Genesis of Highly Active Cobalt Sulfide Catalyst for Hydrogenation and Isomerization: Effect of the Calcination Temperature of Precursor Cobalt Oxide upon the Catalytic Properties of Cobalt Sulfide

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It was found that the catalytic activities and selectivities of cobalt sulfide catalysts are significantly affected by the calcination temperature of precursor cobalt oxide for the hydrogenation of butadiene and the isomerization of 1-butene. When cobalt sulfide was prepared from cobalt oxide calcined at 1473—1573 K, the specific activities per surface area of the sulfide were enhanced by 30—40 times those of cobalt sulfide prepared from cobalt oxide calcined at a conventional temperature, 573—973 K. The reaction selectivities were also strongly modified by the calcination temperature of precursor oxide. It is suggested that two different types of active sites are formed on cobalt sulfide, depending on the calcination temperature of the precursor. On the basis of XPS, XRD, SEM, and NO adsorption techniques, it is concluded that the particle size of the precursor cobalt oxide and sulfiding conditions determine the surface sulfur content and hence the catalytic properties of the sulfide catalysts. The sulfidation mechanism of cobalt oxide and active site models are proposed.

Supported Group 6 metal sulfides, Mo and W, combined with Co or Ni have been widely employed for hydroprocessing of petroleum feedstocks.[1,2] In connection with these catalyst systems, fundamental catalytic properties of metal sulfides have recently received considerable attention.[3] With the hydrodesulfurization (HDS) of dibenzothiophene over unsupported metal sulfides, Chianelli et al.[4—6] have shown that the HDS activity as a function of periodic table yields typical volcano type correlations for second and third raw elements, suggesting that the primary effect in the HDS over metal sulfides is electronic. As for supported metal sulfides, similar volcano type correlations have been reported for HDS[7,8] and HDN (hydrodenitrogenation).[9,10] Elucidation of the intrinsic activities of metal sulfide catalysts is very crucial to examine these correlations.

The effect of preparation method of metal sulfides upon the catalytic properties has received only a little attention in spite of importance in the determination of intrinsic activity. With nickel sulfide, the effect of sulfiding reagent of Ni metal was noted briefly.[11] Takeuchi et al.[12] reported that NiS was inactive for the hydrogenation of acetylene, whereas sulfided Ni metal having a surface composition of Ni_3S_2 was active. Similarly, CoS_2 and CoS did not show any catalytic activities for butadiene hydrogenation and *cis*-2-butene isomerization, while sulfided Co metal was active for these reactions.[13] In the present study, we examined the effect of the calcination temperature of the oxide precursor upon the catalytic properties of cobalt sulfide.

It is shown here that the catalytic properties of unsupported cobalt sulfide, which is one of the most important sulfides, depends strongly on preparation variables. The calcination temperature of precursor cobalt oxide was found to significantly affect the catalytic activities and selectivities of resultant cobalt sulfide for the hydrogenation of butadiene and the isomerization of 1-butene.

The physicochemical aspects of sulfidation process of cobalt oxide have been investigated by using temperature programmed sulfidation (TPS) and X-ray diffraction (XRD) techniques and have been presented elsewhere.[14]

Experimental

Catalyst Preparation. Cobalt oxide was prepared by decomposing cobalt acetate (GR grade, Nakarai Chemicals Ltd.) in air at 573 K for 5 h. The resultant cobalt oxide was calcined again at varying temperatures (T_c: 573—1573 K) for 5 h. Cobalt oxide calcined at T_c is denoted Co–O(T_c) here. Co–O(T_c) was ground into fine powder using a mortar and pestle. X-ray diffraction patterns showed an exclusive formation of Co_3O_4 irrespective of T_c. The BET surface areas of some representative samples were measured at 77 K using an Ar adsorption method.

Sulfidation of the cobalt oxide was conducted as fine powder in an in situ reaction cell at a desired temperature (T_s: 373—673 K) for 90 min using a stream of an atmospheric pressure of H_2S/H_2 (1/10, 550 cm^3 min^{-1}). T_s was 673 K unless otherwise noted. The oxide sample in the cell was exposed to H_2S/H_2 at T_s after a brief evacuation at room temperature. Subsequently, the sulfided sample was treated for 60 min at 673 K in a stream of H_2 (1 atm, 500 cm^3 min^{-1}), which had been passed through a deoxygenation catalyst layer (De-Ox, Alfa) at 573 K, followed by a zeolite packing at a liquid nitrogen temperature. The cobalt sulfide catalyst thus prepared from Co–O(T_c) is designated Co–S(T_c).

Test Reaction. Both hydrogenation of butadiene (H_2/butadiene molar ratio: 2/1) and the isomerization of 1-butene

(H_2/butene: 1/1) were carried out over the cobalt sulfide catalyst (ca. 0.3 g) at 473 K and a total pressure of 15 kPa using a closed circulation system (220 cm^3). The reaction gases were analyzed by glc using a column packing of sebaconitrile. The composition of the reaction gas was analyzed every 15 min after the first analysis at 5 min of the reaction time. The initial activity was calculated from the conversion of the reactant at 5 min. The highest initial conversions of butadiene and 1-butene were 7.5 and 27%, respectively, for cobalt sulfides at T_s=673 K. The rate constant, k, of the 1-butene isomerization was calculated on the basis of an observed reaction order, i.e., reversible first order with respect to butenes. In both reactions, the *initial* selectivity was obtained by extrapolating a conversion- selectivity curve to the conversion=0%.

NO Adsorption. The amounts of NO chemisorption were measured around 300 K for the cobalt sulfide catalyst in the reaction cell. The catalyst was freshly sulfided and H_2-treated at 673 K prior to the adsorption. Nitrogen monoxide (Takachiho Kagaku Kogyo, purity: 99.9%) was supplied from break-seal Pyrex vessels and used after purification by a freeze-and-thaw technique. After contacting the sulfide with NO (ca. 5.3 kPa) for 30 min, the pressure of NO in a gas phase was measured, followed by condensing NO in the gas phase at 77 K to examine evolution of uncondensed products during the adsorption. When any uncondensed gas was not detected, the cobalt sulfide was evacuated at room temperature for 30 min. Subsequently, the amount of physisorbed NO was obtained in a similar way at an approximately same NO pressure. Sometimes a small amount of products uncondensed at 77 K was detected after the first NO adsorption. The amount of the uncondensed gas was volumetrically estimated. After being analyzed by a quadruple mass spectrometer (MSQ 101, ULVAC), the product gas was evacuated, followed by a second NO adsorption. The mass analysis of the uncondensed gas showed the formation of N_2 in addition to a small amount of NO.

