

The operating performance and products distribution of the catalytic oxidation of methyl-isobutyl-ketone over a Pt/ γ -Al₂O₃ catalyst

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Abstract

Catalytic oxidation is one of the cost-effective technologies to solve the troublesome volatile organic compounds. This study treated methyl-isobutyl-ketone (MIBK) by a commercial catalyst, Pt/ γ -Al₂O₃, in a fixed-bed reactor. The effects of operating factors, such as operating temperature, MIBK concentration, space velocity, and O₂ concentration, on the performance of the catalyst were investigated. The products and reactants distributions from the oxidation of MIBK over Pt/ γ -Al₂O₃ were observed. The results show that the products containing carbon atoms are CO, CO₂, and C₃H₆O. Two catalyst life-tests were also carried out to characterize the deactivation effect of MIBK. The result shows that the deactivation effect may be due to the coke on the catalyst surface at 423 K. From the statistical analysis, the operating temperature is the most effective factor on the conversion of MIBK. The catalysts were also characterized by surface area analysis and elemental analysis before and after the test. The results show that the catalytic deactivation may be due to carbon coating. At low temperature (423 K), the phenomenon of carbon coating was more obvious than that at high temperature (573 K). The product distributions from the oxidation of MIBK over Pt/ γ -Al₂O₃ were analyzed by GC. The results indicate that the C₃H₆O is formed from the beginning, presenting a peak at 423 K, 6.54 ppm. The CO concentration also peaked at the same temperature, 6.84 ppm.

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1. Introduction

Volatile organic compounds (VOCs) are defined as the organic compounds that have high vapor pressure and are easily vaporized at ambient temperature and pressure. Most hydrocarbons, including nitrogenous, chlorinated, and sulfonated organics, are determined to be VOCs. These compounds are usually found in the industries that manufacture or utilize organic solvents, e.g., petrochemical, pulp, or coating industries.

In addition to causing harmful effects on human organs, VOCs may also react with NO_x in the atmosphere to form even more toxic photochemical smog and ozone [1]. To remove these hazardous substances, a number of technologies

have been developed. Among them, catalytic incineration has received increasing attention lately because it is a final disposal and an energy saving process [2]. Catalytic incineration is more selective and, as it requires less heating, is more cost effective than the other technologies, such as direct combustion [3], when the VOCs concentration is lower than 10,000 ppm [4]. The major problem with this technique is catalyst deactivation caused by the reactant, by the products of the reaction or by particles present in the effluents [5]. The major parameters affecting catalytic incineration of VOCs include catalyst type, VOC type, VOC concentration, operating temperature, space velocity, and O₂ concentration. From the definition, space velocity is the inverse of residence time of VOCs in the catalytic reactor. Therefore, residence time would decrease as space velocity increases, and the conversion of VOCs would drop. The catalysts can be divided into two categories: precious metals and metal oxides [6,7].

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In the case of the catalytic combustion of carbonyl VOCs, in particular methyl-isobutyl-ketone (MIBK), there is not much work done yet. Gil et al. [8] found total conversions of acetone at 352 °C and of methyl-ethyl-ketone (MEK) at 317 °C in catalysts of 2.3 wt.% Pt/Al pillared clays. Moreover, Pina et al. [9] found total conversion of MEK in air at 200 °C over a 0.19 wt.% Pt/Al₂O₃ catalytic membrane. Gandía et al. [10] studied the catalytic oxidation of acetone and methyl-ethyl-ketone over Mn₂O₃ catalysts. They found that when this oxide is modified by alkali additives, like Na and Cs, the conversion of the ketones are shifted to lower temperatures. Catalytic combustion of C3 hydrocarbons and oxygenates was studied by Baldi et al. [11] over Mn₃O₄. Complete oxidation of these compounds into CO₂ occurs at temperatures below 673 K. Partially oxidised compounds were observed only at temperatures where the VOC conversion was incomplete. In the case of acetone, the conversion into CO₂ is complete at temperatures around 550 K. Tsou et al. [12,13] studied the catalytic oxidation of methyl-isobutyl-ketone over Pt/zeolites catalysts. They found that the rate of MIBK oxidation increases with the reaction temperature, while coke formation decreases. At temperatures between 190 and 195 °C the more reactive coke compounds can also be oxidised into CO₂ at sufficiently high reaction rate to cause a significant increase in the catalyst temperature, leading to cyclic oscillations in the apparent conversion into CO₂.

