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# Synthesis of polysulfides using diisobutylene, sulfur, and hydrogen sulfide over solid base catalysts

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## Abstract

A series of solid base catalysts were prepared with several alkali and alkaline earth metal species. The catalysts were used in one-stage synthesis processes of polysulfides using diisobutylene (DIB), sulfur, and hydrogen sulfide ($H_2S$). The possibility of using solid base catalyst as an alternative for a liquid amine catalyst and the effects of preparation conditions on the catalytic activity were discussed. Alumina-supported potassium catalysts showed a catalytic activity comparable to that of dicyclohexylamine. The alkali metal catalysts proved to be more effective than alkaline earth metal catalysts. Further, a three-stage mechanism for polysulfide synthesis using the system of diisobutylene, sulfur, and hydrogen sulfide in the presence of solid base catalysts was suggested. Moreover, a novel [$^{14}$C]$CO_2$ radioisotope pulse tracer method was developed to determine the amount of $CO_2$ adsorption on solid base catalysts at the temperatures between 100–400 °C and under 0.6–3.1 MPa. The relationship between the uptake amount of $CO_2$ on the alkali metal catalysts and the catalytic activity in syntheses of polysulfides was discussed.

*Keywords:* Polysulfide synthesis; Alkali metal catalyst; Alkaline earth metal catalyst; Bis-(1,1,3,3-tetramethylbutyl)-polysulfide; Solid base catalyst; Carbon dioxide adsorption

## 1. Introduction

Generally, hydrotreating catalysts are presulfided in order to obtain the active phase prior to use [1,2]. The presulfiding stage is typically performed at the beginning of the hydrotreating process by introducing a sulfiding agent such as carbon disulfide ($CS_2$), dimethyldisulfide (DMDS), a sulfur compound-containing oil, or even feedstock under $H_2$ atmosphere [2,3]. In addition to these compounds, it is also possible to use organic polysulfides. Unlike other reagents such as $CS_2$, dimethylsulfide (DMS), DMDS and hydrogen sulfide ($H_2S$), these are stable and exhibit a relatively low toxicity [3–6]. In a previous work, the authors have discussed about hydrodesulfurization (HDS) of dibenzothiophene (DBT) and straight run light gas oil (SRLGO) and also about ultra deep HDS of a hydrotreated light gas oil (HTLGO) over a commercial Co-Mo/$Al_2O_3$ catalyst presulfided with a novel sulfiding agent, bis-(1,1,3,3-tetramethylbutyl)-polysulfide (CS-40) [3,6]. It was found that the catalyst presulfided in situ with CS-40

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showed the same or even higher activity than those observed when using the conventional sulfiding agents such as DMDS and $CS_2$. At the same time, a novel ex situ presulfiding method using CS-40 in the presence of sulfur was also developed [6,7]. Therefore, CS-40 is a promising sulfiding agent that can be substituted for current sulfiding agents such as DMDS.

In general, polysulfides are produced via a two-stage process: the first stage is synthesis of thiol via the addition reaction of hydrogen sulfide to olefin [8]; the second stage is synthesis of polysulfide via the base-catalyzed reaction of sulfur with thiol [9]. In recent years, a one-stage synthesis process of polysulfides by mixing olefins, elemental sulfur and $H_2S$ in a homogeneous system with amine compounds as the catalyst has been developed [10]. The yields of polysulfides obtained by this method are relatively high. However, there are some drawbacks reported, such as a too-long reaction time or some difficulty to separate the amine from the products in order to avoid its contamination. On the other hand, these problems can be avoided by using an heterogeneous catalysis process over a solid catalyst; production cost of polysulfide can then drop down because the solid catalysts can be easily separated from the reaction system and can be reused. Another advantage of using heterogeneous catalyst lies in the fact that it becomes possible to develop a flow type process to manufacture polysulfides, while the present homogeneous process is limited to a batch reaction. Therefore, the present paper deals with the preparation of solid base catalysts and their use in the synthesis of polysulfides. A variety of solid catalysts, mainly solid base catalysts, were prepared and each one's catalytic activity in synthesis of polysulfide-CS-40 was then tested using a batch type reactor. The effects of preparation parameters of catalysts such as types and loadings of active metals or the calcination temperature, on the catalytic activity were investigated.

It is known that acidity and basicity are paired concepts to explain the catalytic properties of divided metal oxides and zeolites [11]. During the past decades, extensive investigations have been devoted to solid acid catalysts [11–15] due to their great importance in the petroleum industry. In contrast, only a few research projects have been performed to study the basicity of solid catalysts despite their potential as environment-friendly industrial catalysts [16–19]. A great number of physical and chemical methods have been developed to determine the number, nature, strength and location of the active sites so as to establish correlations between catalytic activity and surface properties of catalysts. To estimate proton-accepting (basic) properties of the surface, there are principally two groups of methods: titration with various reagents such as benzoic acid [20], and spectral techniques using adsorption of probe molecules such as pyridine or $CO_2$. [21]. A combination of adsorption of $CO_2$ and infrared spectroscopy has been commonly used. Because carbon dioxide is acidic, it adsorbs specifically on basic sites of metal oxides [22,23]. Therefore, $CO_2$ adsorption is more generally used to study the basic properties of metal oxides such as $Al_2O_3$ [24], $ZrO_2$ [25], $ThO_2$ [26] and CeO [27], MgO [28] or of mixed metal oxides such as $TiO_2$-$ZrO_2$ [29], $TiO_2$-$Al_2O_3$ [30], MgO-CaO [31], MgO-$Al_2O_3$ [32]. $CO_2$ adsorption has also been used to study the systems of alkaline zeolites [17,33,34]. However, these studies are only carried out under lower pressure or in vacuum, significantly different from the practical reaction conditions. So far, a measurement method for basic properties of solid catalysts has not been established under higher pressure, i.e. the so-called in situ measurement method. Therefore, in the present study, a more simple approach, $[^{14}C]CO_2$ radioisotope pulse tracer method, by which the $CO_2$ adsorption can be determined under higher pressures, was developed to investigate basic properties of several solid catalysts that were used in the synthesis of polysulfides. Further, the relationships between the catalytic activity in the synthesis of polysulfide and the amount of $CO_2$ uptake on the catalysts were also discussed.

