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Effect of Ga modification on different pore size silicas in synthesis of LLDPE by copolymerization of ethylene and 1-hexene with [*t*-BuNSiMe$_2$Flu]TiMe$_2$/MMAO catalyst

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Abstract Copolymerization of ethylene and 1-hexene for obtaining the linear low-density polyethylene was conducted along with silicas as supports for [*t*-BuNSiMe$_2$Flu]TiMe$_2$/MMAO catalyst. Two silicas with different pore sizes were used to investigate the effect of pore sizes on copolymerization. In addition, gallium was also introduced into both silicas to improve their properties and enhance the catalytic activities of the system. It was found that before modification, the larger pore silica exhibited higher catalytic activity than the smaller one due to low internal diffusion resistance. After modification, both silicas exhibited higher catalytic activity comparing to their pristine condition. However, 1-hexene incorporation in the obtained copolymers was lower. The reduced surface area of silica after modification was the main reason for the decrease in 1-hexene incorporation. The properties of the copolymers by means of differential scanning calorimetry, gel permeation chromatography, and ^{13}C NMR spectroscopy were further discussed in more detail.

Keywords Polymer synthesis · Silica · Metallocene · LLDPE

Introduction

First commercialize in the late 1970s by Union Carbide and Dow Chemical [1], linear low-density polyethylene (LLDPE) has continued a fast growth rate in usage

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from that time to this day. For using LLDPE in an efficient way, the specific properties of LLDPE, such as molecular weight (M_w) distribution, stereoregularity, and comonomer content need to be considered carefully. Metallocene is one of the most widely used catalysts for control those properties, and thus, many studies have been conducted with this type of catalyst [2–4]. However, the industrial application of metallocene is usually processed in a gas or slurry phase, so the development of supported metallocene is very important. Inorganic materials, such as SiO_2, Al_2O_3, and ZrO_2 were applied for supported metallocene. It was, nevertheless, SiO_2 that has been reported as the most attractive support. Therefore, the studies of silica on the role of support for metallocene catalyst have been conducted by many researchers in many aspects. Silveira et al. [5] have reported that textural properties of silica support were shown to influence several parameters and properties of supported metallocene catalysts, for example, the particle size influencing on catalytic activity. Besides the particle size, pore size is another factor that has been investigated. Kumkaew et al. [6, 7] have discovered that pore sizes influence the nature of the catalytic sites for supported metallocene catalyst, and then, also influence the comonomer incorporation rate of copolymerization. Ko et al. [8] reported that the certain pore size of support had different levels of impact on different sizes of (co)monomer. The effect of pore size not only exists in a system during copolymerization, but also does previously during preparation or modification of support. Therefore, properties of support before and after modification need to be considered to further clarify all phenomena occurring in the supported system.

In our previous study, the copolymerization of ethylene/1-hexene using the [*t*-BuNSiMe$_2$Flu]TiMe$_3$/MMAO catalyst under homogeneous system was investigated [9]. However, in this study, the similar copolymerization under the heterogeneous or supported system using silica support was further investigated. In addition, the effects of pore size of silica were studied by using different pore size silica-supported MMAO. Moreover, the effect of gallium (Ga) modification on silica was also examined to give a better understanding on how the catalytic activity apparently changes with Ga modification on different pore size silicas. In fact, the Ga modification on silica was chosen because it can enhance activity in zirconocene/MMAO catalytic system as reported by Wannaborworn et al. [10].

Experimental

Materials

All operations were manipulated under an argon atmosphere using glove box and/or standard Schlenk techniques. [*t*-BuNSiMe$_2$Flu]TiMe$_2$ was synthesized according to the procedure described by Hagihara et al. [11]. Ethylene was obtained from the National Petrochemical Co. Ltd., Thailand. 1-Hexene was purchased from Aldrich Chemical Company. Modified methyl aluminoxane (MMAO) (1.86 M in toluene) was donated by Tosoh Akzo, Japan. Toluene was donated by the Exxon Chemical, Thailand Co. Ltd. It was dried over dehydrated $CaCl_2$ and distilled over sodium/benzophenone. Silica gel from Fuji Silysia Chemical Ltd., Japan (Cariact Q-50 and

P-10) was calcined at 400 °C for 6 h under vacuum. Gallium nitrate was purchased from Aldrich Chemical Company, Inc., and use as received.

