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NOTES

The Mechanistic Relation between Isomerization and Hydrogenolysis of Alkane on Molybdena-Interacted Supported Pt Catalysts

Anchored Pt–Mo–SiO_2 catalysts prepared with Mo(π-allyl)$_4$ and Pt(π-allyl)$_2$ compounds are examined by comparing the activity and selectivity for conversion of alkanes with that of monometallic Pt catalysts in a pulse reactor under hydrogen pressure of 1.5 atm and in the temperature range of 300–340°C. The rule of Pt/Mo ratio dependent product distribution for Pt–Mo–SiO_2 catalysts is interpreted by the preferential formation of 1,3 dehydrogenated species on molybdena-interacted Pt sites leading to a high contribution of the reaction pathway via the bond-shift mechanism. Additional evidence further demonstrating the mutual coupling between bond cleavage and C-skeleton rearrangement on supported platinum catalysts cited in a previous work is described.

INTRODUCTION

It has been well established by Anderson (*1*), Gault (*2*), and others (*3*) that a category of alkane reactions including isomerization, hydrogenolysis, cyclization, and aromatization proceeds via the formation of 1,3 and 1,5 doubly or multiply dehydrogenated species as the intermediates of elementary reactions on Pt catalysts. Systematic and comprehensive studies on the relative contribution of the bond-shift mechanism via 1,3 intermediates and the cyclic mechanism via 1,5 intermediates for alkane isomerization was accomplished and summarized by Gault and his co-workers on the basis of mechanistic examinations using labeled compounds. For instance, it has been substantiated that for supported Pt catalysts of small metal particle size (less than 25 Å), the main reaction pathway for isomerization is through the 1,5 cyclic mechanism, while the 1,3 bond-shift mechanism becomes significant and predominant in the total isomerization on low-dispersion catalysts with Pt particles greater and greater in size.

The mechanistic investigation is of course of great importance to our knowledge of the catalytic reforming process in detail. However, bimetallic catalysts are almost invariantly used in industrial practice. Increasing attention is therefore currently focalized on the characterization of surface behaviors of supported bimetallic catalysts such as Pt–Ir, Pt–Re, Pt–Sn, etc., by means of various physical methods (*4–6*). Recent advances in this respect provide us with a better understanding of the electronic and geometric factors and the relevant metal–metal and metal–support interactions. Further progress along this line will certainly continue to be attractive and encouraging for the development of the "state of the art" catalysis science. At the same time, it is noteworthy to point out that much less effort has been applied recently to the study of the reaction mechanism on bimetallic catalysts, although the reaction of individual isomeric hydrocarbons can be used as a molecular probe for the characterization of bimetallic catalysts as well. For this reason, the product distributions of nC_5, nC_6, and methylcyclopentane conversion over bimetallic Pt–Mo–SiO_2 catalysts prepared with Pt- and Mo-allyl compounds are studied and a mechanistic comparison is made between bimetallic and monometallic Pt catalysts to elucidate if and how the reaction pathways for alkane conversion are affected by the Mo–Pt interaction.

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EXPERIMENTAL

Catalyst

Pt–Al$_2$O$_3$. γ-Al$_2$O$_3$ (290 m^2/g) precalcined in air at 550°C for 4 hr was impregnated with the required amount of aqueous solution of H$_2$PtCl$_6$. The resulting material after standing for 48 hr was filtered, washed, then dried and calcined for 6 hr each at 120° and 500°C, respectively.

Pt–SiO$_2$. SiO$_2$ (390 m^2/g) was immersed in a solution of Pt(π-allyl)$_2$ in pentane for 0.5–1 hr at ambient temperature under moisture (below 10 ppm) and oxygen (below 10 ppm) free nitrogen atmosphere. The SiO$_2$ was pre-evacuated at 500°C for 4 hr. Pt-allyl solution was prepared in this laboratory [see Ref. (*7*)]. The mixture was stirred and the silica became brown and the solution was colorless in 0.5–1 hr. After decanting the overlayer and washing with *n*-pentane several times, the sample was evacuated to remove the occluded solvent. It was finally treated with hydrogen at 200°C for 1 hr and then kept in argon for use.