## 2. Experimental

### 2.1. Materials

Helium (99.9999%) was purchased from Tohei Chemicals and purified through Molecular Sieve 13A (Kishida Chemicals) using a liquid nitrogen trap. Hydrogen sulfide ($H_2S > 99.9\%$) was obtained from Sumitomo Seika Chemicals. Diisobutylene (DIB), a mixture of 75% of 2,4,4-trimethyl-1-pentene and 25% of 2,4,4-trimethyl-2-pentene, was purchased from Maruzen Petrochemical Co. Sulfur, alkali metal hydroxides, alkali metal nitrates, sodium carbonate, potassium carbonate, potassium hydrogen phthalate (K–H–Ph), magnesium nitrate, calcium chloride and barium nitrate were purchased from Kishida Chemicals.

$^{14}$C-labeled $CO_2$ ($[^{14}C]CO_2$) was synthesized using $^{14}$C-labeled barium carbonate ($[^{14}C]BaCO_3$, 185 MBq/mmol, Japan Radioisotope Association) and an HCl solution (36 wt.%, Kishida Chemicals) according to Eq. (1):

$$[^{14}C]BaCO_3 + 2HCl = [^{14}C]CO_2 + BaCl_2 + H_2O \quad (1)$$

A mixture of $[^{14}C]BaCO_3$ of 0.05 g (0.4 MBq) and $BaCO_3$ of 12.1 g was charged into an autoclave (300 cm$^3$). After the autoclave was degassed under vacuum, the solution of 10 M HCl (10.6 cm$^3$) was put in and the reaction was carried out for 12 h at room temperature. The gas of produced $[^{14}C]CO_2$ was purified via degassing and dehydration under vacuum using the freeze–pump–thaw cycles by means of the combination of a liquid nitrogen trap (78 K) and a cooler trap (233 K) of methanol. The gas was then transferred into a 260 cm$^3$ cylinder for use. The purity of $[^{14}C]CO_2$ in the cylinder was identified with a gas chromatograph (Hitachi 263) equipped with a thermal conductivity detector, Porapack Q column ($\phi$3 mm × 4 m); this purity was 99.999+%. The scintillation solvents—Carbosorb and Permafluor for measuring radioactivity were obtained from Packard Japan.

### 2.2. Preparation of catalysts

Commercial dicyclohexylamine was used as a liquid amine catalyst. Solid catalysts used in this study were prepared by the incipient wetness impregnation method of $\gamma$-$Al_2O_3$ with alkali metal or alkaline earth metal precursor solution containing the desired amount of metals. The precursors of catalysts were then dried at 120 °C for 2 h before being calcined in air at 400–700 °C for 2–24 h. Contents of active metals on the catalysts were between 0 and 1.9 mmol per gram of $Al_2O_3$. A commercial $\gamma$-alumina (BET surface area: 256 m$^2$/g) was supplied by Nippon Ketjen. MgO was obtained as a compared catalyst (JRC-MgO-1; surface area: 55 m$^2$/g) from the Japan Catalysis Society.

### 2.3. Synthesis of polysulfides

Polysulfide syntheses were carried out using a stainless steel autoclave of 50 cm$^3$ equipped with a magnetic stirrer. An amount of 13.4 g of diisobutylene (DIB), 6.5 g of sulfur and 1.0 g of catalyst were added to the autoclave. The obtained mixture was then heated to 125–132 °C under stirring, and was kept for 1 h for the complete melting of introduced sulfur. Then, gaseous hydrogen sulfide was introduced into the autoclave under stirring, and reacted for 1–20 h. The reaction pressure was adjusted and kept under a desired pressure (0.6–1.0 MPa) during the reaction. After reaction, the mixture was cooled down to room temperature and $H_2S$ remaining in products was removed by vacuum distillation.

The qualitative analyses of products were made using a GC-MASS system (Shimadzu, GCMS-QP5050). The quantitative analyses of the products were made using a gas chromatograph (Hitachi-263, FID). It is well known that polysulfides ($C_8H_{17}S_nC_8H_{17}$: $n = 1$–7) have a high boiling point and readily decompose at a low temperature [3,8]. Therefore, the conditions of GC-FID analysis must be carefully chosen in order to perform reliable analyses. GC-FID analysis conditions are summarized in Table 1.

### 2.4. Adsorption of $[^{14}C]CO_2$

In order to investigate the basicity of solid catalysts under higher pressure, the authors developed a $^{14}$C labeled $CO_2$ ($[^{14}C]CO_2$) radioisotope pulse tracer method. The pulse apparatus is shown in Fig. 1 [35]. About 0.2–0.6 g of the solid sample was ground to 20–80 mesh and dried at 120 °C for 1 h and calcined at 600 °C for 20 h prior to use. This

Table 1
Analytical conditions of GC-FID

| | |
|---|---|
| Detector temperature | 150 °C |
| Injection temperature | 150 °C |
| Column | OV-17, Unibort B Mesh 60–80 glass column |
| Carrier gas | Nitrogen, 40 ml/min |
| Temperature programs | |
| Initial temperature | 60 °C for 2 min |
| Heating speed | 20 °C/min |
| Final temperature | 150 °C for 80 min |

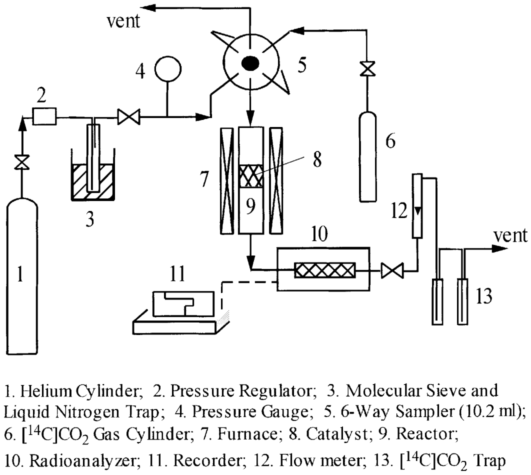


Fig. 1. $[^{14}C]CO_2$ radioisotope pulse tracer apparatus.

was packed into the stainless steel-made reactor (i.d. 4 mm) and fixed with quartz sand and wool at both ends of the reactor. The adsorption with $[^{14}C]CO_2$ pulse (10.2 ml per pulse) was carried out with a pressurized flow reactor. The typical reaction conditions were as follows: total pressure 0.6–3.1 MPa, the flow rate of carrier gas He 20 cm$^3$/min, adsorption temperature 100–400 °C. After being pretreated in He at 600 °C for about 3 h, each catalyst was cooled in He stream to adsorption temperature and was pressurized with the carrier gas to the desired pressure. A pulse of $[^{14}C]CO_2$ was then introduced with a high-pressure gas sampler every 15 min. The radioactivity of $[^{14}C]CO_2$ released from the reactor was directly monitored with a radioanalyzer (Aloka RLC-701). In addition, the unreacted $[^{14}C]CO_2$ that was released at the outlet of the radioanalyzer was recovered by bubbling through the basic scintillation solution-Carbosorb. The total radioactivity of unreacted $[^{14}C]CO_2$ trapped by Carbosorb was measured by a liquid scintillation counter (LSC) (Beckman LS-6500, Beckman), after adding proper scintillator solvent (5 cm$^3$, Permafluor, Packard, Japan) to each fraction (1 cm$^3$). Literature is available for the liquid scintillation counting [36–41]. The amount of radioactivity was consistent with that measured by the radioanalyzer. Several pulses of $[^{14}C]CO_2$ were introduced into the catalyst until the radioactivity in the released pulse became equal to that in the introduced pulse.