MIBK is used as an excellent solvent for the paint industry and an important reagent in dewaxing mineral oils. It is also a hazardous material, which is on the control list of Taiwan Environmental Protection Agency.

This study was carried out by catalytic incineration of MIBK over a Pt/γ-Al₂O₃ fixed-bed reactor. The effects of operating parameters, including inlet temperature, space velocity, MIBK concentration, and O₂ concentration were characterized. A life-test of the catalyst on MIBK was performed to identify the deactivation effect.

2. Materials and methods

The catalytic oxidation of this study was done in a bench-scale fixed-bed reactor system. The system can be divided into three parts: an effluent gas simulation system, a catalytic oxidation system, and a combustion gas analyzing system as shown in Fig. 1. The effluent gas simulation system was composed of an air compressor (1) (SWAN, 1/4 hp), a N₂ cylinder (6) (99.9%, San Fu), three mass flowmeters (4) (Teledyne Hasting-Raydist, HFC-202), two plug-flow mixers (5) (Omega, FMX7106), a water bath (7) (Deng Yng, 253–353 K), and two VOC vapor generators (8) (Pyrex). Flow rates of dilution N₂, purge N₂, and dilution air were controlled by three mass flowmeters, to prepare the desired concentrations of MIBK and O₂. The simulated gas was then preheated by an electrical heating tape before going through the catalytic reactor. The materials of piping, valves, regulators, or fittings used were either SS-316 or polytetrafluoroethylene.

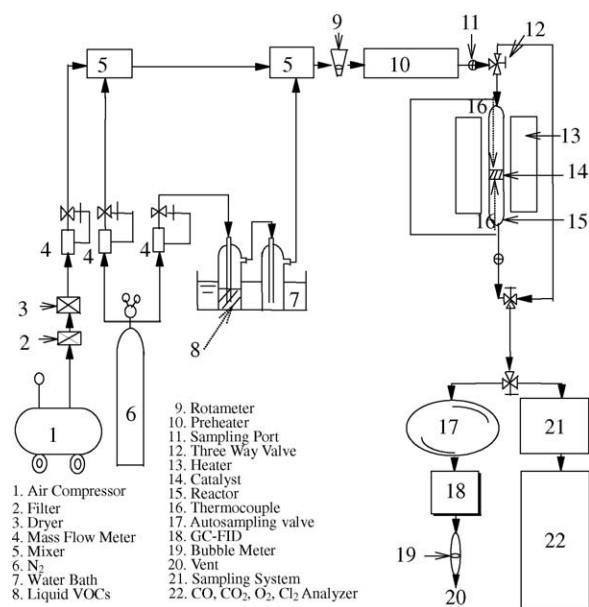


Fig. 1. A schematic diagram of bench-scale catalytic incinerator.

The catalytic incineration system was composed of a custom-made SS-316 tube reactor (15) and an electrical heater (13). The length, internal diameter, and outer diameter of the reactor were 45, 1.5, and 2.0 cm, respectively. A 200-mesh SS-316 sieve was set in the reactor, 24 cm below the top of the tube, to support the catalyst. The weight of Pt/γ-Al₂O₃ catalyst packing was 0.60 g (thickness 0.75 cm and bulk density 0.40 g/cm³). A thin layer of glass fiber and a layer of glass bead with a 2-mm diameter covered the catalyst packing to uniformly distribute the gas. Two K-type thermocouples (16) were inserted into the reactor to the positions on the top and bottom of the catalyst packing, respectively, to measure and control (up position) and measure (down position) the inlet and outlet temperature.

