

SYNTHESIS AND CHARACTERIZATION OF POLYMERIC V₂O₅/AlO(OH)

WITH NANOPORES ON ALUMINA SUPPORT

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Abstract

Polymeric vanadium pentoxide gel was formed via the reaction of V₂O₅ powder with hydrogen peroxide. The polymeric vanadium pentoxide gel was then dispersed in alumina gel. Different vanadium loading composites were coated on alumina support and calcined at 500°C for 1hr. These composite layers were characterized using EDX, FT-IR, XRD, SEM, TGA and Autosorb. It was found that the lamellar structure of polymerized vanadium pentoxide was retained in the inorganic matrix. Crystalline alumina in gamma phase was formed after calcinations. However, crystalline V₂O₅ was not found in the composite layer and it was possibly due to low calcination temperature. Alumina top layer with 21.81 wt% of V₂O₅ gel showed smaller pore diameter (5.483nm) and improved BET surface area (380.4 m²/g).

Keywords: Vanadium pentoxide, Aluminium oxide, Alumina Support

Introduction

Vanadium oxide is one of the most important catalysts in metal oxide catalysis. It plays important roles in oxidation reactions such as selective oxidation of alkanes and alkenes, oxidation dehydrogenation of alkanes and alkenes and oxidative coupling of methane [1]. Supported vanadium oxide shows improved catalytic activity because of an increase in surface area and mechanical strength [2]. By incorporating vanadium oxide in porous membranes, researchers have found that it also improves the efficiency of membrane reactors [3, 4].

Due to the reasons above, several methods have been developed to create a homogeneous and uniform distribution of this transition metal oxide on inorganic supports. The most widely used preparation technique is impregnation using ammonium metavanadate [5, 6]. Besides that, some vanadium based membranes are prepared using sol-gel method or chemical vapor deposition [7 - 9]. In this work, a simple and economical route to prepare vanadium based membrane was reported.

Experimental

Preparation of alumina support layer and intermediate layer

Alumina support layers and intermediate layers were prepared by doctor blade casting method as described elsewhere [10, 11]. An alumina powder (AKP 30, Sumitomo Chemicals, Japan) with an average particle size of 0.4 μm and a specific

surface area of $6.5\text{ m}^2\text{ g}^{-1}$ was used in this study. The alumina powder was dispersed in water and stirred at room temperature for 15 min. Then, an aqueous solution of 8.3 wt% polyethylene glycol (PEG 6000, Merck Company) as plasticizer and 8.3 wt% methyl cellulose (MTC, BDH Laboratory Supplies) as binder was added. The agglomerates and entrapped air in the slurry was removed by wet sieving through a $75\text{ }\mu\text{m}$ sieve. Several dry support tapes were pressed together at 60 MPa to form support with thickness 1-2 mm. The laminated membrane was then sintered at the condition stated below.

- (a) $2^\circ\text{C}/\text{min}$ from 30 to 500°C
- (b) 90 min at 500°C
- (c) $5^\circ\text{C}/\text{min}$ from 500 to 1200°C
- (d) 60 min at 1200°C
- (e) $0.5^\circ\text{C}/\text{min}$ from 1200 to 30°C

Synthesis of vanadium pentoxide gel ($\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$)

Vanadium pentoxide gel was prepared by dissolution reaction of V_2O_5 in H_2O_2 as described elsewhere [12]. The reaction is highly exothermic so diluted hydrogen peroxide solution (10 wt%) was used. 1 g of V_2O_5 powder (Riedel-de Haën) was slowly dissolved in 100 ml hydrogen peroxide solution (Merck Company, Germany). Clear orange solution was formed after about 15 min and it turns to deep red after 2 h. Red polymerized $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ gel was formed after 24 hr aging.

Synthesis of alumina gel ($AlO(OH) \cdot nH_2O$)

Alumina gel was prepared using sol-gel method developed by Yoldas [13]. PEG 10000 (Merk Company) was completely dissolved in the deionized water at 80°C with stirring. The amount of the binder added was designed to be 2%wt of the final solution. Aluminum *sec*-butoxide (Fluka) was then added at 85°C and mixed for 15 min in an open container to evolve butanol. Dilute HCl (1M, Mallinckrodt) was then added as a peptization agent. The time for peptization was 20 h. The final molar ratios were $Al(OC_4H_9)_3 \cdot H_2O \cdot HCl = 1 : 100 : 0.07$. The pH of the sols was proximately 4. The resulting solution was stirred overnight at 80°C in a closed container to form a clear, stable alumina sol.