To confirm the amount of $CO_2$ incorporated into the catalyst, the adsorbed catalysts were desorbed. In the adsorption operation, each catalyst sample was heated to 600 °C in helium stream and was held for 1 h. The radioactivity of $[^{14}C]CO_2$ released from the catalyst was measured by the radioanalyzer. At the same time, the gas of $[^{14}C]CO_2$ eluted was trapped by the Carbosorb solution and its radioactivity was measured by the liquid scintillation counter in the same way as in the adsorption operation.

## 3. Results and discussion

### 3.1. Polysulfides syntheses using dicyclohexylamine

In order to clarify the effect of reaction conditions such as reaction temperature, pressure, and reaction time on conversion of DIB, yields of polysulfides, and selectivities of each sulfur-containing product and to decide the optimum reaction conditions in polysulfides syntheses, the authors carried out polysulfides syntheses in the presence of a conventional homogeneous amine catalyst-dicyclohexylamine under various reaction conditions. The results are summarized in Table 2. The products were pentasulfide ($S_5$) and tetrasulfide ($S_4$), a small amount of monosulfide ($S_1$), disulfide ($S_2$) and trisulfide ($S_3$), and a trace amount of 2,4,4-trimethyl-pentyl-2-thiol (TMPT). There is no significant effect of reaction temperature, pressure of $H_2S$ or reaction time on the conversion of DIB and yield of polysulfides. In contrast, the reaction conditions except for the pressure of $H_2S$ influenced remarkably the selectivities of various polysulfides with different numbers of bridge sulfurs. The longer reaction time resulted in higher ratios of $S_4$ to $S_5$. Similarly, lower reaction temperature also favored the formation of $S_4$.

### 3.2. Polysulfide syntheses using solid base catalysts

Table 3 shows conversions of DIB, yields of polysulfide and selectivities of each sulfur-containing product obtained in reactions over solid base catalysts at 125 °C and under 0.6 MPa for 12 h. The conversions of DIB over ZnO, 1.3 mmol and 2.7 mmol $K/Al_2O_3$ catalysts were 43.3, 89.8 and 89.6%, respectively.

Table 2
Synthesis of polysulfide under various reaction conditions using dicyclohexyl amine (DCHA)

| Reaction time (h) | Temperature (°C) | Pressure (MPa) | Conversion (%) | Yield (g) | Selectivity (mol%) | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | $S_1$[a] | $S_2$[a] | $S_3$[a] | $S_4$[a] | $S_5$[a] |
| 13 | 125 | 0.6 | 87.6 | 20.1 | 1.8 | 1.4 | 1.5 | 42.3 | 53.1 |
| 13 | 125 | 1.0 | 97.8 | 20.3 | 1.8 | 0.7 | 1.0 | 40.3 | 56.1 |
| 13 | 128 | 0.6 | 90.3 | 20.7 | 1.7 | 2.0 | 2.0 | 25.2 | 69.1 |
| 13 | 132 | 0.6 | 89.7 | 20.2 | 2.6 | 1.7 | 1.5 | 25.8 | 68.3 |
| 20 | 128 | 0.6 | 95.6 | 19.9 | 1.4 | 1.4 | 1.6 | 50.4 | 45.2 |

[a] Si: monosulfide; $S_2$: disulfide; $S_3$: trisulfide; $S_4$: tetrasulfide; $S_5$: pentasulfide.

The results clearly indicated that the conversions of the solid base catalysts except for ZnO are almost the same as that of dicyclohexylamine (DCHA). The lower activity of ZnO was attributed to deactivation of the catalyst because of the formation of ZnS in the atmosphere of $H_2S$. Further, it was observed that the selectivities of polysulfides, i.e. the distribution of polysulfides with different numbers of bridging sulfurs, were similar to that in the case of DCHA; the selectivity of $S_4$ in the case of $K/Al_2O_3$ catalysts slightly increased, accompanying a decrease in selectivity for $S_5$.

Regarding the liquid amine-catalyzed alkyl thiol-sulfur reaction, a mechanism similar to that proposed for inorganic nucleophiles and sulfur have been proposed [42–44]. Such a reaction sequence is presented in step 2 in Scheme 1. Interaction of the thiol with base is probably the first step; then nucleophilic attack by the thiolate or developing thiolate on sulfur opens the eight-membered sulfur ring forming a linear alkyl hydrogen polysulfide. Reaction of the thiolate on the alkyl hydrogen sulfur chain occurs and forms alkyl nonasulfide. Further random attack by such thiolate on the alkyl nonasulfide can occur until steric factors and conditions intercede to govern the nature of the final product. Moreover, it was proposed that alkyl thiol could be readily formed via the addition of hydrogen sulfide to olefin, that the reaction should follow Markovnikov's rule in the presence of sulfur, and that the formation rate of thiol increased in the presence of sulfur [45]. Based on these viewpoints, a three-stage mechanism is suggested to interpret the synthesis of polysulfides from DIB, sulfur, and hydrogen sulfide in the presence of solid base catalysts, as shown in Scheme 1: (1′) The ready formation of intermediate—TMPT via the addition reaction of $H_2S$ to DIB according to Markovnikov's rule in the presence of sulfur (2′); the formation of bis-(1,1,3,3-tetramethylbutyl)-nonasulfide via the base-catalyzed TMPT-sulfur reaction (3′); the formation of polysulfides of lower numbers of bridging sulfurs via the reaction of thiol with polysulfides of higher numbers of bridging sulfurs, i.e. re-distribution of various polysulfides in the product depending on the reaction conditions.