Pt–Mo–SiO$_2$. A freshly prepared green solution of Mo(π-allyl)$_4$ (*8*) in pentane was used to impregnate the pre-evacuated SiO$_2$. The same procedure mentioned above was repeated to obtain a dried SiO$_2$-supported Mo-allyl complex. The complex was heated in hydrogen at 600°C for 2 hr, cooled down to 60°C in argon, evacuated for 1 hr, and impregnated with Pt(π-allyl)$_2$ solution with stirring (at r.t.). The mixture was again decanted and washed several times and evacuated to dryness. The dried sample was heated in hydrogen at 200°C, cooled in an Ar stream to ambient temperature, and sealed in argon before use. After heating in hydrogen, the allyl complexes converted to Pt–Mo^{+2}–(O–Si $\equiv$)$_2$ and the Mo^{+2} was oxidized in air to Mo^{+4} (*9*) easily and/or partly during transferring.

The H$_2$ uptake measured by the flow method (*10*) is shown in Table 1 for a few catalyst samples. It is unexpected that the Pt–SiO$_2$ sample (E) is of high dispersion, while the calculated dispersion for Pt–Mo–SiO$_2$ (PM-1) is quite low. Since both samples are prepared by the anchoring method, such surprising differences could be interpreted as the result from the interaction effect between Pt–Mo rather than any appreciable particle aggregation of metal elements which would be caused by thermal factors involved in catalyst preparation. In fact, the "low-"dispersion Pt–Mo–SiO$_2$ sample is able to uptake more hydrogen at some higher temperatures. This implies that hydrogen chemisorption is very complicated and that the H$_2$ uptake at room temperature is not adequate for determining the population of individual Pt sites on Pt–Mo–SiO$_2$ catalysts. In order to examine the Pt–Mo interaction problem in more detail, the surface properties of anchored Pt–Mo–SiO$_2$ catalysts have been studied and compared with conventional supported Pt catalysts. The results achieved in catalyst characterization by TPR, IR, ESR, and other measurements are published elsewhere (*11*).

Reaction. A pulse reactor (i.d. 3 mm) with 50 mg of powder catalyst was used, and each catalyst was reduced with hydrogen (30 ml/min) at 600°C for 2 hr before test

TABLE 1

Catalyst Preparation

Composition	Method	H/Pt	D_{Pt} calc. (Å)
3% Pt–Al$_2$O$_3$(B)	Impregnation	0.75	12
1.5% Pt–SiO$_2$(E)	Anchoring	1.0	10
3% Pt 1.1% Mo–SiO$_2$ (PM-1)	Anchoring	0.5	18

runs. The reaction was carried out in a hydrogen stream (1.5–2 atm) of 180 ml/min flow rate. The experimental details were given in a previous work (*12*). Analytic reagents were used. The total conversion and product distributions for hydrogenolysis and isomerization are calculated in mol percent (*13*).

RESULT

The proportions of hydrogenolysis, isomerization, and cyclization in total conversion of nC_6 and nC_5 were plotted vs the Pt/Pt + Mo atomic ratio of Pt–Mo–SiO_2 catalysts as shown in Figs. 1 and 2. Table 2 shows the results of hydrogenolysis of MCP on Pt–Mo–SiO_2 including the monometallic Pt–SiO_2.

As pointed out earlier (*12*), the anchored Mo–SiO_2 was found to be inactive for alkanes at the reaction condition of the test run; therefore, the Pt–Mo–SiO_2 preparations could be presumably considered as some modifications of the Pt catalyst with their activity solely due to the "Mo-modified" Pt sites. It was also for this reason that catalysts of changed instead of constant Mo content were prepared with the convenience that the Pt/Mo ratio could be varied with neither too large nor too small a content in the final Pt–Mo–SiO_2 preparations.

