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APPENDICES

APPENDIX A

CALCULATION OF THE CRYSTALLITE SIZE

Calculation of the crystallite size by Debye-Scherrer equation

The crystallite size was calculated from the half-height width of the diffraction peak of XRD pattern using the Debye-Scherrer equation.

From Scherrer equation:

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (\text{A.1})$$

where D = Crystallite size, Å

K = Crystallite-shape factor = 0.9

λ = X-ray wavelength, 1.5418 Å for CuK α

θ = Observed peak angle, degree

β = X-ray diffraction broadening, radian

The X-ray diffraction broadening (β) is the pure width of a powder diffraction free from all broadening due to the experimental equipment. α -Alumina is used as a standard sample to observe the instrumental broadening since its crystallite size is larger than 2000 Å. The X-ray diffraction broadening (β) can be obtained by using Warren's formula.

From Warren's formula:

$$\beta = \sqrt{B_M^2 - B_S^2} \quad (\text{A.2})$$

where B_M = The measured peak width in radians at half peak height.

B_S = The corresponding width of the standard material.

Example: Calculation of the crystallite size of γ -Al₂O₃

$$\begin{aligned}
 \text{The half-height width of peak} &= 1.153^\circ \text{ (from the figure C.1)} \\
 &= (1.153 \times \pi) / 180 \\
 &= 0.0201 \text{ radian}
 \end{aligned}$$

The corresponding half-height width of peak of α -alumina (from the B_s value at the 2θ of 67.44° in figure C.2) = 0.0057 radian

$$\begin{aligned}
 \text{The pure width, } \beta &= \sqrt{B_M^2 - B_S^2} \\
 &= \sqrt{0.0201^2 - 0.0057^2} \\
 &= 0.01927 \text{ radian}
 \end{aligned}$$

Scherrer equation:

$$B = 0.01927 \text{ radian}$$

$$2\theta = 67.44^\circ$$

$$\theta = 33.72^\circ$$

$$\lambda = 1.5418 \text{ \AA}$$

$$\begin{aligned}
 \text{The crystallite size} &= \frac{0.9 \times 1.5418}{0.01927 \cos 33.72} \\
 &= 86.6 \text{ \AA} \\
 &= 8.7 \text{ nm}
 \end{aligned}$$

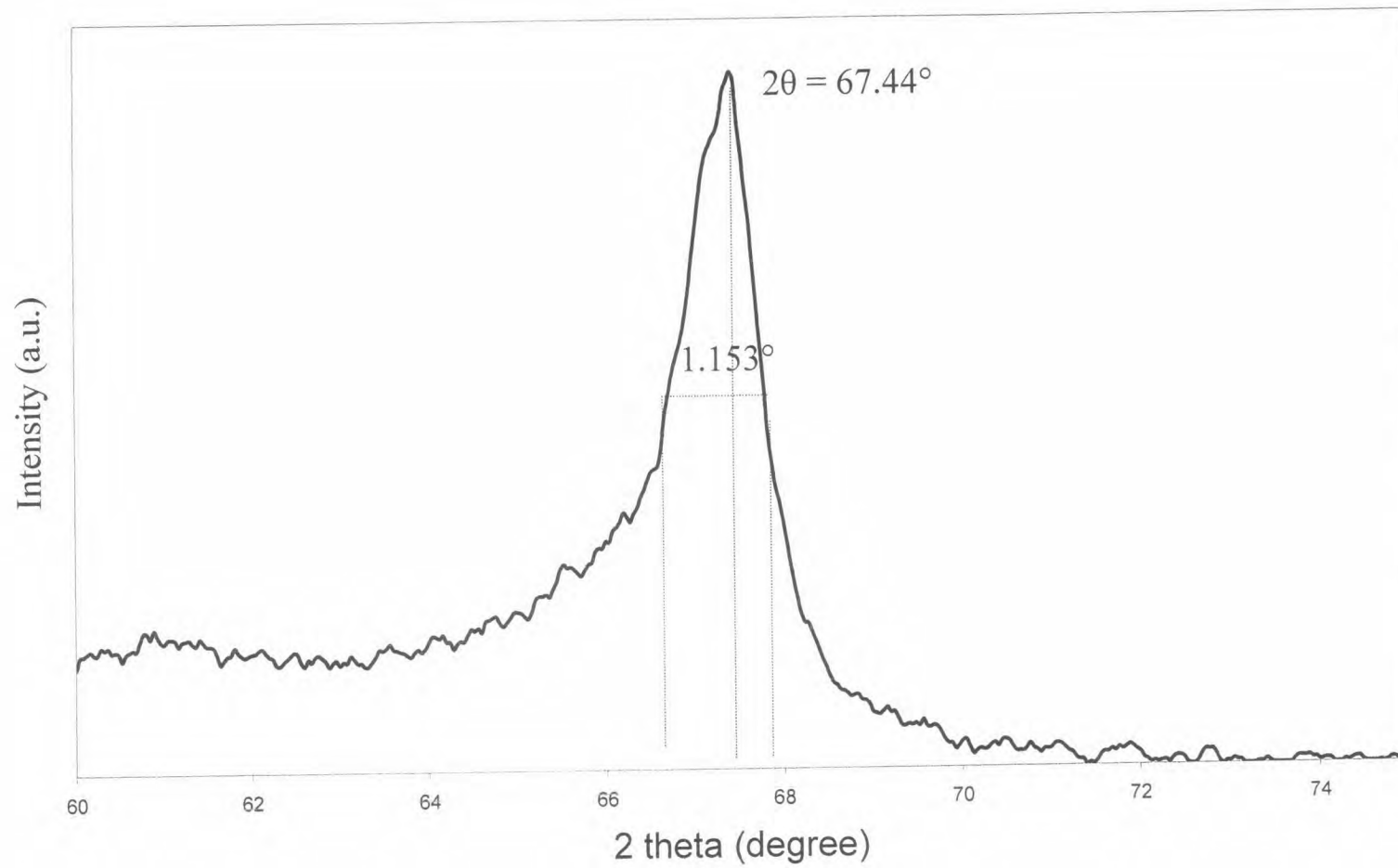


Figure A.1 The diffraction peak of pure chi alumina for calculation of the crystallite size.