In order to verify the mechanism of polysulfide synthesis mentioned above, the effect of the reaction time on conversion and product selectivity in the case of

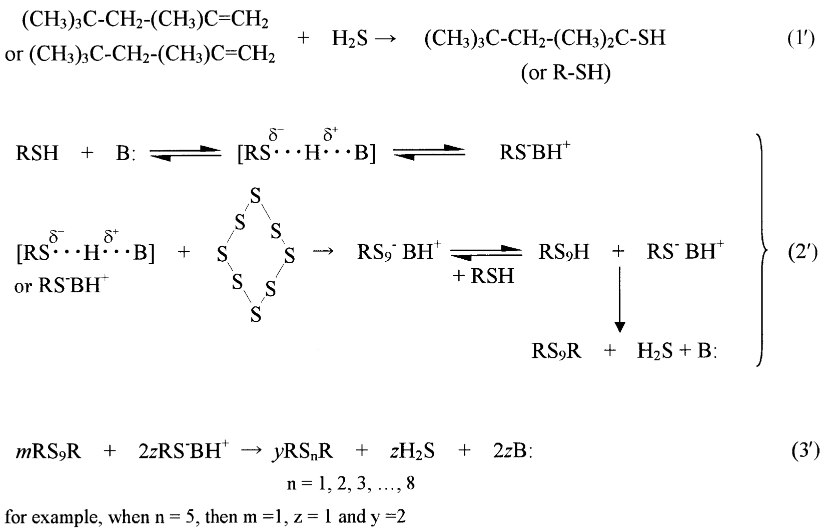
Table 3
Comparison of amine and base solid catalysts on catalytic activity in synthesis of polysulfide

| Catalyst | Amount of catalyst (g) | Conversion (%) | Yield (g) | Selectivity (mol%) | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | $S_1$[a] | $S_2$[a] | $S_3$[a] | $S_4$[a] | $S_5$[a] |
| DCHA | 0.05 | 87.6 | 20.1 | 1.8 | 1.4 | 1.5 | 42.3 | 53.1 |
| ZnO[b] | 0.54 | 43.3 | 5.9 | 1.8 | 0.7 | 1.0 | 40.3 | 56.1 |
| 1.3 mmol $K/Al_2O_3$[c] | 1.00 | 89.6 | 17.4 | 2.6 | 1.5 | 2.0 | 47.7 | 46.2 |
| 2.7 mmol $K/Al_2O_3$[c] | 1.00 | 89.8 | 16.9 | 2.2 | 1.1 | 1.5 | 47.8 | 47.4 |

[a] $S_1$: monosulfide; $S_2$: disulfide; $S_3$: trisulfide; $S_4$: tetrasulfide, $S_5$: pentasulfide.

[b] Calcining conditions: 450 °C/20 h.

[c] Metal salt: K–H–Ph; calcining conditions: 450 °C/20 h.



Scheme 1. Mechanism of polysulfide synthesis.

solid base catalyst was investigated. The syntheses of polysulfides were performed at 125 °C under 0.6 MPa pressure during 1–12 h in the presence of 1.3 mmol $K/Al_2O_3$ catalyst, which was prepared with K–H–Ph and calcined at 600 °C for 2 h. The changes in the mole fraction of each component in liquid products with reaction time are shown in Fig. 2. The formation of TMPT was observed for all reactions, although the quantity detected was very small during all reactions. Moreover, the formation of pentasulfide was observed in the reactions for 3 h or over and increased with an increase in reaction time. In contrast, tetrasulfide and trisulfide were detected only in the reactions for 6 h or over. This clearly indicates that the formations of thiol and $S_5$ are in the initial stage of the reaction, which is consistent with the mechanism shown in Scheme 1. Moreover, if one considers the similarity between the liquid amine catalyst and solid base catalysts, one could predict that the formation of $S_5$ would decrease and yields of $S_4$ and $S_3$ would increase with increasing reaction time by comparing with the results obtained for 13 h and 20 h using an amine catalyst, as shown in Table 2. This further supports the mechanism proposed in Scheme 1. Further, in every reaction, only a little amount of thiol was detected, indicating that the reaction rate of step ((1′)) in Scheme 1 is far slower than those of step (2′, 3′). Therefore, these results suggested that the thiols formation step is likely to be the rate-determining step governing the reaction rate. That is, once the thiols were formed, they quickly react with sulfur, and gave polysulfides of greater numbers of bridging sulfurs ($S_5$, $S_6$, etc.), each of which was subsequently transformed to one containing lower number of sulfur atoms ($S_3$, and $S_4$).

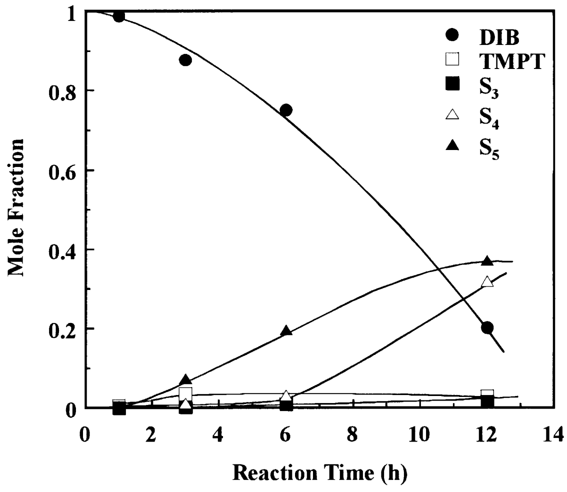


Fig. 2. Changes in distribution of products with reaction time during polysulfide syntheses.

### 3.3. Effect of preparation parameters on activity of catalysts

In order to investigate the influence of preparation parameters of solid base catalysts on the activity, the authors performed experiments over the base catalysts calcined at temperature between 400 and 700 °C for 2–24 h. Firstly, potassium hydrogen phthalate (K–H–Ph) was dissolved in water and impregnated into γ-alumina and samples were calcined at 600 °C for 2–24 h. The metal loadings of all the catalysts were 1.33 mmol of K per gram of catalyst. Syntheses of polysulfides were then performed at 125 °C and under 0.6 MPa for 6 h over the obtained catalysts. The results are shown in Table 4. The conversion of DIB increased from 40 to 79% with increasing calcination time from 2 to 17 h, and then only slightly increased with increasing the calcination time to 24 h. The result indicates that the number of active basic sites increases with an increase in the calcination time, resulting in the increase in the activity. Hence, the calcination time was fixed at 17 h and the polysulfide syntheses were performed on catalysts calcined at temperatures between 400 and 700 °C. Nevertheless, no significant activity modification was observed, as shown in Table 4. This is explained by the fact that moisture and acid gases adsorbed on the catalysts were sufficiently removed after calcination at 400 °C for 17 h; and number of basic sites formed did not change with further rise of calcination temperature. Hence, the calcination conditions of solid base catalysts at 600 °C for 17 h were chosen in developing the various basic catalysts.

