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Effect of Ag addition into the Activity of Titanium Silicate-1 Catalyst in Cyclohexanone Reaction

Dyah Fitasari*[1], Didik Prasetyoko[2], Suprapto[2]

[1]Universitas Islam Negeri Walisongo Semarang, Jawa Tengah, Indonesia
[2]Institut Teknologi Sepuluh Nopember, Surabaya, Jawa Timur, Indonesia
*E-mail: dyahfitasari@walisongo.ac.id

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Abstract

Titanium Silicate-1 (TS-1) has been successfully modified by combining Silver (Ag) metals. In this study, the preparation of Ag/TS-1 was carried out by impregnation method using a solution of silver nitrate (AgNO3) as a precursor to TS-1 with a loading variation of 0.5%, 1%, 2%, and 4%. Impregnation carried out on TS-1 aims to disperse Ag (1) only attached to the surface of TS-1 particles (before calcination/TK) and (2) on the entire surface of TS-1 particles (after calcination/K). The synthesized catalyst was then characterized by X-ray diffraction, infrared spectroscopy, and pyridine adsorption techniques. The XRD pattern shows that all the catalysts have high crystallinity with MFI structure, and there is no other crystalline phase. The infrared spectra showed that the titanium tetrahedral in TS-1 remained after Ag impregnation. The TS-1 and Ag/TS-1 catalysts were analyzed for their surface acidity using pyridine adsorption on the sample. The pyridine adsorption technique showed the presence of Lewis sites on Ag/TS-1. In this study, the presence of Ag loading on the Ag/TS-1 catalyst affected the TS-1 catalytic activity. The amount of cyclohexanone oxime product produced in XAg/TS-1 was more than in Ag/TS-1.

Keywords: Ag/TS-1; catalyst; cyclohexanone; acidity

Introduction

Titanium Silicate-1 (TS-1) can catalyze various organic mixtures by using hydrogen peroxide (H_2O_2) as an oxidant. It is environmental-friendly because it only produces water as a by-product (Clerici, 2015). TS-1 also has excellent performance against a variety of hydrocarbon selective oxidation processes by using H_2O_2 as an oxidant and has high activity and selectivity against cyclohexanone oxime (Yang et al., 2008).

TS-1 catalyst has been doped by using Fe metal and investigated its surface properties (Saxena et al., 2007). Saxena proved that the amoximation reaction using TS-1 catalyst resulted in 56.50% conversion and 99.29% selectivity, while the amoximation reaction using TS-1 catalyst doped with Fe resulted in 69.89% conversion and 99.72% selectivity. Amoximation reaction using TS-1 catalyst doped with Fe has high conversion and selectivity due to the higher number of active sites and higher reduction potential of Fe than Ti.

Silver (Ag) is a good catalyst for oxidation reaction, such as ethylene epoxidation, formaldehyde synthesis, selective catalytic oxidation of ammonia, partial oxidation of benzyl alcohol, methane combined oxidative, styrene oxidation, selective oxidation of ethylene glycol, and CO oxidation. The performance of Ag catalyst depends on the surface structure and the surface-active sites, which are strongly influenced by the preparation method, pretreatment, reaction conditions, and the size of Ag nanoparticles. Ag catalyst activation is the result of various Ag-O interactions, like the presence of molecular, surface, and sub-surface of oxygen atoms (X. Zhang et al., 2010).

This research aimed to know how the effect of adding Ag metal which is loaded on the TS-1 catalyst. Ag was chosen because it is an oxidizing agent that helps oxidation. In addition, Ag has a higher reduction potential value than Fe. It is expected that the use of Ag Metal will increase conversion and high selectivity as well.

Amoximation of cyclohexanone to cyclohexanone oxime is a reaction between cyclohexanone and hydroxylamine sulfate. This reaction is a non-catalytic reaction that has several weaknesses, including oxime production goes through many stages so that it takes a long time and high production costs, and produces ammonium sulfate as a by-product that can cause problems in the environment (Xia et al., 2017). To cope with the increasing demand for nylon-6 in the world market, as well as to overcome the drawbacks of non-catalytic reactions, the researchers developed new methods to increase the production of cyclohexanone oxime through an environmental-friendly process.