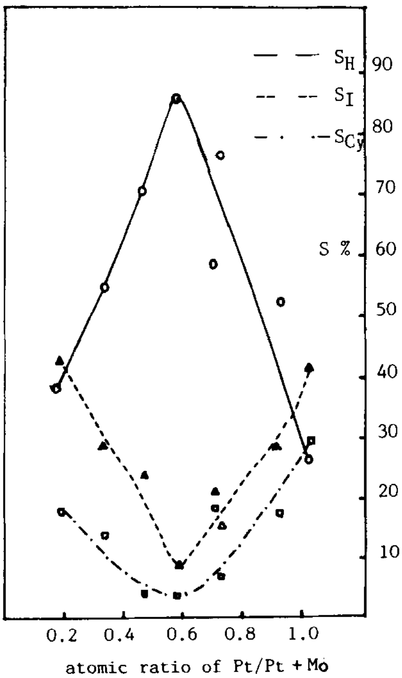


FIG. 1. Reactions of C_6 on the Pt–Mo–SiO_2 proportion of hydrogenolysis (S_H), isomerization (S_I), and cyclization (S_{Cy}) in total conversion.

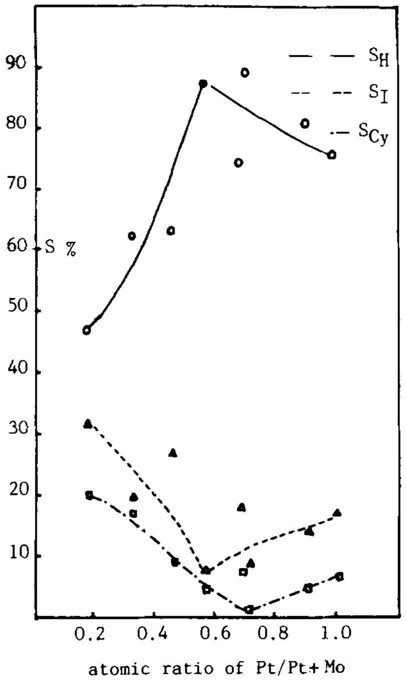


FIG. 2. Reactions of C_5 on the Pt–Mo–SiO_2 proportion of hydrogenolysis (S_H), isomerization(S_I), and cyclization (S_{Cy}) in total conversion.

DISCUSSION

(1) As shown in Fig. 1, the hydrogenolysis in total conversion of *n*-hexane increases to a maximum as the Pt/Pt + Mo ratio is increased up to 0.5–0.6, then decreases with the Pt/Pt + Mo ratio from 0.6 to 1.0. At the same time, the isomerization and cyclization are changed in a reverse direction. For *n*-pentane, however, the changes for each reaction within the Pt/Pt + Mo ratio range of 0.6–1.0 become much less remarkable than for *n*-hexane (Fig. 2). Since *n*-pentane will not convert to isopentane through a cylic mechanism, the difference between Figs. 1 and 2 is an indication

TABLE 2

Hydrogenolysis of MCP on Pt–Mo–SiO$_2$ Catalysts

Catalyst	Contents		Pt/Pt + Mo	Conv.[a] mol%	3-MP/nC$_6$	3-MP/2-MP
	Pt wt%	Mo				
PM-3	0.41	0.40	0.33	3.05	0.22	0.42
PM-5	0.79	0.45	0.46	2.54	0.23	0.53
MP-1[b]	2.82	1.31	0.51	10.71	0.44	0.43
PM-1	2.96	1.08	0.57	5.69	0.50	0.36
PM-7	2.53	0.55	0.69	4.87	0.50	0.33
PM-6	2.64	0.53	0.71	9.19	0.50	0.47
PM-4	4.28	0.22	0.91	12.07	0.44	0.50
PT-1	1.50	—	1—	23.42	0.50	0.51

[a] Reaction temperature = 340°C.

[b] Impregnating with Pt allyl before the Mo allyl.

of the steady trend of the increasing contribution of the 1,5 cyclic mechanism to the total conversion of n-hexane on the catalysts of high Pt/Mo ratios. This is in conformity with the previous result that the Pt–Mo–SiO$_2$ catalyst exhibits a profound contribution of the 1,3 bond-shift mechanism to isomerization of heptanes in comparison with the monometallic platinum catalysts [see Table 4 of (*12*)].