XPS and XRD Measurements. The X-ray photoelectron spectra (XPS) of sulfided catalysts were measured after the hydrogenation reaction on a Hitachi 507 photoelectron spectrometer using Al$K\alpha_{1,2}$ radiation (1486.6 eV). The anode was operated at 9 kV and 50 mA. The sample was mounted on a copper holder using a double-sided adhesive tape without an exposure to air in a N_2-filled glovebox (nominal composition of N_2; N_2: >99.999%, O_2: <0.0005%, H_2: <0.0002%, and H_2O: <10 mg m^{-3}). Assuming linear backgrounds, XPS intensity ratios were calculated by using the planimetered peak areas of the Co2$p_{3/2}$ and S2p bands. Binding energies (BE) were referenced to the Cls band at 285.0 eV due to adventitious carbon.

XRD patterns of the calcined and sulfided cobalt were obtained on a Shimadzu VD-1 diffractometer using Cu $K\alpha$ radiation with a Ni filter (scan speed; 0.5 degree min^{-1}). The XRD measurements of the sulfided catalysts were made in air soon after an exposure to air. The crystallite sizes of Co_3O_4 and Co_9S_8 were estimated from the line widths using a Scherrer's equation (K=0.9). A correction was made for the instrumental line broadening.

Results

Morphology of Cobalt Catalyst. BET surface areas of some cobalt oxide precursors are summarized in Table 1 together with the crystallite size of Co_3O_4. The area decreased greatly as T_c increased from 573 to 1173 K and gradually at the higher T_c. The T_c dependence of the surface area is consistent with that expected from the crystallite size of Co_3O_4.

When the sulfidation and subsequent H_2-treatment were conducted at 673 K, a significant increase in the surface area was observed and the extent of increase amounted to 65—100-fold at T_c=1173—1573 K as presented in Table 1. The XRD measurements showed the formation of a crystalline Co_9S_8 phase in all the sulfide catalysts. Besides, a very weak hump was observed at 44.2° only with Co–S (1473) and (1573), indicating the formation of metallic cobalt. However, no XRD peaks due to cobalt oxides were detected for Co–S (573—1573) *after* the H_2-treatment at 673 K. The crystallite size of Co_9S_8 decreased with increasing T_c contrary to the change in the surface area, suggesting the formation of a noncrystalline cobalt sulfide phase, particularly, for Co–S (1473—1573). The difference in the surface area was only 4-fold at most between Co–S (573—1173) and Co–S (1473—1573) as opposed to a more than 50 times difference in the oxidic state.

SEM micrographs of cobalt oxide calcined at 573 and 1573 K and of their sulfided forms are shown in Fig. 1. Co-O (1573) is apparently well crystallized as compared to Co-O (573). The morphology of Co-O (573) seems essentially invariant on sulfiding at 673 K. With Co-O (1573), on the other hand, surface roughness significantly developed on the sulfidation at 673 K. It is likely that a rapid expansion of the sample volume due to exchange of

Table 1. BET Surface Areas and Crystallite Sizes of Cobalt Oxide and Sulfide and the Amount of NO Adsorption on Cobalt Sulfide

T_c	BET surface area/m^2 g^{-1}		Crystallite size[a)]/nm		Amount of NO adsorption	
K	Oxide	Sulfide[b)]	Oxide	Sulfide[b)]	10^{18} mol g^{-1}	10^{18} mol m^{-2}
573	14.1	38	14	48	83	2.2
973	3.2	24	64			
1173	0.41	41	79	31	121	3.0
1473	0.21	17	113	20	149[c)]	8.8[c)]
1573	0.17	11	113	19	105[d)]	9.5[d)]

a) Crystallite diameters of Co_3O_4 (2θ=36.9°) and Co_9S_8 (2θ=51.9°) for oxide and sulfide, respectively. b) T_s=673 K and H_2-treatment temperature=673 K. c) 20% of NO was decomposed during the adsorption experiments. d) 18% of NO was decomposed during the absorption experiments.

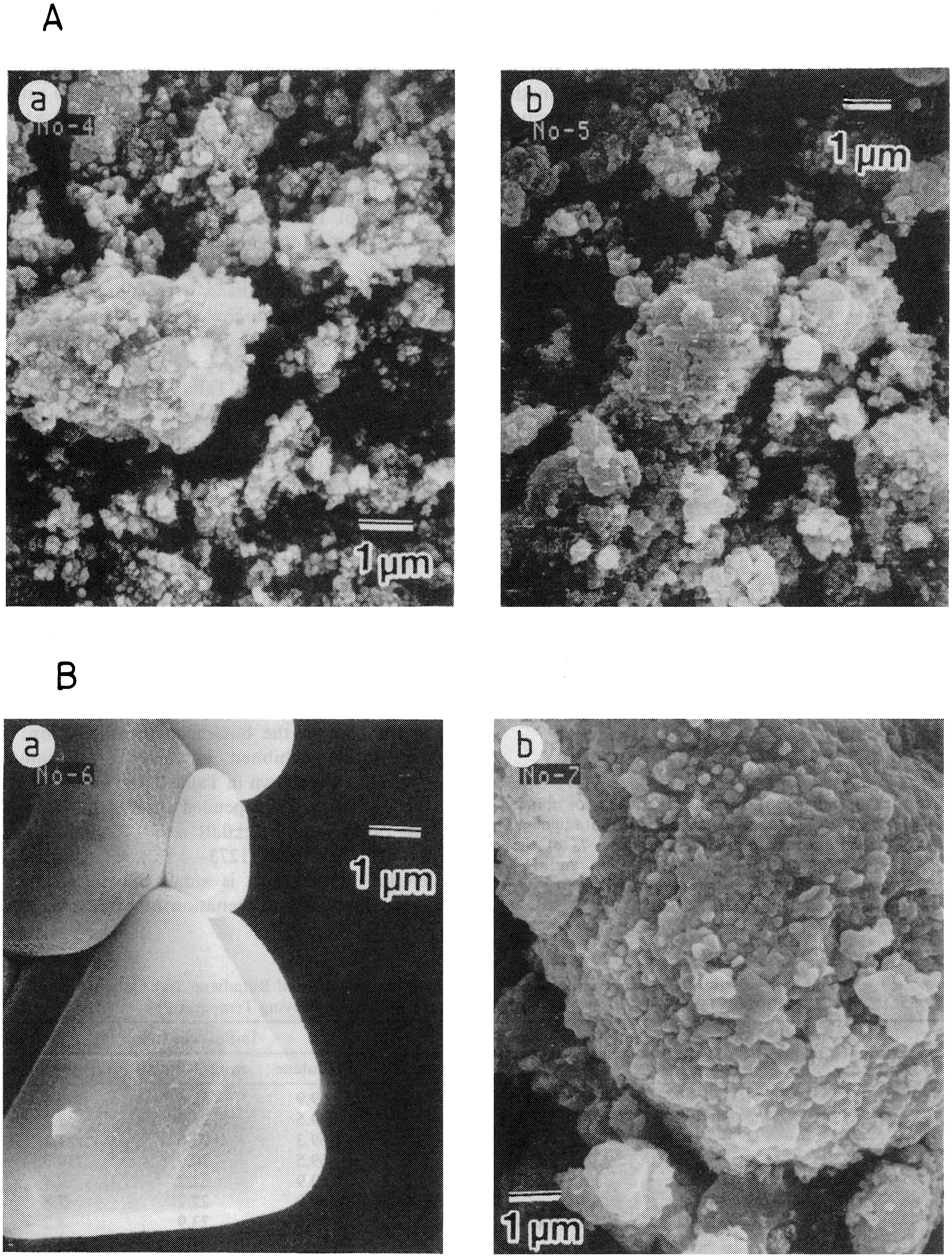

Fig. 1. Scanning electron micrographs of Co–O (573) (A) and Co–O (1573) (B) calcined (a) and sulfided and H_2-treated (b). Both sulfidation and H_2-treatment temperatures were 673 K.

oxygen anions (*r*: 0.132 nm)[15] with considerably larger sulfur anions (0.184 nm) results in crack formations in the sulfide phase and hence the surface area increase.

