Isopropyl Alcohol Combustion on Ferrite Catalyst NiFe₂O₄

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Abstract: Feasibility of combustion of volatile organic compounds (VOCs) using ferrite catalyst NiFe₂O₄ are investigated. A systematic catalytic evaluation study as a function of various process parameters is performed. Isopropyl alcohol (IPA) was used as a simulated model compound VOC herein. It includes the preparation of the ferrite catalyst, the screening of catalytic activity, catalytic combustion testing and 72 hr-decay testing of the catalyst. The results demonstrated that over 95% IPA conversion was obtained at a space velocity of 24000 hr⁻¹, an O₂ content of 21%, 1700 ppm of isopropyl alcohol and a reaction temperature of 230 \square . It is supposed that Ni-ferrite catalyst (NiFe₂O₄) has a great potential in treating isopropyl alcohol streams, helping industrial plants to reduce the emission of VOC derived from isopropyl alcohol.

Key-words: VOC, combustion, isopropyl alcohol, ferrite, catalyst, NiFe₂O₄

1 Introduction

Volatile organic compounds (VOCs) are a group of anthropogenic or biogenic organic compounds with high vapor pressures. There are thousands of different VOCs produced in our daily lives. One of them is derived from isopropyl alcohol (IPA).

Isopropyl alcohol is a common organic solvent that can be used as an industrial raw material, as a dehydrating agent, as antifreeze, as an anticorrosive and in dry jets. However, IPA is associated with problems of VOCs.

The ferrite process (FP) method has been used for many years to treat heavy metal wastewater [1-5]. In 1959, Feitknecht considered the addition of air to Fe(OH)₂ suspension solution to form Fe_3O_4 . This work marked the beginning of manufacturing ferrite spinel by the wet method. Its reaction is showed as Equation 1.

 $3 \text{ Fe}^{2+} + 6 \text{ OH} \quad 1/2 \text{ O}_2 \rightarrow \text{Fe}_3 \text{O}_4 \quad 3 \text{ H}_2 \text{O}$ (1)

When the solution has other coexisting metal ions, the reaction must be showed as Equation 2.

x M^{2+} (3-x) Fe^{2+} 6 OH 1/2 $O_2 \rightarrow$

 $M_x Fe_{(3-x)}O_4 \ 3 H_2O$ (2)

Equation 2 is the principle of FP in treating heavy metal wastewater [5]. The heavy metal ions can be removed from a solution by situating at the lattice point in a spinel structure. Japan has numerous examples of using FP in this way [3,4,6,7].

In recent years, the sludge generated from ferrite process has been used as recycled products, such as magnetic signs, absorbent of electric waves, and catalysts. Some investigations have addressed the results of activity and characteristic despite the catalytic combustion of IPA with ferrite catalysts [8-14]. Our previous work has proven that the Mn-ferrite catalyst (MnFe₂O₄) has a highly potential in combustion of VOCs [15].

The cited works addressed preparing Ni-ferrite catalyst from FP, and combustion IPA using prepared catalysts in the laboratory. This work covers the preparation of ferrite catalyst, the screening of catalytic activity, the catalytic combustion test and the 72 hr-decay testing.

2 Materials and Methods 2.1 Experimental apparatus

Figure 1 presents the experimental apparatus, which include an IPA feeding system, a catalytic reaction system and a product sampling and analysis system.



Figure 1 The schematic diagram of the catalytic combustion

2.1.1 IPA feeding system

The IPA feeding system used herein involved three gases - isopropyl alcohol, nitrogen and air - which were carried to the reaction system through individual stainless steel pipes. The gases were filtered using a filter (GF-IMS 100, SGE, Australia) to eliminate moisture and impurities to prevent damage to the flow meter. Besides, the mass-flow meter was used to control precisely the rate of flow. The gases were uniformly mixed in a mixing chamber before they entered the reaction system.

2.1.2 Catalytic reaction system

A catalytic reaction system was set up to heat a catalytic reaction tube in a furnace. The reaction tube was quartz, with a length of 30 cm and a diameter of 2.54 cm; a quartz spacer was placed in the center of the tube to support the catalysts. Before the catalysts were installed, a layer of glass wool and 5 g of glass sand were introduced to prevent the catalysts (5 g) from being removed and clogging the pores of the catalytic bed, causing a pressure drop. The catalysts were screened to ensure they were of uniform size before they were packed. After they had been packed, a layer of glass sand was placed above the catalysts to ensure that the gases entered the catalytic bed uniformly, to prevent turbulence on the catalytic bed. A K-type thermocouple was placed above the catalytic bed to measure the temperature in the tube. Besides, a temperature controller was used to control heating in the furnace. 2.1.3 Sampling and analysis of products

As the mixed gases passed the catalytic reaction system, they reacted and then were collected in sampling bags, before being injected into a GC to analyze the concentration of IPA using a flammable ionic detector (FID). A flue gas analyzer (IMR 2000, Germany) and GC/TCD (GC-14A TCD system, Shimadzu, Japan) were utilized to monitor O_2 content and measure the amount of CO_2 produced.