The gas analyzing system was composed of a gas chromatograph (18) (GC) (Shimadzu, GC-14B) and three combustion gas analyzers (22): O₂ analyzer (Signal Model magneto dynamic type), CO analyzer (Signal Series 2000), and CO₂ analyzer (Signal Series 2000). The GC column was a 30-m long capillary column with diameter of 0.53 mm (J&W Scientific #115–3432). A 1:1 splitter was connected with the column to split the sample gas into a flame ionization detector (FID) and a flame photometry detector (FPD). An icebox impingement condenser (Pyrex) and two particle filters (Balston, 95S6 and 45G) were installed between the sampling port and three combustion gas analyzers. This arrangement was designed to prevent the analyzers from being damaged by condensed water and particles. All mass flowmeters and rotameters were calibrated by a bubble meter (19) (Humonic digital flowmeter 650) or a dry gas meter (Shinagawa DK-SCF-T) at their proper ranges. The catalyst samples were taken before and after the reaction to determine the changes of their specific surface area and organic coating composition, by a BET specific surface area analyzer (ASAP 2000)

Table 1
Basic properties of NIKKI NS-10 catalysts

Catalyst	Pt
Support	γ -Al ₂ O ₃
Shape	Pellet
Pellet diameter (cm)	0.3–3.5
Bulk density (g/ml)	0.395
BET (m ² /g)	149
Pore volume (cm ³ /g)	0.674
Average pore diameter (Å)	181

and elemental analyzer (EA) (Elementar Vario EL). The catalyst was also analyzed by a thermo-gravimetric analysis (TGA) to determine its weight loss by thermal effect. MIBK standard was a product of Chem Service Inc. (99%). The catalyst used was commercial product of NIKKI NS-10 Pt/ γ -Al₂O₃. The commercial catalyst was ground to 50–100 mesh (250–150 μ m) particle size range and the basic properties of Pt/ γ -Al₂O₃ catalyst are shown in Table 1. Liquid MIBK used for the catalytic incineration system was a product of Merck Chemical Inc. (purity > 99.5%). Standard gases included zero gas (N₂, 99.9995%, San Fu) and O₂ span gas (21%, San Fu).

The experiments were divided into three parts. The first part was performed to investigate the performance of the better catalyst, Pt/ γ -Al₂O₃, on catalytic conversion of MIBK. The operating parameters and ranges tested were inlet temperature (373–573 K), MIBK concentration (50–200 ppm), space velocity (50,000–120,000 h⁻¹), and O₂ concentration (0.1–20.8%). The second part was the products distribution for the oxidation of MIBK over Pt/ γ -Al₂O₃. The last part was a life-test of the catalyst by catalytic incineration of MIBK to identify its deactivation effect.

Reagent grade liquid MIBK was injected into the VOC generator, which was kept at a constant temperature of 298 K in the water bath. Purged N₂ carried the vaporized MIBK to mix with dilution air and N₂ in the mixture to simulate the waste gas, from a typical chemical coating plant, at a certain flow rate and O₂ concentration. The simulated gas was injected into the catalytic reactor heated by an electrical furnace. One milliliter of gas samples was taken before and after the reaction, by an on-line autosampler, to be injected into the GC to determine the conversion of MIBK. The gas samples before and after the reaction were also analyzed by three combustion gas analyzers to determine the extent of complete oxidation. A series tests were performed earlier on conversion of methanol over the same Pt catalyst with three size ranges [14]. The results showed that the conversion differences were not significant. Therefore, the catalyst being ground to 50–100 mesh was chosen to carry out the experiments for this study in order to reduce both the interfacial mass transfer limitation and intraparticle mass transfer resistance. The conversion (X) of MIBK and the yield (Y_C) of carbon products are defined as follows [15,16]:

$$X = \frac{C_{in} - C_{out}}{C_{in}} \times 100\% \quad (1)$$

$$Y_C = \frac{C_{CO}}{6C_6H_{12}O} \times 100\%, \quad \frac{C_{CO_2}}{6C_6H_{12}O} \times 100\%, \quad \frac{3C_{C_3H_6O}}{6C_6H_{12}O} \times 100\% \quad (2)$$

3. Results and discussion

The MIBK conversions over the Pt/ γ -Al₂O₃ catalysts and a blank test by replacing catalyst packing with glass fiber are shown in Fig. 2. The Pt catalyst and blank test are active in the range of 373–573 K. The results indicate that the MIBK conversion over the Pt catalyst is higher than the blank test at all temperature in the operating range of this study. The Thermo-gravimetric analyses for the Pt/ γ -Al₂O₃ catalyst were recorded. There are significant weight losses from 323 to 373 K, but no more large weight losses at higher temperatures no matter which thermo-program was used. The results show that the water adsorbed by the catalyst desorbs from the catalyst at a temperature range of 323–373 K. Above 373 K, the Pt/ γ -Al₂O₃ catalyst shows a stable characteristic.