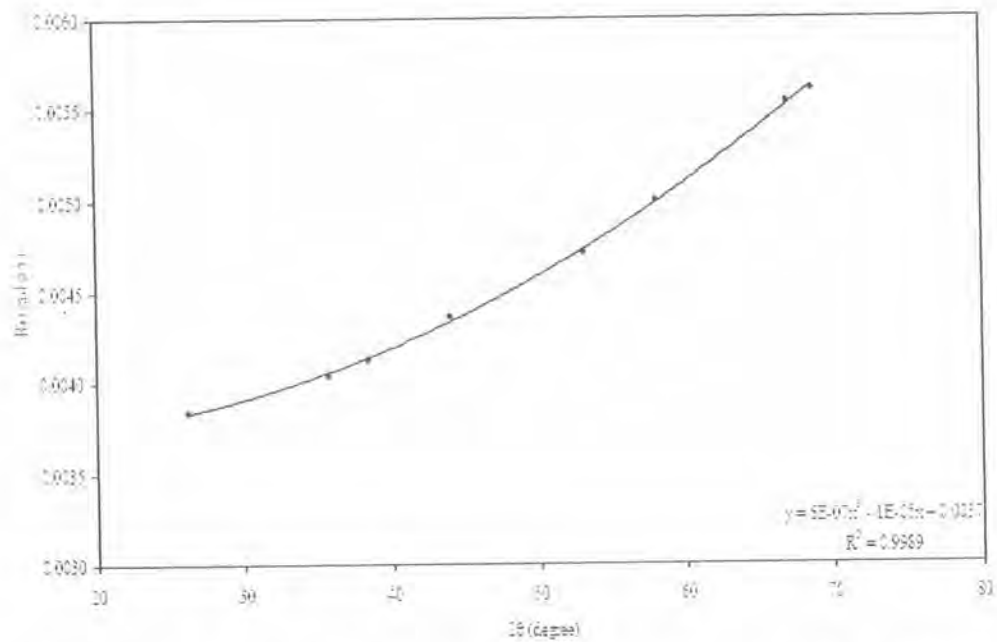


Figure A.2 The plot indicating the value of line broadening due to the equipment. The data were obtained by using α -alumina as a standard.

APPENDIX B

CALCULATION OF THE ACIDITY

This appendix showed the calculation of the acidity of alumina catalysts from the NH₃-TPD Profiles and Titration with ion exchange of alumina catalysts.

$$\text{The acidity} = \frac{\text{mole of NH}_3}{\text{amount of dry catalyst}}$$

Example: Calculation of the acidity of χ -Al₂O₃

The NH₃-TPD Profiles:

From the Figure B.1, area 1 = 0.00083 and area 2 = 0.001572

$$\begin{aligned} \text{Under area of the NH}_3\text{-TPD Profiles of } \chi\text{-Al}_2\text{O}_3 &= \text{area 1} + \text{area 2 (from Figure B.1)} \\ &= 0.00083 + 0.001572 \\ &= 0.002402 \end{aligned}$$

The mole of NH₃ was calculated from the calibration curves of NH₃ in Figure B.2.

$$\begin{aligned} \text{The mole of NH}_3 \text{ of } \chi\text{-Al}_2\text{O}_3 &= 0.002402 \times 0.0003 \\ &= 7.216 \times 10^{-7} \text{ mole} \end{aligned}$$

$$\text{Amount of } \chi\text{-Al}_2\text{O}_3 = 0.1011 \text{ g}$$

$$\begin{aligned} \text{The acidity of } \chi\text{-Al}_2\text{O}_3 &= (7.216 \times 10^{-7}) / 0.1011 \text{ mol NH}_3 / \text{g catalyst} \\ &= 7.14 \times 10^{-6} \text{ mol NH}_3 / \text{g catalyst} \\ &= 7.14 \text{ } \mu\text{mol NH}_3 / \text{g catalyst} \end{aligned}$$