Preparation of Ga-modified silica support

The Ga modification of the silica support was prepared by the conventional incipient-wetness impregnation method according to the procedure described previously [12]. The Ga source in this case was $Ga(NO_3)$. Ga was impregnated onto silica gel (Cariact Q-50 and P-10) by 1.0 wt% of Ga. The support was dried in oven at 110 °C for 12 h, and then calcined in air at 400 °C for 2 h.

Preparation of supported MMAO

The silica supports were prepared by in situ impregnation method which was described by Wannaborworn et al. [10]. Silica (0.1 g) was allowed in contact with 4 mmol of MMAO for at least 2 h in a reactor with magnetic stirring, and then the slurry of MMAO/support was obtained and ready to be used in polymerization. To verify that all MMAO was immobilized onto the support, a batch test was conducted together with the preparation method for the entire samples. For the batch test, after stirring the mixture of support and MMAO for 2 h and leaving for precipitate for 1 h, 1 mL of clarified liquid was taken and injected into the polymerization reactor, where a desired amount of catalyst was already present. If no formation of any amount of polymer is observed, it will be evident that this clarified liquid does not contain the free MMAO. Thus, all MMAO was immobilized on the supports completely.

Polymerization procedure

The prepared MMAO/support (0.1 g support and 4 mmol MMAO) and toluene were introduced into the reactor. The titanium complex in toluene (10 μmol mL^{-1}) was put into the reactor to make the $[Al]_{MMAO}/[Ti]_{cat} = 400$. Then, the reactor was immersed in liquid nitrogen. 0.018 mol of 1-hexene was added into the frozen reactor (to stop or prevent possible polymerization of 1-hexene). The reactor was heated up to the polymerization temperature at 70 °C. The polymerization was started by feeding ethylene into the reactor, and then stopped when ethylene consumption reached to 0.018 mol (6 psi on the pressure gauge). The reactor temperature was kept constant during the polymerization. The reaction was terminated by adding acidic methanol and the material was stirred for 30 min. After filtration, the copolymer obtained was washed with methanol and dried at room temperature.

Characterization

Characterization of supports

N_2 physisorption: Measurement of BET surface area, average pore diameter, and pore size distribution were determined by N_2 physisorption using a Micromeritics

ASAP 2000 automated system. *X-ray diffraction*: XRD was performed to determine the bulk crystalline phases of samples. It was conducted using a SIEMENS D-5000 X-ray diffractometer with Cu K_α (l = 1.54439 Å). The spectra were scanned at a rate of 2.4 min^{-1} in the range of $2\theta = 10°–80°$.

Characterization of polymers

^{13}C NMR spectroscopy: The copolymers were characterized using ^{13}C NMR spectroscopy (BRUKER AVANCE II 400) to determine the 1-hexene incorporation. Each sample solution was prepared by dissolving 50 mg of copolymer in 1,2,4-trichlorobenzene and $CDCl_3$. Spectra were taken at 60 °C operated at 100 MHz with an acquisition time of 1.5 s and a delay time of 4 s.

Differential scanning calorimetry (*DSC*): Thermal analysis measurements were performed using a Perkin-Elmer DSC P7 calorimeter. The DSC measurements reported here were recorded during the second heating/cooling cycle with the rate of 20 °C/min. This procedure ensured that the previous thermal history was erased and provided comparable conditions for all samples. Approximately, 10 mg of sample was used for each DSC measurement.

Gel permeation chromatography (*GPC*): The M_w of polymer was determined using GPC (GPC, PL-GPC-220). Samples were prepared having approximately concentration of 1–2 mg/mL in trichlorobenzene (mobile phase) by using the sample preparation unit (PL-SP 260) with filtration system at a temperature of 140 °C. The dissolved and filtered samples were transferred into the GPC instrument at 140 °C. The calibration was conducted using the universal calibration curve based on narrow polystyrene standards.