The effect of MIBK concentration on its conversion by the Pt/ γ -Al₂O₃ catalyst at various temperatures is shown in Fig. 3. It suggests that the conversion of MIBK increases as inlet temperature increases in the range of 373–573 K. It also can be found that the conversion of MIBK decreases as its concentration increases from 50 to 200 ppm. Fig. 4 shows that the lower the space velocity is, the higher the conversion of MIBK is. The effect of O₂ concentration on the conversion of MIBK is shown in Fig. 5. It is found that the O₂ concentration has a positive effect on the conversion of MIBK.

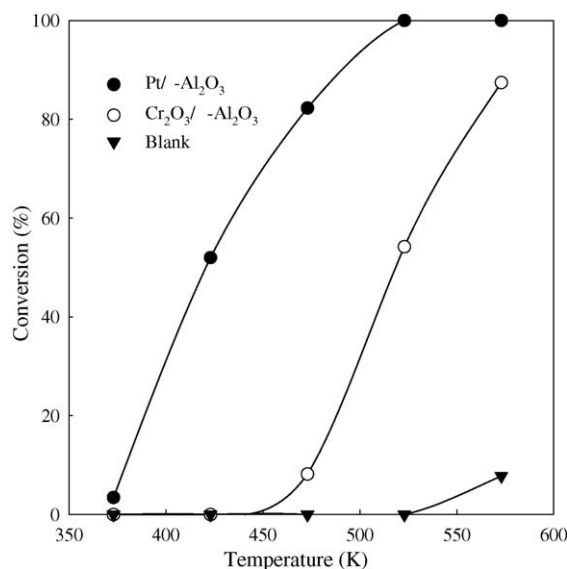


Fig. 2. Comparisons of the catalytic incineration of MIBK on the Cr₂O₃/Al₂O₃ catalyst, Pt/ γ -Al₂O₃ catalysts and a blank test at various temperatures (inlet concentration: 100 ppm; gas hourly space velocity (GHSV): 80,000 h⁻¹; temperature: 373–573 K; O₂ concentration: 20.8%).

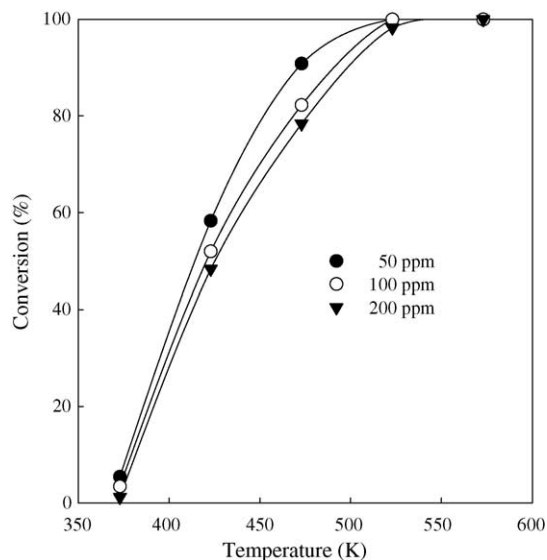


Fig. 3. Effect of MIBK concentration on the catalytic conversion of MIBK over the Pt/γ-Al₂O₃ catalyst (inlet concentration: 50–200 ppm; GHSV: 80,000 h⁻¹; temperature: 373–573 K; O₂ concentration: 20.8%).