2.2 Experimental plan

The four parts of this study herein were preparing ferrite catalysts; screening catalyst activity, performing the combustion conversion of IPA with various operating parameters, and conducting the 72 hr-decay testing of catalyst. Each part is described below.

2.2.1 Preparing ferrite catalysts

Three ferrite catalysts were prepared (Cr/Fe, Zn/Fe, Ni/Fe, at molar ratio 1/5, 1/10, 1/20, respectively). All of the catalysts were synthesized in the laboratory. For instance, the Ni and Fe in the Ni/Fe catalyst were obtained from the pure chemicals NiSO₄·6H₂O and FeSO₄·7H₂O. We add 1 liter solution with 002 mole of NiSO₄·6H₂O and 0.1mole of FeSO₄·7H₂O into the reactor, agitating the solution and mixing it uniformly. Adjust the pH value of solution in advance by adding NaOH, then heat the solution until reaching the preset reaction temperature. Supply air and begin measuring the reaction time. The method of preparation involved mixing NiSO₄·6H₂O with FeSO₄·7H₂O at pH=9, temperature= $80\Box$, air supply rate=3 L/min and reaction time=60 min.

2.2.2 Analysis of SEM/EDS

The scanning electron microscope (SEM) and energy dispersive X-Ray spectrum (EDS) (JEOL, JSM-6400) were used to observe the surface of catalysts, especially on the particle size and the component of the catalysts.

2.2.3 Screening catalytic activity

The IPA conversion on three metallic spinel catalysts were compared at operating temperatures of $150\Box$ and $200\Box$, an IPA inlet concentration of 1700 ppm and an oxygen content of 21%. The catalyst with the highest activity was chosen to examine the combustion of IPA in dependence of different operating parameters.

2.2.4 Combustion conversion of IPA with various operation parameters

The section discusses various operation parameters that affect the combustion of IPA conversion. The blank test, the Ni loading, the IPA inlet concentration, and the space velocity, were considered.

2.2.5 72 hr decay test of Catalyst

The combustion efficiency over 72 hr was investigated at $175\Box$, $200\Box$ and $225\Box$, at the following operating parameters - IPA=1700 ppm, oxygen content =21% and space velocity=24000 hr⁻¹

3 Results and Discussions

3.1 Screening catalyst activity

Figure 2 shows the conversion obtained using the above catalysts at temperatures 150 and 200. The order of IPA conversion was Ni/Fe > Zn/Fe > Cr/Fe; Ni/Fe was the optimum catalyst, with a 30% IPA conversion at 150 and 85% at 200.

The comparisions in Figure 2 demonstrate that the differences among the conversion efficiency of IPA oxidation were significant. Accordingly, the Ni in a catalyst is probably important in the combustion of IPA. Therefore, the performance of the Ni-ferrite catalyst is examined further below.



Figure 2: Effect of temperature on conversion of IPA in different metal catalysts. Test conditions: Inlet Conc.=1700 ppm, $SV=24000 \text{ hr}^{-1}$, 21% O₂.

3.2 Catalytic combustion system test 3.2.1 Blank test of combustion system

The catalyst was replaced with the same volume of glass wool on a reactive bed as a blank. Figure 3 plots the IPA conversions at various reaction temperatures. Figure 3 shows that the conversion of IPA was only 10% at 200 \square and 75% at 500 \square in the absence of catalyst, indicating that the destruction of IPA is associated with the consumption of much energy when no catalyst was used.



Figure 3: Effect of temperature on conversion of IPA in blank test. Test conditions: Inlet Conc.=1700 ppm, $SV=24000 \text{ hr}^{-1}$, 21% O₂.

3.2.2 Ni loading

After Ni/Fe had been chosen as the catalyst for further testing, various loads were compared and molar ratios of Ni/Fe (molar ratio=1/5; 1/10 and 1/20) were considered, yielding the results in Figure 4. The effects of the Ni/Fe ratio and temperature on IPA conversion were thus determined.



Figure 4: Effect of temperature on conversion of IPA in different molar ratios of Ni/Fe catalyst. Test conditions: Inlet Conc.=1700 ppm, $SV=24000 \text{ hr}^{-1}$, 21% O₂.

