Study on the Characteristics and Performance Assessment of Prepared Mesopourous Metal MCM-41 Catalyst for Treating Di-chloromethane

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Abstract — *Most VOCs are toxic to humans in some manner. Generally, transitional metal catalysts have better conversion rates for controlling VOCs. However, catalyst activity will decay at high temperature, though the oxidizing catalyst is cheap. SiO_2 is the main framework composition of MCM-41, which has good performance for controlling VOCs. MCM-41 has high surface area, high thermal stability, and uniform pore size. Further, pore sizes in MCM-41 can be controlled. In this research, the iron catalyst, platinum catalyst, and MCM-41 were used to treat VOCs. The concentration of ethanol was controlled from 2000 to 5000ppm. The reaction temperature ranged from 25 to 400 degrees under retention times of 2~6 sec to evaluate optimum operating conditions.*

After learning nanotechnology with experiment in nanoparticle formation, the recognition of nanotechnology can be promoted largely. The effect of learning nanotechnology with experiment is also good in urban student. It suggests this method of learning can be continued to understand more nanotechnology.

The results showed that the thermal efficiency is approximately 22% under 400 degrees with a blank test. The temperature must be higher than 250, 300, and 350 degrees with platinum catalyst, Fe-MCM-41, and iron catalyst, respectively, at a conversion rate of 90 %. The conversion rate ranged from 99.5 to 100, 96 to 99, and 96 and 99% with Pt, Fe, and Fe-MCM-41 catalysts, respectively, when the inlet concentrations were controlled from 2000 to 5000ppm under 400 degrees. The Fe catalyst displayed the worst performance. Following the Langmuir-Hinshelwood kinetics model, the second-order rate constant kc of Fe catalyst, Fe-MCM-41, and Pt catalyst were 39.1, 375.5 and 1877.6 mg/m3-min, respectively. In addition, the equilibrium adsorption constant K value of the three catalysts were 5.65, 0.59 and 0.12 L mg^{-1}, individually. The activity energy of iron catalyst, Fe-MCM-41 and platinum catalyst were 3.31, 0.41 and 1.83 kcal, respectively, using the Arrhenius equation. Furthermore, the order of collision factor A of catalysts was 1.16 x 10^4, 102 and 1.87 x 10^4 sec^{-1}, respectively.

Index Terms — *Mesoporous metal catalyst, metal catalyst, volatile organic compounds, kinetics analysis*

Introduction

Volatile organic compounds (VOCs) are defined as the organic compounds that have high vapor pressure, greater than 0.1 mmHg, and are easily vaporized at ambient temperature and pressure (20 °C, 760 mmHg). VOCs are widely used as solvents in industrial and household products manufacturing processes. VOCs are one of the main sources of photochemical reaction in the atmosphere, leading to various environmental hazards. Easily inhaled, most VOCs are toxic in some manner. For example, ethanol a central nervous system depressant, may cause slowed cognition, stupefaction, unconsciousness, and possible death at progressively higher dosages. Catalysts for controlling VOCs can generally be divided into noble metal catalysts, such as platinum, rhodium, silver, and gold, and oxidizing metal catalysts, such as Copper (II) oxide, iron oxide, and molybdenum oxide. Generally, transitional metal catalysts have better conversion rates for controlling VOCs. Catalyst activity will be decayed at high temperatures, though the oxidizing catalyst is inexpensive. SiO_2 is the main structural component of MCM-41. MCM-41 has good performance for controlling VOCs since it has high surface area, high thermal stability, and uniform pore size. Furthermore, MCM-41 pore size may be easily controlled. The metal catalyst deposited on the MCM-41 surface can be used to form surface modifications of mesoporous molecular sieves with the sol-gel process and hydrothermal method. The efficiency of the

packing bed reactor can be increased since the metal catalyst deposited on MCM-41 has a larger particle size and a smaller pressure drop.