Syntheses of polysulfides were carried out at 125 °C and under pressure of 0.6 MPa for 2 h over a series of $K/Al_2O_3$ catalysts, which were prepared with potassium hydroxide and calcined at 600 °C for 17 h. As shown in Fig. 3, the conversion of DIB linearly increased with increasing the content of potassium on the catalyst up to 1.33 mmol K and then slightly decreased. If one looks at the ideal surface of hydrated γ-alumina from the side, as proposed by Peri [46], one observes that the surface is terminated by hydroxyl groups, each of which is directly above an aluminum ion in the next layer of the crystallite. Since there are 12.5 hydroxyl groups on the surface per 100 Å, this corresponds to 5.3 mmol of hydroxyl groups per gram of an alumina with a surface area of 256 $m^2$/g. Higher activation temperatures result in the production of greater quantities of water. At 600 °C, about 80% of the hydroxyl groups are lost [46,47]. Further, if one considers that K ion replaces the proton in hydroxyl groups on the surface of alumina, the maximum loading of K on the alumina for monolayer distribution should be about 1.1 mmol per gram of alumina (5.3 mmol × (1–80%) = 1.1 mmol). This value is close to the K loading of 1.33 mmol $K/Al_2O_3$ catalyst, which showed the maximum activity in Fig. 3.

Table 4
Effect of preparation parameters on the activity of solid base catalysts

| Metal source | Metal loading (mmol/g catalysis) | Calcination conditions | | Conversion (%) |
|---|---|---|---|---|
| | | Temperature (°C) | Time (h) | |
| K–H–Ph | 1.33 | 600 | 2 | 40.0 a |
| | | 600 | 17 | 79.0 a |
| | | 600 | 24 | 85.0 a |
| $K_2CO_3$ | 1.33 | 400 | 17 | 28.0 b |
| | | 500 | 17 | 28.9 b |
| | | 600 | 17 | 30.3 b |
| | | 700 | 17 | 27.4 b |
| $NaOH_3$ | 1.33 | 600 | 17 | 26.3 b |
| NaOH | 1.33 | 600 | 17 | 27.5 b |
| $Na_2CO_3$ | 1.33 | 600 | 17 | 25.9 b |
| | | | | 82.2 a |
| $Mg(NO_3)_2$ | 1.33 | 600 | 17 | 68.1 a |
| $CaCl_2$ | 1.33 | 600 | 17 | 65.3 a |

Synthesis condition: a, 125 °C, 0.6 MPa, 6 h; b: 125 °C, 0.6 MPa, 2 h.

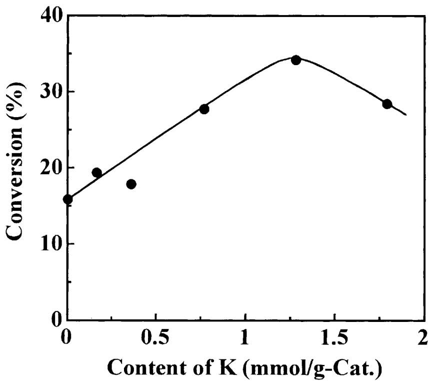


Fig. 3. Effect of potassium content supported on γ-alumina on catalytic activity in synthesis of CS-40.

On the other hand, if the K loading were increased over this value, the interaction between K ion surplus to the monolayer distribution and support would become weak, resulting in the sintering of K and scattering when the catalyst was calcined at 600 °C. Such reasons brought about the decrease in the activity of 1.8 mmol K/$Al_2O_3$ catalyst, as shown in Fig. 3.

### 3.4. Effect of active metals on catalytic activity

In order to investigate the effect of types of active metal salt on the activity of prepared catalyst, the authors prepared Na/$Al_2O_3$ catalysts of 1.33 mmol of Na per gram of catalyst using sodium carbonate, sodium hydroxide, and sodium nitrate. As shown in Table 4, there is no significant effect of type of metal salts on the conversion of DIB. Syntheses of polysulfides were also conducted at 125 °C and under 0.6 MPa for 6 h over several catalysts impregnated with different alkali and alkali earth metal agents. Results are summarized in Table 4. The alkali metal catalysts show higher catalytic activity than alkaline earth metal catalysts.

In order to more accurately compare the activity of the catalysts prepared with alkali metal hydroxides, activity tests were also conducted in a similar way, but total reaction time was chosen at 2 h as so to get lower DIB conversions. All catalysts were of the same loadings—1.33 mmol of metal per gram catalyst—and were calcined at 600 °C for 17 h. The catalytic activities of alkali metal catalysts increased in the order of $Li/Al_2O_3 < Na/Al_2O_3 < K/Al_2O_3 < Cs/Al_2O_3 < Rb/Al_2O_3$, as shown in Fig. 4. The loadings of Rb and Cs catalysts were determined by means of XRF (X-ray fluorescence, Shimadzu Rayny EDX-800). The metal loadings were 1.2 and 1.7 mmol of metal per gram of catalyst for Rb and Cs catalysts, respectively. As mentioned above, it was found that the optimal loading of active metal for alkali metal catalyst was about 1.3 mmol per gram of catalyst and that the surplus metal loading would inversely result in a decrease in catalytic activity, as shown in Fig. 3. Further, if one considers that the atomic radius of Cs is much greater than that of K, the inverse effect of higher loading of Cs should be more effective than that in the case of K. Based on these results, it is suggested that the activity of solid base catalysts depends on the basicity and basic strength of active metal, which originates from the electronegativity of the supported active metals.

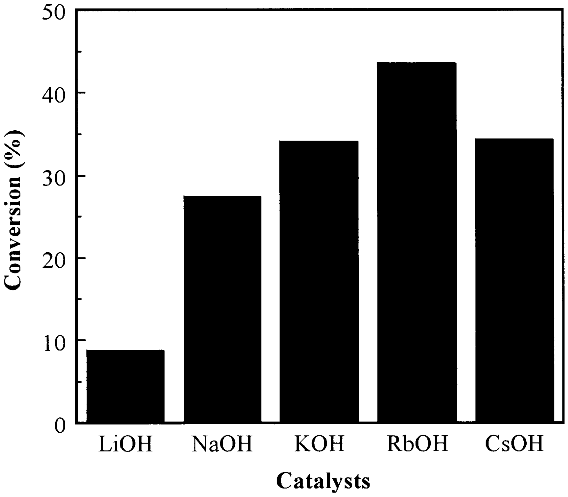


Fig. 4. Polysulfide synthesis activities over solid base catalysts.