Cyclohexanone oxime can be obtained from several mechanisms, namely through the formation of hydroxylamine and imine. The reaction mechanism does not only form cyclohexanone oxime products but also produces many by-products, including organic and inorganic ones.

(Gabrysch, 2019) proposed a mechanism of the amoximation process through unstable intermediates. The same mechanism had been reported for the gas phase amoximation reaction of cyclohexanone in the presence of NH_3 and O_2 and had been supported by IR spectroscopy which proved the formation of adsorbed imine species on the surface of TS-1. The imine intermediate is then oxidized by the titanium active site to oxime. Besides limiting the diffusion of cyclohexanone and oxime in the zeolite pores, good catalytic performance was observed by several groups by using TS-1 (Wu et al., 2014).

The use of metal Ti combined with various supporting substances like Ti, Na-ZSM5, Ti, Na-USY, Ti, Na-erinite, and Ti, Na-zeolite as catalysts in the amoximation reaction of cyclohexanone. Amoximation of cyclohexanone had also been carried out with SiO_2-TiO_2 (Xia et al., 2017), amorphous silica, and supported-titanium silicate, as well as non-redox reactions. Enichem had developed a catalytic process by using a titanium silicalite 1 (TS-1) catalyst for the amoximation reaction of cyclohexanone to cyclohexanone oxime. The structure of TS-1 was similar to zeolite, which has the same MFI structure. Zeolite contains Si and Al atoms, while TS-1 contains only Si and Ti atoms. The purpose of this study was to determine the effect of adding Ag to TS-1 on the structure and properties as well as its activity in the amoximation reaction of cyclohexanone.

Research Methods

Materials and Tools

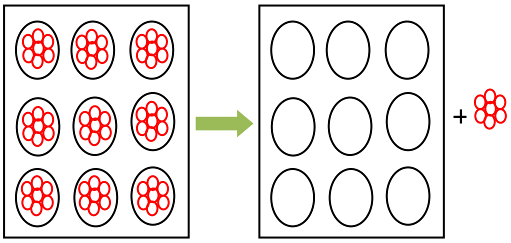
The materials used were tetraethyl orthosilicate (TEOS, Merck, 98%), tetrabutyl orthotitanate (TBOT, Merck, 99%), tetrapropilamonium hydroxide (TPAOH, Merck, 40% in water), distilled water, 2-propanol, and silver nitrate (Merck). The equipment used in this study were the Phillips Expert X-Ray Diffraction Instrument, and FTIR, beaker glass 250 ml, hotplate magnetic stirrer, test tube, measuring cup, thermometer, dropper pipette, stirring rod, oven, analytical balance, and stainless-steel autoclave reactor.

Procedure

TS-1 catalyst (1% mole titanium) was synthesized based on the procedure obtained from a patent (T. Zhang et al., 2016) by replacing TEOT as a titanium source with Tetrabutyl orthotitanate (TBOT) (Kimia & Iii, n.d.). The addition of metal Ag to the catalyst TS-1 used the impregnation method. It is adding titanium silicalite (TS-1 in a solution of silver nitrate ($AgNO_3$) obtained by dissolving silver nitrate in distilled water. The titanium silicalite mixture in the silver nitrate solution was stirred using a magnetic stirrer at 80ºC for 3 hours. The mixture was then evaporated at a temperature of 80-100ºC to remove water. This step was repeated according to the predetermined composition. The solid obtained was then dried at a temperature of 110ºC for 24 hours and calcined at a temperature of 550ºC for 5 hours (Shylesh et al., 2005) and (Chary et al., 2003). Ag/TS-1 catalyst was made by weight percentage of $AgNO_3$ 0.5%, 1%, 2%, and 4%.