Preparation of $V_2O_5/AlO(OH)$ on alumina support

The $V_2O_5 \cdot nH_2O/AlO(OH) \cdot nH_2O$ xerogel composite was prepared by mixing 50ml alumina gel with different amounts of polymerized vanadium pentoxide: 5ml, 15ml and 30ml. The mixture is labeled as V01, V03 and V06. The mixtures were stirred using magnetic stirring bar at room temperature for 24hr. The alumina support was dipped into mixture for 5-10s. The coated supports were dried overnight at room temperature. After drying, the coated supports were calcined at 500°C for 1hr. Besides that, pure alumina gel (labeled as $AlO(OH)$) and pure vanadium pentoxide gel (labeled as V_2O_5) were also coated on alumina supports separately for further study.

Characterization techniques

The chemical composition of the mixed oxide was determined by using energy dispersive X-ray analysis (EDX) using Leo Supra 55VP Ultra High Resolution Analytical FESEM. The samples were coated with pure gold and placed on aluminium-gold plating for analyses. Fourier-transform infrared spectra (FT-IR) were recorded at $4000 - 400\text{cm}^{-1}$ using a Fourier Transform Infra Red (FTIR) spectrophotometer (model Perkin Elmer). The spectra were taken from thin KBr pellets containing approximately 1% weight of samples. X-ray diffraction patterns of the samples were measured at room temperature using Philips Goniometer PW1820, diffractometer PW 1710 and x-ray generator PW1729. The phase analysis was done in the range of $10^\circ < 2\theta < 150^\circ$ at a wavelength $\lambda = 1.54060\text{\AA}$. The samples were ground into fine powders before analysis. Thermogravimetric analyses were performed using Thermogravimetric analyzer model Perkin Elmer (TGA 7) to study the weight loss of membrane as a function of temperature. A platinum pan was used to hold the sample with weight around 5mg. Nitrogen was flowed through the furnace which was heated at a rate of $20^\circ\text{C}/\text{min}$ up to a final temperature 550°C . Scanning electron microscopy (SEM) studies were carried out using Leo Supra 55VP Ultra High Resolution Analytical FESEM. The same samples prepared for EDX were used for SEM analyses. The BET surface area, average pore diameter and total pore volume for the samples were determined using Quantachrome Autosorb automated gas sorption system. The system was accompanied by Micropore version 2.48 data acquisition software. The

samples were feed into sampling tube and outgas for 24hr before analyzed

Result and discussion

The FT-IR spectra for the differently synthesized samples are shown in Fig 1 Pure alumina layer shows bands at 3475, 2055 and 1646cm⁻¹ Band at 3475 cm⁻¹ is corresponded to Al-OH group and band at 1646 cm⁻¹ is corresponded to the O-H bond stretching vibration of adsorbed water and coordinated water [14]. Meanwhile, band at 2055 cm⁻¹ is possibly due to the adsorption of CO₂ because CO₂ is strongly chemisorbed by alumina at 25°C [15] V01, V03 and V06 have peaks that are similar to the alumina top layer However, they also show bands at 538, 860, 836 cm⁻¹ which can be associated with δ(VOV) [16] The result indicates that the polymeric structured of the layered vanadium pentoxide is retained in the alumina matrix after the calcinations Besides that, V03 and V06 show peaks at 604 and 593cm⁻¹ which are associated with monomeric V₂O₅ [17] However, the composite samples do not show bands in the range 1050 – 950 cm⁻¹ which are due to the V=O stretching [18] Only V₂O₅ top layer showed bands at 1019, 812 and 522 cm⁻¹ respectively

Powder x-ray diffraction patterns for V01, V03 and V06 are shown in Fig 2 All three samples show peaks at 1.4 Å or 2.0 Å which are corresponded to crystalline alumina in gamma phase [15] Although the samples show the formation of crystalline γ-Al₂O₃ after calcined at 500°C, no crystalline vanadium pentoxide (2θ = 15.4°, 20.3°, 22°, 25.6°, 26.2°, 31°) [3] or aluminium vanadium oxide phase (d = 3.3, 7.1, 3.5 Å) [15]

was found Fig. 3 showed the SEM images of the samples The images also showed no formation of crystalline vanadium pentoxide on the surface of V01, V03 and V06 These three composite surfaces showed amorphous structure similar as alumina top layer With the addition of binder in the alumina sol, no crack was found on these samples

