Hydrogenation by CoMo/Al₂O₃ Catalyst (Part 1)

Effect of Catalyst Pretreatment on Hydrogenation of Monoaromatic Hydrocarbons

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Effects of reduction and sulfidation pretreatments on the hydrogenation activity of Co-Mo/alumina catalysts were studied. Reactions adopted for the activity tests were hydrogenation of benzene, toluene, and *o*-xylene, carried out over pretreated catalysts at 400°C under flowing H₂ or H₂S/H₂ at 5 MPa. The hydrogenation was followed by skeletal isomerization, irrespective of the substrate and reaction conditions. The activity sequence among the variously pretreated catalysts in descending order was: sulfided > presulfided/reduced > prereduced/sulfided > fresh > reduced. The reaction of *o*-xylene was most sensitive to pretreatment, and attained its maximum conversion when the reaction was carried out over the sulfided catalyst and under flowing H₂S/H₂. Catalysts sulfided at higher temperatures exhibited higher catalytic activities. The catalytic activity was determined principally by the amount of sulfur incorporated in the catalyst.

1. Introduction

A commercial Co-Mo/alumina catalyst, supplied in the oxide form, is commonly sulfided prior to use in hydrotreatment of heavy stocks. Efforts have been made, therefore, to unveil surface modifications caused by sulfidation.¹⁾ In their FT-IR study of adsorbed nitric oxide on Co-Mo/alumina catalysts, the authors have shown that relative abundance of Co and Mo exposed on the catalyst surface changed when a fresh catalyst was converted into a sulfide form.²⁾ Such structural change should affect both the activity and selectivity of the catalyst. To date, however, Co-Mo/alumina catalysts modified by various pretreatments have been tested only for hydrodesulfurization of a few selected model compounds.³⁾

The present article deals with hydrogenation of benzene, toluene, and *o*-xylene over variously pretreated Co-Mo/alumina catalysts. Since hydrogenation of these monoaromatic hydrocarbons

has been known to be difficult,⁴⁾ the reaction may serve as an acid test for catalyst performance. It is also expected that, through controlled modifications by well-established means of pretreatment, the role played in the hydrogenation by each metallic component may be envisaged.

2. Experimental

2.1 Catalyst

The base material used was a single charge of commercial Co-Mo/alumina catalyst KF 742, supplied by Nippon Ketjen Co., in the form of distorted cylinders of sizes (1.16–1.36) × 2.8 mm. Chemical composition and physical properties of the catalyst are listed in **Table 1**. The catalyst crushed to 32/42 mesh particles was used in all the runs made.

2.2 Apparatus and Procedure

A conventional trickle bed flow reactor was used. The reactor was made of a 7.4 mm i.d. stainless steel tube and it was packed with about 3 g of catalyst. Unless otherwise stated, pretreatment of the catalyst was carried out under flowing H₂ at 1

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MPa or H₂S(5%)/H₂(95%) with the rate of 400 cm³ · min⁻¹ and treated continuously at three temperature stages: at ambient temperature for 1 hr, at increasing temperatures from the ambient temperature to 400°C in 40 min, and finally at 400°C for 2 hr. In this paper, pretreatments under flowing H₂ and under flowing H₂S(5%)/H₂(95%) are simply expressed as “reduction” and “sulfidation”, respectively. Reactions of benzene, toluene, and *o*-xylene were subsequently carried out in situ under the following conditions: 400°C, 5 MPa, LHSV 4.5 hr⁻¹, and H₂/feed ratio 1,000 vol/vol. H₂ or H₂S(5%)/H₂(95%) was introduced into the system at such a rate that the overall rate was 300 cm³ · min⁻¹. The substrate compound was metered into the system at a rate of 0.3 cm³ · min⁻¹ from a measuring buret using a high pressure pump. Conversion of

the substrate was limited far below equilibrium in order to avoid possible interference caused by reverse reaction. Reaction products were separated from the effluent by using a train of traps chilled with liquid N₂.

2.3 Analysis

Condensable products were collected for 10 min, before the time on stream had reached the prescribed points. The product collected was analyzed as such using a gas chromatograph equipped with a 50 m OV-101 glass capillary column.

3. Results and Discussion

3.1 Reactions under Flowing H₂

3.1.1 Product Pattern

Benzene, toluene, and *o*-xylene were hydrotreated under the prescribed conditions(2.2) and over the sulfided catalyst, untill the time on stream had reached 2 hr. Compositions of the products are summarized in Table 2. In agreement with those reported hitherto,⁴⁾ cyclohexane and methylcyclopentane were the exclusive products from benzene. The product pattern indicated that the reaction comprised ring saturation and subsequent skeletal isomerization. A similar conclusion is reached for the reactions of toluene and *o*-xylene.