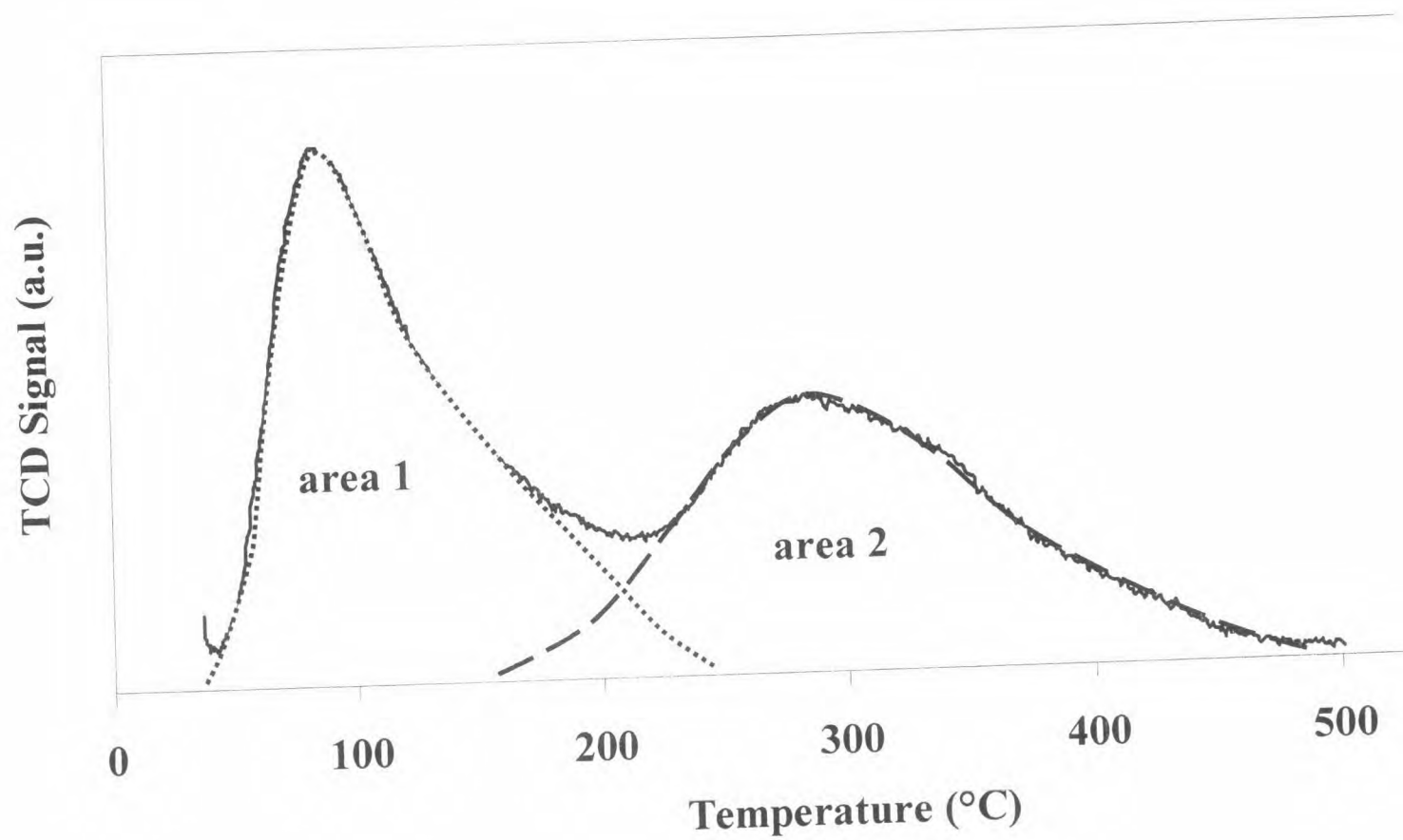


Figure B.1 The NH_3 -TPD Profiles of pure chi alumina for calculation of the acidity

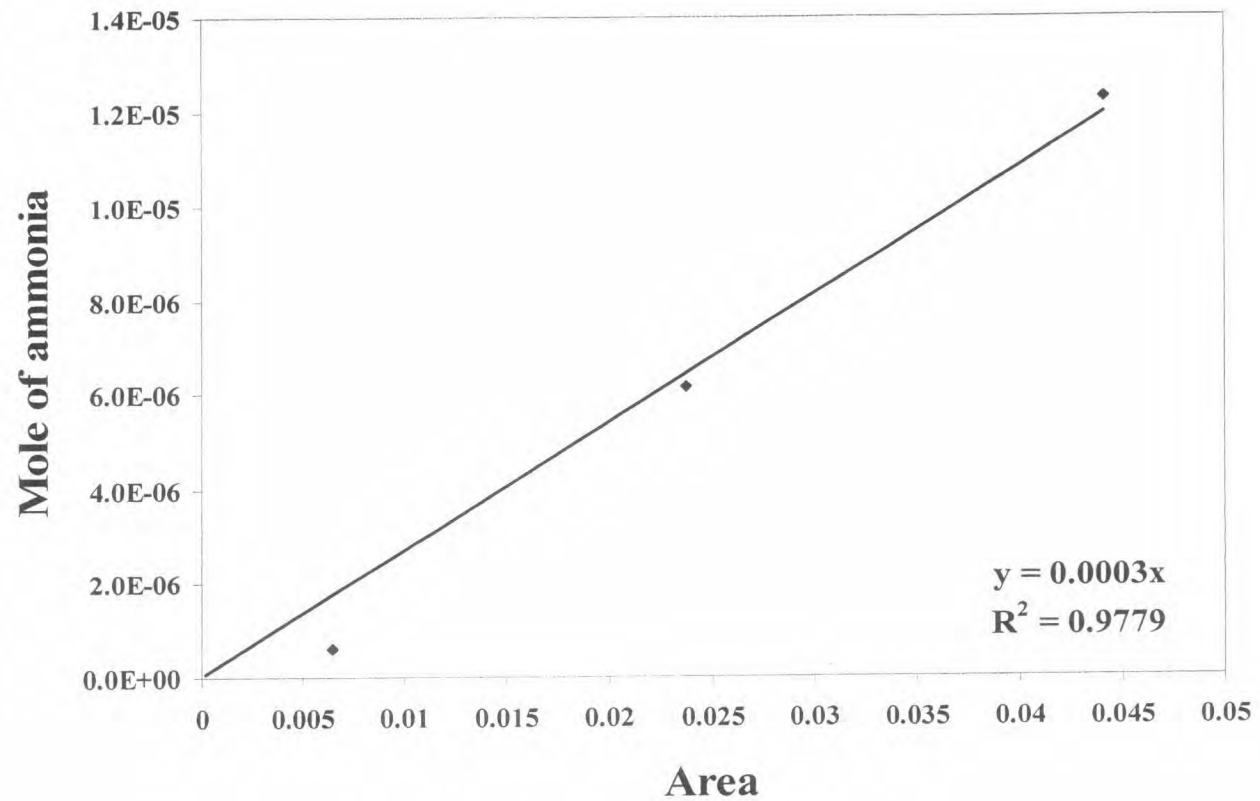


Figure B.2 The Calibration curve of ammonia

APPENDIX C

CALCULATION FOR METAL ACTIVE SITES AND DISPERSION

Calculation of the metal active sites and metal dispersion of the catalyst measured by CO adsorption is as follows:

Let the weight of catalyst used	= W	g
Integral area of CO peak after adsorption	= A	unit
Integral area of 50 μ l of standard CO peak	= B	unit
Amounts of CO adsorbed on catalyst	= B-A	unit
Volume of CO adsorbed on catalyst	= $50 \times [(B-A)/B]$	μ l
Volume of 1 mole of CO at 30°C	= 24.86×10^6	μ l
Mole of CO adsorbed on catalyst	= $[(B-A)/B] \times [50/24.86 \times 10^6]$ mole	
Molecule of CO adsorbed on catalyst	= $[1.61 \times 10^{-6}] \times [6.02 \times 10^{23}] \times [(B-A)/B]$ molecules	
Metal active sites	= $9.68 \times 10^{17} \times [(B-A)/B] \times [1/W]$ molecules of CO/g of catalyst	
Molecules of Pt loaded	= $[\%wt \text{ of Pt}] \times [6.02 \times 10^{23}] / [MW \text{ of Pt}]$ molecules/g of catalyst	
Metal dispersion (%)	= $100 \times [\text{molecules of Pt from CO adsorption} / \text{molecules of Pt loaded}]$	

APPENDIX D

CALIBRATION CURVES

The thermal conductivity detectors (TCD) independently connected with two gas chromatographs (SHIMADZU GC 8ATP and SHIMADZU GC 8AIT) were used to analyze the concentration of the sampling gases in the catalytic activity test. It is note the operating condition of gas chromatograph for making the calibration curves is maintained to be similar to that for testing the reaction. These calibration curves are given in Figures D.1- D.5.