The thermogravimetric curves of the fresh V01, V03 and V06 xerogel composite were shown on Fig 4 All the samples showed four weight loss events The first weight loss in the 30 – 100°C region could be related to the loss of adsorbed water molecules. Weight loss in the second region (100 – 200°C) was possibly due to loss of weakly bound water molecules, coordinated water molecules and interlayer water molecules. The major weight loss event occurs from 200 – 450°C and it corresponds to dehydration and dehydroxylation of the hydrous aluminium oxide Above 450°C, all the samples still showed continue weight loss that was possibly due to hydroxylation of aluminium oxide [19] S I Hong et al [3] have showed that pure vanadium pentoxide will crystallized at temperature higher 320°C However, the result of XRD, SEM and TGA showed that crystalline vanadium pentoxide was not formed in the composite layer at 500°C. Thus, higher temperature of calcinations is possibly needed to grow crystalline V₂O₅ which is the active site for reactions such as selective oxidation [20] More research on different calcinations temperature should be carried out to increase the catalytic structure of vanadium pentoxide in alumina matrix

Specific surface area, average pore diameter and total pore volume of the calcined samples are reported in Table 1. It was found that the specific surface area of top layer

has the highest specific surface area and the smallest average pore diameter if 21.81 wt% vanadium pentoxide gel was added to alumina gel in sample V03. The specific surface area of V03 was 10% higher than pure alumina top layer. Besides that, it is noticed that average pore diameter of V03 and V06 are much smaller compared to pure alumina top layer. However, increasing the vanadium loading will decrease the total pore volume of the composite layer. Among all samples, V03 showed the highest specific area and the smallest average pore diameter. Besides that, the total pore volume of V03 did not decrease more than 7% compared to pure alumina top layer.

Conclusion

FT-IR result has shown that the polymerized V_2O_5 was embedded in alumina matrix without strongly affecting the lamellar structure. Crystalline alumina in gamma phase was formed after 1hr calcinations at 500°C even though polymerized V_2O_5 was embedded in the alumina matrix. However, crystalline V_2O_5 did not form in alumina matrix. More studies on calcinations temperature should be carried out to increase catalytic structure of V_2O_5 . Using Quantachrome Autosorb, it was found that the imbedded 21.81wt% V_2O_5 gel improved the specific area and average pore diameter of the composite layer. V03 showed the optimized specific area of $380.4 \text{ m}^2/\text{g}$ and average pore diameter of 5.483 nm .