As reported by Picasso et al.[1, 2], the performance of the Fe_2O_3 catalyst for treating methyl ethyl ketone was studied with Knudsen's method. The concentration of methyl ethyl ketone was controlled from 500 to 2000ppm and the reaction temperature was set at 225 degrees for complete combustion. As reported by Zhu et al.[3], Ethylbenzene were analyzed with potassium-promoted Iron(III) oxide by gas chromatography-mass spectrophotometer(GC-MS) connected to a computer to understand the transition reaction process of the dehydrogenases. Ethylbenzene showed high conversion rates to form Styrene only under Fe^{3+} cooperation conditions. Lin reported that Pt/AC catalysts could raise the activity of oxygen atoms and the adsorption ability of organic compounds to make organic compounds oxidized at low temperature. As reported by Tichenor and Palazzolo [4], the performance of Pt/ Pd catalysts with ceramic support was assessed for treating volatile organic compounds. At a reaction temperature of 260 ~ 425 degrees and a space velocity of 5000 ~ 18000 hr^{-1}, the oxidation capability of the catalysts ranked in the order was: alcohol > aldehyde > aromatic compound > ketone > ester > alkane > chlorine compound. The aim of this study was to assess the performance of a platinum catalyst, Fe-MCM-41, and an iron catalyst in a plug flow continuous system for treating ethanol. Furthermore, the concentrations, the reaction temperatures, and the retention time were tested to confirm reaction feasibility and to evaluate optimum operating conditions.

Experimental

1.1. Preparation of Materials and Catalysts

(1) Ethanol

The performance of catalysts for treating ethanol was assessed. Ethanol A.R. (95% C_2H_5OH) is manufactured by the Taiwan Tobacco & Liquor Corporation. Its molar mass is 46.07g mol^{-1} and boiling point is 78.4 degrees. It has a vapor pressure of 44.3 mmHg at 20 degrees.

(2) Iron catalyst

The performance of the iron catalyst with aluminum oxide support was also assessed (28.8% Fe). Bulk density is 9.98 g/mL. The average particle diameter is 3 mm. The specific surface areas were 1.5 m^2/g. The total pore volume and the average pore diameter were 0.342 cm^3/g and 30.0 nm, respectively.

(3) Platinum catalyst

The characteristics of the platinum catalyst with aluminum oxide, DASH-220N, support were also tested. The content and bulk density of Pt in the catalyst were roughly 1.8 g/L and 770 g/L, respectively. Furthermore, the average particle diameter and specific surface area was 4 mm and 161.6 m^2/g, individually. The total pore volume and the average pore diameter were 0.439 cm^3/g and 7.61 nm, respectively.

(4) Fe-MCM-41 catalyst

The Fe-MCM-41 catalyst synthesis was preformed as follows. 8 g of CTABr was dissolved by stirring in 100mL of distilled water at 55 ^oC. Then, Na_2SiO_3 was added. After 2 h of stirring, the pH was adjusted to 11 using HCl solution. The crystallization was done at 160 ^oC for 48 h after the $FeNO_3$ was added. The powder Fe-MCM-41 catalyst was obtained by washing with a centrifuge and calcining at 650 ^oC for 6 h.

1.2. Operating conditions

The operating conditions are listed in Table 1. This study assessed the performance of the platinum catalyst, Fe-MCM-41, and iron catalyst in a plug flow continuous system for treating ethanol. The reaction temperature was set from 25 to 400 degrees, while retention times ranged from 2 to 6 secs, to evaluate optimum operating conditions.

1.3. Plug Flow Continuous System

This was conducted in a tubular flow reactor. The reactor is a quartz tube and was positioned in a furnace. The ID and length of the quartz tube were 2.0cm and 40cm, respectively. The temperature of the reactor can be set between 298 K to 673 K. It is controlled by a furnace multi-stage heater.

Results and discussion

3.1. Blank test

The blank test was run to assess the degradation efficiency without the catalyst across different temperatures (25, 100, 150, 200, 250, 300, 350, and 400 ^{o}C). The results showed that the highest degradation efficiency is approximately 22% under 400 degrees (Figure 1).

3.2. The influence of reaction temperature on degradation efficiency

As shown in Figs. 2, 3, and 4, the degradation efficiency at 100 degrees was low with the Pt, Fe, and Fe-MCM-41 catalysts. The temperature must be higher than 250, 300, and 350 degrees with platinum catalyst, Fe-MCM-41, and iron catalyst, respectively, to obtain a degradation efficiency higher than 90%. In addition, the degradation efficiency was 95%, 94% and 90%, at 300 degrees with the platinum catalyst, Fe-MCM-41, and iron catalyst, individually. The performance of the catalysts ranked as follows: platinum catalyst > Fe-MCM-41 > iron catalyst, under identical conditions.