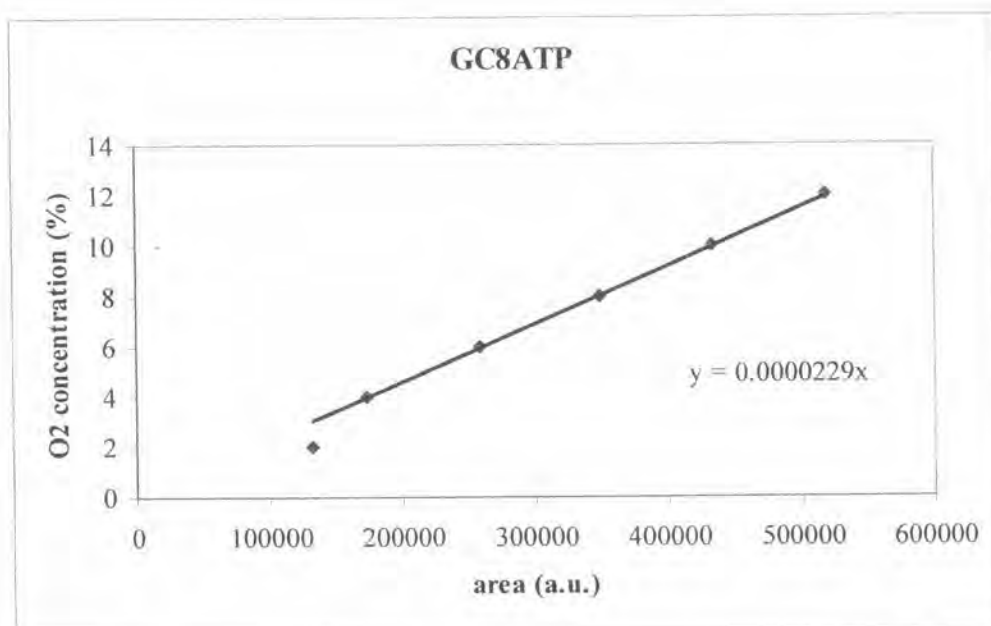


Figure D.1 The calibration curve of oxygen from TCD of GC 8ATP

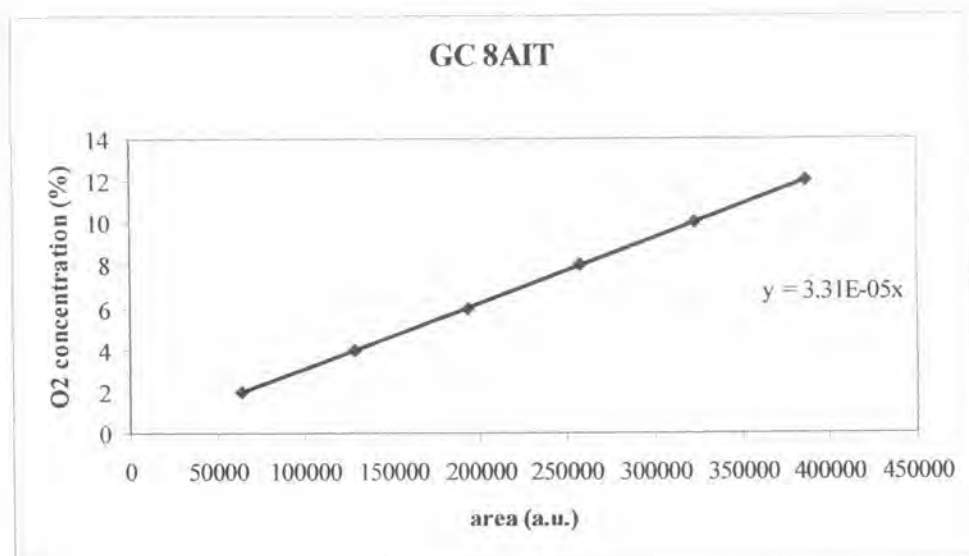


Figure D.2 The calibration curve of oxygen from TCD of GC 8AIT

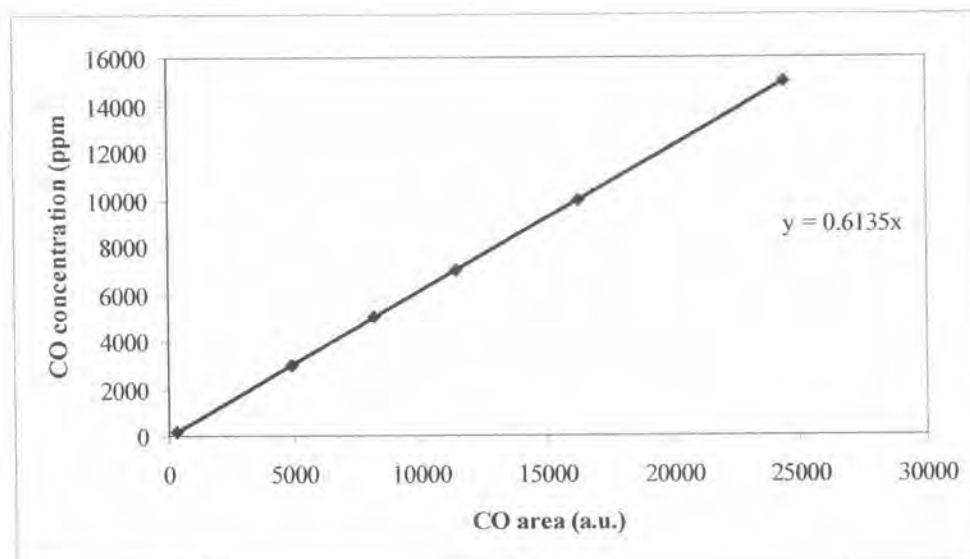


Figure D.3 The calibration curve of carbon monoxide

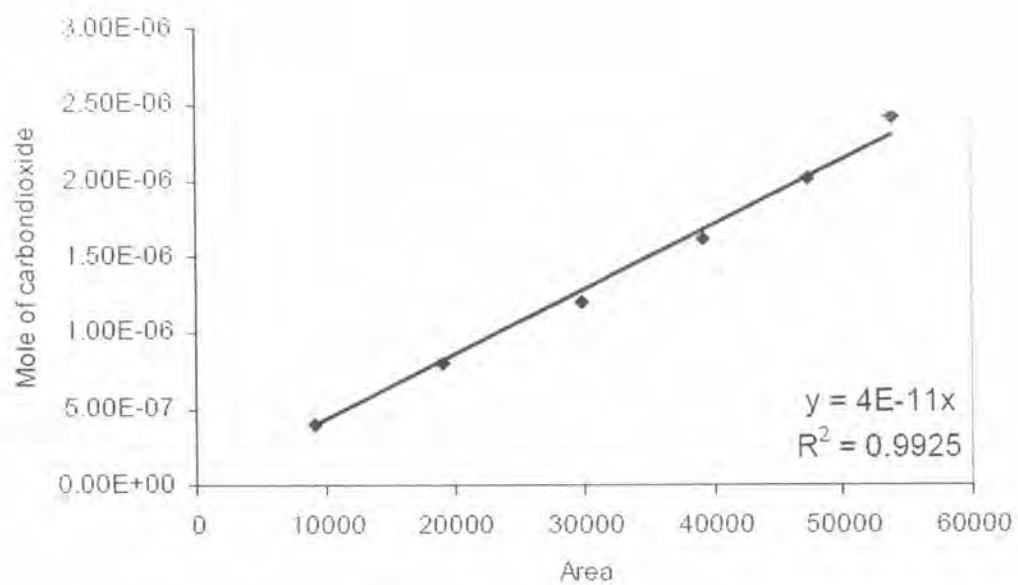


Figure D.4 The calibration curve of carbon dioxide

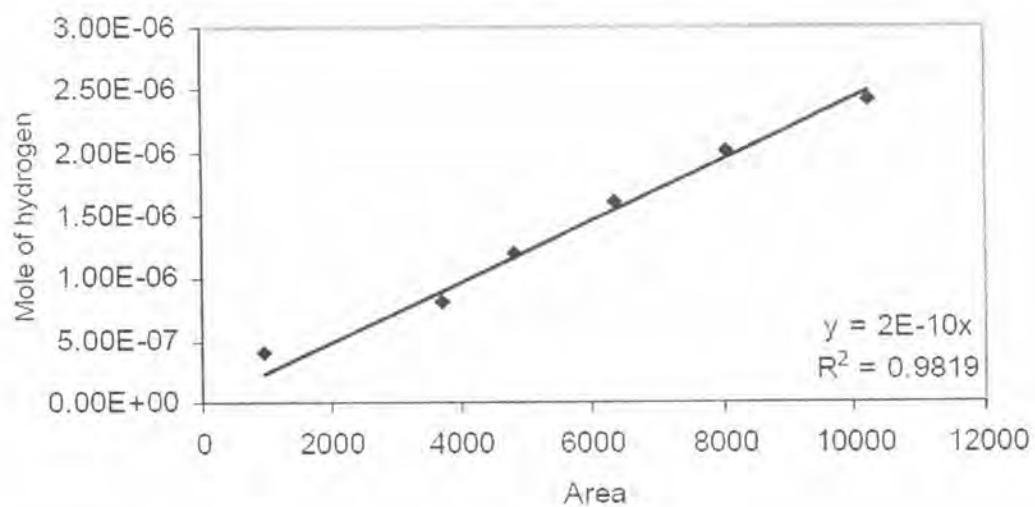


Figure D.5 The calibration curve of hydrogen

APPENDIX E

TEMPERATURE PROGRAM DESORPTION OF AMMONIA

The raw data of the ammonia desorption are shown in the Figure E.1.

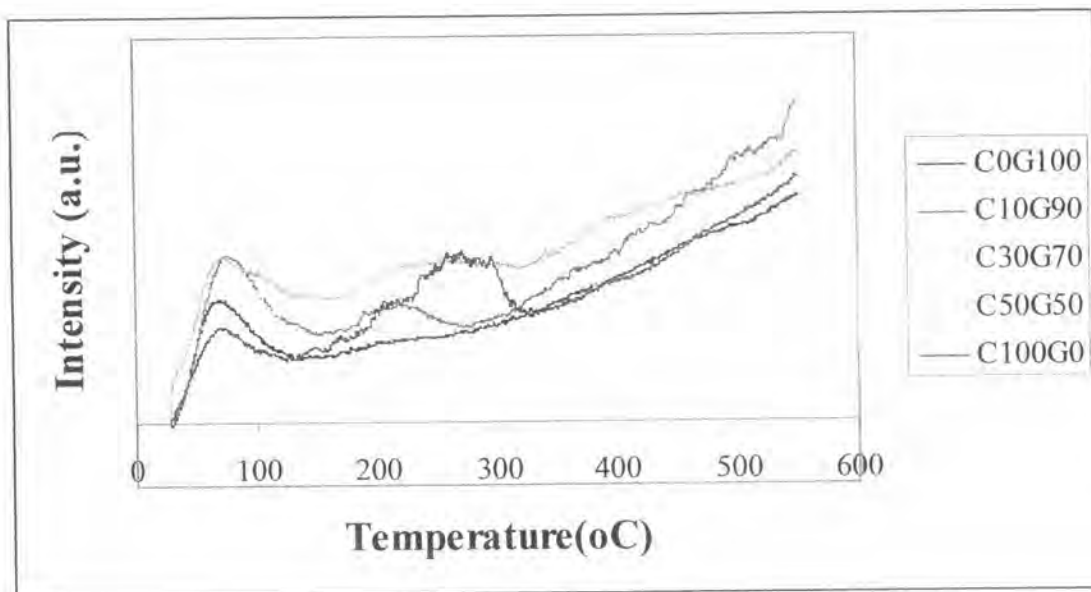


Figure E.1 The ammonia desorption profile of alumina supports

APPENDIX F**LIST OF PUBLICATIONS**

1. Chatchai Meephoka, Choowong Chaisuk, Panida Samparnpiboon, Piyasan Prasertthdam "Effect of phase composition between nano γ - and χ - Al_2O_3 on $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst in CO oxidation", *Catalysis Communications*, 9, 2008, 546-550.

2. Chatchai Meephoka, Choowong Chaisuk, Panida Samparnpiboon, Piyasan Prasertthdam "Effect of phase composition between nano γ - and χ - Al_2O_3 on $\text{Ag}/\text{Al}_2\text{O}_3$ catalyst in SCR of NO by propane under lean-burn condition", The 13th Regional Symposium on Chemical Engineering, *Advances in Chemical & Biomolecular Engineering*, 3-5 December 2006, Singapore.