### 3.5. Adsorption of [$^{14}C$]$CO_2$ on solid catalysts

In order to investigate the basicity of solid catalysts under higher pressure, a $^{14}C$-labeled $CO_2$ ([$^{14}C$]$CO_2$) radioisotope pulse tracer method was developed. A Rb/$Al_2O_3$ catalyst with 1.33 mmol Rb per gram of catalyst was prepared using rubidium nitrate and calcined at 600 °C for 17 h. Fig. 5a–d show the change in radioactivity of recovered [$^{14}C$]$CO_2$ with the number of introduced pulses which was directly monitored by the radioanalyzer, when a pulse of [$^{14}C$]$CO_2$ (10.2 $cm^3$) with a constant radioactivity (660 cps per pulse) was introduced into Rb/$Al_2O_3$ catalyst under 3.1 MPa every 15 min. After the first pulse was introduced, the radioactivity of the recovered pulse was only 320 cps at 100 °C, as shown in Fig. 5a. This indicates that a part of $^{14}C$ was incorporated into Rb/$Al_2O_3$. Further, the radioactivity in the recovered pulse increased with the number of introduced pulses and approached a constant value (660 cps per pulse) when the third pulse was introduced. Therefore, it could be considered that the adsorption at this temperature was almost completed. Under the typical condition, five pulses were introduced to insure the radioactivity in the pulse recovered being equal to that in the pulse introduced. In addition, the [$^{14}C$]$CO_2$ eluted at the outlet of the radioanalyzer was recovered by bubbling through the basic scintillation solution of Carbosorb. The total [$^{14}C$]$CO_2$ trapped by Carbosorb in every recovered pulse was

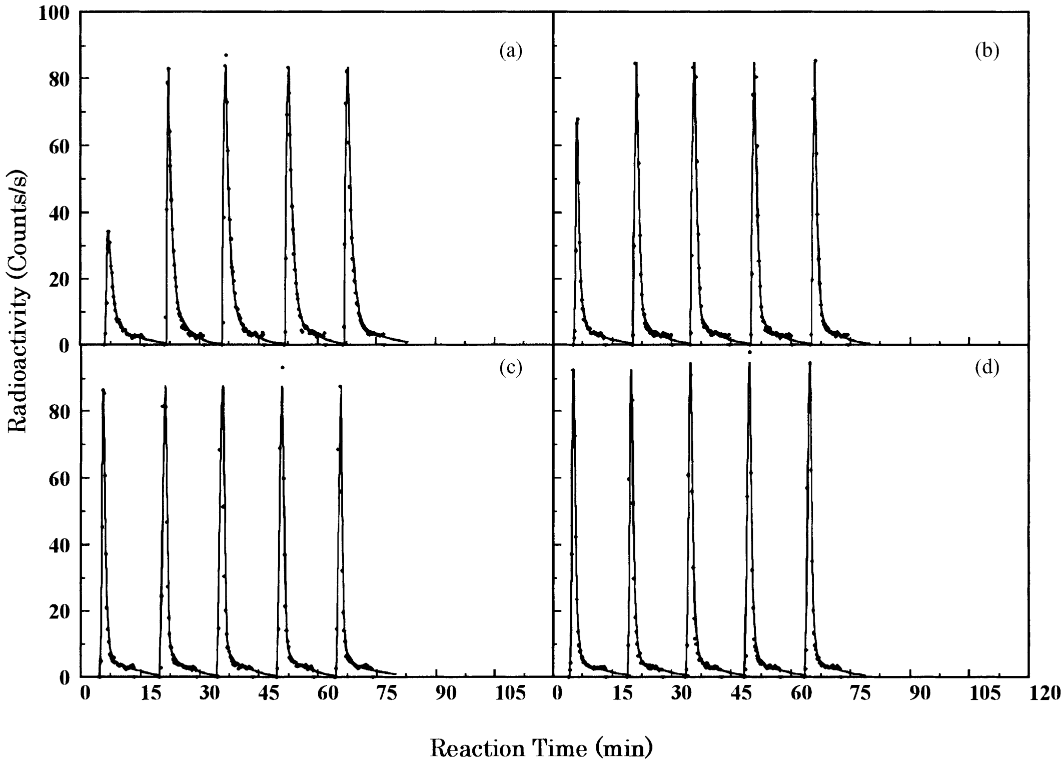


Fig. 5. Changes in radioactivities of [$^{14}$C]CO$_2$ measured by the radioanalyzer in recovered pulse with reaction time (0.5 g Rb/Al$_2$O$_3$, 3.1 MPa). (a)100 °C; (b) 200 °C; (c) 300 °C; (d) 400 °C.

measured by the LSC. The change in radioactivity of recovered [$^{14}$C]CO$_2$ with the number of introduced pulses, which was measured by LSC, was shown in Fig. 6. This amount of radioactivity was consistent with that measured by the radioanalyzer. The number of pulses ($N_T$) incorporated into the catalyst could be calculated from the balance of radioactivity between introduced and recovered [$^{14}$C]CO$_2$:

$$N_T = N_P - \sum_{i=1}^{5} \frac{R_{\text{trapi}}}{R_{\text{input}}} \tag{2}$$

where $N_P$ is the number of introduced pulses, $R_{\text{input}}$ the amount of radioactivity in a standard pulse, and $R_{\text{trapi}}$ the radioactivity in the $i$th pulse collected by the trap at the outlet of the reactor, which was measured by either radioanalyzer (cps) or LSC (dpm). The uptake amount of [$^{14}$C]CO$_2$ to the catalyst was obtained from:

$$S_T = N_T S_P \tag{3}$$

Here $S_P$ is the amount of CO$_2$ in a standard pulse (mmol/g catalyst). Further, the adsorbed catalyst was desorbed to further verify the amount of CO$_2$ accumulated into the catalyst. When the adsorbed catalyst was heated to 600 °C in helium stream and was held for 1 h the [$^{14}$C]CO$_2$ adsorbed on the catalyst desorbed from the catalyst after the adsorption of [$^{14}$C]CO$_2$ was completed at every temperature. The radioactivity of [$^{14}$C]CO$_2$ desorbed from the catalyst was measured by the radioanalyzer and by LSC in the same way as in the adsorption operation. It was found that the radioactivity of [$^{14}$C]CO$_2$ released from the catalyst in the desorption operation was approximately the same as that incorporated into the catalyst in the adsorption operation at every temperature, as shown in Fig. 6. This indicates that the uptake of CO$_2$ to the catalyst is reversible. Similarly, the amount of CO$_2$ desorbed could be calculated from the total radioactivity using the same method as described previously.