Effects of T_c and T_s on Catalytic Properties of Sulfided Cobalt. Shown in Fig. 2 is the effect of the calcination temperature (T_c) of precursor oxide upon the activity of cobalt sulfide for the hydrogenation of butadiene. Both sulfidation (T_s) and subsequent H_2-treatment were conducted at 673 K. The reaction rate and *initial* distribution of products for the hydrogenation are summarized in Table 2. Only a negligible amount of butane was detected during the hydrogenation (<0.1% and <0.5% at 80% butadiene conversion for Co–S (573) and (1573), respectively). In contrast, when cobalt oxide was H_2-reduced at 673 K, the hydrogenation rate was too large to measure even at 373 K and 1-butene and butane were predominantly produced. Of significance in Fig. 2 and Table 2 are the findings that the catalytic activity of cobalt sulfide greatly increases at $T_c \geqslant 1473$ K after taking a shallow minimum around 1000—1100 K as T_c increases from 573 to 1573 K and that the selectivity remarkably shifts at $T_c=1473$ K from a predominant production of 1-butene to that of *trans*-2-butene. A predominant production of *trans*-2-butene was reported by Tanaka et al.[13] and Wells et al.[16] for the hydrogenation of butadiene over sulfided Co metal. Wells et al.[16] have found that cobalt catalysts exhibiting similar catalytic properties are also prepared by reducing a mixture of CoS and CoO.

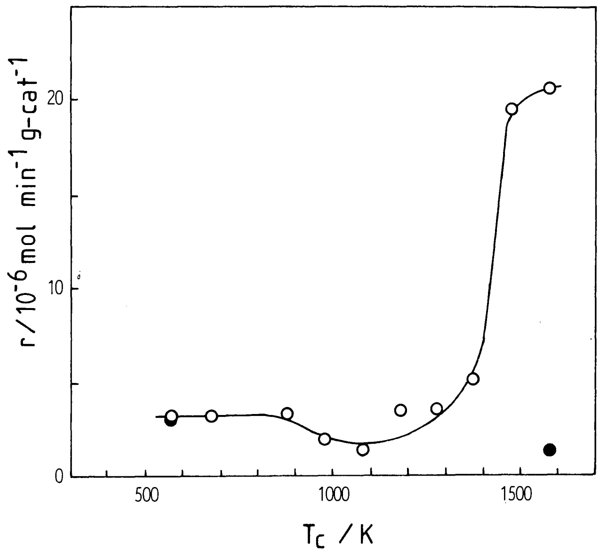

Fig. 2. Dependence of the reaction rate, *r*, of cobalt sulfide catalyst for the hydrogenation of butadiene at 473 K upon the calcination temperature T_c of the precursor cobalt oxide. Both sulfidation and H_2-treatment temperatures were 673 K. ○; after H_2 treatment and ●; before H_2 treatment.

As shown in Fig. 2 and Table 2, the activity of Co–S (573) was not considerably altered by omitting the H_2-treatment at 673 K after the sulfidation. Besides, no appreciable activity change was observed even on a prolonged H_2-treatment at 673 K (5 h). In contrast, when the H_2-treatment was not applied, the activity of Co–S (1573) remained significantly low and 1-butene was predominantly produced, indicating that the high activity of Co–S (1573) emerges only during the H_2-treatment following the sulfidation.

Figure 3 illustrates the catalytic activity of cobalt sulfide for the isomerization of 1-butene as a function of T_c. The rate constant and selectivity are summarized in Table 3. No appreciable amount of butane was found as in the case of the butadiene hydrogenation. The cobalt sulfide exhibited an activity maximum at $T_c=1473$ K. As shown in Table 3, the *initial* selectivity of the isomerization depended on T_c; the *cis*/*trans*-2-butene ratios were 0.83±0.01 and 0.72±0.02 for Co–S (573—1073) and Co–S (1273—1573), respectively. The difference in the ratio is small but significant. As observed for the hydrogenation of butadiene, the H_2-

Table 2. Reaction Rate and Initial Selectivity of the Hydrogenation of Butadiene over Cobalt Sulfide Catalysts Prepared from Cobalt Oxides Calcined at Varying Temperatures

Calcination temperature/K	Reaction rate[a]/10^{-6} mol min^{-1} g-cat^{-1}	Initial selectivity[a]/%		
		1-Butene	*trans*-2-Butene	*cis*-2-Butene
573	3.20 (0.084[b])	69.9	23.6	6.5
573[c]	2.98	69.5	23.3	7.2
673	3.22	69.3	23.6	7.1
873	3.29	69.5	20.2	10.3
973	1.85 (0.077[b])	69.9	22.7	7.4
1073	1.44	70.0	22.2	7.8
1173	3.43 (0.084[b])	67.9	23.9	8.2
1273	3.49	69.3	24.7	6.0
1373	5.17	62.7	29.3	8.0
1473	19.5 (1.2[b])	38.6	50.4	11.0
1573	21.6 (2.0[b])	24.2	67.5	8.3
1573[c]	1.33	69.3	23.5	7.2

a) At 473 K. Initial selectivity was obtained by extrapolation of selectivity-conversion curves to conversion=0%. Only a negligible amount of butane was observed. b) 10^{-6} mol min^{-1} m^{-2}. c) Without H_2-treatment after sulfidation.

treatment at 673 K was found to cause a great increase in the isomerization activity for Co–S (1573), whereas essentially no change was observed for Co–S (573).

Comparisons of the catalytic activities in Figs. 2 and 3 and the surface areas of sulfide catalysts in Table 1 inidicate that the T_c dependences of the catalytic activities cannot be explained simply in terms of the change in the surface area of cobalt sulfide. On the contrary, the difference in the activities between Co–S (573—1173) and Co–S (1473—1573) is greatly enhanced when the activities are evaluated in terms of the specific activities per surface area as presented in Tables 2 and 3 for some typical catalysts. It is noteworthy that the specific activities of Co–S (573), Co–S (973), and Co–S (1173) are nearly equivalent, while those of Co–S (1473) and Co–S (1573) are very close. The specific activities of the latter catalysts are about 20 and 40 times larger than those of the former catalysts for the hydrogenation and isomerization, respectively.

