

Oxidative dehydrogenation of isobutyric acid over 12-molybdophosphoric acids modified by tetrahydrofuran

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Received 24 May 2000; received in revised form 20 September 2000; accepted 11 October 2000

Abstract

In this work, $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ (PMo) and $\text{Cs}_{2.75}\text{H}_{0.25}\text{PMo}_{12}\text{O}_{40}$ (CsPMo) were modified via the polymerization of tetrahydrofuran (THF), followed by thermal treatment to be used as model catalysts for the oxidative dehydrogenation of isobutyric acid (IBA) into methacrylic acid (MAA). The THF-treated catalysts retained partially reduced stable structures with high surface areas. The THF-treated catalysts showed higher IBA conversions and MAA yields than the corresponding mother catalysts. The THF-treated CsPMo catalyst showed the best catalytic performance among the catalysts tested. It is concluded that the high surface area, the suitable acidity, and the partially reduced stable structure of the THF-treated CsPMo catalyst were responsible for this catalytic performance. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Heteropolyacid; Isobutyric acid; Methacrylic acid; Tetrahydrofuran; Oxidation

1. Introduction

Heteropolyacids (HPAs) are used as acid as well as oxidation catalysts [1–3]. The vapor-phase oxidation of methacrolein into methacrylic acid (MAA) and liquid-phase polymerization of tetrahydrofuran (THF) into polytetramethyleneglycolether (PTMG) are typical commercial processes which utilize HPA as a heterogeneous oxidation catalyst and as a homogeneous acid catalyst, respectively [4–6]. It is also well known that HPAs are promising catalysts for environmentally benign chemical processes. For example, attempts have been made to replace the acetone cyanohydrin process for the production of MAA. The oxidative dehydrogenation of isobutyric acid (IBA)

has been investigated as a possible route for the production of MAA over solid HPAs [7]. V-containing HPAs and their insoluble Cs salts have been reported to be active for the oxidative dehydrogenation of IBA into MAA due to their high surface area, enhanced thermal stability, surface acidity and suitable redox capability [7–10]. It has also been reported that MAA is formed via a bulk-type oxidation and that acetone is produced via a surface-type reaction, while propylene arises via the acid catalysis by HPA [11]. As one of the modification methods for the oxidation catalysis of HPAs, Ueda et al. prepared highly reduced and stable HPA catalysts by precipitation with an organic base, followed by thermal treatment. They reported that the reduced HPAs showed enhanced catalytic activities for the oxidation of propane into acrylic acid compared to the mother catalyst [12].

HPAs are highly soluble in various polar solvents such as water, amines and alcohols [1]. Taking

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advantage of the fact that HPAs are highly soluble in THF and efficiently catalyze THF polymerization [13], 12-molybdophosphoric acid and its insoluble Cs salt were modified by treatment with THF to be used as model catalysts for the oxidative dehydrogenation of IBA in this work. The effects of THF treatment on both the catalytic properties and activities were investigated in this report.

2. Experimental

2.1. Catalyst modification

$\text{H}_3\text{PMo}_{12}\text{O}_{40}$ (hereafter referred to as PMo) was obtained from Aldrich Chem. Co. Inc. $\text{Cs}_{2.75}\text{H}_{0.25}\text{PMo}_{12}\text{O}_{40}$ (hereafter referred to as CsPMo) was prepared by titration of an aqueous solution of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ (0.08 mol/dm^3) with an aqueous solution of Cs_2CO_3 (0.2 mol/dm^3), as described in literatures [14–16]. To the solution of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$, an appropriate amount of the aqueous solution of Cs_2CO_3 was added dropwise at a rate of $1 \text{ cm}^3/\text{min}$ at room temperature. The resulting solution was allowed to stand overnight at room temperature, and then it was evaporated at 45°C to a solid. The prepared catalysts were thermally treated with air for 2 h at 350°C prior to modification by THF. HPA catalysts were modified by two successive processes: (i) by the polymerization of THF; and (ii) by subsequent thermal treatment. THF (50 ml) was initially polymerized with PMo (2 g) in a stirred batch reactor for 12 h at room temperature, and the polymerized product was then dried at 45°C for 10 h by evacuation to obtain a solid mixture of PMo-PTMG (MW $\approx 3,900$). In a second step, PTMG was eliminated from the solid mixture by the thermal treatment at 300°C for 3 h to obtain the final form of the modified PMo. The resultant PMo catalyst was referred to as PMo-THF. CsPMo was also modified by the same procedures to obtain CsPMo-THF.