3.1.2 Effect of Pretreatment

Conversions observed with the reactions of benzene, toluene, and *o*-xylene under flowing H₂ and

Table 1 Chemical Composition and Physical Properties of Co-Mo/Alumina Catalyst

Chemical composition (wt%):	
MoO ₃	14.9
CoO	4.42
Na ₂ O	0.08
Fe ₂ O ₃	0.03
SiO ₂	0.95
Al ₂ O ₃	79.1
SO ₄	0.53
Physical properties:	
surface area (m ² · g ⁻¹)	268
pore volume (cm ³ · g ⁻¹)	0.52
bulk density (g · cm ⁻³)	0.73

Table 2 Hydrogenation and Isomerization Products of the Reactions at 400°C under Flowing H₂ over Sulfided Co-Mo/Alumina^{a)}

Substrate	Product (mol%)	
Benzene (Conversion 11.8%) (Isomerization 0.125 ^{b)})	Cyclohexane	87.0
	Methylcyclopentane	12.0
	Others ^{c)}	1.0
Toluene (Conversion 11.0%) (Isomerization 0.249 ^{b)})	Methylcyclohexane	75.0
	Ethylcyclopentane	15.0
	Dimethylcyclopentane	7.7
	Cyclopentane	0.9
	Others ^{d)}	1.4
<i>o</i> -Xylene (Conversion 12.3%) (Isomerization 0.612 ^{b)})	<i>trans</i> -1, 2-Dimethylcyclohexane	15.3
	<i>cis</i> -1, 2-Dimethylcyclohexane	10.2
	1, 3- + 1, 4-Dimethylcyclohexanes	11.6
	1, 1-Dimethylcyclohexane	4.7
	1, 1, 2-Trimethylcyclopentane	0.7
	1, 1, 3-Trimethylcyclopentane	1.2
	1, 2, 3-Trimethylcyclopentane	1.3
	1, 2, 4-Trimethylcyclopentane	2.5
	<i>trans</i> -1-Methyl-2-ethylcyclopentane	2.3
	<i>cis</i> -1-Methyl-2-ethylcyclopentane	2.5
	1-Methyl-3-ethylcyclopentanes	7.2
	Isopropylcyclopentane	4.8
	Others ^{e)}	35.7

a) Time on stream 2 hr.
b) Isomerization = (Conversion to Isomerization)/(Total Conversion).
c) Includes toluene (0.3%).
d) Includes benzene (0.4%), and methylcyclopentane (0.2).
e) Includes toluene (7.6%), methylcyclohexane (0.4%), ethylcyclohexane (0.9%), *m*- and *p*-xylenes (9.8%), and trimethylbenzenes (8.5%).

over the presulfided catalyst are compared with those observed over the prereduced catalyst in **Table 3**. With all the three substrates tested, the presulfided catalyst was more active than the pre-reduced catalyst. It was also noted that the reaction of *o*-xylene was more susceptible to the catalyst's pretreatment. The effect of pretreatment was, therefore, examined in more detail with this reaction. The results are shown in **Fig. 1**. The sulfided catalyst exhibited the highest activity at the beginning of run, but the activity faded away rather quickly; and the conversion dropped, more or less, to the same levels as those attained by variously pretreated catalysts. The initial activity sequence among the variously pretreated catalysts in descending order was: sulfided > prereduced/sulfided > fresh > reduced.

It is noteworthy that, in this study, the promoting effect of sulfidation was suppressed significantly once the catalyst was reduced. It is reported that, by the same sulfidation treatment considerably higher sulfur content resulted with a fresh catalyst than with a prereduced catalyst.⁵⁾ In their FT-IR study on nitric oxide adsorbed on the Co-

Mo/alumina, the authors found that reduction prior to sulfidation decreased specifically the active-Co-site population.²⁾ It is also reported that hydrogenation activity can be ascribed to Co of the Co-Mo/alumina catalyst.⁶⁾ Therefore, deterioration of the catalyst by reduction may be due to the decrease in the active-Co-site population.

3.1.3 Effect of Sulfidation Time

Conversions of *o*-xylene hydrogenation observed after 2 hr on stream under flowing H₂ and over the catalyst sulfided for varying lengths of time are summarized in **Table 4**. Sulfidation beyond 2 hr showed no further improvement in the catalyst activity.

To convert 3.00 g of fresh CoO-MoO₃/alumina into a completely sulfided form, Co₉S₈-MoS₂/alumina, 174 ml/(NTP) of H₂S is required. The theoretical amount required corresponds to a H₂S(5%)/H₂(95%) gaseous mixture flowing for about 9 min in the pretreatment. The present result implies that the fresh catalyst can be sufficient-

Table 3 Conversions at 400°C under Flowing H₂ and over Sulfided and over Reduced Co-Mo/Alumina^{a)}

Substrate	Conversion (mol%)	
	Reduced	Sulfided
Benzene	5.4	11.8
Toluene	5.7	11.0
<i>o</i> -Xylene	4.6	12.3

^{a)} Time on stream 2 hr.