Results and Discussion

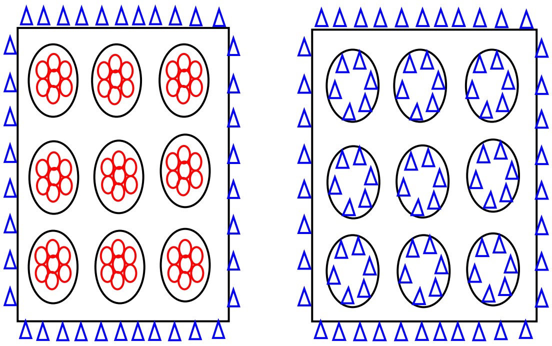
In this research, the preparation of Ag/TS-1 was carried out by impregnation method by using a solution of silver nitrate ($AgNO_3$) as a precursor to TS-1 with a loading variation of 0.5%, 1%, 2%, and 4%. Impregnation was carried out on TS-1 before calcination aimed to disperse Ag only on the surface of TS-1 particles/crystallites because there was still an organic template in the pores of TS-1, namely TPA (Figure 1 (a)). Therefore, $AgNO_3$ could not enter the pores which were already full of templates, and only stuck to the crystal surface (Figure 2 (a)) which was depicted in 2 dimensions. In addition, impregnation was also carried out on TS-1 after calcination, which aimed to disperse Ag on the entire surface of TS-1 including in the pores of TS-1 because the template in the TS-1 pores would be decomposed (Fig. 1 (b)). Therefore, Ag could enter the pores (Figure 2 (b)). However, in this impregnation, it is expected that Ag will be deposited on the surface of TS-1, so that the initial structure of TS-1 does not change.



a. Before Calcination

b. Before calcination

Figure 1. Pore Description of TS-1



Note: △= Ag

a. on the surface of crystalline

b. on the entire surface of crystalline

Figure 2. Description of Ag dispersion on the surface of the catalyst

Infrared spectroscopy was applied to the catalyst to identify the adsorbed species and determine the way the species bonded chemically to the catalyst surface. FTIR was used to identify materials, determine the composition of mixtures, and help to provide information in estimating molecular structures.

The catalyst samples TS-1 and X Ag/TS-1 that showed absorption bands at wavenumbers around 1100, 800, and 450 cm^{-1} were lattice vibrational modes associated with internal bonds in SiO_4 or AlO^4 tetrahedral. The absorption band at a wavenumber of about 1100 cm^{-1} was the Si-O-Si asymmetrical vibration mode, while the absorption band at a wavenumber of around 800 cm^{-1} was the symmetrical one. The absorption band that appeared at a wavenumber of around 1230 and 547 cm^{-1} was the characteristic of the tetrahedral structure in a zeolite framework with MFI type (Mulyatun & Prasetyoko, 2011). The absorption band that appeared at a wavenumber of around 970 cm^{-1} was the characteristic of TS-1. It indicated that the presence of titanium atoms in the structure of the TS-1 catalyst. The absorption band in the wavenumber of about 970 cm^{-1} was the stretching vibration mode of the Si-O- group of the $[SiO^4]$ unit bound to the Ti^{IV} atom with tetrahedral coordination in the TS-1 framework (Li et al., 2001). Besides that, it is also the asymmetric stretching vibration mode of the Si-O-Ti (Budiarti et al., 2017) and (Gabrysch, 2019). It can be concluded that the absorption band in the wavenumber of about 970 cm^{-1} was evidence of the inclusion of titanium in the structure of the TS-1 catalyst.

The results of the FTIR analysis on the TS-1 and X Ag/TS-1 catalyst samples shown in Figure 3 showed the same absorption band. The absorption band at 970 cm^{-1} was narrower than the absorption band at 800 cm^{-1}.

The X-ray diffraction pattern of the XAg/TS-1 sample showed similarities to the structure of TS-1. The highest peaks that appeared were also in the range of 2q = 23.04º; 23.08º; 23.12º; 23.24º; 23.28º; and 23.32º. This indicated that the XAg/TS-1 catalyst also belongs to the MFI structure type and ~~is~~ orthorhombic symmetry. The similarity of the X-ray diffraction pattern between XAg/TS-1 and TS-1 samples indicated that the addition of Ag metal did not change the MFI framework. This indicated that the MFI framework was stable.