The degradation efficiency was different due to the differences in the specific surface areas of the catalysts as determined by the BET. The specific surface areas of the catalyst ranked as follows, platinum catalyst> Fe-MCM-41 > iron catalyst, with values of 161, 151, and 1.50 m^2/g, respectively. In addition, the conversion rate ranged from 96 to 99, 96.4 to 99, and 99.5 to 100% with Fe-MCM-41, Fe, and Pt catalysts, respectively, at inlet concentrations controlled from 2000 to 5000ppm under 400 degrees. Therefore, the reaction rate of the C_2H_5OH increased with the increase of temperature, due to the lower activation energy and higher frequency factor at higher temperatures.

3.3. Effects of ethanol concentration on degradation efficiency

Concentrations of ethanol were controlled from 2000 to 5000ppm, as shown in Fig. 5. The degradation efficiency ranged from 96 to 99, 96.4 to 99, and 99.5 to 100%, with Fe-MCM-41, Fe, and Pt catalysts, respectively, under 400 degrees. Among the three catalysts, the degradation efficiency of the Pt catalyst was the highest as it had the largest specific surface areas. In addition, degradation efficiency increased with the increase in concentration.

3.4. The effects of catalysts on degradation efficiency

The degradation efficiency was higher than 96, 97, and 99%, with Fe, Fe-MCM-41, and Pt catalyst, respectively, under 400 degrees and at inlet concentrations of 3000ppm. The Fe catalyst has the lowest performance, while the degradation efficiency of the Pt catalyst was the highest as it has the largest specific surface area, 161 m^2/g.

3.5. Analysis of kinetics

The Langmuir- Hinshelwood kinetics model was used to investigate the reaction characteristics of the metal catalysts. It is expressed as follows:

$$\mathrm{R} = -\frac{dC}{dt} = \frac{k_c K C}{1 + K C_o} = K_{obs} C \qquad (1)$$

Where

R is the reaction rate (ppm/min),

kc is the second-order reaction rate constant (ppm/min),

K is the adsorption equilibrium constant (ppm-1),

Co and C are the initial concentration and the reaction concentration (ppm), respectively.

Kobs is . $\dfrac{k_c K}{1 + K C_o}$

The second-order reaction rate constant kc and K were obtained with the Langmuir-Hinshelwood kinetics model. The kc of the Fe, Fe-MCM-41, and Pt catalysts was 39.1, 375 and 1878 mg/m^3-min, respectively. Moreover, the degradation efficiency of the catalyst ranked as follows: platinum catalyst > Fe-MCM-41 > iron catalyst. In addition, the equilibrium adsorption constant K of the three catalysts was 5.65, 0.59, and 0.12 L/mg, individually. Thus, the removal capacity of the catalysts ranked as follows: iron catalyst > Fe-MCM-41 > platinum catalyst.

The activation energy was evaluated with the Arrhenius Equation by determining the relationship between the reaction rate constant and temperature. The reaction rate was increased with an increase in temperature since the molecular collision probability was increased at higher temperatures. The higher collision rate resulted in a higher kinetic energy,

which has an effect on the activation energy of the reaction. The Arrhenius equation may be expressed as follows:

$$k_c = A\exp\left(-\frac{Ea}{RT}\right) \quad (2)$$

Where kc is the rate coefficient,
A is a constant,
Ea is the activation energy,
R is the universal gas constant,
and T is the temperature (in kelvin).
R has the value of 8.314 x 10^{-3} kJ mol^{-1} K^{-1}.
The Equation (3) can be developed by taking natural logarithm of the Arrhenius equation and illustrated as follows:

$$\ln kc = \ln A - (Ea/RT) \quad (3)$$

The Ea and A were determined by plotting the relationship between ln (kc) and T^{-1}. The activation energy of the iron catalyst, Fe-MCM-41, and platinum catalyst was 3.31, 0.41, and 1.83 kcal, respectively, and shown in Table 3. Further, the value of the constant A of the three catalysts was 1.16 x 10^4, 102, and 1.87 x 10^4 sec^{-1}. The reaction rate of the metal catalysts was:

Fe catalyst：k =1.16 x 10^4exp(-3.31 /RT)
Fe-MCM-41 catalyst：k = 102 exp(-0.41 /RT)
Pt catalyst：k = 1.87 x 10^4 exp(-1.83/RT)

3.6. The recognition of nanotechnology Assessment

The differences of recognition of nanotechnology between different grade students are listed as in the Table 4 and Figure 7. Before learning the nanotechnology, the students in rural and in urban got the average score 47.6 and 56.4, respectively, among the highest score 100. The grade 1 students got the lowest score 41.0 and 48.4 in the rural and urban, respectively. In contrast, the grade 3 students could promote the scores to 52.2 and 65.0 in the rural and urban, respectively. It means the elder students have more chance to learn nanotechnology.