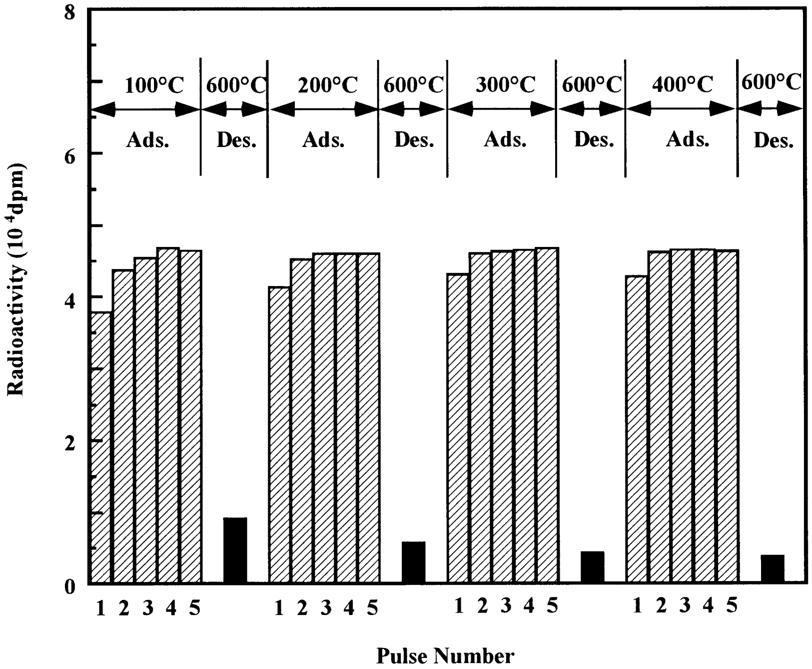


Fig. 6. Changes in radioactivities of [$^{14}C]CO_2$ measured by the liquid scintillation counter in recovered pulse with number of [$^{14}C]CO_2$ pulses introduced at the temperature between 100 and 400 °C, and changes in radioactivities of [$^{14}C]CO_2$ desorbed from the catalyst at 600 °C.

The uptake amounts of $CO_2$ on Rb/$Al_2O_3$ catalyst at several temperatures are shown in Table 5. The results based on the measurements using the radioanalyzer are approximately the same as those obtained using LSC. Further, the results obtained in the adsorption operation are also consistent with those obtained in the desorption process at 600 °C. This indicates that the uptake of [$^{14}C]CO_2$ on the catalyst is a reversible process. Moreover, the uptake amount of $CO_2$ on the catalyst decreased with an increase in temperature.

Table 5
Uptake amount of $CO_2$ measured in adsorption and desorption processes over Rb/$Al_2O_3$ catalyst

| Temperature (°C) | 100 | 200 | 300 | 400 |
|---|---|---|---|---|
| Adsorption | | | | |
| RA a | 0.470 | 0.350 | 0.257 | 0.216 |
| LSC b | 0.497 | 0.367 | 0.291 | 0.203 |
| Desorption | | | | |
| RA a | 0.464 | 0.334 | 0.225 | 0.204 |
| LSC b | 0.459 | 0.318 | 0.257 | 0.203 |
| Average | 0.472 | 0.342 | 0.258 | 0.206 |

Uptake amount of $CO_2$ measured by means of a: radjoanalyzer; b: liquid scintillation counter.

### 3.6. Effect of amount of catalyst and total pressure on the uptake amount of $CO_2$

Fig. 7a shows the effect of amounts of catalyst on the uptake amounts of $CO_2$ on MgO where the amounts of the catalyst used were 0.200, 0.450, 0.05 and 0.600 g, respectively. The uptake amount of $CO_2$ at every temperature increased linearly with an increase in the amount of MgO. Further, the intercepts of all straight lines were 0.0205, 0.0128, 0.0089, and 0.0070 mmol/g catalyst. at 100, 200, 300 and 400 °C, respectively. These values were considered to represent the background of the adsorption device. Moreover, a blank test in which the quartz sand was substituted for the catalyst, i.e. the amount of the catalyst used was zero, was carried out; the results were also plotted in Fig. 7a. The values of intercepts were approximately the same to those obtained in the blank

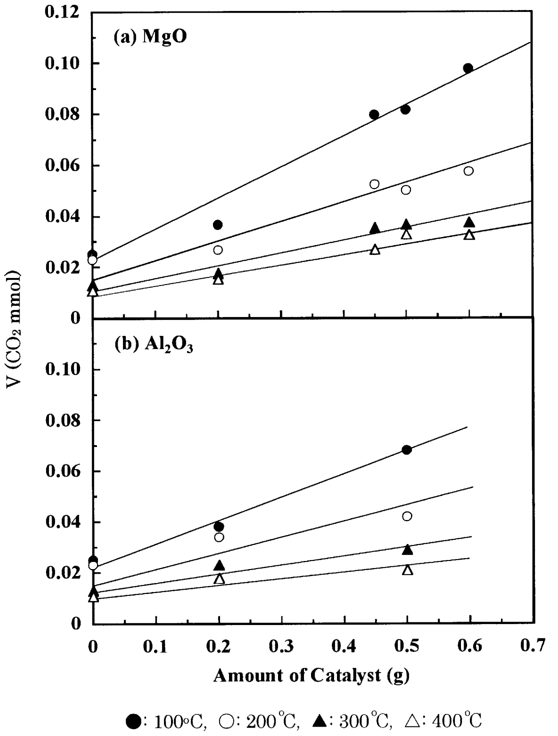


Fig. 7. Changes in adsorbed amounts of $[^{14}C]CO_2$ with amount of MgO and alumina at several temperatures.

test, as shown in Fig. 7a. In addition, similar results were obtained when $Al_2O_3$ was used, as shown in Fig. 7b. Therefore, these values were defined as the background values for the adsorption device at each temperature. For all the uptake amounts of $CO_2$ described below, these background values were taken into account.

The effect of operating pressure on the uptake amount of $CO_2$ on the 1.33 mmol $Rb/Al_2O_3$ catalyst was also investigated when the operating pressure was varied from 0.60 to 3.10 MPa; the results at several temperatures are shown in Table 6. No significant change in the uptake amount of $CO_2$ on the catalyst was observed at any temperature, although the operating pressure was varied from 0.60 to 3.10 MPa. This suggested that the adsorption of $CO_2$ on the catalyst only occurred on the basic sites, which eventually was an acid–basic neutralization reaction and was not affected by the pressure. In the meantime, this also reveals the feasibility of $CO_2$ pulse tracer method to measure the basicity of the solid catalysts.