Table 4 Conversions at 400°C under Flowing H₂ over Variously Pretreated Co-Mo/Alumina^{a)}

Catalyst pretreatment	Conversion (mol%)
Sulfided (2 hr)	12.3
Sulfided (14 hr)	13.5
Presulfided (2 hr)/reduced (10 hr)	8.3
Presulfided (2 hr)/reduced (40 hr)	7.5
Presulfided (2 hr)/reduced (10 hr)/sulfided (2 hr)	11.0
Prereduced (10 hr)/sulfided (2 hr)	6.6
Prereduced (10 hr)/sulfided (10 hr)	7.8

^{a)} Time on stream 2 hr.

Fig. 1 Hydrogenation of *o*-Xylene at 400°C under Flowing H₂

ly sulfided within at least 2 hr.

3.1.4 Effect of Sulfidation Temperature

Conversions of *o*-xylene hydrogenation under flowing H_2 and over the catalyst sulfided at three different temperatures are compared in **Fig. 2**. Under such experimental conditions, the catalyst sulfided at higher temperatures gave higher activity. Deterioration in the activity of all the catalysts concerned was associated with the length of time on stream.

All the results described above suggest that surface sulfide be closely related to the catalyst activity. The surface sulfide is formed by catalyst presulfidation and it is lost by catalyst reduction and by reaction under flowing H_2 .

3.1.5 Effect of Sulfidation Sequence

Effects of reduction prior to and subsequent to sulfidation was also examined. The results are included in **Table 4**. Reduction of the presulfided catalyst resulted in a considerable decline in activity which was restored to its original value when the catalyst was resulfided. Reduction of the fresh catalyst prior to its sulfidation, on the other hand, resulted in a sulfided catalyst with even poorer activity. The result suggests that, to attain the maximum activity, the Co-Mo/alumina catalyst is to be kept away from any strongly reductive environment.

3.1.6 Isomerization

The reaction of *o*-xylene under the present conditions yielded considerable amounts of 1,3-dimethylcyclohexane, 1,4-dimethylcyclohexane, methylethylcyclopentane, and trimethylcyclopentane in addition to 1,2-dimethylcyclohexane, a

ring-hydrogenation product. As mentioned earlier, the isomerization was conspicuous with *o*-xylene reaction as compared with benzene and toluene reactions (**Table 2**). Conversions pertaining to the isomerization over variously treated catalysts are summarized in **Table 5**. Sulfidation clearly enhanced the catalyst activity with respect to the skeletal isomerization.

This enhancement suggests the formation of new acid sites by catalyst sulfidation. It is reported that sulfidation creates strong acid sites on the surface of alumina support.⁷⁾ It is reported, on the other hand, that a mixture comprising sulfided CoO and MoO₃ without alumina support exhibited some skeletal isomerization activity.⁸⁾ Therefore, the active sites responsible for isomerization is still controversial. In light of the recently developed knowledge about the functions of the valence-shell expanded sulfur atom,⁹⁾ the authors may add another interpretation to the above. The sulfur atoms implanted on the catalyst surface facilitate the diffusion of partially hydrogenated intermediate of the sulfided metal and the acidity-reinforced

Table 5 Conversion and Isomerization of *o*-Xylene at 400°C under Flowing H_2 over Variously Pretreated Co-Mo/Alumina^{a)}

Catalyst pretreatment	Conversion (mol%)	Isomerization ^{b)}
Fresh	7.7	0.158
Reduced (10 hr)	5.0	0.267
Prereduced (10 hr)/ sulfided (10 hr)	7.0	0.420
Sulfided (2 hr)	11.0	0.592

^{a)} Time on stream 3 hr.

^{b)} Isomerization = (Conversion to Isomerization)/(Total Conversion).

Fig. 2 Hydrogenation of *o*-Xylene at 400°C under Flowing H_2 over Sulfided Co-Mo/Alumina

Fig. 3 Hydrogenation of *o*-Xylene at 400°C under Flowing H₂S(5%)/H₂(95%)

support, while hydrogenation and isomerization take place on the sulfided metal and on the reinforced support, respectively.

3.2 Reactions under Flowing H₂S/H₂

Figure 3 shows the effect of catalyst pretreatment on the conversion of *o*-xylene under a flowing H₂S/H₂ gaseous mixture. A comparison of this figure and Fig. 1 reveals that gas phase addition of H₂S considerably enhanced the activity of the fresh and reduced catalysts. As the time on stream increased, the initial activity of the fresh catalyst increased gradually and approached to the level attained by the sulfided catalyst. A similar trend was observed between the reduced and prereduced/sulfided catalysts.