3.7. The recognition of nanotechnology after learning

After learning nanotechnology with experiment in nanoparticle formation, the recognition of nanotechnology can be promoted largely. For example, the score can be promoted to 57.5 from 40.8 and 74.4 from 52.9 among the grade 1 and grade 3 rural students, respectively, before and after learning, as listed in the Figure 8. The effect of learning nanotechnology with experiment is also good in urban student as shown in the Tables 5 and 6. The score can be promoted to 62.1 from 48.4 and 80.2 from 65.0 among the grade 1 and grade 3 urban students, respectively. It suggests this method of learning can be continued to understand more nanotechnology.

Conclusion —

1. The thermal efficiency was approximately 22% under 400 degrees with the blank test.
2. The temperature must be higher than 250, 300, and 350 degrees with the platinum catalyst, Fe-MCM-41, and iron catalyst, respectively, to obtain a degradation efficiency higher than 90%.
3. The degradation efficiency ranged from 96 to 99, 96.4 to 99, and 99.5 to 100%, with the Fe-MCM-41, Fe, and Pt catalysts, respectively, under 400 degrees.
4. The performance of the catalysts ranked as follows: platinum catalyst > Fe-MCM-41 > iron catalyst.
5. Following the Langmuir-Hinshelwood kinetics model, the second-order rate constant kc of the Fe catalyst, Fe-MCM-41 and Pt catalysts was 39.1, 375, and 1878 mg/m^3-min, respectively. In addition, the equilibrium adsorption constant K of the three catalysts was 5.65, 0.59 and 0.12 L/mg, individually.
6. The activity energy of the iron catalyst, Fe-MCM-41, and platinum catalyst was 3.31, 0.41 and 1.83 kcal, respectively, from the Arrhenius equation. The order of collision factor A of the catalysts was 1.16 x 10^4, 10^2, and 1.87 x 10^4 sec-1.