2.2. Reaction and characterization

The vapor-phase oxidative dehydrogenation of IBA into MAA was carried out in a continuous flow fixed-bed reactor. IBA was vaporized and fed into the reactor with air (50 cc/min). Air was used as both an

oxygen source and a carrier gas. The feed composition was IBA 4.6% and O_2 20.2% in N_2 balance. W/F was maintained at $38.72 \text{ g HPA h/IBA mol}$, and the reaction temperature was in the range from 260 to 320°C . All the catalysts were thermally treated with air (50 cc/min) at the given reaction temperature for 2 h prior to reaction. The products were analyzed with an online GC (HP 5890). Steady state IBA conversions and product yields were calculated on the basis of mole balance. Each HPA sample was characterized by XRD, IR, BET, TPD, NMR and ESCA measurements.

3. Results and discussion

3.1. XRD, BET, NMR and TPD measurements

Fig. 1 shows the XRD patterns and surface areas of the bulk and THF-treated catalysts. All catalysts were thermally treated at 300°C in air before obtaining the XRD data. The XRD patterns of PMo-THF were different from those of bulk PMo and pure MoO_3 . In order to verify the presence of MoO_3 in the PMo-THF catalyst which might be formed during the modification process, the ^{31}P -MAS NMR spectra of the bulk PMo and PMo-THF catalysts were measured. As shown in Fig. 2, the ^{31}P chemical shift for bulk PMo was -2.67 ppm (singlet) while major shift for PMo-THF was -5.02 and -13.15 ppm (doublet). The major doublet observed in PMo-THF catalyst strongly indicates the existence of two types of P compounds. The peak at -13.15 ppm can be assigned to the decomposed PMo catalyst yielding P_2O_5 and MoO_3 . The peak area of this signal was less than 3% of the total area. It, thus, appears that negligible amounts of PMo catalyst were decomposed during the preparation of the PMo-THF catalyst. Although, one shoulder peak was also observed between two major peaks in the PMo-THF, its identity was not fully elucidated yet. The BET surface area of PMo-THF was higher than that of the bulk PMo. On the other hand, the XRD patterns of the CsPMo and CsPMo-THF catalysts were identical. Both catalysts formed very stable crystal structures and retained high surface areas compared to the PMo catalysts. It was also confirmed from ^{31}P -MAS NMR data that both CsPMo and CsPMo-THF catalysts showed

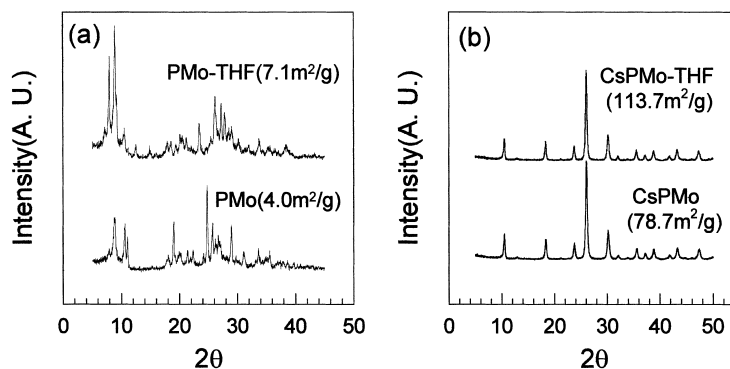


Fig. 1. XRD patterns and surface areas of bulk and THF-treated catalysts: (a) PMo and PMo-THF; (b) CsPMo and CsPMo-THF.

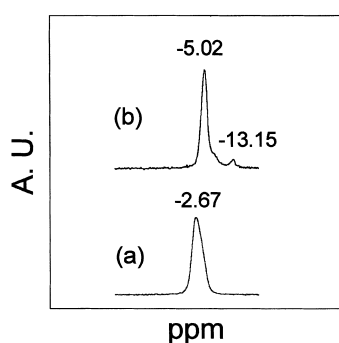


Fig. 2. ³¹P-MAS NMR spectra of (a) PMo, and (b) PMo-THF with respect to H₃PO₄.

only singlet signals. The surface area of CsPMo was increased after the modification by THF. CHNS analyses on the THF-treated catalysts revealed that the

negligible amounts of carbon, less than 1 wt.% of the total catalyst weight, remained in both catalysts.