Table 6
Effect of operating pressure on uptake amount of $CO_2$ on $Rb/A1_2O_3$ catalyst

| Pressure (MPa) | Temperature (°C) | | | |
|---|---|---|---|---|
| | 100 | 200 | 300 | 400 |
| 0.6 | 0.448 | 0.337 | 0.237 | 0.192 |
| 1.6 | 0.471 | 0.339 | 0.236 | 0.191 |
| 3.1 | 0.472 | 0.342 | 0.258 | 0.206 |

### 3.7. *Uptake of $CO_2$ on alkali metal catalysts and relationship with catalytic activity*

Similar adsorption experiments on a series of $\gamma$-$Al_2O_3$-supported alkali metal catalysts using $[^{14}C]CO_2$ pulses were carried out. All alkali metal catalysts of the same loadings −1.33 mmol per gram of catalyst—were prepared using nitrate salts and calcined at 600 °C for 17 h. Fig. 8 shows the uptake amounts of $CO_2$ on these catalysts at several temperatures. The amount of $CO_2$ accumulated onto the catalyst decreased with adsorption temperature for all catalysts. Moreover, the uptake amount of $CO_2$ at 300 and 400 °C was significantly less than the amounts at 100 and 200 °C. The amount of adsorption of $CO_2$ increased in the order of $Li/Al_2O_3 < Na/Al_2O_3 < K/Al_2O_3 < Rb/Al_2O_3 < Cs/Al_2O_3$.

As mentioned above, the catalytic activities of alkali metal catalysts depended upon the types of active metals. In order to investigate the relationship between

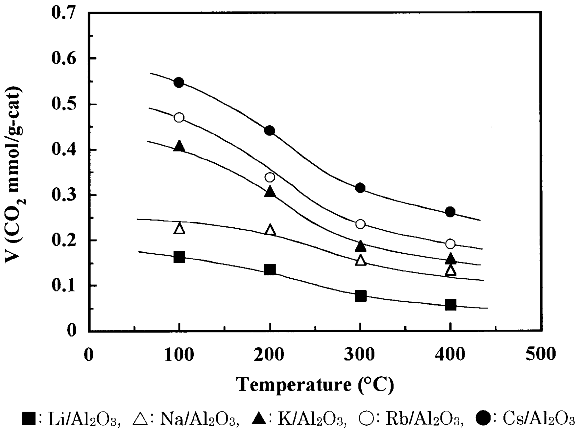


Fig. 8. Amount of $CO_2$ uptake on a variety of solid basic catalysts at several temperatures.

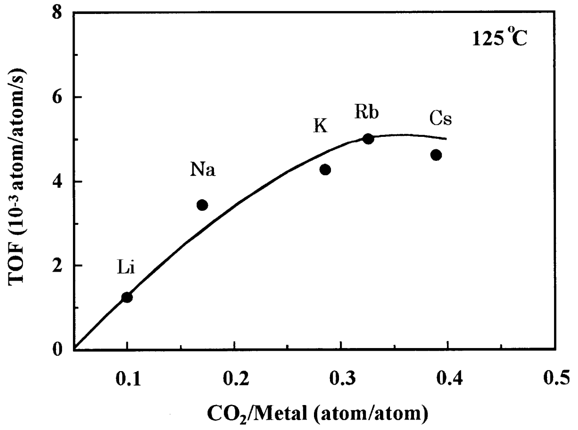


Fig. 9. Relationship between the adsorption amount of $[^{14}C]CO_2$ and catalytic activity in the syntheses of polysulfides over several catalysts at 125 °C.

the catalytic activity and the amount of $CO_2$ uptake, conversion of diisobutylene in the synthesis of polysulfide on the catalysts were transferred to turnover frequency (TOF, atom number of converted diisobutylene per atom of active metal per second). At the same time, the number of $CO_2$ atoms taken up per atom of active metal at 125 °C on every alkali metal catalyst was calculated via interpolation from the curves shown in Fig. 8. As shown in Fig. 9, the turnover frequency increased with the amount of $CO_2$ taken up on every active metal atom, and a very good relationship was obtained between the uptake amount of $CO_2$ and the catalytic activity except for the Cs catalyst. Taking into account that the Cs catalyst showed a lower catalytic activity than Rb catalyst (Fig. 4) due to the effect of Cs and Rb loadings, which brought about the overlapping of point for Cs catalyst in Fig. 9, one can conclude that the amount of $CO_2$ uptake should represent the number of active sites on solid base catalysts. At the same time, this also reveals the feasibility of the $[^{14}C]CO_2$ pulse tracer method in studies on the catalytic activity of solid base catalysts in syntheses of polysulfides.

## 4. Conclusions

It was found that the solid base catalysts could be applied to syntheses of polysulfides with diisobutylene, sulfur, and hydrogen sulfide in the one-stage process. The conversions of diisobutylene, yields of polysulfides, and the distribution of products, i.e. the selectivity for various polysulfides of different numbers of bridging sulfurs in the syntheses of polysulfides using solid base catalysts (1.3 mmol $K/Al_2O_3$ catalyst) were almost the same as the results obtained using a liquid amine catalyst (DCHA). Further, it was found that the optimal preparation conditions for the solid base catalysts were as follows: calcination temperature of 600 °C; calcination time of 17 h; the loadings of 1.33 mmol of alkali metal per gram of catalyst. It was also found that the type of active metal salt did not significantly affect the catalytic activity and that the alkali metal catalysts were more effective than alkaline earth metal catalysts. The catalytic activities of alkali metal catalysts increased in the order of $Li/Al_2O_3 < Na/Al_2O_3 < K/Al_2O_3 < Cs/Al_2O_3 = Rb/Al_2O_3$.

Based on the changes in the distribution of various polysulfides of different numbers of bridging sulfurs in the product with the reaction time using 1.3 mmol $K/Al_2O_3$ catalyst, a three-stage mechanism is suggested as follows: (1) the formation of intermediate—thiol (TMPT) via the addition reaction of $H_2S$ to DIB according to Markovnikov's rule; (2) the formation of polysulfides of higher numbers of bridging sulfurs; (3) the formation of polysulfides of lower numbers of bridging sulfurs via the reactions of thiol with those of higher numbers of bridging sulfurs, i.e. re-distribution of various polysulfides in the product.

A novel method for determining the adsorption of $CO_2$ using a $[^{14}C]CO_2$ pulse tracer method on solid base catalysts was developed. There was no significant effect of pressure on the amount of $CO_2$ adsorption on $Rb/Al_2O_3$. For the $\gamma$-$Al_2O_3$-supported alkali metal catalysts, the uptake amount of $CO_2$ at all temperatures increased in the order: $Li/Al_2O_3 < Na/Al_2O_3 < K/Al_2O_3 < Rb/Al_2O_3 < Cs/Al_2O_3$. The order is in good agreement with the catalytic activities of the catalysts in syntheses of polysulfides.

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