Figure 4 illustrates the effect of sulfiding temperature (T_s) on the hydrogenation of butadiene for Co–S (573). The H_2-treatment temperature after the sulfidation was 673 K. It was found that the hydrogenation activity

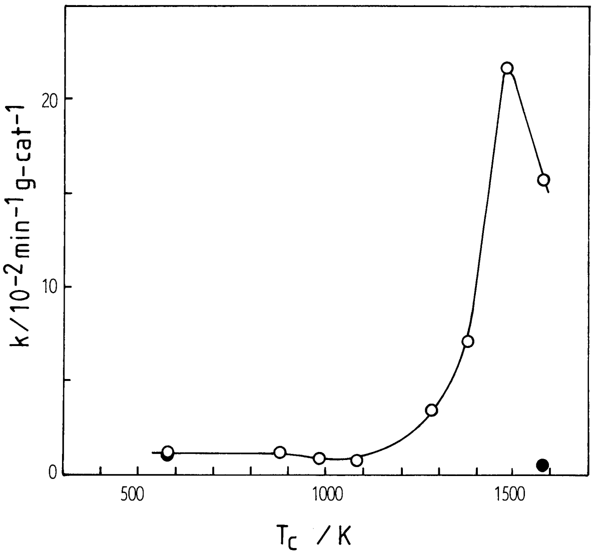

Fig. 3. Dependence of the rate constant, k, of cobalt sulfide catalyst for the isomerization of 1-butene at 473 K upon the calcination temperature of the precursor oxide. Both sulfidation and H_2-treatment temperatures were 673 K. ○; after H_2 treatment and ●; before H_2 treatment.

Table 3. Rate Constant and Initial Selectivity of the Isomerization of 1-Butene over Cobalt Sulfide as a Function of Calcination Temperature of Precursor Cobalt Oxide

Calcination temperature	$k^{a)}$	Initial selectivity$^{a)}$
	10^{-2} min^{-1} g-cat^{-1}	*cis*-2-butene/ *trans*-2-butene
573	1.27 (0.033$^{b)}$)	0.83
573$^{c)}$	1.05	0.84
873	1.31	0.83
973	0.97 (0.040$^{b)}$)	0.83
1073	0.90	0.78
1273	3.57	0.70
1373	7.27	0.69
1473	21.8 (1.3$^{b)}$)	0.73
1573	15.8 (1.4$^{b)}$)	0.73
1573$^{c)}$	0.63	0.83

a) At 473 K. Initial selectivity was obtained by extrapolation of selectivity-conversion curves to conversion=0%. b) 10^{-2} min^{-1} m^{-2}. c) Without H_2-treatment after sulfidation.

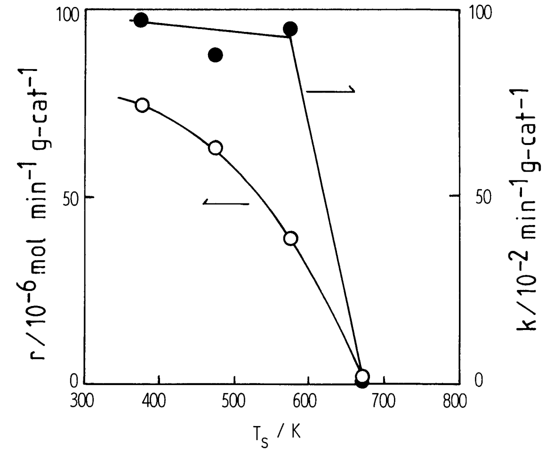

Fig. 4. Activities of cobalt sulfide catalyst for the butadiene hydrogenation and 1-butene isomerization as a function of sulfidation temperature T_s. The H_2-treatment temperature was 673 K. ○; hydrogenation at 473 K and ●; isomerization at 473 K.

Table 4. Surafce Area, $S2p/Co2p_{3/2}$ Ratio, Specific Activity, and Initial Selectivities in the Butadiene Hydrogenation and 1-Butene Isomerization for Cobalt Sulfide Catalysts Sulfided at Varying Temperatures (T_s)

T_s	Surface area	$S2p/Co2p_{3/2}$ intensity ratio		Specific activity and initial selectivity			
K	m^2 g^{-1}	Before H_2 treatment	After H_2 treatment	Hydrogenation		Isomerization	
				$r^{b)}$	*trans*-2-b/%$^{b)}$	$k^{c)}$	*cis*/*trans*$^{c)}$
373	34	0.082$^{d)}$	0.21	2.2	68	2.9	0.73
473	42	0.33$^{d)}$	0.36	1.5	65	2.1	0.74
573	77		0.39	0.51	59	1.2	0.71
673	41	0.40	0.40±0.01	0.084	22	0.033	0.83

a) H_2-treated at 673 K for 60 min. b) $r/10^{-6}$ mol min^{-1} m^{-2} at 473 K. Proportion of *trans*-2-butene. c) $k/10^{-2}$ min^{-1} m^{-2} at 473 K. *cis*-2-butene/*trans*-2-butene ratio. d) Sulfate sulfur is included.

greatly increased as T_s decreased from 673 to 373 K, accompanying a selectivity shift from 1-butene at T_s=673 K to *trans*-2-butene at $T_s \leqslant 573$ K as summarized in Table 4. The catalytic activity of Co–S (573) for the isomerization of 1-butene is also shown in Fig. 4 as a function of T_s. The *cis*/*trans*-2-butene ratio decreased from 0.83 to 0.72±0.02 when T_s was reduced to the temperatures lower than 573 K (Table 4).

NO Adsorption on Sulfided Cobalt. Nitric oxide adsorption capacities of cobalt sulfides are presented in Table 1. The adsorption capacity depends weakly on T_c and reaches a maximum for Co–S (1473). The surface density of NO adsorption (NO molecules m^{-2}) increased considerably for Co–S (1473—1573) as compared with those for Co–S (573) and (1173). Of significant difference in the NO adsorption properties between Co–S (573—1173) and Co–S (1473—1573) is the production of N_2 on Co–S (1473—1573) during the adsorption at room temperature. This fact suggests that at least part of NO adsorbs dissociatively on Co–S (1473—1573).

XPS Characterization. The XPS characterization of cobalt sulfide catalysts sulfided at 673 K was conducted to disclose the surface characteristics of the catalysts as a function of T_c. The spectroscopic features of the Co2p and S2p bands and their BE values (Co2p$_{3/2}$: 778.6±0.2 eV and S2p: 162.9±0.2 eV) were typical for Co_9S_8[17—19] irrespective of T_c of the precursor cobalt oxide (vide infra). The S2p/Co2p$_{3/2}$ XPS intensity ratio is presented in Fig. 5 against T_c. The surface sulfur content seems invariant (S2p/Co2p$_{3/2}$=0.40±0.01) between T_c=573 and 1273 K within experimental reproducibility. The H_2-treatment did not affect the ratio for Co–S (573). It is considered that the XPS ratio for Co–S (573—1273) corresponds to the formation of stoichiometric Co_9S_8 in surface, taking into consideration thermodynamic stability of Co_9S_8 under the present sulfidation conditions[20] and the XRD results showing exclusive Co_9S_8 formation for these cobalt sulfides. It is likely from Fig. 5 that the surface sulfur content for Co–S (1473—1573) is decreased by several % with respect to that for Co–S (573—1273). As shown in Fig. 5, the S2p/Co2p$_{3/2}$ intensity ratio for Co–S (1573) prior to the H_2-treatment was close to that for Co–S (573).