Fig. 3 shows the NH₃-TPD spectra of the PMo and CsPMo catalysts before and after THF treatments. It was previously reported that thermal decomposition temperatures of PMo and CsPMo were above 400 and 600 °C [15,17,18], respectively, and NH₃ desorption from Cs_{2.75}H_{0.25}PMo₁₂O₄₀ occurred even at the temperature of ca. 570 °C [19]. As shown in Fig. 3, the acid properties of bulk catalysts were modified slightly by the THF treatment. Although, two acid sites were observed in both bulk PMo and PMo-THF catalysts, the acid strengths of the catalysts were different. The two sites of the PMo-THF catalyst appeared in a narrow temperature region, compared to those of the bulk PMo. CsPMo and CsPMo-THF catalysts also showed slight differences in acid strength.

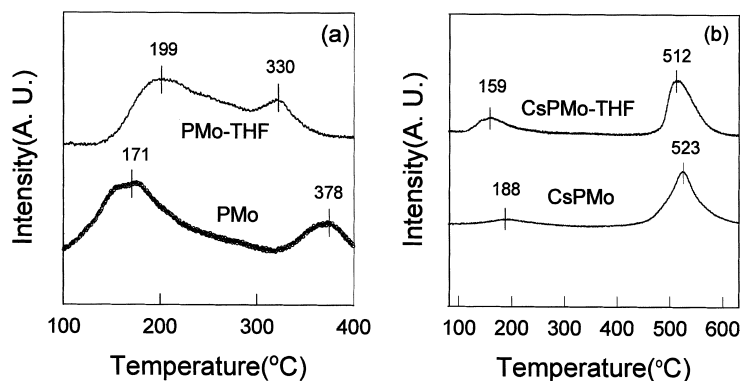


Fig. 3. NH₃-TPD spectra of (a) PMo, (b) PMo-THF, (c) CsPMo and (d) CsPMo-THF: heating rate = 10 °C/min; helium carrier = 50 cc/min.

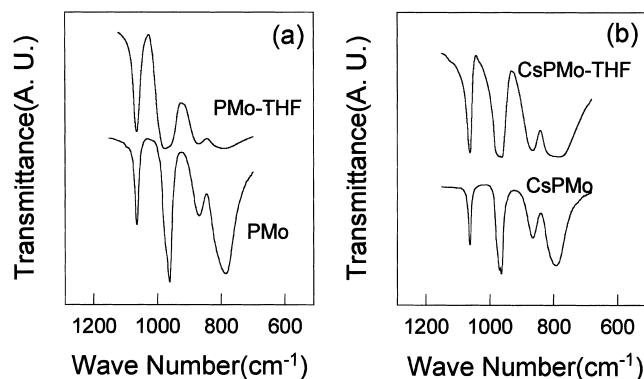


Fig. 4. IR spectra of bulk and THF-treated catalysts: (a) PMo and PMo-THF; (b) CsPMo and CsPMo-THF.

3.2. IR observation

Fig. 4(a) shows the IR spectra of the PMo and PMo-THF catalysts. Four characteristic IR bands of bulk PMo representing a Keggin anion appeared at 1064 (P–O), 961 (Mo=O), 866 (Mo–Oc–Mo, corner-sharing) and 781 cm^{-1} (Mo–Oe–Mo, edge-sharing). It is noteworthy that a great difference in peak intensities of Mo–O–Mo bands was observed between PMo and PMo-THF, although, no significant shift in band positions was observed between two catalysts. As is also shown in Fig. 4(b), the IR spectra of CsPMo and CsPMo-THF catalysts revealed that the four characteristic IR bands of the Keggin anion appeared at the same positions regardless of the modification processes. However, peak intensities of the Mo–O–Mo bands with reference to the Mo=O band in CsPMo-THF was small, compared to those in the bulk CsPMo catalyst.