The order of IPA conversions was Ni/Fe (molar ratio=1/5) > Ni/Fe (molar ratio=1/10) > Ni/Fe (molar ratio=1/20). Clearly, a greater Ni content corresponded to a higher conversion of IPA. Hence, the Ni metal was the important constituent of this catalytic reaction. At 230 \square , Ni/Fe (molar ratio=1/5) and Ni/Fe (molar ratio=1/10) both yielded conversions of 95%. In this work, the catalyst was Ni/Fe with a spinel structure and the chemical formula (NiO)Fe₂O₃. It is a composite with one Ni⁺² ion, two Fe⁺³ ions and four O⁻² ions. Importantly, a higher loading of Ni corresponds to better performance of IPA, according to the results of the tests.

3.2.3 IPA inlet concentration

Figure 5 plots the relationship between the rate of conversion and the temperature at various inlet concentrations. Clearly, the conversion decreases as the IPA concentration increases. At $210\Box$, the conversion was 93% at an IPA of 400 ppm, but 82% at an increased IPA of 1700 ppm. However, the concentration became irrelevant when the temperature was increased to $250\Box$, because both conversions were near 100%.



Figure 5: The relationship between temperature and conversion in different inlet concentrations of IPA. Test conditions: SV=24000 hr⁻¹, 21% O₂, Ni/Fe=1:5.

3.2.4 Space velocity

Figure 6 plots the relationship between the rate of conversion and the space velocity. The figure demonstrates that a lower conversion is associated with a greater space velocity at a given temperature. The conversion was 92% at a temperature of 210 $^{-1}$ and the space velocity was 6000 hr⁻¹. However, the conversion fell to 87% and 76% when the space velocity was increased to 12000 hr⁻¹ and 24000 hr⁻¹, respectively. Hence, in the range of interest, the conversion declined as the space velocity increased, but when the temperature exceeded 250 $^{-1}$, the space velocity only slightly affected the conversion.



Figure 6: The relationship between temperature and conversion in different space velocities. Test conditions: Inlet Conc.=1700 ppm, 21% O₂, Ni/Fe=1:5.

3.3 Selectivity of the catalyst

The catalysts and reactants typically determine the products of catalytic combustion. Equation 3 describes the combustion of IPA to acetone. Equation 4 specifies the complete combustion of IPA to CO_2 .

$$C_{3}H_{8}O + 1/2 O_{2} \rightarrow C_{3}H_{6}O + H_{2}O$$
 (3)

$$C_3H_8O + 9/2 O_2 \rightarrow 3 CO_2 + 4 H_2O$$
 (4)

The experimental findings reveal that CO_2 was the final product when IPA was oxidized with Ni/Fe=1/5 catalyst. In the range $130\Box$ -230 \Box , IPA was oxidized into an intermediate, acetone, but the amount of acetone decreased as the temperature rose; when the temperature was increased to 250 \Box , IPA was completely converted into CO_2 .

3.4 72 hr test of catalyst decay

Figure 7 compares the IPA conversions in the 72 hrdecay test (Ni/Fe=1/5). The results revealed that the activity of catalysts was stable at 24 hour later and a stable reaction rate was reached at a fixed temperature in the 72 hr-decay test.



Figure 7: The comparison of conversion with time at different temperatures in 72 hr-decay test of catalyst. Test conditions: Inlet Conc.=1700 ppm, SV=24000 hr⁻¹, $O_2=21\%$, Ni/Fe=1:5.

3.6 SEM/EDS test

Figure 8 displays the SEM photograph of the Ni/Fe catalyst. It demonstrates that the primary particle size of the Ni/Fe catalyst was nearly 30 -70 nm. The results of the EDS test showed that the major components were indeed Ni and Fe, in a ratio of about 1:5. The measured real element contents in the catalyst were highly consistent with the predicted value.

4 Conclusions

The combustion of VOC derived from isopropyl alcohol using ferrite catalyst NiFe₂O₄ is described. The results reveal that Ni/Fe (molar ratio=1:5) catalyst is effective. Over 95% conversion was obtained at a space velocity of 24,000 hr⁻¹, an O₂ content of 21%, 1700 ppm of isopropyl alcohol and a reaction temperature of $230\square$. Importantly, isopropyl alcohol was completely converted into CO₂ at a temperature of $250\square$. This work addresses NiFe₂O₄ catalytic combustion, which has potential

in treating isopropyl alcohol streams, helping industrial plants to reduce the emission of VOC derived from of isopropyl alcohol.



Figure 8: SEM photograph of Ni/Fe catalyst (Ni/Fe=1:5)

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