It is quite likely, therefore, that catalyst activity is largely determined by the initial pretreatment whether the catalyst in question was presulfided or prereduced. The initial prereduction may cause an irreversible change in the catalyst surface in such a way that even the subsequent prolonged sulfidation fails to reproduce its intrinsic activity. Acceleration by gas phase H₂S observed with the fresh and reduced catalysts may be due to the sulfidation of the catalysts during the reaction, and

therefore it should be considered as a secondary effect.

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要 旨

CoMo/Al₂O₃ 触媒による水素化反応 (第 1 報) 単環芳香族の水素化反応
に及ぼす触媒前処理の影響

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重質油の水素化処理には, Co-Mo/アルミナ触媒が用いられているが, 高活性を得るためには適切な前処理が必要とされている。本研究では比較的水素化されにくい単環芳香族化合物であるベンゼン, トルエンおよび *o*-キシレンの水素化反応を利用して, Co-Mo/アルミナ触媒の水素化活性に及ぼす還元, 硫化の前処理の影響を検討し, さらに前処理方法の違いによる活性の違いを触媒表面と関連させて考察した。

触媒は日本ケッチェン社製の Co-Mo/アルミナ (KF-742) を用いた。その性状を **Table 1** に示した。このものを高圧流通式反応装置により還元あるいは硫化処理を施した後反応に供した。還元あるいは硫化処理は 1 MPa, 400 cm³・min⁻¹ の水素あるいは硫化水素 (5%)/水素 (95%) の流通下で室温 (1 時間) ~400°C の条件で行った。反応条件は 400°C, 5 MPa, LHSV=4.5 hr⁻¹, H₂/Feed = 1,000 vol/vol とした。また, 硫化水素 (5%)/水素 (95%) 気流中での反応も行った。反応生成物の分析にはガスクロマトグラフ法を用いた。

硫化した触媒上, 水素気流中でベンゼン, トルエン, *o*-キシレンの水素化反応を行った。得られた生成物の組成を **Table 2** に示す。反応は, いずれの化合物においても基質→水素化物→骨格異性化物のように逐次的に進行していると推定される。**Table 3** にこれら単環芳香族化合物の反応の転化率を示す。還元した触媒を用いた場合では, これらの化合物の転化率はほぼ同じで約 5% であるのに対して, 硫化した触媒では転化率がかなり向上した。特に *o*-キシレンでは, 還元した触媒に比べて約 3 倍の値となり, *o*-キシレンの水素化は触媒の前処理に敏感であるといえる。そこで *o*-キシレンの水素化を利用して触媒活性と前処理との関係を詳細に検討した。**Fig. 1** に種々の前処理を施した触媒上での *o*-キシレンの反応の結果を示す。触媒活性は前処理に大きく依存し, 硫化>還元後硫化>未処理

>還元の順であることがわかった。最初に還元してしまうと, それに引き続いて硫化を施してもその効果は小さい。さらに硫化された触媒の活性が通油時間とともに低下していくのが認められた。

最近著者らは本触媒上への一酸化窒素吸着を FT-IR 法で観測した結果, 硫化だけを施した触媒に比較して還元後硫化を施した触媒では Co 側への一酸化窒素の吸着量が著しく少ないことを報告している。したがって, 最初に還元処理を施すことによる硫化処理効果の低下は, 活性な Co サイトの減少に由来すると考えられる。水素化脱硫に関する各種のモデル反応から, 水素化反応は Co-Mo/アルミナ触媒の Co 側で起こると推測されているが, 本実験結果はこの推測とも符合する。

Table 4 に水素化活性に及ぼす硫化, 還元処理時間の影響を示した。硫化処理を 2 時間以上施しても活性に影響しなかったことから, 本触媒は 2 時間の硫化処理で十分な硫化度に到達しているといえる。硫化後の還元時間を長くすると活性が低下するのが認められた。また, 最初に還元してしまうと, その後硫化処理を長時間施しても活性は回復しなかった。**Fig. 2** は硫化温度の異なる触媒上での反応の結果を示したもので, 硫化温度の高いほど水素化活性が高くなることが認められた。

前処理の異なる触媒上での反応生成物に占める骨格異性化物の割合を **Table 5** に示した。硫化処理は, 水素化に引き続いて起こる骨格異性化をも促進することがわかる。硫化処理によって新たな酸点が形成されたか, あるいは反応中間体の担体酸点への移動が硫化によって容易になったとも推測される。

硫化水素/水素気流中における *o*-キシレンの反応の結果を **Fig. 3** に示す。**Fig. 1** の水素気流中での結果に比して触媒活性は明らかに向上しているが, 活性は主として前処理によって決定されていることがわかる。

Keywords

Aromatic compound, Cobalt molybdenum alumina, Hydrogenation, Isomerization, Reduction, Sulfiding