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FIGURES AND TABLES

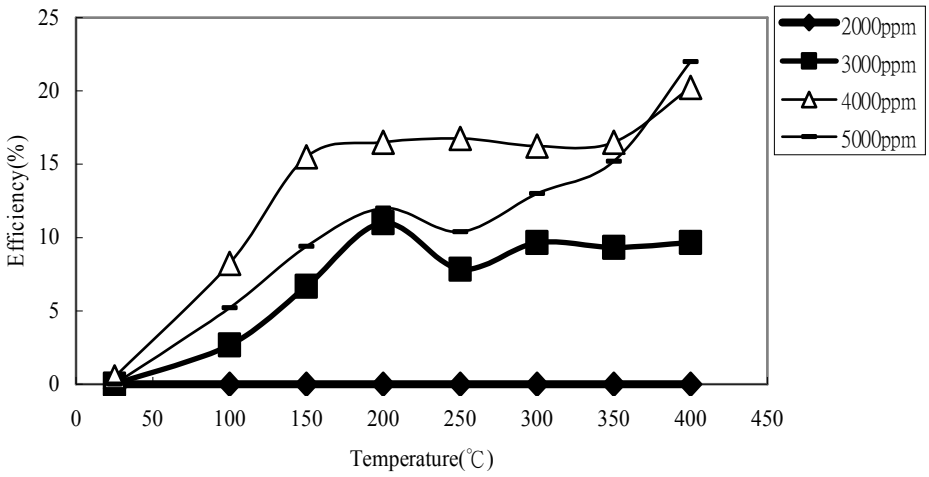

FIGURE 1
THE DEGRADATION EFFICIENCY WITHOUT CATALYST IN DIFFERENT TEMPERATURE

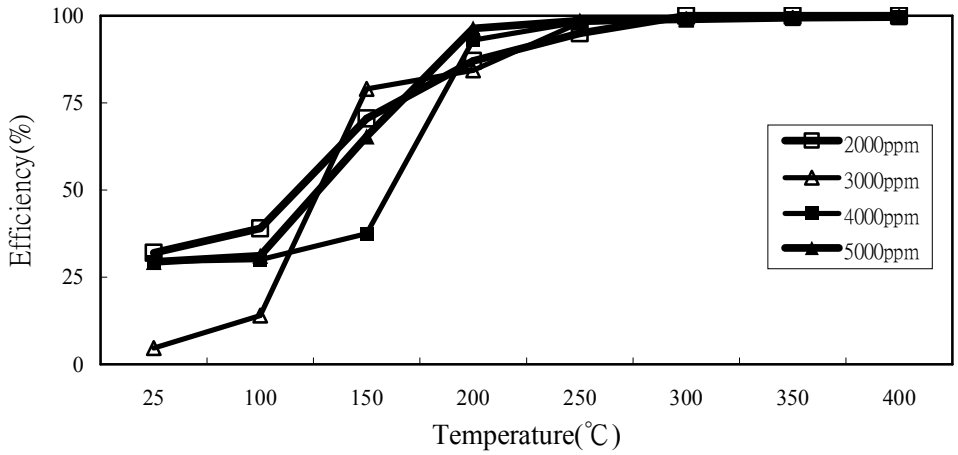

FIGURE 2
THE DEGRADATION EFFICIENCY WITH PT CATALYST IN DIFFERENT TEMPERATURE

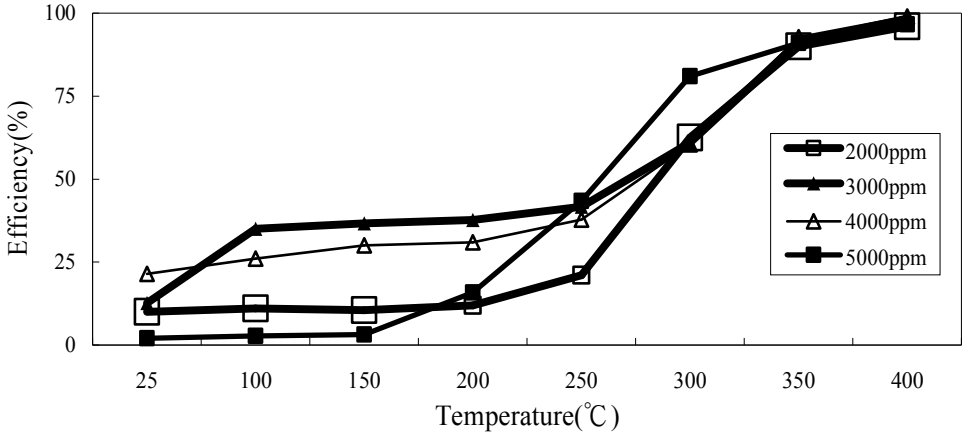

FIGURE 3
THE DEGRADATION EFFICIENCY WITH FE CATALYST IN DIFFERENT TEMPERATURE

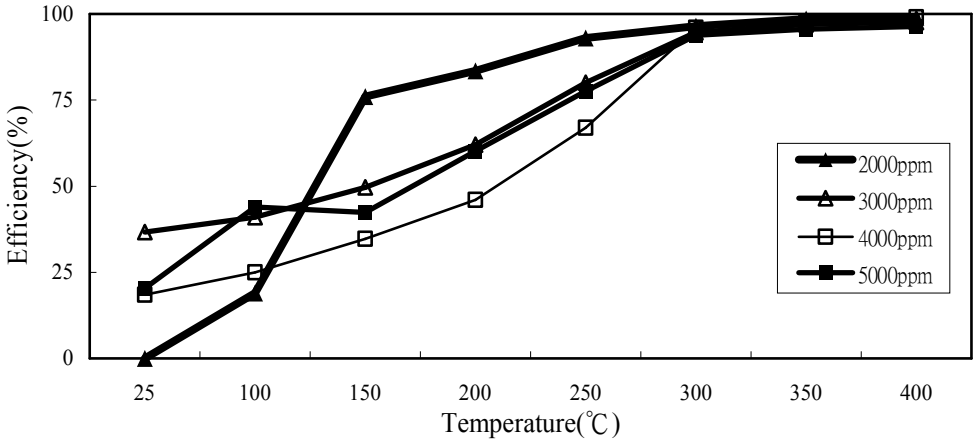

FIGURE 4
THE DEGRADATION EFFICIENCY WITH FE-MCM-41 IN DIFFERENT TEMPERATURE

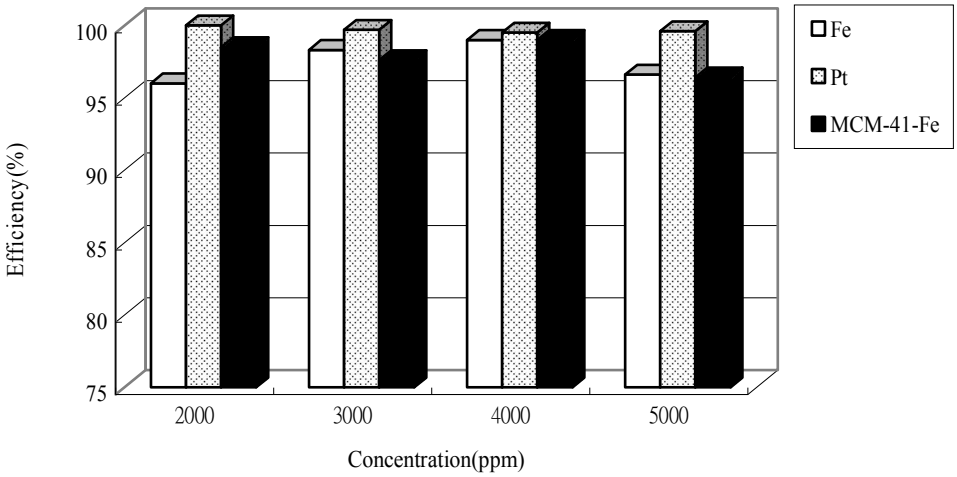

FIGURE 5
THE EFFECTS OF CONCENTRATIONS ON DEGRADATION EFFICIENCY

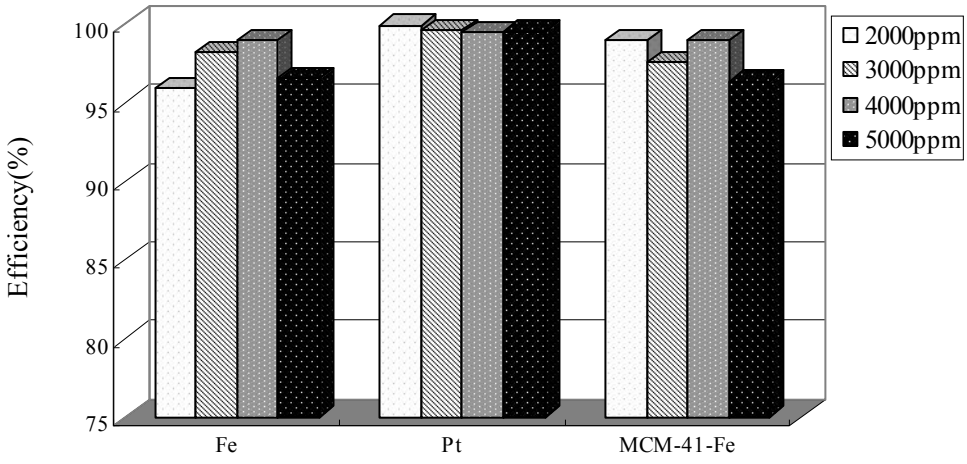

FIGURE 6
THE DEGRADATION EFFICIENCY WITH CATALYSTS