The surface state of cobalt catalysts sulfided at varying temperatures was also analyzed by XPS. The Co2p spectra for Co–S (573) are shown in Fig. 6 (a—c) before an H_2-treatment. Figure 7 illustrates the corresponding S2p XPS spectra. When Co–O (573) was contacted with H_2S/H_2 at 373 K, a new set of Co2p bands appeared at 780.5 and 796.5 eV at the expense of the peaks due to Co_3O_4 (779.6 and 794.6 eV).[21—23] On the basis of the BE, spin-orbit splitting (16.0 eV), and intense satellites ($\Delta\varepsilon_{3/2}$: 5.3 eV, $\Delta\varepsilon_{1/2}$: 6.6 eV),[21—23] the cobalt species

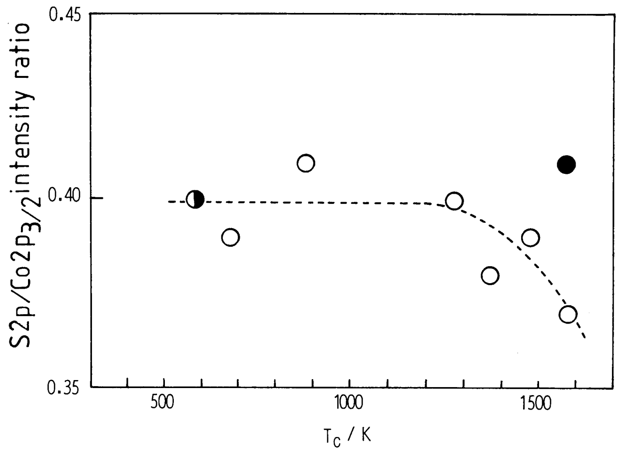

Fig. 5. Dependence of the S2p/Co2p$_{3/2}$ XPS intensity ratio for cobalt sulfide catalysts upon T_c. Both sulfidation and H_2-treatment temperatures were 673 K. ○; after H_2-treatment and ●; before H_2-treatment. The ratios were averaged over 2—5 independent measurements.

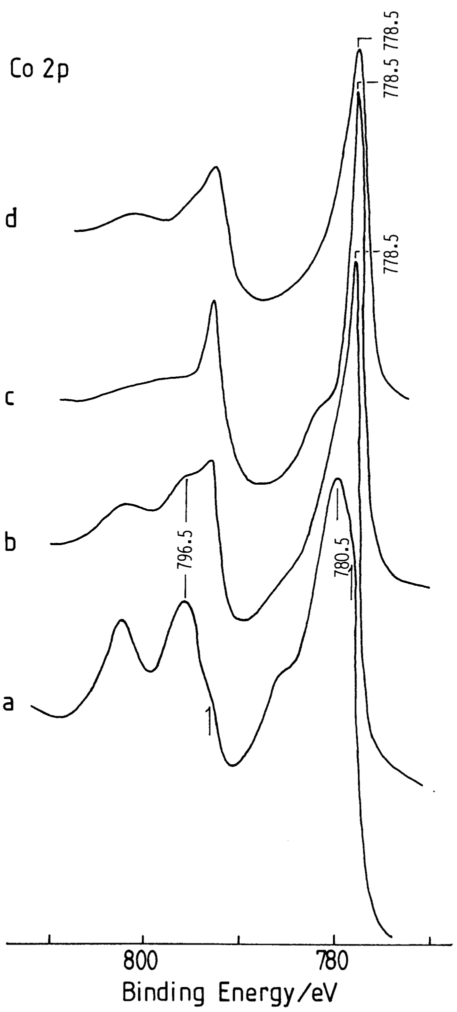

Fig. 6. X-Ray photoelectron spectra of the Co2p band for cobalt sulfide Co–S (573) before H_2-treatment. The calcination temperature of cobalt oxide was 573 K. Sulfidation temperatures were a) 373 K, b) 473 K, and c) 673 K. Spectrum d) was measured after an H_2-treatment of a) at 673 K.

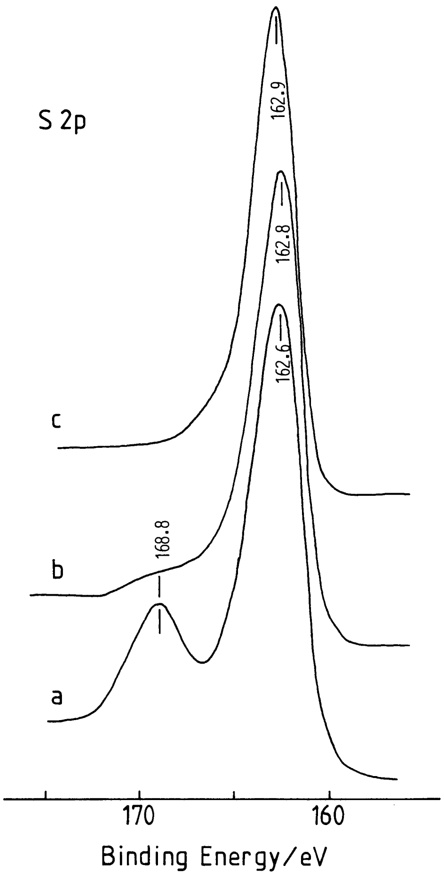

Fig. 7. X-Ray photoelectron spectra of the S2p level for the cobalt sulfide Co–S (573) in Fig. 6. Sulfidation temperatures were a) 373 K, b) 473 K, and c) 673 K. No H_2-treatment was conducted after the sulfidation.

produced is most likely assigned to CoO. A partial formation of Co(II) oxide sulfide species is not ruled out. When T_s=473 K, the Co2p bands appeared at 778.5 and 793.5 eV. Although the BE values for Co-metal and Co_9S_8 are very close each other,[17—19] the new bands are attributed to sulfided cobalt species on the basis of the observation of a considerable amount of sulfide sulfur at 162.8 eV[17—19] as shown in Fig. 7. Weak shoulder peaks due to cobalt sulfide are also detected for Co–S (573) sulfided at 373 K as indicated by the arrows in Fig. 6. When Co–O (573) was sulfided at 673 K, cobalt sulfide became predominant and no cobalt oxide was discernible in the catalyst surface. It is obvious that the thickness of the sulfide phase increases with increasing T_s.