Effect of phase composition between nano γ - and χ - Al_2O_3 on Pt/ Al_2O_3 catalyst in CO oxidation

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Received 21 September 2006; received in revised form 30 March 2007; accepted 17 April 2007
Available online 30 April 2007

Abstract

Alumina supports were prepared by solvothermal method of a mixed solution of toluene and butan-1-ol for various chi/gamma phase compositions and the Pt/ Al_2O_3 catalyst was prepared by the incipient wetness impregnation technique. The catalysts were evaluated in the carbon monoxide oxidation. Increasing amount of %chi phase in the alumina supports has roughly the same BET surface area. The different alumina supports were affected on the Pt dispersion on alumina. The pure chi alumina and pure gamma alumina supports had the same effect of catalyst activity. In the various chi/gamma phase compositions, it was found that Pt dispersion and catalyst activity are lower than pure gamma and chi phases for alumina support with 10% chi. The alumina supports with 30–70% chi gave higher dispersion and activity than pure phase and 10% chi support.

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Keywords: γ - Al_2O_3 ; χ - Al_2O_3 ; Phase composition; Pt/ Al_2O_3 ; CO oxidation

1. Introduction

Alumina (Al_2O_3) has been considered as one of the most promising advanced materials for variety of applications because of its distinctive chemical, mechanical and thermal properties. Alumina is widely used as ceramic, ceramic coating, catalyst, catalyst support, wear-resistance material, soft abrasive, medicinal material, filler, crucible, and adsorbent. Many preparation methods have been developed to produce alumina powder that possesses the required characteristics. Examples of these methods are precipitation from solution [1], sol–gel synthesis [2], hydrothermal synthesis [3], microwave synthesis [4], emulsion

evaporation [5] and solvothermal synthesis [6–12]. In such methods, the characteristics of alumina are tailored-made by controlling the crystal type, crystal size, particle shape, particle size distribution, degree of agglomeration and porosity of particles [13–16]. Among various methods, the products obtained by solvothermal synthesis show uniform morphology, well-controlled chemical composition and narrow size distribution. It was also found that crystal structures, grain sizes and morphologies can be controlled by process conditions such as solute concentration, reaction temperature, reaction time and the type of solvent [17–20].

In general, nature of the catalyst support, especially phase types, is very important to provide the catalytic properties and performances. Chary et al. [21] reported that MoO_3 dispersed better on anatase TiO_2 than when it was supported on rutile TiO_2 . It is interesting to investigate

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this topic in order to obtain the useful information for developing the catalysis field. In this work, the alumina support is focused. The gamma phase is well-known supports because it shows a high surface area. The structure of gamma alumina has been described as defect spinal structure [22]. The ideal spinal structure AB_2O_4 is represented by $2 \times 2 \times 2$ array of an fcc closet packing, with A and B cations occupying the $8a$ (of the 64 available) tetrahedrally and the $16d$ (of 32) octahedrally coordinated interstitial sites. In addition to the gamma phase, other phases have been also used as the supports. The alpha alumina is usually used as the thermal stabilizing material but it shows low surface area. Many researchers have reported the promising properties of other transition phases. Mekasuwandumrong et al. [23] found that the γ - Al_2O_3 synthesized by the solvothermal method gave both high thermal stability and large surface area. In our preliminary work [23,24], it was found that its surface chemistry is different from that of α - and γ - Al_2O_3 . The common metastable of chi alumina crystal structures are based on hcp close packing of the oxygen atom. Hexagonal chi alumina seems to possess a layer structure, the arrangement of anions being inherited from gibbsite, whereas the aluminum cations occupy octahedral site within the hexagonal oxygen layers [25]. Hence, the chi phase may be possible to make a dispersed metal catalyst. In this research, the characteristics of gamma, chi and mixed alumina phase are investigated. Platinum was selected as the dispersed metal on these supports. The physicochemical properties of alumina and Pt supported on alumina consisting of various chi/gamma phase compositions were investigated by X-ray diffraction (XRD), N_2 physisorption, temperature programmed reduction (TPR) and pulse CO chemisorption methods. Furthermore, the catalytic properties of the Pt/ Al_2O_3 catalysts were evaluated by CO oxidation.

2. Experimental

2.1. Preparation of Al_2O_3 and Pt/ Al_2O_3 catalyst samples

Al_2O_3 supports with various chi/gamma phase compositions were obtained by solvothermal synthesis of a mixed solution of toluene and 1-butanol in aluminum isopropoxide. The autoclave was purged completely by nitrogen before heating up to 300 °C at a rate 2.5 °C min^{-1} and holding at that temperature for 2 h. After the system was cooled down, the resulting powders were repeatedly washed with methanol and subsequently dried in air. The as-synthesized powders were subsequently calcined by 100 $cm^3 min^{-1}$ of air flow with a heating rate of 10 °C min^{-1} until the temperature reached 600 °C and holding at that temperature for 6 h.

The Pt/ Al_2O_3 catalyst was prepared by incipient wetness impregnation technique with hexachloroplatinic acid hexahydrate ($H_2PtCl_6 \cdot 6H_2O$) obtained from Aldrich. The platinum loading was fixed as 0.3 wt% on a dry basis. After impregnation, the resulting samples were dried at 110 °C

overnight and calcined in air at 380 °C for 2 h. The size range of the powdered catalysts is between 37 and 74 μm (200/400 mesh size).

2.2. Catalyst characterization

The BET surface areas of the samples were determined by N_2 physisorption using a Micromeritics ASAP 2020 automated system. Each sample was degassed under vacuum at $<1.3 Pa$ in the Micromeritics ASAP 2000 at 150 °C for 4 h prior to N_2 physisorption. The XRD spectra of the catalyst samples were measured from 20° to 80° 2θ using a SIEMENS D5000 X-ray diffractometer and Cu $K\alpha$ radiation with a Ni filter.

Temperature programmed reduction (TPR) study was performed in a Micromeritic ChemiSorb 2750 automated system attached with ChemiSoft TPx software. A 0.1 g of a calcined catalyst was placed in a quartz tube in a temperature-controlled oven and connected to a thermal conductivity detector (TCD). The catalyst was first purged under 100 $cm^3 min^{-1}$ of N_2 flow at 200 °C for 1 h (using a ramp rate of 10 °C min^{-1}) and cooled down to room temperature. The carrier gas was 10% H_2 in Ar. During reduction, a cold trap was placed before the detector to remove produced water. The temperature programmed reduction was performed with a constant heating rate of ca. 10 °C min^{-1} from 35 °C to 600 °C. The thermal conductivity detector was conducted to measure the amount of hydrogen consumption.