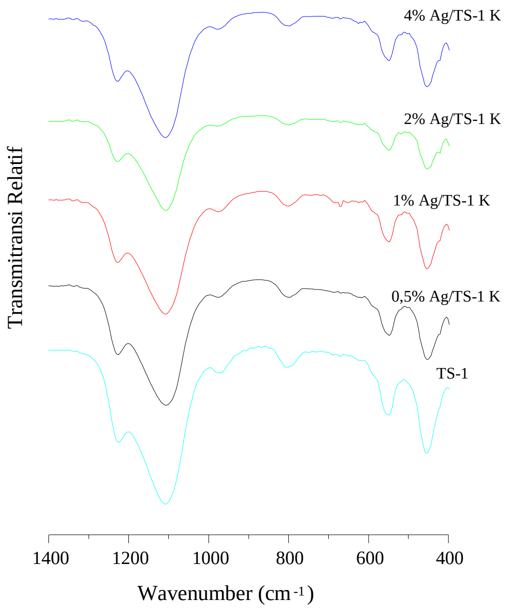


Figure 3. Transmittance analysis of FTIR TS-1 and X Ag/TS-1

The addition of Ag metal on the surface of the TS-1 catalyst only caused the crystallinity of the material to decrease slightly, so it did not change the crystal structure of the MFI catalyst. The peak intensity at 2θ around 23.14º of the catalyst samples showed a decrease as well as the increasing Ag loading on TS-1 as summarized in Table 1. This was due to the decrease in the percentage of TS-1 in the sample along with the increased percentage of additional Ag. Impregnation of Ag on the surface of the TS-1 particle caused the partial closure of the surface of the TS-1 particle. This is what caused a decrease in peak intensity at 2θ around 23.14º (Treacy & Higgins, 2001).

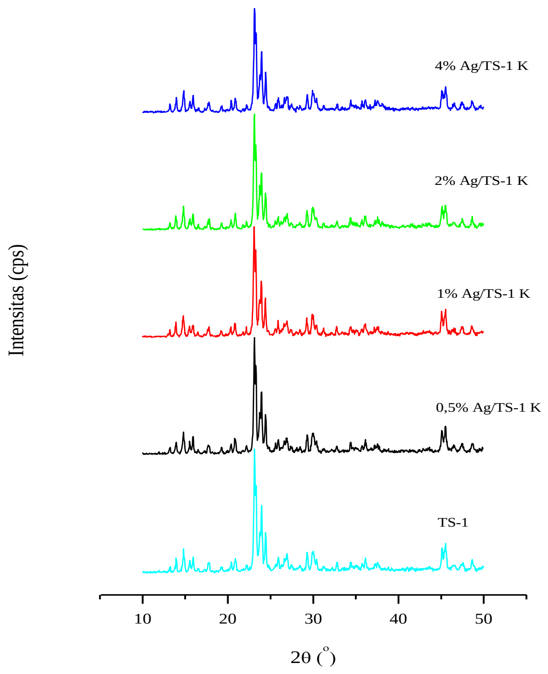


Figure 4. X-Ray Diffractogram of TS-1 and X Ag/TS-1

X-ray diffraction results up to loading 4% Ag/TS-1 did not show any detectable Ag or Ag2O diffraction peaks. This is possible due to the small particle size and low Ag content. Loading Ag did not form large particles due to evidence of the absence of peaks indicating Ag metal that was observed yet dispersed in the micropores of the TS-1 structure. Ag peaks were seen at 38.2, 44.2, 64.4, and 77.1 appeared on the 8% Ag/SiO_2 catalyst (X. Zhang et al., 2010).

Acidity test was carried out by adsorption of pyridine at room temperature after the evacuation of 400°C to remove the adsorbed water on the sample. Soon after the adsorption of pyridine at room temperature, the sample was then heated at 150°C for 3 hours to remove the physically bound pyridine. Following this, the samples were analyzed using infrared spectroscopy techniques. The amount of adsorbed pyridine was observed using infrared spectroscopy technique in the area of 1700-1400 cm-1. The absorption band of the sample in the pyridine region (1700-1400 cm-1) is shown in Figure 5.