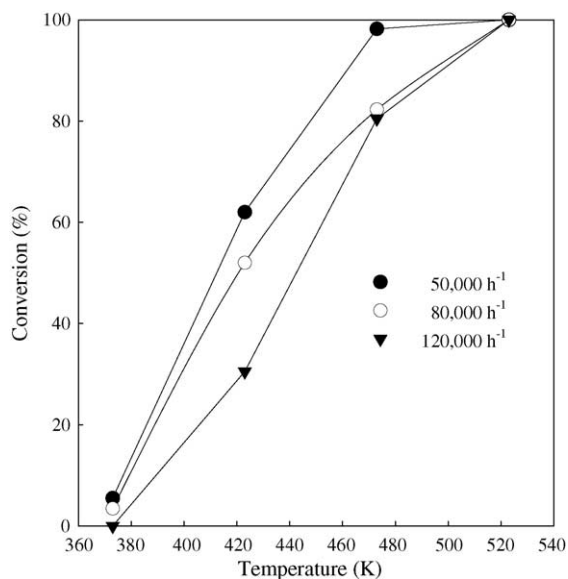


Fig. 4. Effect of space velocity on the catalytic conversion of MIBK over the Pt/γ-Al₂O₃ catalyst (inlet concentration: 100 ppm; GHSV: 50,000–120,000 h⁻¹; temperature: 373–573 K; O₂ concentration: 20.8%).

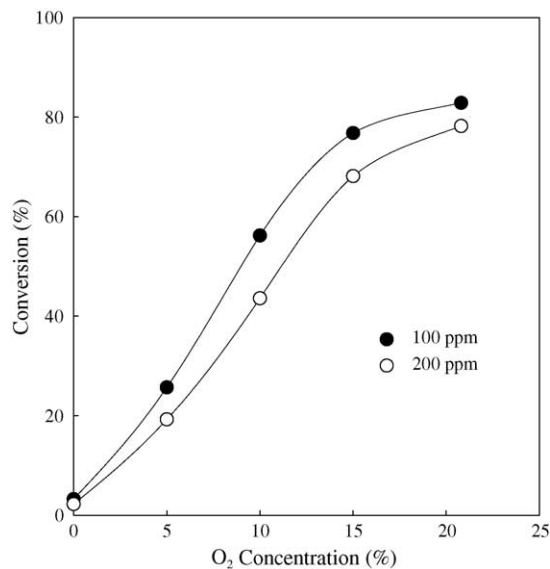


Fig. 5. Effect of O₂ concentration on the catalytic conversion of MIBK over the Pt/γ-Al₂O₃ catalyst (inlet concentration: 100–200 ppm; GHSV: 80,000 h⁻¹; temperature: 473 K).

The distributions of the products and reactants for the oxidation of MIBK over Pt/γ-Al₂O₃ were conducted and shown in Table 2. The conversion of MIBK was extremely low, below 373 K. As the temperature exceeds 423 K the conversion rapidly increases and CO₂ is the main products, with only some trace amounts of incomplete combustion products (e.g., C₃H₆O and CO). According to Table 2, the C₃H₆O is presented a peak at 423 K, 6.54 ppm. The concentration of CO is also peaked at the same temperature, 6.84 ppm. From the results shown in Table 2, to correlate concentrations of different components in the figure, the following reaction scheme can be proposed for the destruction of MIBK:

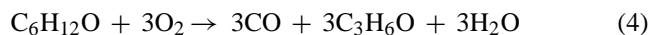
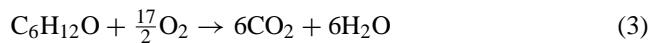


Fig. 6 shows the MIBK conversion and product yield at vary temperature for Pt/γ-Al₂O₃ catalyst. To thoroughly understand the reaction pathway of the decomposition of MIBK, the mass balance on C atoms was performed. The MIBK sim-

Table 2
Carbon recovery of the catalytic incineration of MIBK

Temperature (K)	Initial MIBK (ppm)	Conversion (%)	CO ₂ (ppm)	CO (ppm)	Acetone (ppm)	Carbon recovery (%)
373	100.16	3.45	13	4.32	0.24	99.55
423	101.97	52.12	250	6.84	6.54	93.07
473	99.84	85.14	448	3.50	5.87	93.17
523	100.38	99.21	598	1.25	0.00	100.29
573	101.25	99.76	602	0.98	0.00	99.50