Results and discussion

Characterization of supports

In this study, two kinds of silica with different pore diameters were used as a supporting material for catalyst. By investigating their porous properties with N_2 physisorption, they were classified according to the size of pores. Large pore (LP) denotes the Q-50 silica having an average pore diameter of 380 Å, and small pore (SP) denotes the P-10 silica having an average pore diameter of 170 Å. Besides using both silicas in pristine condition, they were modified by gallium (SP-Ga and LP-Ga) for improving some specific properties before use. Thus, there were four kinds of supports used in this polymerization system. The specific properties of them are shown in Table 1. It can be seen from this table that after modification by Ga, both supports (SP and LP) exhibited decreased surface area and also pore volume compared to the supports before modification (SP-Ga and LP-Ga). This was due to the partial blockage of pore by Ga nitrate used for the modification procedure. In addition, according to the XPS investigation on Ga-modified supports conducted by Campos et al. [13], it was suggested that Ga modifiers were mostly deposited at the surface of the supports, but some of them can penetrate into the

Table 1 Specific properties of various supports obtained from N_2 physisorption

Supports	Pore diameter (Å)	Pore volume (cm^3/g)	Surface area (m^2/g)
SP	171	6.5	216.8
LP	369	1.36	70.9
SP-Ga	190	1.4	169.7
LP-Ga	320	0.2	68.8

surface and being present in the bulk of the support. The average pore diameters of the supports before and after modification slightly changed. The XRD patterns (not shown) for all supports were similar exhibited only a board peak between 20° and 30°, as seen typically for the conventional amorphous silica. No XRD peaks of Ga were observed after impregnation due to its highly dispersed form.

Effect of pore size of silica supports

As seen in Table 2, the LP silica exhibited higher catalytic activity than that of the SP silica. Although most MMAO is presumed located mostly at the external surface [10], some is located at the internal surface too. This can be observed from the effect of pore size of the silica support which still existed in this comparison. To grasp the effect of pore size, the internal diffusion resistance needs to be considered. In general, the supports with SP size result in poor intra-pellet diffusion efficiency and slow transportation of reactants and products due to strong diffusion resistance [14], contrasting with the supports with LP size, which are able to diminish the diffusion resistance by their large pores. Then, copolymerization conducted with LP size support exhibited higher catalytic activity than that with SP size support. Another parameter which provides compelling evidence is the copolymerization time of the systems. It can be obviously seen that copolymerization time of the LP silica system (LP and LP-Ga) was shorter than that of the SP silica system (SP and SP-Ga) indicating that propagation rate of system with the LP silica was higher, due to monomer and comonomer being able to reach to the catalytic active sites more easily even located inside the pores. In addition, silica with smaller diameters could

Table 2 Catalytic activities in ethylene/1-hexene copolymerization with different supports

Supports	Time[a] (s)	Yields (g)	Catalytic activity[b] (kg polymer/mol Ti h)
SP	233	0.8681	1341
LP	170	0.7941	1682
SP-Ga	186	0.9919	1920
LP-Ga	140	0.7632	1893

[a] Time when all ethylene (0.018 mol) was consumed

[b] Copolymerization condition: Ti = 10 μmol, Al/Ti = 400, temperature = 70 °C, 50 psi of ethylene pressure was applied

display the lower catalytic activities probably due to the higher probability of formation for the bimolecular species as described by Silveira et al. [15].

Effect of Ga modification on silica surface

To investigate an effect of Ga as modifying agent for silica support, comparisons were drawn between modified and unmodified supports on both types of silica. As seen from Table 2 (SP vs. SP-Ga, LP vs. LP-Ga), Ga modification can increase catalytic activity in both types of silica. It has been known that adding Ga into silica surface normally increases acidic sites to the silica support [13, 16]. These sites are required to activate metallocene catalyst to be an active species in supported system. Many inorganic supports which possess the strong Lewis acidic property, such as Al_2O_3 and $MgCl_2$ have been used as support for this purpose [17]. For silica, directly using as a support for metallocene catalysts preparation resulted in inactive catalysts formation [18]. However, in this method, MMAO took charge of main activating agent as usual in metallocene catalyst system and Ga can assist in the activation by increase Lewis acidity in support as mentioned. Furthermore, Ga can be anchored on the surface of silica, thus lower interaction between active sites and support. The result of higher catalytic activity by Ga modification accorded with the finding of Campos et al. [19], which found that introducing Ga into supports can improve the ability of the supports to immobilize metallocene, and then enhancing the catalytic activity of the systems. Improving ability to immobilize (grafting the substances) by Ga was also reported by Morrow and McFarlane [20]. They found that the introduction of species such as PH_3 and AsH_3 into the silica surface was more strongly adsorbed when silica was first reacted with the Ga.