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Table 1 Specific surface area, average pore diameter and total pore volume of
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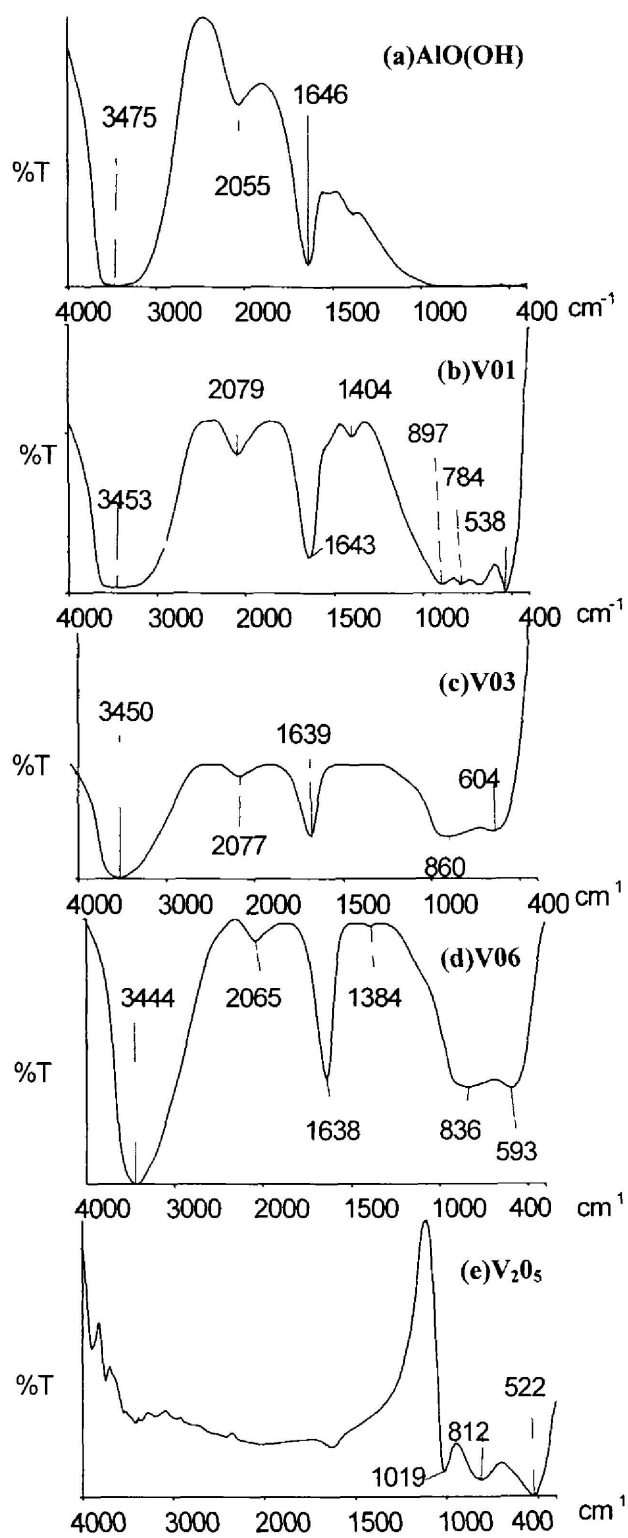