In order to confirm the nature of the oxygen species involved in the redox process of PMo and to ensure the stability of the THF-treated catalysts, IR spectra of used, reduced, and spent PMo catalysts were taken as shown in Fig. 5. Fig. 5(a) shows the IR spectra of PMo catalyst which was reduced at 300°C for 5 h in a stream of H₂ (50 cc/min). The reduction of PMo by H₂ at high temperature yields H₂O by consuming the lattice oxygen atoms. It was observed that the Mo=O band was quite stable even after the reduction process, while P–O band became slightly reduced after the reduction. However, Mo–O–Mo bands nearly disappeared after reduction by H₂. Further, IR observation (Fig. 5(b)) on the spent PMo, which was previously used for the

IBA conversion for 7 h with an O₂-free stream of N₂ at 300°C, revealed that Mo–O–Mo bands in the catalyst were greatly decreased after the reaction, although, the P–O and Mo=O bands still remained quite strong. The above results strongly indicate that the oxygens in Mo–O–Mo bands are the key oxygen species involved in the oxidative dehydrogenation of IBA. A new band at 1031 cm^{-1} in the spent PMo catalyst is believed to be due to the partial decomposition of heteropolyanion [7], which was caused by severe reduction. The stability of PMo and PMo-THF catalysts in relation to the actual reaction could also be confirmed by the IR analyses, as shown in Fig. 5(c) and (d). A direct comparison of Fig. 5(a) and (c) clearly shows that the IR spectrum of the used PMo catalyst was similar to that of

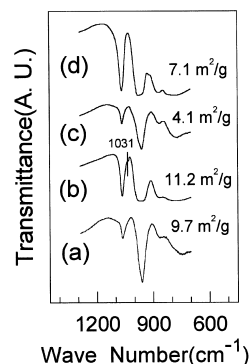


Fig. 5. IR spectra and surface areas of (a) reduced PMo (reduced at 300°C for 5 h by H₂), (b) spent PMo (after 7 h reaction with O₂-free N₂ stream at 300°C), (c) used PMo (after 4 h reaction under actual reaction conditions at 300°C), and (d) used PMo-THF (after 4 h reaction under actual reaction conditions at 300°C).

the reduced PMo catalyst. Moreover, a great difference in peak intensities was observed in the PMo catalyst before and after the reaction, as is shown in Figs. 4(a) and 5(c). Nearly all the Mo–O–Mo bands in the bulk PMo disappeared and the P–O band in the bulk PMo became a little small after the actual reaction, which suggests that the PMo catalyst was not completely stable in the reaction. On the other hand, however, the IR spectrum of the used PMo-THF catalyst was nearly identical to that of the unused PMo-THF catalyst, as shown in Figs. 4(a) and 5(d). These results strongly indicate that the PMo-THF catalyst is highly stable, even after the completion of the catalytic reaction. It was also found that the surface areas of PMo and PMo-THF were nearly constant before and after the catalytic reaction, as shown in Figs. 1 and 5.

3.3. Modified state of THF-treated catalysts

The modified state of the THF-treated catalysts was confirmed by quantification of the IR spectra in Fig. 4, as shown in Fig. 6. The IR peak intensity of Mo=O band was used as a reference for the comparison of peak intensity, because the Mo=O band is a predominant acid center [20] for the polymerization of THF and it is quite stable after the reduction and reaction as observed in Fig. 5. It was found that $I(\text{Mo-Oe-Mo})/I(\text{Mo=O})$ and $I(\text{Mo-Oc-Mo})/I(\text{Mo=O})$ in PMo-THF were smaller than those in bulk PMo. This result means that the PMo-THF was slightly reduced, as also inferred from the IR analysis of the reduced PMo in Fig. 5. Moreover, $I(\text{Mo-Oe-Mo})/I(\text{Mo=O})$ and $I(\text{Mo-Oc-Mo})/I(\text{Mo=O})$

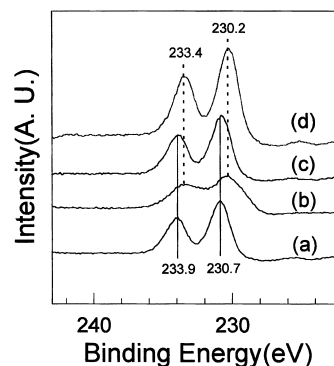


Fig. 7. Binding energies of Mo $3d_{3/2}$ and Mo $3d_{5/2}$ in bulk and THF-treated catalysts: (a) PMo; (b) PMo-THF; (c) CsPMo; (d) CsPMo-THF.