When comparing the activities of system with Ga modification on both silica types, it revealed that the SP silica showed slightly higher catalytic activity. This was opposite to the result of activities before modifying the support. This is because the SP silica has higher surface area than that of the LP silica. Then, Ga modification, which mainly affected on the surface properties of support, can more efficiently influence catalytic behavior in higher surface area support than the lower surface area support. Therefore, after modification the SP silica would give the higher activity than that of the LP silica due to higher surface area.

Characterization of copolymers

The triad distribution for all copolymers investigated by ^{13}C NMR is also shown in Table 3. The triad block of comonomer (HHH) was not detected for all samples. This suggests that the good distribution of comonomer throughout the copolymer chain existed in the systems. In addition, the products of reactivity ($r_E r_H$) of some sample (SP-Ga) also showed the characteristic of random copolymers ($r_E r_H > 1$), and the rest of them showed the typical alternating copolymer character ($r_E r_H < 1$). Both silicas provided higher M_ws for the copolymers after Ga modification. This was probably due to Ga modifier enhanced propagation rate, but reduced termination rate (chain transfer) in polymerization. It was also observed that Ga had more effect on the M_w of polymer obtained by the smaller pore silica than the larger one due to higher surface area of the smaller pore silica as mentioned earlier.

Effect of pore size of silica supports

It can be observed from Table 3 that both pore size silicas produced copolymers with nearly the same incorporations of 1-hexene (SP and LP). In general, the LP silica should supply more comonomer for propagating the copolymer chain than the SP silica due to lower diffusion resistance within the pores. However, another factor which can influence on the incorporation of comonomers is the surface area of the supports. Regarding to surface area, the support with large surface area is expected to produce copolymers with high incorporation of comonomer as a result of more space between active sites dispersed on its surface area compared to the support with smaller surface area, as seen in Fig. 1. Then, the SP size silica with higher surface area would probably result in high comonomer incorporation with this effect. Therefore, from the result that showed a roughly equal amount of 1-hexene comonomer incorporation for two different textures of silicas indicated that both effects (pore size and surface area) have a profound impact at the same level upon the incorporation of 1-hexene in the obtained copolymers.

Table 3 Properties of the obtained copolymers examined by ^{13}C-NMR and GPC

Supports	EEE	EEH	HEH	EHE	EHH	HHH	$r_\mathrm{E}r_\mathrm{H}$[a]	% H[b]	M_w[c]
SP	0.367	0.269	0.041	0.156	0.166	0.000	0.969	32.2	26
LP	0.359	0.272	0.046	0.163	0.159	0.000	0.873	32.3	24
SP-Ga	0.410	0.246	0.038	0.149	0.157	0.000	1.108	30.6	37
LP-Ga	0.422	0.280	0.039	0.159	0.099	0.000	0.737	25.8	27

[a] Relative comonomer reactivities (r_E for ethylene and r_H for 1-hexene) calculated by $r_\mathrm{E} = 2[\mathrm{EE}]/[\mathrm{EH}]X$, $r_\mathrm{H} = 2X[\mathrm{HH}]/[\mathrm{EH}]$, $[\mathrm{EE}] = [\mathrm{EEE}] + 0.5[\mathrm{HEE}]$, $[\mathrm{HH}] = [\mathrm{HHH}] + 0.5[\mathrm{EHH}]$, $[\mathrm{EH}] = [\mathrm{HEH}] + 0.5[\mathrm{HEE}] + [\mathrm{EHE}] + 0.5[\mathrm{EHH}]$