When T_s=373 K and no H_2-treatment was applied, the S2p spectrum in Fig. 7 exhibited the formation of sulfate sulfur at 168.8 eV[24—26] in addition to sulfide sulfur at 162.6 eV. The proportion of sulfate species significantly decreased at 473 K and disappeared at 673 K.

When Co–S (573) sulfided at 373 K was treated with H_2 at 673 K, the CoO phase in Fig. 6(a) was greatly decreased in proportion and sulfided cobalt and/or metallic phase became predominant as presented in Fig. 6(d). With cobalt sulfides prepared at $T_s \geqslant 473$ K and H_2-treated at 673 K, the Co2p spectra resemble a typical one (e.g. Fig. 6(c)) reported for Co_9S_8[17—19] except for a difference in the S2p/Co2p$_{3/2}$ intensity ratio. During the H_2-treatment at 673 K, the sulfate species disappeared completely and only the sulfide sulfur was detected irrespective of T_s (373—673 K). The absence of sulfate sulfur on the H_2-treated catalysts indicates that the sulfate species are not formed by oxidation of sulfide sulfur during the XPS measurement procedures.

The S2p/Co2p$_{3/2}$ XPS intensity ratios for Co–S (573) catalysts sulfided at varying T_s are summarized in Table 4. The ratio decreased considerably as T_s decreased both before and after the H_2-treatment at 673 K. The intensity ratio was found to increase at low T_s ($\leqslant$473 K) upon the H_2-treatment. This indicates that in these cases a surface sulfur segregation occurs during the reduction of the Co(II) oxide phase, which has been produced during the sulfidation at the low temperatures (Fig. 6 (a,b)).

The specific activities per surface area of Co–S (573) for the butadiene hydrogenation and 1-butene isomerization are summarized in Table 4 and plotted in Fig. 8 against the S2p/Co2p$_{3/2}$ intensity ratio. The specific activities of Co–S (1473) and Co–S (1573) in Tables 2 and 3 are also presented in Fig. 8. Both series of results seem to be delineated to the S2p/Co2p$_{3/2}$

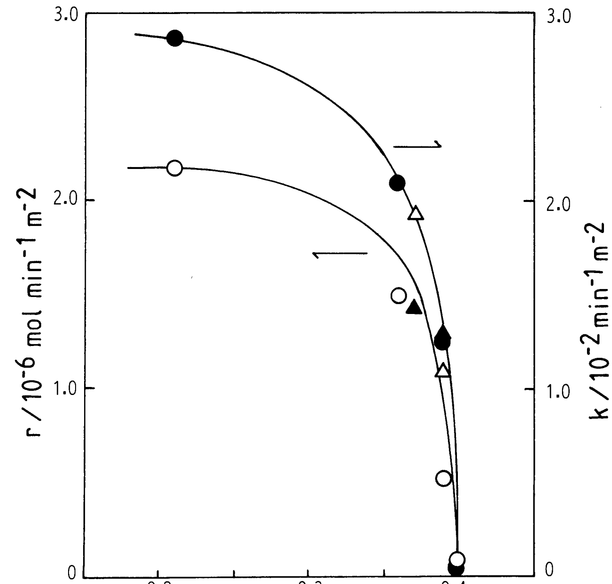

Fig. 8. Dependences of the specific activities of cobalt sulfide catalyst for the butadiene hydrogenation and 1-butene isomerization at 473 K upon the S2p/Co2p$_{3/2}$ XPS intensity ratio. ○; hydrogenation over Co–S (573) at varying T_s, △; hydrogenation over Co–S (1473—1573), ●; isomerization over Co–S (573) at varying T_s, and ▲; isomerization over Co–S (1473—1573).

intensity ratio, suggesting that the surface sulfur content controls the catalytic properties of the cobalt sulfide. It is worth of note that a small decrease in the surface sulfur content with respect to that of Co_9S_8 brings about a great increase in the specific activity, while a further considerable decrease in the sulfur content causes only a smaller increment in the activity.

Discussion

Of great significance in the present study is the finding that catalytic behaviors of cobalt sulfide for the hydrogenation of butadiene and the isomerization of 1-butene depend strongly on the calcination tempeprature of the precursor cobalt oxide. The catalytic and physicochemical properties of cobalt sulfide are compared in Table 5. The distinct differences in the *initial* selectivities in both reactions and NO adsorption properties may suggest that the active sites are significantly different between Co–S (573—1273) and Co–S (1473—1573). For simplicity, the active sites on Co–S (573—1273) and Co–S (1473—1573) for the present reactions are denoted here Co(L) and Co(H), respectively. The selectivity in the butadiene hydrogenation on Co(H) sites was completely different from that on cobalt metal (*trans*- vs. 1-butene and butane), indicating that Co(H) is not assigned to unmodified, pure Co-metal species dispersed on cobalt sulfide.

Tanaka and coworkers[27] have shown using single crystals of MoS_2 that the edge planes of MoS_2 are catalytically active for isomerization and hydrogen exchange reactions of olefins, while the basal plane of MoS_2 shows activity only for acid-mediated isomerization of olefin such as 2-methyl-1-butene. The edge planes of MoS_2 have also been shown to be NO-adsorption sites.[28] An angle resolved photoemission study on the edge plane of MoS_2 clearly demonstrated the presence of dangling bonds of surface molybdenum ions, that is, the formation of coordinatively unsaturated (cus) molybdenum atoms.[29] Accordingly, it is rational to assume that surface sulfur vacancies are responsible for the formations of NO-adsorption and catalytically active sites for the hydrogenation and isomerization over cobalt sulfide. On the basis of the correlations between the specific activity and surface sulfur content in Fig. 8, it is deduced that the surface sulfur content determines the catalytic properties of cobalt sulfide. The decrease in the surface sulfur content by several per cent with respect to that of Co_9S_8 may lead to a notable genesis of Co(H) sites (Figs. 5 and 8).

Nature of Co(L) Sites. In the case of Co(L) sites, sulfur vacancies are produced during the sulfidation of cobalt oxide rather than a surface sulfur removal during the H_2-treatment, since the subsequent H_2-treatment at 673 K did not significantly alter the catalytic activity of the resultant cobalt sulfide. TPR results followed by TPS up to 673 K clearly indicated that no H_2S evolution occurs at <700 K during H_2-treatment of sulfided cobalt.[14] Since XRD results showed exclusively the formation of crystalline Co_9S_8 on Co–S (573—1273), it is considered that surface sulfur-defect sites on Co_9S_8 are responsible for the formation of Co(L) sites.

The catalytic properties of Co(L) sites are considered to be described by the active site model proposed by Siegel.[30] The hydrogenation site is assumed to be an isolated, single cobalt atom site having three sulfur vacancies[27,29—32] for olefin adsorption and concurrent dissociative adsorption of H_2. The prominent production of 1-butene suggests the formation of a *s*-butenyl intermediate on Co(L) sites as proposed for the hydrogenation of butadiene over MoS_2.[27]

The *cis*/*trans*-2-butene ratio of the 1-butene isomerization over Co(L) sites (0.83) is very close to those on Ni-sulfide[12] and MoS_2,[27] where the formation of *s*-butyl[27] is well established as the reaction intermediate of 1-butene isomerization. It is likely that the isomerization of 1-butene on Co(L) sites proceeds also via *s*-butyl intermediate.