in CsPMo-THF were also smaller than those in bulk CsPMo, although, both catalysts still retained stable crystal structures and high surface areas. This result also indicates that CsPMo-THF was partially reduced by THF treatment as in the case of PMo-THF. The modified state of the THF-treated catalysts was also confirmed by the ESCA measurements, as shown in Fig. 7. The binding energies of Mo $3d_{3/2}$ and Mo $3d_{5/2}$ in the THF-treated catalysts were smaller than those in the corresponding untreated catalysts. Once again, this result directly shows that both PMo-THF and CsPMo-THF catalysts were partially reduced.

3.4. Activities of bulk and THF-treated catalysts

It was reported that MAA is formed via a bulk-type oxidation and that acetone is produced via

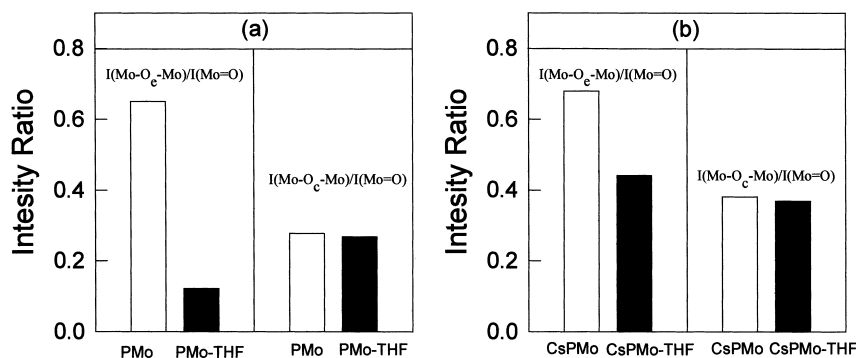


Fig. 6. Ratio of IR band intensity in the bulk and THF-treated catalysts: (a) PMo and PMo-THF; (b) CsPMo and CsPMo-THF; (open) bulk catalyst; (closed) THF-treated catalyst.

Table 1
Typical catalytic activities of PMo and PMo-THF catalysts for the oxidative dehydrogenation of IBA into MAA at 300°C

Catalyst	IBA conversion ^a (%)	Product yields (%)			
		MAA	Acetone	Propylene	CO + CO ₂
Bulk PMo	26.9	11.3	5.9	9.6	0.05
PMo-THF	45.0	27.1	9.4	8.4	0.14

^a $W/F = 38.72$ g HPA h/IBA mol, catalyst weight = 0.1 g, IBA:O₂:N₂ = 4.6:20.2:75.2 (mol%).

a surface-type reaction, while propylene arises via the acid function of HPA [11]. Both acid–base and redox properties of HPA are known to be very important for the reaction. Table 1 summaries the steady state IBA conversions and product yields over the bulk PMo and PMo-THF catalysts at 300°C. The reaction was quite unstable at the initial stage of the reaction, but a steady state was attained after ca. 4 h from the start-up. IBA conversions and MAA yields over both PMo and PMo-THF catalysts decreased with time on stream in a similar manner in literatures [21,22] until the reaction reached steady state. Steady state IBA conversion and MAA yield over bulk PMo catalyst were 69.2 and 55.5% of the initial (1 h reaction) conversion and yield, respectively. Steady state IBA conversion and MAA yield with respect to the corresponding initial values over PMo-THF were 87.9 and 83.6%, respectively. This means that PMo-THF showed more stable catalytic activity than bulk PMo catalyst. As listed in Table 1, PMo-THF showed a higher IBA conversion than PMo. It also showed the higher yields for MAA and acetone than the mother catalyst. However, the propylene yield over PMo-THF was slightly lower than that over the mother catalyst. The enhanced performance of PMo-THF for the formation of MAA might be due to its enlarged surface area and partially reduced stable structure. This catalytic behavior of the PMo-THF catalyst may be understood in a manner similar to the previous work [12] where the partially reduced heteropolyacid catalyst with a high surface area efficiently activated molecular oxygen atoms for the vapor-phase oxidation of propane.