(2) The hydrogenolysis of MCP is increased remarkably on catalysts of a high Pt/Pt + Mo ratio. The total conversion and the ring-opening selectivity of MCP are illustrated in Fig. 3 and Table 2. For catalysts with atomic ratios of 0.6–1.0, the curve for hydrogenolysis in Fig. 3 has a similar feature to the curve for isomerization and/or cyclization in Fig. 1. It implies that a parallel relationship exists between the isomerization and/or cyclization of hexane and the ring opening of methylcyclopentane, while for catalysts of a low Pt/Pt + Mo ratio such parallelism is not obtainable. In other words, by increasing the Pt/Pt + Mo ratio, the isomerization of hexane via 1,5 dehydrogenated intermediates is facilitated so that its rate becomes high enough to compete with that of hydrogenolysis and isomerization reactions via 1,3 dehydrogenated intermediates.

It is interesting that the ratio of 3-Mp/nC$_6$ in the hydrogenolysis product of methylcyclopentane never exceeds 0.6 for all Pt–Mo catalysts. This means that only nonselective ring opening is adequate for hydrogenolysis of MCP over Pt–Mo–SiO$_2$ catalysts. According to Gault *et al.* (*2*), the nonselective ring opening of cyclopentanes should occur only when the monometallic Pt catalyst is of high dispersion, and in this case the 1,5 cyclic mechanism would have to be

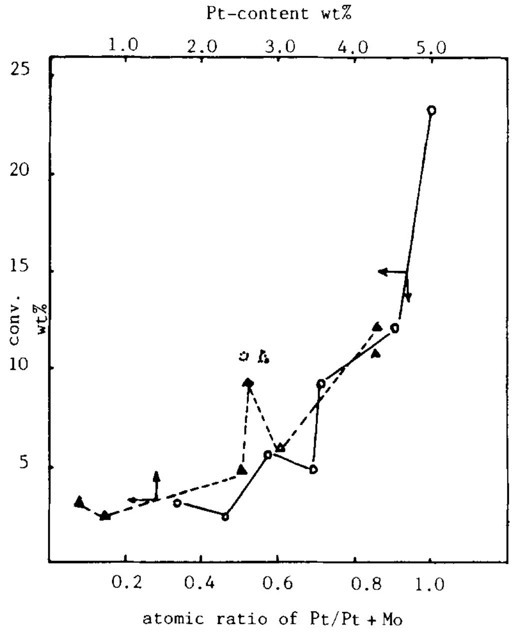
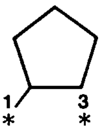


FIG. 3. Hydrogenolysis of methylcyclopentane.

predominant for the isomerization of "*n*-/iso-" alkanes. However, for our low Pt/Pt + Mo ratio samples, values as small as 0.2–0.3 for 3-MP/$n\text{C}_6$ are observed while no obvious deviation from the normal value of 0.5 is observed for the relative proportion of 3-MP to 2-MP. This extraordinary enhancement of the ring opening at the C_{ter}–C_{sec} position to yield more *n*-hexane plausibly resulted from the formation of the 1,3 dehydrogenated species of



which provides an additional chance to produce *n*-hexane via the 1,3 bond-cleavage mechanism. In other words, a relative preponderance of 1,3 adsorbed species could be suggested on Pt–Mo–SiO_2 catalysts. If so, we can further anticipate that at least for the molybdena-interacted platinum catalysts, the isomerization of C_6 and higher alkanes is by no means always mainly due to the 1,5 cyclic mechanism even if the catalyst is of low Pt content and high dispersion. In fact, as shown in the left branches of Figs. 1 and 2, for the catalysts of low atomic ratio, no priority of the 1,5 cyclic mechanism could be depicted. Here the 1,3 bond-shift mechanism is obviously contributory to total conversion and will account not only for the hydrogenolysis but also for the major part of isomerization products.

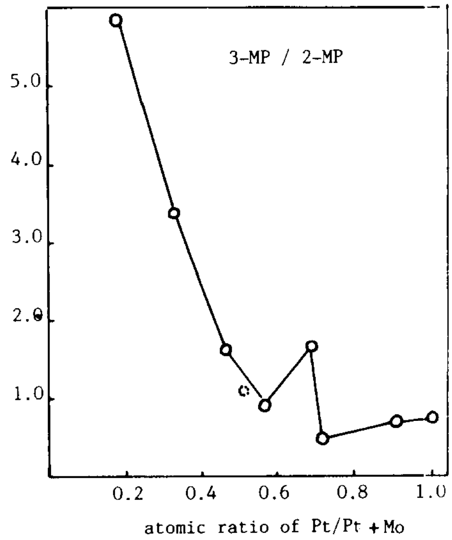


FIG. 4. 3-MP/2-MP in the product of the isomerization of $n\text{C}_6$ on Pt–Mo–SiO_2.