Nature of Co(H) Sites. The generation of Co(H) sites is correlated to a surface sulfur depletion with respect to the surface sulfur density of Co_9S_8. Co(H) sites formed on Co–S (1473—1573) are characterized by a preferential production of *trans*-2-butene in the hydrogenation of butadiene. Analogous selective *trans*-2-butene formations have been reported for butadiene hydrogenation over sulfided cobalt metal catalysts[13,16] and sulfided nickel catalysts.[16,33] Wells and

Table 5. Catalytic and Physicochemical Properties of Cobalt Sulfide Catalysts Sulfided at 673 K

	Co–S (573—1273)	Co–S (1473—1573)
Hydrogenation of butadiene (473 K)		
Specific activity/mol min^{-1} m^{-2}	0.077—0.084$\times10^{-6}$	1.2—2.0$\times10^{-6}$
Selectivity	1-Butene; ca. 70%, *cis*/*trans*; ca. 3	*trans*-2-Butene; 60—70%, *cis*/*trans*; 5—8
Isomerization of 1-butene (473 K)		
Specific activity k/min^{-1} m^{-2}	0.033—0.040$\times10^{-2}$	1.3—1.4$\times10^{-2}$
Selectivity	*cis*/*trans*; 0.83±0.01	*cis*/*trans*; 0.72±0.02
NO adsorption	No N_2 formation	N_2 production
S2p/Co2$p_{3/2}$XPS intensity ratio	0.40±0.01	0.38±0.01
Effect of H_2 treatment after sulfidation	Very weak	Very strong

coworkers[16)] described the catalytic behavior of sulfided cobalt metal as "type B" to distinguish from the hydrogenation characteristics of pure cobalt metal (type A). 1-Butene is produced on Co-metal as a major product with a concomitant total hydrogenation to butane, as observed in the present experiments. Comparing Co(H) and type B, it is concluded that they show essentially identical characteristics of butadiene hydrogenation, that is, a high *trans*-2-butene/*cis*-2-butene ratio (5—8). Accordingly, it is reasonable to propose that cobalt metal overlayers modified by sulfur are responsible for the formation of Co(H) sites.

It is well established[34)] that sulfided metal surfaces have well-defined surface structures, depending on the fractional coverage of sulfur. Since the specific activity for the hydrogenation seems to reach a maximum for Co–S (573) sulfided at 373 K and H_2-treated at 673 K (Fig. 8), it is likely that fully developed Co(H) sites form a well defined two-dimensional surface structure with a S/Co atomic ratio of ca. 0.5 (calculated from the S2p/Co2$p_{3/2}$ ratio assuming that the ratio=0.40 for Co_9S_8 as shown in Fig. 5). In the case of sulfided nickel metal catalysts, it has also been shown by using XPS[33)] that good "type B" behaviors are established at S/Ni=0.4—0.5. However, sulfidation of single crystal surface of cobalt metal and the catalytic properties of the resulting two-dimensional sulfide structure have not been well studied yet. Accordingly, definitive conclusions must await a further surface science study on S-Co systems.

The difference between type A and type B catalysts in the selectivity of butadiene hydrogenation has been proposed to result from an electronic effect of sulfur.[16,33)] Surface modifications by sulfur in type B catalysts bring about electron deficient cobalt metal atoms and facilitate a preferential formation of π-allyl intermediate, eventually leading to the production of *trans*-2-butene. However, it seems difficult to explain the difference in the catalytic behaviors between Co(H) and Co(L) simply in terms of an electronic effect of sulfur, since the surface sulfur concentration is not very different.

It is considered that Co(H) and Co(L) sites are different in structure. The dissociation of CO on cobalt metal is inhibited by the presence of sulfur.[34)] On the basis of the partial decomposition of adsorbed NO at room temperature (Table 1) on Co–S (1473—1573), it is deduced by analogy to the CO adsorption that Co(H) sites consist of the ensemble of cus-cobalt atoms in contrast to Co(L) sites consisting of a single Co-atom. The high density of NO adsorption sites on Co–S (1473—1573) (Table 1) is in conformity with the model. Assuming that the catalytically active sites are probed by NO adsorption, it is suggested that in contrast to *s*-butenyl intermediate on isolalted single Co-atom site, the adjacent electron deficient cobalt atoms in Co(H) sites enable butadiene hydrogenation to proceed effectively via a π-allyl intermediate utilizing a dissociatively adsorbed H_2 molecule on the neighbor site for a further hydrogen atom addition. This mechanism is expected to result in a predominant formation of *trans*-2-butene. In the case of homogeneous hydrogenation systems using $Co(CN)_5^{3-}$, a similar cooperation between two cobalt complexes is claimed.[35)] When CN/Co ratio is lower than 5.5, trans-2-butene is predominantly formed via reactions between π-allyl-$Co(CN)_4^{2-}$ intermediate and $HCo(CN)_5^{3-}$.

The slightly but definitely different *cis*/*trans*-2-butene ratios in the 1-butene isomerization between Co(L) and Co(H) sites apparently reflect the changes in the electronic state and/or configuration of the active sites. However, it is premature in the present study to estimate the controlling factors and reaction mechanism.

Slight differences in the T_c and T_s dependences of the activity between the hydrogenation and isomerization are ascribed to the difference in the configurations of the active sites required for these reactions. The hydrogenation is believed to require a higher cus-sites than the isomerization.[27,30,31)]

Sulfidation Mechanism of Cobalt Oxide. The sulfidation mechanism of cobalt oxide has not been well established. With the sulfidation of a CoO (100) surface at room temperature-873 K and 1.3×10^{-4} Pa H_2S, Dumas et al.[36)] have suggested that an epitaxial formation of cobalt metal takes place first, followed by H_2S adsorption on the metal surface. On the other hand, Arnoldy et al.[37)] suggested using TPS techniques ($H_2S/H_2/Ar$; 3.4/28.7/67.9, 1.1 bar) that the sulfidation of cobalt oxide proceeds via an O–S anion exchange. In our previous study on sulfidation of CoO/SiO_2 prepared from cobalt acetate, we have proposed a similar sulfidation process via O–S anion exchange.[38)] Under the present sulfidation conditions, the O–S anion exchange seems more appropriate than the reduction-sulfidation mechanism to account for the SO_4^{2-} formation during the sulfidation of Co_3O_4 at 373—473 K (Fig. 7). The sulfidation mechanism is proposed as follows.