Relative percentages of platinum dispersion were determined by pulsing carbon monoxide over the reduced catalyst. A 0.1 g of the catalyst was placed in a quartz tube in a temperature-controlled oven. The amounts of CO chemisorbed on the catalysts were measured using a Micromeritic Chemisorb 2750 automated system attached with ChemiSoft TPx software at room temperature. Prior to chemisorption, the sample was reduced in a H_2 flow at 500 °C for 2 h and then cooled down to ambient temperature in a He flow.

2.3. Reaction study

The reaction tests were performed in a quartz tube with 6 mm inside diameter. This tube was filled with 0.2 g of catalyst held in place with quartz wool. It was placed inside an electrically heated sleeve furnace equipped with a temperature controller. Composition of the reactor off gases was measured chromatographically using two 6 port sampling valves and two TCD GCs (SHIMADZU GC 8A), one equipped with a molecular sieve 5A column (for separating O_2 and CO) and the other with a Porapak QS column (for separating CO_2).

Temperature programmed reaction was performed to observe the catalyst activity as a function of temperature. The gas feed was obtained by mixing three gas sources. They consisted of $5.47 \pm 2\%$ CO in He, $10.4 \pm 0.2\%$ O_2 in He and ultrahigh pure He (99.99%). The composition

of gas mixture is 0.2 vol% CO + 0.9 vol% O₂ + 98.9 vol% He. The total volumetric flow rate of 100 cm³ min⁻¹ was corresponding with GSHV of 16,000 h⁻¹. The reaction gases were introduced to the reactor whose temperature was raised from ambient temperature to 350 °C stepwise. At each step, the catalyst bed was held at constant temperature until the steady state was reached. This was achieved within 20 min.

3. Results and discussion

Alumina supports were prepared by the solvothermal synthesis. The gamma and chi phases were produced using the different solvent precursor, i.e. 1-butanol and toluene, respectively. Various chi/gamma phase compositions were controllably obtained by mixing 1-butanol and toluene in an appropriate ratio. XRD pattern of the alumina supports is shown in Fig. 1. For the pure gamma phase, XRD peaks at 32°, 37°, 39°, 45°, 61° and 66° were evident. When adding toluene in 1-butanol, XRD peaks were appeared at 37°, 40°, 43°, 46°, 60°, and 67°. The peak at 43° is dominant. This peak showed characteristics of the chi phase and thus the increase of %chi alumina phase leads to larger peak area at 43°. Certainly, the pure gamma alumina did not show the peak area at 43°. The results are in agreement with the work previously reported by our group on the effect of solvent on the preparation of alumina [24]. In this paper, the alumina samples consisting of 0%, 10%, 30%, 50%, 70% and 100% chi phase are named as C0G100, C10G90, C30G70, C50G50, C70G30 and C100G0, respectively. The phase compositions of alumina supports were determined by area of chi major peak (43°) from XRD pattern. The calibration curve of this peak was obtained by varying the ratio of pure gamma and pure chi alumina in the physical mixtures. Therefore, we can calculate %chi phase in sample from this calibration curve. The calculation method gave an error in a range of ±10%.

The physical properties of the alumina products are summarized in Table 1. The BET surface area decreased slightly when the chi phase was in the alumina structure. This method gave an error in a range of ±10%. The pure gamma and pure chi phases showed 226 and 168 m² g⁻¹,

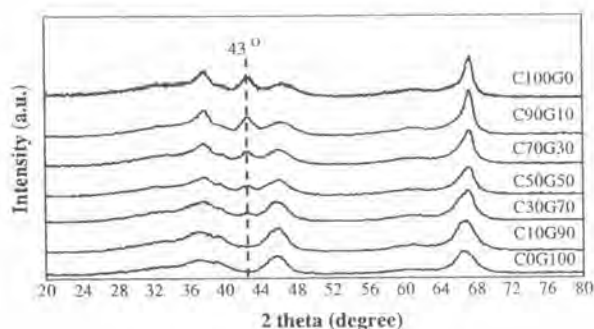


Fig. 1. XRD patterns of alumina samples.

Table 1
Surface area of alumina supports

Sample	Crystallite size (nm)	BET surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Average pore diameter (nm)
C0G100	5	226	0.63	8
C10G90	5	213	0.50	8
C30G70	5	203	0.53	9
C50G50	6	182	0.44	7
C70G30	6	177	0.42	6
C100G0	6	168	0.57	9

respectively. The average pore diameter was rather similar for the different ratio of phase composition.

The aluminas with various phase compositions were used as the catalyst support. The platinum was impregnated on them at about 0.3 wt%. In this paper, the catalysts samples were also addressed. For example, when the support is C30G70, the catalyst is named as Pt/C30G70. Dispersion of active surface Pt on these supports was measured by CO pulse chemisorption. The results are given in Table 2. The BET surface areas of the alumina supported Pt catalysts were slightly less than those of the original alumina supports. This indicates plugging of the loaded platinum on some of the alumina pores. After loading the Pt, decrease of the BET surface area with increasing the fraction of chi phase was observed similar to behavior of the unloaded alumina support. The metal active sites on the aluminas with pure phase were rather equivalent at approximately 3.2 × 10¹⁸ molecule CO g⁻¹ catalyst. The mixed phase aluminas can assist high dispersion of platinum on them except the 10% chi phase. Surprisingly, the metal dispersion was maintained constant in a wide range between 30% and 70% chi phase composition. This phenomenon can be useful for the insensitive-structure reaction. However, a low content of the chi phase in the alumina could promote formation of larger platinum particle size. This effect was also observed on the other metal oxides. Panpranot et al. [26] have studied effect of the phase composition of TiO₂ on the amount of palladium active sites. They reported that when the rutile phase of TiO₂ was increased, the amount of chemisorbed CO decreased.