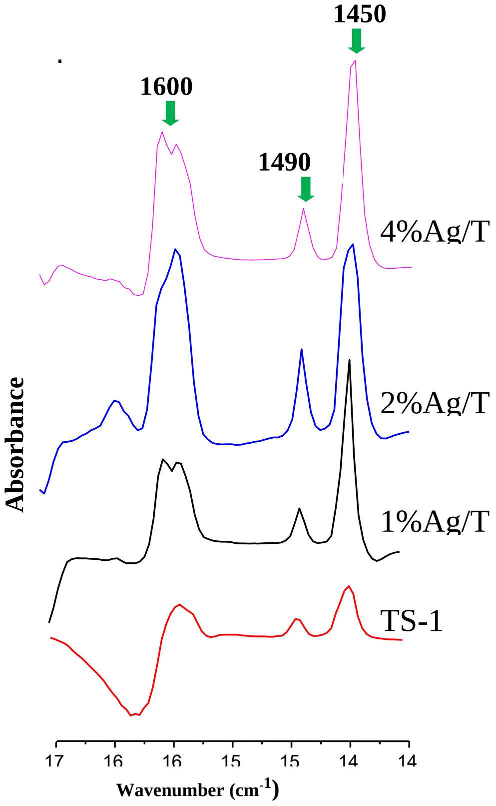


Figure 5. FTIR spectra for samples TS-1 and XAg/TS-1

Table 1. Crystallinity and peak intensity of samples TS-1 and X Ag/TS-1 (XRD data)

Catalyst	Intensity at 2θ = 23,14 Cps	Relative Crystallinity (%)
TS-1	1392.26	100.00
0.5% Ag/TS-1 K	1338.8	96.16
1% Ag/TS-1 K	1236.28	88.80
2% Ag/TS-1 K	1281.36	95.68
4% Ag/TS-1 K	1249.82	89.77
0.5%Ag/TS-1TK	1338.8	96.16
1% Ag/TS-1 TK	1367.99	98.26
2% Ag/TS-1 TK	1322.56	94.99
4% Ag/TS-1 TK	1291.13	92.74

The results of the acidity test in this study can be seen in Figure 5. The FTIR-pyridine TS-1 spectrum showed an absorption band at wavenumber~~s~~ around 1445 cm-1, while the absorption band in the 1540 cm1 region did not appear. This proves that TS-1 has only Lewis acid sites and no Brønsted acid sites. This result is in line with the research of Nur et al., (2004) which states that the FTIR-pyridine peak for TS-1 and SO4/TS-1 only appears at the Lewis acid site. The Lewis acid site in TS-1 appeared due to the presence of a tetrahedrally coordinated titanium atom in the TS-1 lattice structure (Nur et al., 2004) and (Zhuang et al., 2004).

The adding of Ag on the surface of TS-1 did not cause the appearance of a Brønsted acid site which was indicated by the absence of an absorption band at 1546 cm-1, yet only an absorption band at 1445 cm-1 which indicated the presence of a Lewis acid site (Figure 5).

In this study, the presence of Ag loading on the Ag/TS-1 catalyst affected the TS-1 catalytic activity. Ag which is an oxidizing agent helps the oxidation process, thereby increasing the catalytic activity of TS-1 where Ti is also an oxidizing agent. $AgNO_3$ added to TS-1 due to the heating process will turn into Ag_2O. Although Ag_2O theoretically decomposes at a temperature of 280 °C, based on research by Zhang et al., (2010) at 550 °C heating not all Ag_2O turns into Ag, so it is still possible for the reduction reaction of Ag_2O to become Ag so that it can help the oxidation reaction process.

In Table 2. it can be seen that in the amoximation reaction of cyclohexanone, 1%Ag/TS-1 K catalyst showed the highest activity compared to other catalysts in producing cyclohexanone oxime. The 1%Ag/TS-1 K catalyst was able to produce much more cyclohexanone oxime than other catalysts. A total of 0.7385 mmol cyclohexanone oxime was successfully produced using 1%Ag/TS-1 K, the highest among the production using other catalysts.

Table 2. Effect of catalyst on the amount of cyclohexanone oxime product and TOF value on amoximation reaction of cyclohexanone with H_2O_2

catalyst	mol Ti (10^{-5})	TOF (hour^{-1})
TS-1	5,3260	4,28
0,5%Ag/TS-1 TK	5,2738	4,41
1%Ag/TS-1 TK	4,7721	2,61
2%Ag/TS-1 TK	5,3560	3,37
4%Ag/TS-1 TK	4,8769	1,99
0,5%Ag/TS-1 K	5,4302	1,78
1%Ag/TS-1 K	5,2551	7,03
2%Ag/TS-1 K	5,3475	4,80
4%Ag/TS-1 K	5,1645	2,19

Conclusion

The addition of Metal Ag on the TS-1 catalyst did not change the crystal structure of the MFI catalyst. The decrease of the intensity of the diffraction peak (crystallinity) of TS-1 after the addition of AgNO3 indicated that Ag was already on the surface of the TS-1 catalyst.

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