$$3Co_3O_4 + 8H_2S \longrightarrow Co_9S_8 + 4(O) + 8H_2O \tag{1}$$

$$4(O) + H_2S \longrightarrow SO_3 + H_2O \tag{2}$$

$$SO_3 + O^{2-}_{\text{lattice}} \longrightarrow SO_4^{2-} \tag{3}$$

The first step denotes an anion exchange process, where excess oxygen atoms (O) are evolved due to the reduction of Co(III) to Co(II). Part of oxygen atoms are instantaneously consumed in reaction (2), eventually producing SO_4^{2-} by reaction (3), although most of the oxygen atoms may be reduced by H_2. The removal of oxygen atoms by H_2 predominates over reaction (2) at $T_s \geqslant 473$ K. The TPS results on unsupported cobalt oxide[14)] were found to support the above reaction mechanism, that is, at a low sulfiding temperature (350—450 K, β=2 K min^{-1}) the amount of consumption of H_2S

considerably exceeded that of H_2. When H_2-reduction of Co_3O_4 to Co metal precedes sulfidation, no formation of SO_4^{2-} is expected, which is contradiction to the findings in Fig. 7.

$$3Co_3O_4 + 3H_2 \longrightarrow 9CoO + 3H_2O \quad (4)$$

$$9CoO + 9H_2 \longrightarrow 9Co + 9H_2O \quad (5)$$

$$9Co + 8H_2S \longrightarrow Co_9S_8 + 8H_2 \quad (6)$$

A proposed mechanism of sulfidation of Co_3O_4 is schematically presented in Fig. 9. Sulfidation of cobalt oxide is considered to proceed from the outer surface of the oxide particle forming a passivating sulfide layer. When the particle size of Co_3O_4 is small enough, bulk like Co_9S_8 is produced as observed for Co–S (573—1173). On the other hand, when the radius of Co_3O_4 particle is much larger than the thickness of the cobalt sulfide passivating film, a selective H_2-diffusion into the bulk through the film during the contact with H_2S/H_2 produces reduced cobalt oxide (XPS results in Fig. 6 and XRD[14]) and, in consequence, metallic cobalt at a higher temperature (reactions 4 and 5). This process is accompanied by sulfur diffusion from the surface layer into bulk and a subsequent H_2-formation in the resultant sulfur deficient surface layer (reaction 7).

$$Co_9S_{8-x} + xH_2S \longrightarrow Co_9S_8 + xH_2 \quad (7)$$

It was shown[14] that with Co–O (1473—1573) an intense H_2-production peak appeared in TPS profiles with a concomitant H_2S consumption during sulfidation in H_2S/H_2, just after a strong H_2-consumption (Co-metal formation evidenced by XRD). The presence of a residual cobalt metal phase was actually confirmed here by XRD with Co–S (1473) and (1573) catalysts. In contrast, no H_2-evolution process occurred with Co–O (573)[14] having a smaller particle size of Co_3O_4 (Fig. 1)

Mechanism of Co(H) Site Formation. The generation of Co(H) sites is restricted to Co–S (1473—1573) when sulfided at 673 K. In addition, the H_2-treatment is essential to the Co(H) site formation. Good Co(H) catalysts are also prepared when Co–O (573) is sulfided at 373—473 K and subsequently reduced at 673 K. After sulfidation at the low temperature, CoO and, probably, Co(II) oxide sulfide are formed in surface as illustrated in Fig. 6. In separate experiments,[14] it has been shown by XRD that only with good Co(H) catalysts CoO is produced also in the bulk during sulfidation (*before* the H_2-treatment at 673 K). Co(L) sites are formed prior to the H_2-treatment at 673 K as illustrated in Figs. 2 and 3. The H_2-treatment reduces CoO to cobalt metal as shown by XPS in Fig. 6 and XRD. Accordingly, the genesis of Co(H) sites on Co–S (1473—1573) are considered to correlate to the formation of metallic cobalt within the cobalt sulfide particles. This is in accord with the preparation of "type B" catalyst from a H_2-reduction of a mixture of CoS and CoO.[16]

A mechanism of Co(H) site formation is schematically presented in Fig. 9. The sulfur diffusion from surface to a bulk metallic cobalt phase results in the productions both of a sulfur deficient metallic surface layer, that is, Co(H) sites and of non-stoichiometric and, accordingly, non-crystalline bulk phase ($CoS_{0.89-x}$ in Fig. 9). No H_2S formation was detected at 673 K by TPS during the H_2-treatment of Co–O (573—1573) which had been sulfided at 673 K but not H_2-treated,[14] substantiating that the removal of surface sulfur is a consequence of sulfur diffusion into the bulk rather than H_2S formation upon the H_2-treatment.

The XPS results in Fig. 6 indicate that the thickness of a sulfided layer is controlled by the sulfidation temperature. When T_s is low (373—473 K) and the sulfided layer is thin, Co(H) sites can be generated even for small particles of Co_3O_4 as demonstrated for Co–S (573). In these cases, where surface sulfur concentrations are relatively low, the surface segregation of sulfur

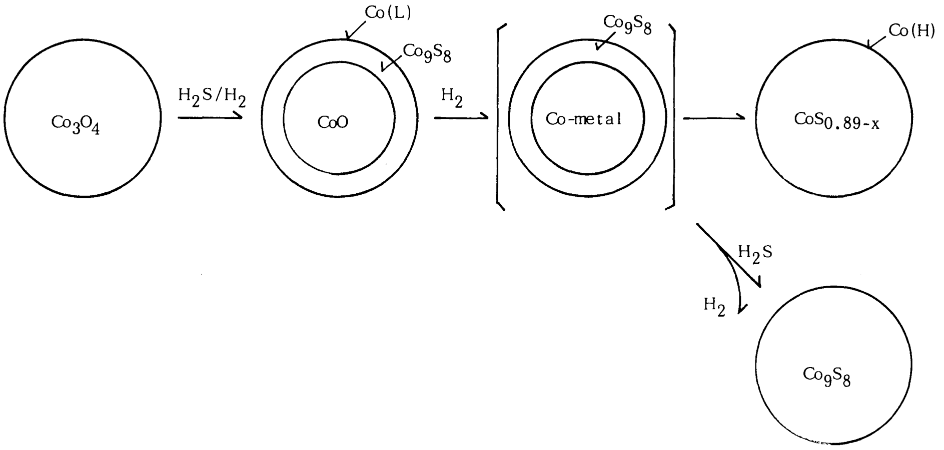

Fig. 9. A plausible model for the generation of Co(L) and Co(H) sites on sulfided cobalt catalysts.

takes place, conversely, constructing a certain, stable surface Co–S phase as discussed above.

Summary

It has been demonstrated that the catalytic properties of cobalt sulfide catalysts prepared by sulfidation of cobalt oxide depend on the calcination temperature of the oxide. This is explained in terms of the change in the surface sulfur content of the sulfide catalyst, which results in the formation of two kinds of active sites with different structures on cobalt sulfide catalysts. The sulfidation mechanism of cobalt oxide, generation of catalytically active sites, and active site models are proposed.

Recently, a sulfidation method was found to affect strongly the amount of Co(H) sites at 673 K. In addition, the sulfidation mechanism of Co_3O_4 has been revealed in more detail using TPS techniques combined with XRD. These results has be presented elsewhere.[14]

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