[b] 1-Hexene incorporation

[c] Molecular weight (kg/mol) obtained from GPC

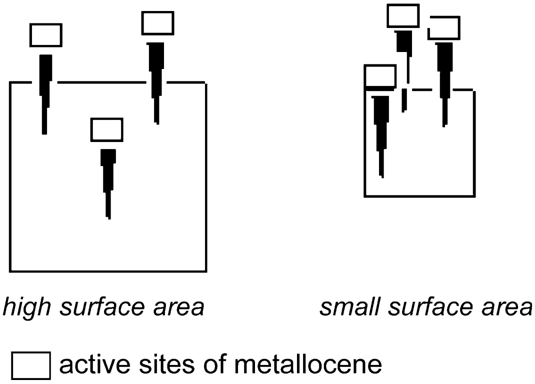

Fig. 1 Comparison of active site dispersion on the different surface areas

Effect of Ga modification on silica surface

Comparing between SP and SP-Ga alongside LP and LP-Ga, we found that when modifying surface of silica support with Ga, the 1-hexene incorporations were decreased in both types of silica. This can be explained by the effect of surface area. Since both silicas had lower surface area through modifying procedure by Ga as follows; in LP 70.9 to 68.8 m^2/g and in SP 216.8 to 169.7 m^2/g. Although incipient-wetness impregnation used in the modification is the easiest method of introducing a metal precursor, it results in the precipitation of small particles of the salt onto the support surface [21]. Therefore, the decrease in the surface area may be due to the partial blockage of pore by excess Ga nitrate. As seen from Fig. 2, the excess substances more seriously affect on the decrease in surface area of the SP silica than the LP silica because the SPs can be blocked by the deposit easier compared to the LP. Therefore, after modification with Ga, the significant decrease in surface area occurs in the SP silica, contrasting to that with the LP silica, which has only slight decrease. The average pore diameter shown in Table 1 also reveals that the blockage seriously affects on the smaller pore sizes by decreasing the population of the smaller pore sizes (the SPs become shallower until disappear), and then the average pore sizes are shifted to higher value (from 171 to 190 Å).

The decrease in 1-hexene incorporation in the copolymer obtained from both silicas after modification by Ga was opposite to the decrease in surface area. The significant decrease was observed for the LP silica instead. The reason for this can be explained as seen in Fig. 2. The active sites with high enough space for high 1-hexene incorporation were indicated in the figure by an open square while a filled square indicated the active sites with insufficient space for high 1-hexene incorporation. It can be seen that high space sites (open square) in the LP silica

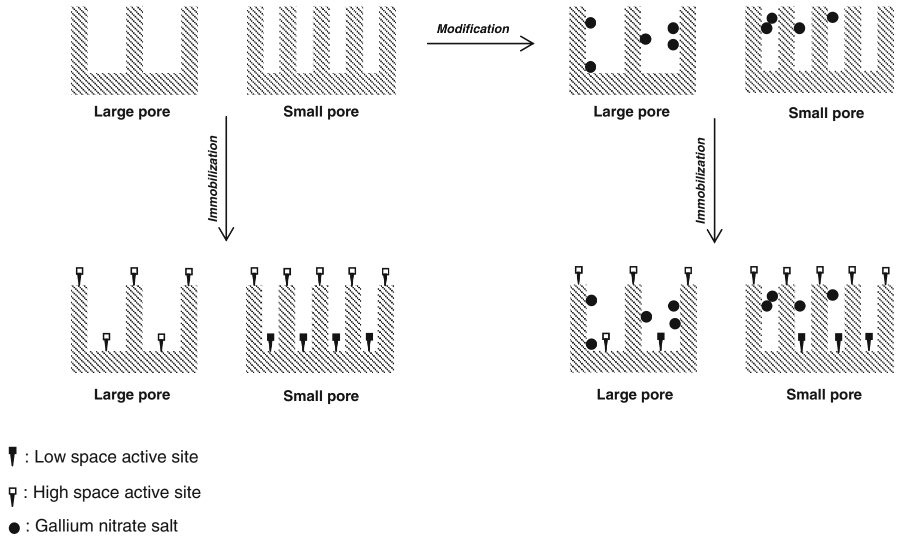

Fig. 2 Conceptual model for impact of pore blockage on supports with different pore sizes

were decreased noticeably after modification, whereas the number of the high space sites in the SP silica remained the same. The high space sites in the SP silica are always located outside the pores, and therefore they can not be affected by the deposit of excess Ga inside the pores. On the other hand, in the LP silica, these sites are sometimes located inside the pores, then the deposit on the wall of pores can hinder them from being reached by a large size molecules, especially for 1-hexene comonomer. Hence, the incorporation of 1-hexene in the LP silica system decreased significantly after the support was modified by Ga.

In addition, this proposed model (Fig. 2) can explain the previous results reported by our research group that sites with no or low 1-hexene incorporation rates (insufficient space site, filled square) were more prevalent at short polymerization times [7]. It can be seen from the model that the said sites usually located inside the pore, so therefore at initial time of polymerization it still had an impact in polymerization. After the long period of polymerization, the supports were covered by the growing chain of polymer and then, hindered the (co)monomer to reach inside of pores, thus decreasing the impact of the sites located inside the pores in polymerization. So if the polymerization time was longer, it would be found the fraction of polymer producing from sites with no or low 1-hexene incorporation rates. However, this model should be used together with the multigrain model [22] and the fragmentation of the particles should be neglected.