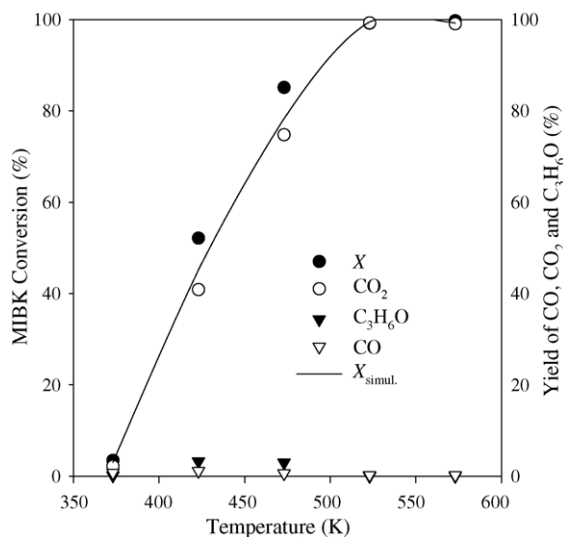


Fig. 6. Relationship between the yield of CO, CO₂, and C₃H₆O and the conversion of MIBK (inlet concentration: 100 ppm; GHSV: 80,000 h⁻¹; O₂ concentration: 20.8%).

ulation conversion ($X_{\text{simul.}}$) and the yields (Y_C) of products are defined as the Eq. (7).

$$X_{\text{simul.}} = \sum Y_C \quad (7)$$

where Y_C is the experiment data (Table 2) of products yield obtained from Eq. (2). The $X_{\text{simul.}}$ can be calculated by summation of the yields (Y_C).

As shown in the Fig. 6 that the MIBK simulation conversions are attached with the raw MIBK conversion data. It reveals that carbon atoms measured at outlet and inlet of the reactor remains balanced at all temperature. In fact, the carbon atoms recovery in all case was within 93–100% (shown in Table 2). This finding consists with reactions (3)–(6) that the products containing carbon atoms are CO, CO₂, and C₃H₆O. The dominant product is CO₂. Table 3 shows the elemental analysis of the fresh and deactivated Pt/ γ -Al₂O₃ catalyst. As this figure shows, the results indicated that the carbon species on the catalyst was ca. 2.5% at 423 K. This phenomenon, maybe, can explain the unfitted carbon atoms balance.

At 423 K, the conversion of MIBK (above 50%) is obtained with some amounts of C₃H₆O (which is destroyed by reaction (4) in the range 373–523 K).

Formation of CO from incomplete oxidation of MIBK, reaction (4), can be observed over Mn₂O₃/ γ -Al₂O₃ catalysts at lower temperatures around 423 K but not found at high

Table 3
Elemental analysis results for the fresh (298 K) and deactivated (423 and 573 K) Pt/ γ -Al₂O₃ catalysts

Carbon element (wt.%)	298 K	423 K	573 K
1st test	0.057	2.48	0.49
2nd test	0.056	2.13	0.49

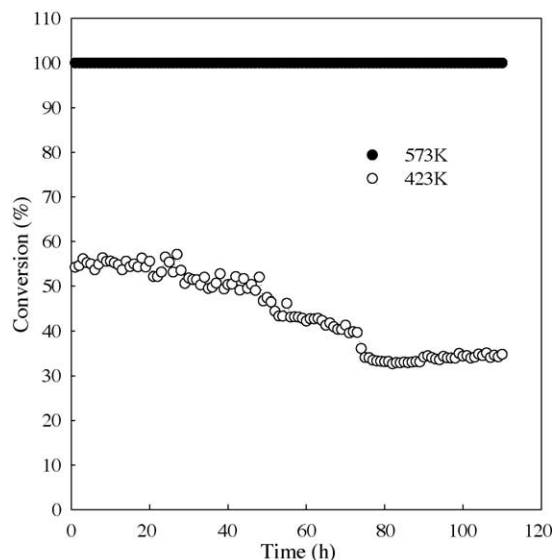


Fig. 7. Deactivation effect of MIBK on the Pt/ γ -Al₂O₃ catalyst (inlet concentration: 100 ppm; GHSV: 80,000 h⁻¹; O₂ concentration: 20.8%; temperature: 423–573 K).

temperature, due to the reaction (6). The peak around 423 K obtained with the catalyst corresponds to the oxidation of MIBK, reaction (4), since formation of CO coincides with the decrease of MIBK concentration.