Figure 1 FT-IR curves of (a) AlO(OH) (b) V01, (c) V03, (d) V06 and (e) V₂O₅

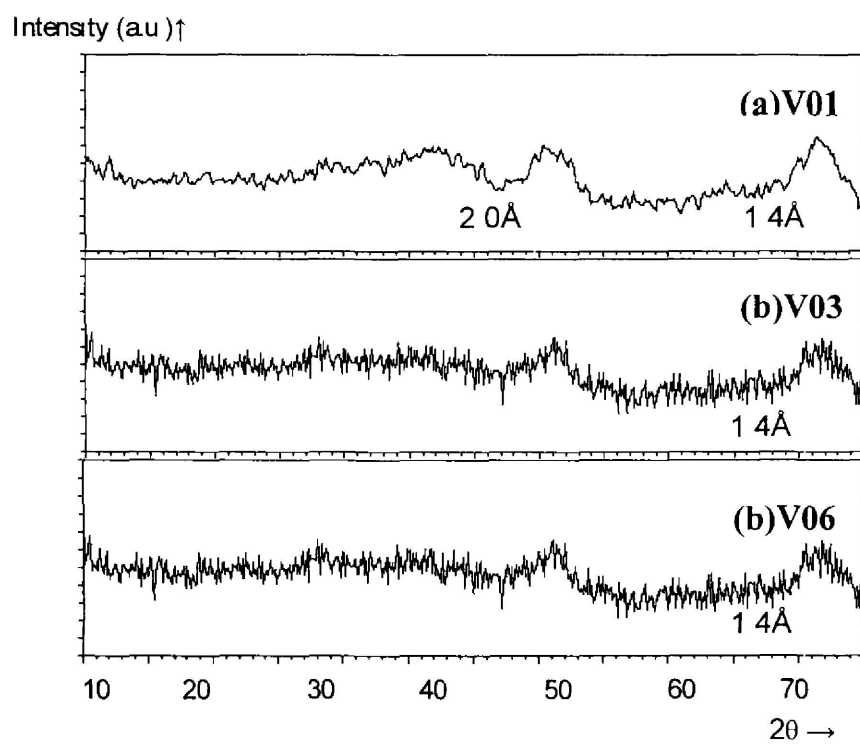


Figure 2 X-ray diffraction patterns of (a) V01, (b) V03 and (c) V06

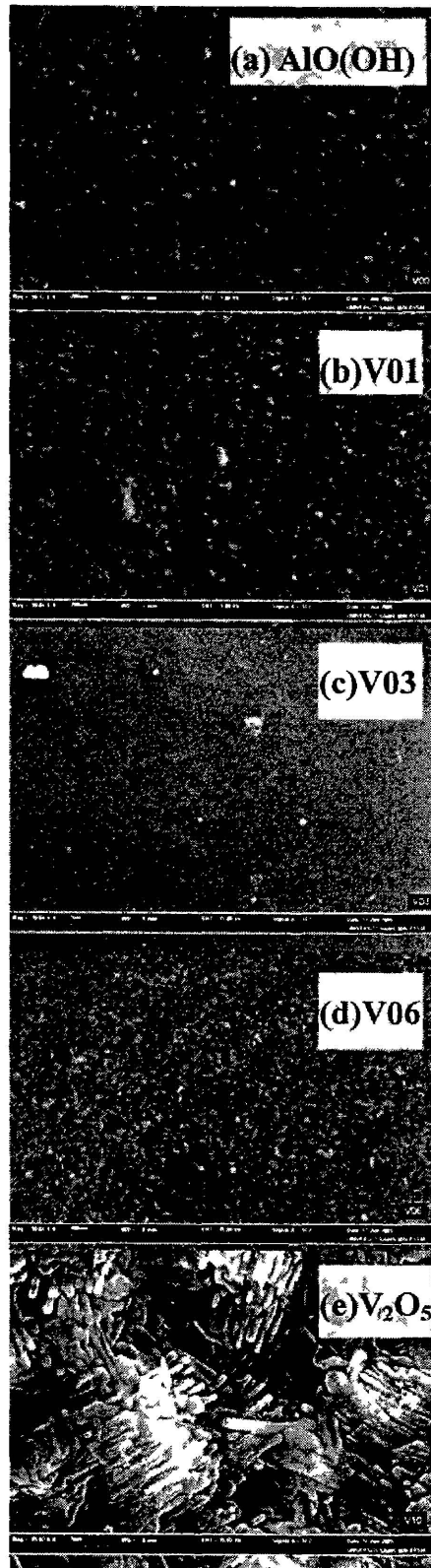


Figure 3 Scanning electron micrographs of (a) AIO(OH) (b) V01, (c) V03, (d) V06 and (e) V₂O₅

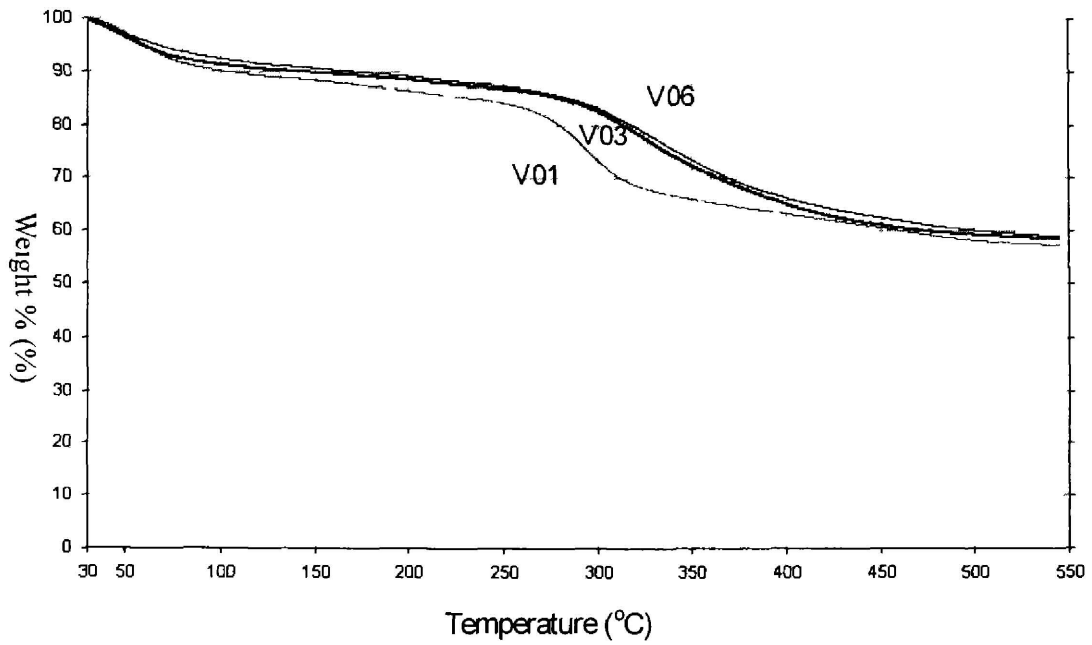


Figure 4 Thermogravimetric curves of V01, V03 and V06

Table 1

Specific surface area, average pore diameter and total pore volume of calcined samples