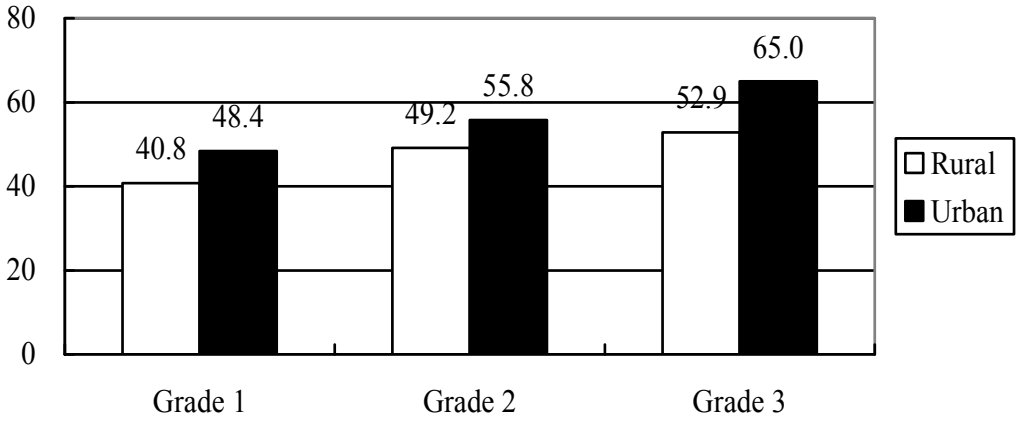

FIGURE 7
THE DIFFERENCES OF NANOTECHNOLOGY RECOGNITION BETWEEN DIFFERENT GRADE STUDENTS

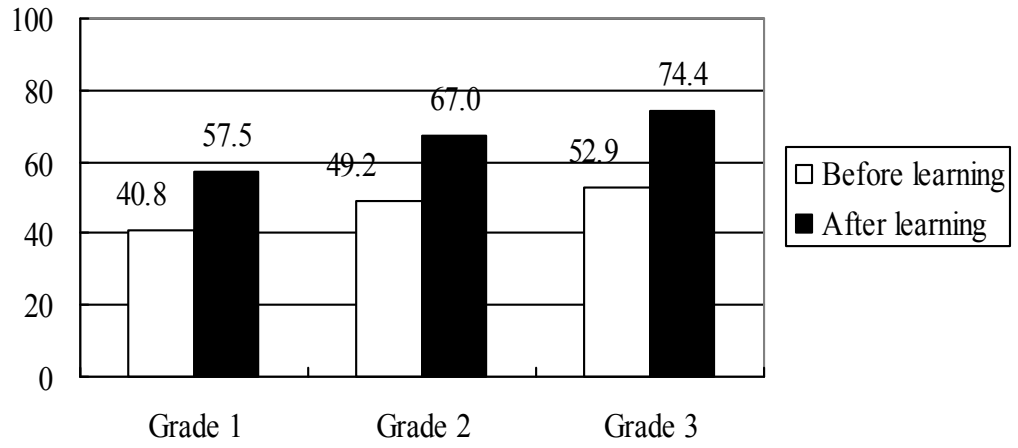

FIGURE 8
THE DIFFERENCES OF NANOTECHNOLOGY RECOGNITION BEFORE AND AFTER LEARNING IN RURAL STUDENTS

Parameter	Conditions
Pollutant	ethanol
Catalyst	platinum catalyst, Fe-MCM-41, iron catalyst
Temperature (℃)	25~ 400
Retention Time (sec)	2~ 6

TABLE 1
OPERATION CONDITIONS

Parameter	Fe	MCM-41-Fe	Pt
K (L/mg)	5.65	0.59	0.12
kc (mg/m3/min)	39.1	375.5	1877.6

TABLE 2
THE SECOND-ORDER REACTION RATE CONSTANT AND THE ADSORPTION EQUILIBRIUM CONSTANT OF METAL CATALYSTS

Parameter	Fe	MCM-41-Fe	Pt
Activity Energy (Ea, kcal)	3.31	0.41	1.83
constant (A, sec-1)	1.16×10^4	102	1.87×10^4

TABLE 3
ACTIVITY ENERGY AND CONSTANT OF CATALYSTS

Area	Persons	Number of questions	Lowest Score	Highest Score	Average	Standard deviation
Rural	180	24	8.3	83.3	47.6	2.4
Urban	892	24	12.5	100	56.4	3.3

TABLE 4
THE SCORES OF NANOTECHNOLOGY RECOGNITION IN RURAL AND URBAN STUDENTS

Status	Persons	Number of questions	Lowest Score	Highest Score	Average Score	Standard deviation
Before learning	180	24	8.3	83.3	47.6	2.4
After learning	180	24	25.0	100	66.3	4.4

TABLE5
THE SCORES OF NANOTECHNOLOGY RECOGNITION BEFORE AND AFTER LEARNING IN RURAL STUDENTS

Status	Persons	Number of questions	Lowest Score	Highest Score	Average Score	Standard deviation
Before learning	892	24	12.5	100	56.4	3.3
After learning	892	24	29.2	100	75.1	4.2

TABLE 6
THE SCORES OF NANOTECHNOLOGY RECOGNITION BEFORE AND AFTER LEARNING IN URBAN STUDENTS