A series of life-tests of the Pt/ γ -Al₂O₃ catalyst under the condition of 100 ppm MIBK were conducted to identify its deactivation effect and the results are shown in Fig. 7. At 423 K, the performance of the catalyst declines gradually for about 70 h and then reaches a stable condition. Fig. 8 shows that the BET specific surface area of the deactivated Pt/ γ -Al₂O₃ catalyst incinerated at 423 K is significantly less

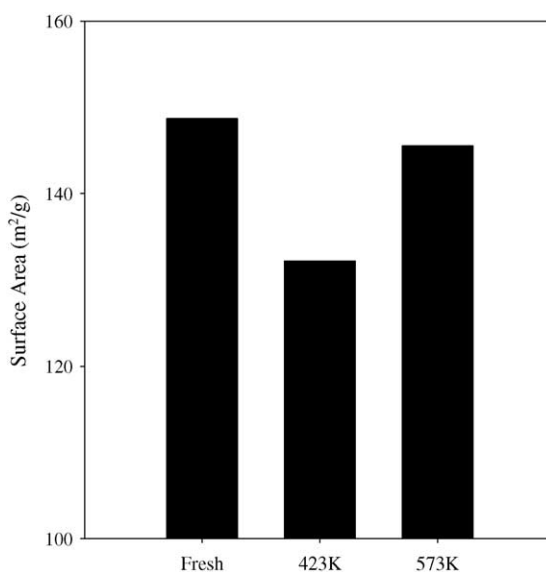


Fig. 8. Specific surface areas of the fresh and poisoned Pt/ γ -Al₂O₃ catalysts (temperature: 423–573 K for 110 h).

than the fresh catalyst. This phenomenon may be due to the following: certain active sites of the catalyst would lose the active at 423 K. At 573 K, however, no deactivation effect is applied. According to the elemental analysis, this also suggests that carbon compounds may cover the catalyst surface after the reaction. The specific surface area of the deactivated Pt/ γ -Al₂O₃ catalyst incinerated at 573 K is almost the same as the fresh catalyst. This suggests that the adsorbed carbon compounds may react with O₂ to produce CO₂ at high temperature. This consists with the result of Tsou et al. [12], which showed that the rate of MIBK oxidation increases with the reaction temperature, while the coke formation decreases. The result also suggested that at temperatures between 190 and 195 °C the more reactive coke compounds can also be oxidised into CO₂ at sufficiently high reaction rate to cause a significant increase in the catalyst temperature, leading to cyclic oscillations in the apparent conversion into CO₂. At temperature lower than 190 °C the rate of coke combustion is extremely low, and there is very little or no coke formation at the temperature higher than 195 °C.

4. Conclusions

The catalytic incineration of MIBK on the Pt/ γ -Al₂O₃ catalysts and blank test were conducted over a variety of operating conditions. The results show that Pt/ γ -Al₂O₃ is a good catalyst for conversion of MIBK compared to the blank test. The results of the operation parameters test show that the higher the concentration and space velocity of MIBK are the lowest of its conversion. The O₂ concentration has a positive effect on the conversion of MIBK.

The products distributions from the oxidation of MIBK over Pt/ γ -Al₂O₃ were observed. The results show that the MIBK conversion starts from 5% at 373 K and rises to very high values in the 523–573 K ranges, the CO₂ yield also pushes to 100% at the same temperature ranges. C₃H₆O and CO are the incomplete combustion products. The results indicate that the C₃H₆O is formed from the beginning, presenting a peak at 423 K, 6.54 ppm. The CO concentration also peaked at the same temperature, 6.84 ppm.

According to the results of the BET specific surface area analysis, elemental analysis, and the life-tests, the deposition of carbon compounds on the catalyst may be the reason causing the deactivation effect.

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