Sample	BET surface (m ² /g)	Average pore diameter (nm)	Total pore volume (cm ³ /g)
AlO(OH)	3 461x10 ²	6 338	0 5484
V01	3 024x10 ²	6 535	0 4940
V03	3 804x10 ²	5 483	0 5124
V06	3 332x10 ²	5 500	0 4582

ICMAT 2005 - Symposium O (Parallel Session OA) Programme-at-a-glance

Time	4-Jul 05	5-Jul-05	6-Jul 05	7 Jul 05	8-Jul 05	
0730 0830	Registration	Registration	Registration	Registration		
0830 0845	Opening Ceremony G o H Balaji Sadasivan	Plenary 2 Nobel Laureate Steven Chu Chair Lim Kheng Wee IMRE	Plenary 4 Nobel Laureate Alan MacDiarmid Chair Lim Seh Chun NUS	Plenary 6 Nobel Laureate Carl Wieman Chair Lai Choy Heng NUS	Plenary 8 Masuo Aizawa Chair Keith Carpenter ICES	
0845 0900		Plenary 3 Subra Suresh Chair William R Schwallier NUS	Plenary 5 C N R Rao Chair Tan Eng Chye NUS	Plenary 7 Bernard Raveau Chair Yoon Soon Fatt NTU	Plenary 9 Chenming Hu Chair Kwong Dim Lee IME	
0900 0915						
0915 0930		Plenary 1 Nobel Laureate Roald Hoffmann Chair Shih Choun Fong NUS	Coffee Break			
0930 0945						
0945 1000						
1000 1030	Coffee Break					
1030 1100		Session 3 Nanosystems M Yoshimura (Keynote) N Padture (Invited) Oral presentations Chairs N Padture & G Goh	Session 5 Growth & Processing II K Okada & P Pramanik (Invited) Oral presentations Chairs K Okada & G Goh	Session 7 Piezoelectrics I R Stevens & D Q Xiao (Invited) Oral presentations Chairs R Stevens & G Goh	Session 10 Piezoelectrics II M R Shen (Invited) Oral presentations Chairs M R Shen & X Gao	
1100 1130	Session 1 Growth & Processing I F Lange (Keynote) Oral presentations Chairs J Wang & M Yoshimura	Lunch	Lunch	Lunch	Lunch	
1130 1200						
1200 1240						
1230 1300						
1300 1330	Theme Lecture Paul C W Chu Chair Lim Hock Temasek Lab	IUMRS Somya Award Lecture	Theme Lecture Denis Fichou Chair Freddy Boey NTU	Theme Lecture Teruo Okano Chair Lee Eng Hin NUS		
1330 1400						
1400 1430	Session 2 Composites L Gao & D Green (Invited & Chairs) Oral presentations	Session 4 Poster Session	Session 6 Growth & Processing III T Sato & H Wang (Invited & Chairs) Oral presentations	Session 8 - Multidisciplinary I Y Yue & R Kaltyar (Invited) Oral presentations Chairs Y Yue & X Gao	Session 11 Growth & Processing IV K Bryappa (Invited) Oral presentations Chairs K Bryappa & H P Soon	
1430 1500						
1500 1530						
1530 1600						
1600 1630						
1630 1700	Coffee Break / Buses to UCC		Coffee Break			
1700 1730	Buses to UCC		Free Time	Session 9 Electrical Properties I W Zhu (Invited) Oral presentations Chairs J Wang & W Zhu	Session 12 - Electrical Properties II Oral presentations Chairs P Pramanik & X Gao	
1730 1800						
1800 1830	Public Lectures by Nobel Laureates Steven Chu Alan MacDiarmid Chair Tan Chorh Chuan NUS	Public Lectures by Nobel Laureates Carl Wieman Roald Hoffmann Chair Tony Woo Cheng Hsian NTU		Conference Banquet		
1830 1900						
1900 1930						
1930 2000						
2000 2030	Bus back to hotels					
2030 2100						
2100 2130						
2130 2200						
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2230 2300				Bus back to hotels		