Fig. 8 shows the IBA conversions and MAA yields over the PMo and PMo-THF catalysts with respect to reaction temperatures. Both IBA conversions and MAA yields were increased with increasing reaction temperatures. The PMo-THF catalyst showed a higher catalytic performance than the bulk PMo

catalyst in terms of IBA conversion and MAA yield. It can be reiterated that the enhanced performance of PMo-THF catalyst is due to its enlarged surface area and stable reduced state achieved by THF treatment.

It has been reported that the Cs salt of HPA, especially when the Cs content is 2.75, was highly active for IBA conversion due to its enhanced thermal stability, high surface area and suitable redox capability [7]. In this work, Cs_{2.75}H_{0.25}PMo₁₂O₄₀ (CsPMo) was also modified by THF in order to ensure the effect of Cs substitution and THF treatment. Fig. 9 shows data on IBA conversions and product yields over the bulk and THF-treated catalysts. IBA conversions and MAA yields were in the following order; CsPMo-THF > CsPMo > PMo-THF > PMo. The bulk CsPMo catalyst showed a better catalytic performance than the bulk PMo catalyst, which is in good agreement with a previous report [7]. The performance of the THF-treated catalysts was superior to the corresponding untreated catalysts. Among the

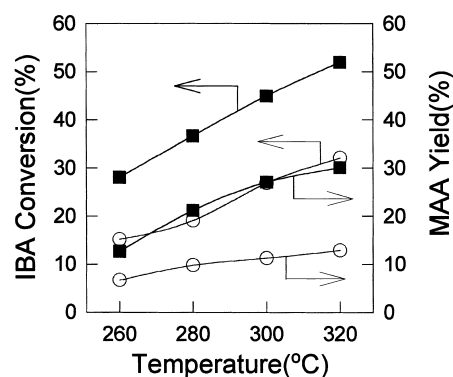


Fig. 8. IBA conversions and MAA yields over PMo and PMo-THF with respect to reaction temperature: PMo (○); PMo-THF (■); $W/F = 38.72$ g HPA h/IBA mol; catalyst weight = 0.1 g; IBA:O₂:N₂ = 4.6:20.2:75.2 (mol%).

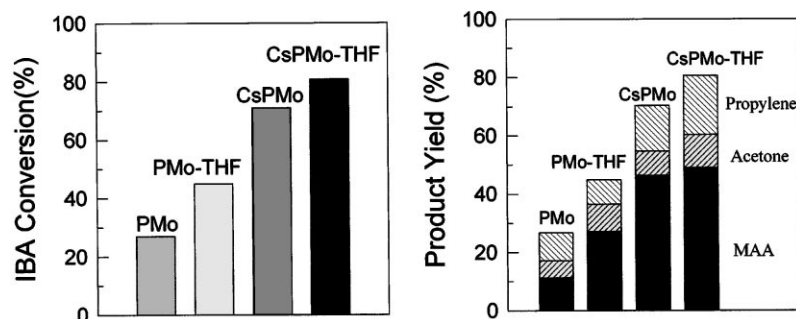


Fig. 9. IBA conversions and product yields over bulk and THF-treated catalysts at 300°C: $W/F = 38.72$ g HPA h/IBA mol; catalyst weight = 0.1 g; IBA:O₂:N₂ = 4.6:20.2:75.2 (mol%).

catalysts tested, the CsPMo-THF catalyst recorded the highest IBA conversion and MAA yield. We conclude that the high surface area, the suitable acidity, and the partially reduced stable structure of the CsPMo-THF catalyst are responsible for this catalytic performance.

4. Conclusions

In this work, 12-molybdophosphoric acid (PMo) and its insoluble Cs salt were successfully modified by THF polymerization, followed by thermal treatment. It was found that the THF-treated catalysts retained a partially reduced stable structure and a high surface area. The THF-treated catalysts showed the higher IBA conversions and MAA yields than the corresponding mother catalysts. Among the catalysts tested, the CsPMo-THF showed the best catalytic performance. The enhanced performance of the THF-treated catalysts for the MAA production was attributed to their enhanced surface areas and the partially reduced stable structures.

Acknowledgements

The authors wish to acknowledge the financial support from LG Chemical Ltd. for this work.

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