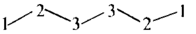
(3) Another specific performance of Pt–Mo interaction is the high 3-MP/2-MP ratio observed in the isomerization product of *n*-hexane. The experimental data are illustrated in Fig. 4 and also in Table 3 for a comparison between Pt–Mo–SiO_2 and the monometallic catalysts. This result can hardly be rationalized on the basis of current viewpoints of either 1,5 cyclic or 1,3 bond-shift mechanisms (*1–3, 14*). In the following discussion we offer a reasonable explanation based on the postulate of the coupling or the competition effect between 1,3 and 1,5 reaction mechanisms.

As pointed out previously (*12*), the selectivity should not be an intrinsic property of

TABLE 3

Reaction of $n\text{C}_6$ on Platinum Catalysts [Reproduced from Table 6 of Ref. (*12*)]

Catalyst	Bond-rupture probability			Product distribution	
	1–2	2–3	3–3	2-MP	3-MP
Pt–Mo–SiO_2(A)	0.11	0.24	0.30	49	51
Pt–Al_2O_3(B)	0.15	0.16	0.38	67	33
Pt–SiO_2(C)	0.19	0.16	0.30	63	37

the catalyst only, but should also depend on the C skeleton of the reacting molecules. Under the same condition, isomers with less branched C skeletons are more favorable to 1,5 adsorptions than to 1,3 adsorptions and vice versa. It can be anticipated on a similar understanding that the relative probability for primary C atoms at the ends of C skeletons to form 1,3 adsorbed species would be small in comparison with secondary and/or tertiary C atoms. This is because the primary C atoms are able to form 1,5 adsorbed species, while for secondary or tertiary atoms at the mid-position of the C skeleton, 1,5 adsorption is in some cases prohibited. For instance, if the C_3 atom on the C skeleton of *n*-hexane is attached on the Pt site at first, then only 1,3 adsorption is possible. Consequently, the C_2–C_3 and C_3–C_3 bonds are more feasible to cleave and/or to participate in 1,3 isomerization than are the C_1–C_2 bonds. If more bond rupture occurs at the C_2–C_3 bond instead of at the C_3–C_3 bond, then the bond-shift isomerization of the C_2–C_3 adsorbed species  to 2-MP would be depressed. The relative bond-rupture probability of the nC_6 skeleton (Table 3) just confirms the higher cleavage at the C_2–C_3 position especially for Pt–Mo–SiO_2 catalysts. Moreover, since 1,5 species are of trivial importance for hydrogenolysis, high selectivity for hydrogenolysis indicates a relatively large abundance of 1,3 adsorbed species on the surface of the catalyst, although the reverse is not necessarily true. Therefore, the high ratio of 3-MP/2-MP in the product is more evidence of the preponderance of the 1,3 adsorption and the bond-shift mechanism of Pt–Mo–SiO_2 in comparison with monometallic Pt catalysts. Moreover, it seems very probable that the selectivity of catalysts for isomerization of alkanes is affected by the mutual mechanistic coupling between hydrogenolysis and isomerization on the one hand and the different abilities of the carbon atoms on the C skeleton to form various 1,3 and 1,5 adsorption species on the other hand.

(4) To further the interpretation of the mechanistic relationship mentioned above, it is worthwhile to review the sulfur poisoning effect in the previous work (*12*) (see Table 4). It is interesting to note that the selectivity changes with S poisoning and the rate of deactivation during sulfur tiration is in the order of hydrogenolysis > isomerization > cyclization. However, the declination of isomerization after the first dosages of thiophene is much slower for Pt–Mo–SiO_2 than for Pt–Al_2O_3. These observations can be rationalized by the postulated mechanistic coupling between hydrogenolysis and isomerization which could be described qualitatively by the following diagram:

The Mutual Coupling Diagram of 1,3 and 1,5 Reaction Mechanisms

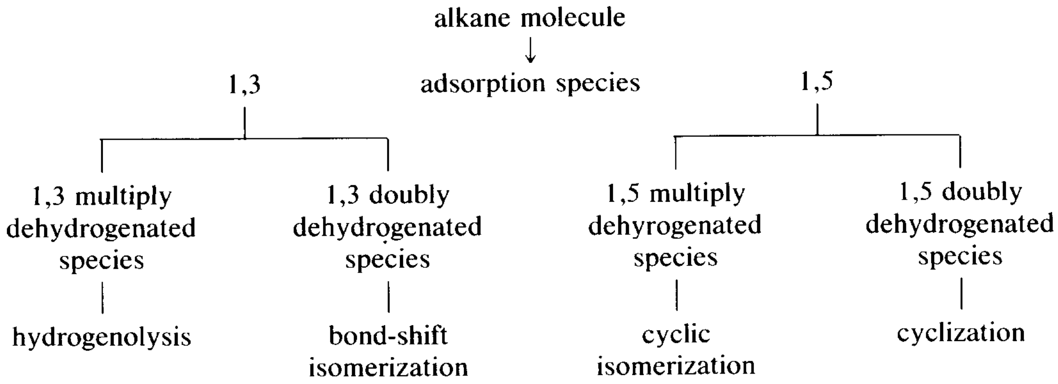


TABLE 4

Sulfur Titration Test [Reproduced from Table 3 of Ref. (12)]

Catalyst	Thiophene accum. (μ liter)	Conv. %	Deactivation rate (%)			
			T	H	I	Cy
Pt–Mo–SiO_2(A)	—	7.0				
	0.225	5.1	27.1	33.3	26.9	25.0
	0.525	2.0	71.5	77.8	73.0	62.5
	0.725	1.0	85.8	88.9	88.8	81.2
	0.807[a]					
Pt–Al_2O_3(B)	—	15.5				
	0.075	10.4	33.0	50.0	35.6	7.7
	0.175	7.1	54.2	72.1	60.6	16.9
	0.225	3.4	78.1	88.8	84.1	54.5
	0/275	1.3	91.5	97.0	95.2	80.8
	0.30[a]					

[a] Extrapolated value of S-tolerance limit: T = total conversion; H = hydrogenolysis; I = isomerization; Cy = cyclization.

According to the diagram, all reactions of alkane conversion demand the formaton of dehydrogenated surface species, but the severity of dehydrogenation is different for different reactions. Because of the greater severity of dehydrogenation involved in hydrogenolysis, it is expected that upon S poisoning, the hydrogenolysis would be retarded to a greater extent than the 1,3 bond-shift isomerization. Similarly, the 1,5 isomerization (or cyclic isomerization) would be retarded to a greater extent than cyclization. For this reason, when 1,3 intermediates predominate, the hydrogenolysis would be deactivated at a fast rate. The sulfur poison effect encountered on Pt–Mo–SiO_2 could be substantially explained in this aspect, since the deactivation of hydrogenolysis (H) is much greater than the deactivation of total conversion (T), while the deactivation of isomerization (I) is less than or at about the same level with that of total conversion. Similarly, when 1,5 adsorbed intermediates become more contributory to the total reactions, isomerization would be deactivated at a faster rate than total conversion and cyclization. This is consistent with the result observed on Pt–Al_2O_3, i.e., the deactivation is in the order of I > T > Cy. The highest deactivation of H on both catalysts may be regarded as due to the greatest demand of dehydrogenation severity for the hydrogenolysis reaction. It seems very plausible that S poisoning depresses the dehydrogenation power of active sites, the S poisoned sites are, consequently, no longer capable of forming the 1,3 multiply dehydrogenated species and the reaction mechanism on the S-modified sites is gradually shifted to isomerization and/or cyclization mechanisms of less dehydrogenation severity.

CONCLUDING REMARKS

Two new conceptions are attempted in this work. First, the hydrogenolysis, isomerization, and cyclization are mechanistically mutually coupled due to the prerequisite to form dehydrogenated species of different severities of dehydrogenation. Second, the interaction of molybdena on platinum is to enhance the severity of dehydrogenation of the surface intermediates and thus facilitate the cleavage of the C skeleton of alkane molecules particularly at the positions of secondary and/or tertiary C atoms.

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