH₃-temperature programmed desorption (NH₃-TPD) that is conducted in Table 3.

Three kinds of desorption peaks are marked as I, II, and III, which are attributed to weak acid sites (including physical adsorption of NH₃), medium-strong acid sites, and strong acid sites, respectively [19]. These three kinds of acid sites are all present on the Ce-Ti catalyst. The desorption peak III is missing in the K/CeTi and Cu/CeTi catalysts and leaves only two desorption peaks.

From the amounts in Table 3, it can be shown that the total acid content of the K/CeTi catalyst is 849 a.u. which is lower than Ce-Ti catalyst with 3026 a.u. The results show that K seriously damages the surface acidity of the Ce-Ti catalyst. The total amount of acid in the Cu/CeTi catalyst is 2016 a.u. that can be seen it is clearly not as high as K/CeTi. The result of this Cu can further protect the surface acidity of the Ce-O-Ti component in the Cu/CeTi catalyst [12].

It is worth noting that the total acid content of the Fe/CeTi has the highest acid content among all samples. This suggests that Fe³⁺ doping can effectively increase the surface acidity of Ce-Ti, but is strongly influenced by other inhibitors. The Zr/CeTi has the

strongest acidic center (S_{III}), and Zr⁴⁺ doping can effectively reduce the adverse effects on surface acidity [12].

Identify the surface properties (surface constituents and element oxidation states) of those catalyst samples can be characterized by x-ray photoelectron spectroscopy (XPS) that is shown in Table 4. XPS was used to test the atomic conversion of the active site and the atomic properties of the tested catalyst. Each binding energy (B.E.) was calibrated using C 1s (B.E. = 284.8 eV) as a standard [11]. It is known that the surface composition and oxidation state of the catalyst is very important for the NH₃-SCR reaction and can have a significant effect on the adsorption and activation of reactant molecules [20].

Sampla	Acid a	mount	(a.u.)	Total acid amount (a.u.)			
Sample	Sı	Sıı	SIII	S ₁ + S ₁₁ + S ₁₁₁			
Ce-Ti [12]	968	1937	121	3026			
Fe/CeTi [13]	1289	2749	324	4362			
Zr/CeTi [13]	1158	2287	415	3860			
Cu/CeTi [12]	927	1089	-	2016			
K/CeTi [12]	365	484	-	849			

Table 3. The amount of surface acidity on the catalysts tested using NH₃-TPD

Table 4. Surface atomic concentration and ratio of the catalysts by XPS

Sample	Atomic concentration (%)						Atomic ratio (%)				
	Ce	Ti	0	Fe	Zr	Cu	к	Ce/Ti	Fe/Ti	Zr/Ti	Cu/Ti
Ce-Ti [12]	0.65	28.06	72.05	-	-	-	-	3.52	-	-	-
Fe/CeTi [13]	0.77	24.88	69.86	4.49	-	-	-	3.09	18.05	-	-
Zr/CeTi [13]	0.44	25.25	71.38	-	2.93	-	-	1.74	-	11.60	-
Cu/CeTi [12]	0.63	25.26	72.16	-	-	1.95	-	2.92	-	-	9.64
K/CeTi [12]	0.87	24.33	70.21	-	-	-	4.59	3.34	-	-	-

In Table 4, we can see that the Cu/CeTi content is the lowest at 9.64%. While the result of atomic ratio on K-doping is not detected, it probably has some negative effect on the electron interaction between Ce and Ti species [12]. The surface Ce/Ti atomic ratio of the Ce-Ti catalyst decreases after adding the component. This may be due to the added component covering the surface of Ce species, thus reducing the active Ce-O-Ti species

further reduces the SCR activity of Ce-Ti. The atomic ratio of Ce/Ti becomes the lowest compared to Zr/Ti, and it can be pointed out that Zr⁴⁺ doping can effectively suppress Ce species on the surface [13].

The Ce³⁺ ratios could be ranked as follows: Ce-Ti (3.52) > K/CeTi (3.34) > Fe/CeTi (3.09) > Cu/CeTi (2.92) > Zr/CeTi (1.74). The highest Ce³⁺ ratio of 3.52 was observed for Ce-Ti. An excellent SCR activity was achieved at higher Ce³⁺ ratios [11]. The presence of more Ce³⁺ species was beneficial in creating more oxygen vacancies, promoting the redox conversion between Ce³⁺ and Ce⁴⁺ [21]. Moreover, the enrichment of Ce³⁺ species could result in more charge imbalance and unsaturated chemical bonds, which increase the number of oxygen species adsorbed and further improve the performance of NH₃-SCR [22].

4. CONCLUSION

The excellent catalytic activity has been shown by the Ce-Ti catalyst over a broad operating temperature window. Furthermore, the doping components of Fe, Zr, and Cu performed in good catalytic activity. The textural features, reductive behaviors, surface acidity, and properties have slightly different results. But, overall can efficiently protect the reduction ability of the catalyst. On the other hand, K/CeTi has poor catalytic activity, and doping K to the Ce-Ti oxide catalyst causes decreasing of surface acidity and reducibility. Since the doping component could improve the activity and characteristics of the Ce-Ti oxide catalyst, the reaction will have significant enhancements and perform more effectively.

It should be noted that, despite significant progress, there are still challenges in the use of doping components on the Ce-Ti oxide catalyst in NH_3 -SCR. The improvement of this study is very helpful for the future. Future research should concentrate on the significant advancements in the improvement of the doping component and the other factors that influence the catalyst, such as the preparation method, the gas hourly space velocity, and the mole ratio.

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