Temperature programmed reduction (TPR) is a powerful tool to study the reduction behavior of the catalysts. The TPR profiles of various chi/gamma phase

Table 2
Catalyst properties of 0.3%Pt/Al₂O₃

Sample	BET surface area (m ² g ⁻¹)	CO chemisorption × 10 ⁻¹⁸ (molecule CO g ⁻¹ catalyst)	%Pt dispersion (%)	Metal size (nm)
Pt/C0G100	203	3.25	38.9	2.92
Pt/C10G90	195	2.53	30.3	3.74
Pt/C30G70	189	3.56	42.6	2.66
Pt/C50G50	177	3.55	42.5	2.67
Pt/C70G30	163	3.58	42.8	2.65
Pt/C100G0	151	3.18	38.1	2.98

compositions of alumina supported platinum catalysts are shown in Fig. 2. The TPR profiles of platinum species were rather complex. They indicated differences in the interaction between the platinum species and the supports. All the catalyst samples exhibited two main reduction regions in ranges of 200–300 and 400–500 °C. Navarro et al. [27] found two main reduction peaks at 110 and 239 °C and a minor peak at 377 °C over 0.75 wt% Pt/Al₂O₃. They pronounced that the low-temperature peak, only observed for this platinum-supported sample, was assigned to the reduction of PtO₂ species [27,28] and the peaks at 239 and 377 °C were attributed to oxychlorinated species in the bulk and two-dimensional phase, with a strong interaction with alumina, respectively [27–29]. To confirm the presence of the PtO_xCl_y species on our catalyst surface, the amount of Cl was first determined by EDX technique. EDX results showed no Cl element in every catalyst samples. Therefore, all of our TPR profiles did not show the reduction of the PtO_xCl_y species. Both of the reduction peaks were assigned to the reduction of PtO_x species. The 200–300 °C peaks were bulk phase of the PtO_x while the 400–500 °C peaks were addressed as its strong interaction dispersive phase. This speculation is in agreement with some literatures [30,31]. Tiernan et al. [30] found two reduction peaks at 220 and 420 °C over Pt/Al₂O₃. Two reduction peaks were assigned to the reduction of dispersed PtO_x. Santos et al. [31] reported that the TPR profile of Pt/Al₂O₃ sample showed two peaks at 287 and 434 °C. They pronounced that the peak at 287 °C was assigned to a reduction of Pt-oxide species and/or to a reduction of oxychlorplatinum surface complex [PtO_xCl_y]_s. The peak at 434 °C was assigned to a reduction of dispersed Pt in isolated patches PtO_x on alumina. From Fig. 2, the presence of the chi phase in the γ-Al₂O₃ can lower the reduction temperature of PtO_x species. The amount of H₂ consumption for each sample was different as shown in Table 3. It was significantly larger when the chi phase composition exceeded 30%, especially at 50% and 70% of chi phase. This implied a high chemical stoichiometric value of O/Pt in PtO_x complex or formation of PtAl₂O₄ spinal species

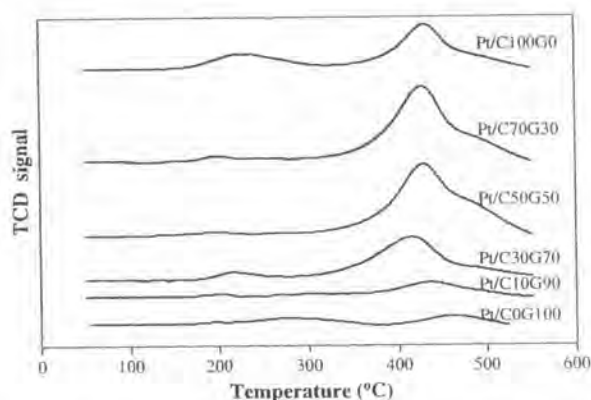


Fig. 2. Temperature program reduction profiles of catalyst samples.

Table 3
The H₂ volume of the reduction peaks

Sample	Temperature (°C)	H ₂ volume (mL g ⁻¹)	N _O /N _{Pl}
Pt/C0G100	280	0.15	0.8
	463	0.16	
Pt/C10G90	202	0.02	0.7
	437	0.24	
Pt/C30G70	216	0.07	1.7
	415	0.59	
Pt/C50G50	200	0.05	2.8
	428	1.01	
Pt/C70G30	197	0.05	2.8
	427	1.02	
Pt/C100G0	229	0.22	2.0
	432	0.55	

[32]. Effect of the phase composition on the reduction characteristics on the other catalysts was also reported in the literature [33]. Jongsomjit et al. [33] have studied cobalt dispersion on TiO₂ and found that the presence of 19% rutile phase in titania facilitated the reduction of highly dispersed cobalt oxide to cobalt metal.

CO oxidation was carried out as an insensitive-structure probe reaction to determine the catalytic activity of the catalyst samples. The results are shown in Fig. 3. As expected, the CO oxidation activities were followed by the amount of platinum active sites. The presence of 30–70% chi phase composition can lower the light-off temperature by 15 °C. On the other hand, the 10% chi phase showed the worst catalytic activity in this reaction. These results can confirm CO chemisorption measurement as well. Besides the promotional effect of the insensitive-structure reaction, introduction of the chi phase in the γ-Al₂O₃ should be possible to be a promising support for some structure-sensitive reaction as studied afterwards.

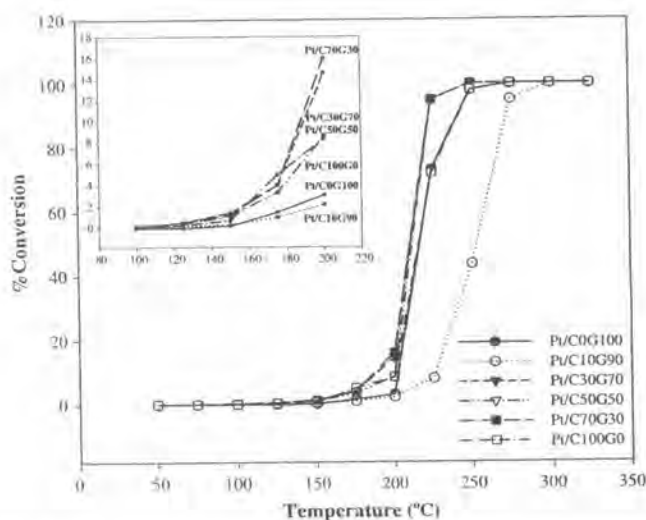


Fig. 3. CO₂ conversion profiles of 0.3 wt% Pt/Al₂O₃ for the CO oxidation.

4. Conclusion

The chi phase was added in the γ -Al₂O₃ to change some properties of the support. It increased the platinum dispersion, except the 10% chi phase composition, and certainly improved the catalytic activity for the insensitive-structure reaction such as CO oxidation. In addition, the chi phase changed the reduction characteristics of platinum oxides on the γ -Al₂O₃. It lowered the reduction temperature. The ratio of oxygen and platinum can be increased when a high composition of the chi phase was introduced.

Acknowledgement

Financial supports from the Commission of higher Education, Ministry of Education, Thailand.

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