The model in Fig. 2 also indicated that different types of catalytic sites are present in these catalysts, according to the findings of Kumkaew et al. [7] which suggested that pore sizes can influence the type of catalytic sites present in the supports. The various sites derived from different environments which mainly point to steric hindrance as seen in the model. The hindrance is not just to the monomer to attack the site, but also to MMAO in forming cocatalysts-counterion fit and salvation, which plays a significant role in the structures and energetic of the ion pairing proposed by Lanza et al. [23]. Therefore, the alteration of selectivity by different pore sizes may be one of the reasons for the change in 1-hexene incorporations.

To support that the copolymers were obtained from different catalytic sites, one simple technique that can be used for this purpose is the DSC. As known, the DSC endotherms were influenced by many factors such as the crystallinity and M_w of polymer, then being difficult to identify each peak occurring clearly. However, they could brief necessary information about characteristic of catalyst as recommended by Kumkaew et al. [7] that DSC of nascent polymer may provide information on heterogeneity of supported polymerization catalysts.

From Fig. 3, it can be seen that the copolymers obtained from the unmodified supports exhibited several DSC endotherm peaks, whereas the ones obtained from the Ga-modified supports exhibited broader peaks. Nevertheless, all of them indicate multiple types of catalytic sites. The slight difference in characteristic of peaks between the Ga-modified support and the unmodified one may be derived from the change in surface nature of the support after modification, particularly the heterogeneous nature. Another parameter that provides information about heterogeneity of the support is the molecular weight distribution (MWD) of the obtained polymers. The MWD as measured by GPC of the samples are; SP = 2.8, SP-Ga = 2.9, LP = 1.8, and LP-Ga = 2.3. It can be seen that after modification both silicas

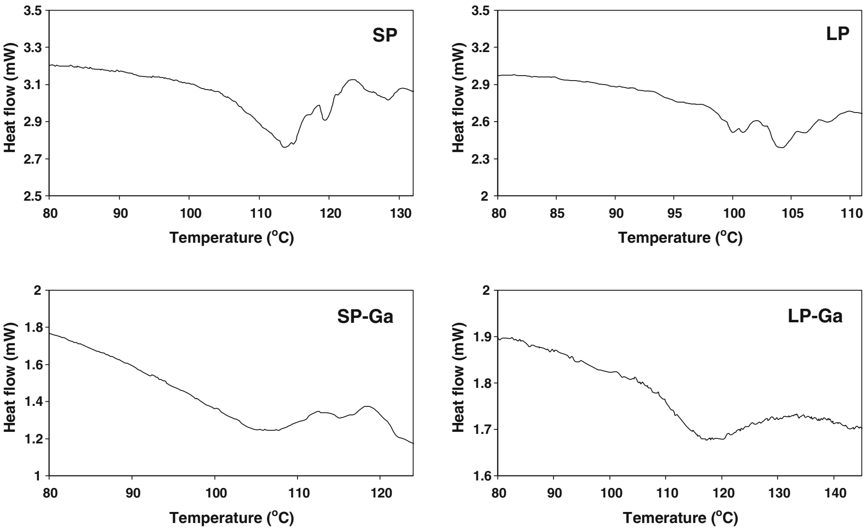

Fig. 3 DSC endotherms of LLDPE synthesized with various SiO_2 supports

exhibited broader MWD values, suggesting more heterogeneous nature. This may imply that silicas after modification by Ga have a greater degree of heterogeneity in catalytic sites. Therefore, it can be concluded that Ga addition into silica also changed the nature of catalyst and provide more heterogeneity in catalytic sites to supported system.

Conclusion

The higher catalytic activity of the LP silica was observed as a result of low internal diffusion resistance. However, after Ga modification, the SP silica exhibited higher catalytic activity. This is because Ga modification, which mainly improves properties of surface, more efficiently influences properties on silica with higher surface area. Then, the SP silica with higher surface can receive more improvement from Ga and raising more catalytic activities than the LP silica with lower surface area. Moreover, effect of surface area also caused change in 1-hexene incorporation, where a decrease in 1-hexene incorporation was evident with decreased surface area. In addition, different types of catalytic sites were observed, and then used to construct a model which helped explain the results.

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