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Isomerization and Metathesis of *n*-Butenes on Reduced Molybdena–Alumina Holding Preadsorbed Hydrogen

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The isomerization reactions of *n*-butenes were studied over molybdena–alumina previously reduced with hydrogen at 823 K, without removal of the hydrogen adsorbed during reduction. The rate of isomerization and hydrogen scrambling increased, but the rate of metathesis decreased significantly due to the effect of preadsorbed hydrogen. This is explained by formation of sites on which transformation of Mo-butyl species (direct intermediates for isomerization) to Mo-butylidene species (initiators for the chain reaction of metathesis) are hindered.

INTRODUCTION

Isomerization of *n*-butenes has been studied over molybdena–alumina catalyst in order to gain insight into the character of the catalyst surface.

Over freshly oxidized catalyst isomerization proceeded by an acidic mechanism (*1*, *2*). Metathesis activity was induced by contacting the catalyst with butenes; the conversion of 2-butenes via an acidic mechanism decreased and most of the *cis–trans* transformation proceeded via metathesis (*1*). In the case of 1-butene as reactant, the decrease of the conversion via the acidic mechanism was not significant; isomerization, metathesis, and cross-metathesis of reactants with primary isomerization products yielded a rather complex product distribution (*3*, *4*).

Over molybdena–alumina reduced with hydrogen, on the contrary to the behavior of the oxidized catalyst, both metathesis and isomerization was observed in the early stage of reaction; the latter was the prevailing process (*5*). Nonmetathetic isomerization was found to proceed by a hydride insertion mechanism via alkyl intermediate. After a short induction period metathesis and nonmetathetic isomerization played an equal part in the transformation of 2-butenes (*6*).

The metathesis of propene was found to be suppressed, but isomerization of *n*-butenes was enhanced by hydrogen adsorbed at the temperature (773–823 K) of catalyst reduction (*7*). Formation of cross-metathesis products in the course of isomerization of *n*-butenes was also suppressed over such catalysts (*8*).

According to temperature-programmed desorption data of hydrogen adsorbed on reduced molybdena–alumina (*9*), strict distinction has to be made between the hydrogen adsorbed at high temperature, and that adsorbed near room temperature. Hydrogen adsorbed below 423 K enhances not only the isomerization of butenes, but the metathesis as well.

In the present paper we intend to clarify the role of hydrogen preadsorbed at high temperature on molybdena–alumina in the transformation of *n*-butenes.

EXPERIMENTAL

Catalyst and Pretreatment

The same catalyst (containing 9.1 wt% MoO_3 on Ketjen CK 300 γ-Al_2O_3 [particle size 0.2–0.4 mm]) was used as in Ref. (*10*). First, oxygen was recirculated for 1 h through the catalyst bed at 823 K and a trap cooled with liquid nitrogen; then the cata-

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lyst was evacuated for 1 h at the same temperature. Reduction was carried out for the desired time by recirculation of hydrogen at atmospheric pressure through the catalyst bed at 823 K and a trap cooled with liquid nitrogen.

Two different treatments were applied after reduction. When the catalyst was evacuated at 823 K for 1 h, catalyst without hydrogen adsorbed at high temperature (CAT) was obtained. When the reactor with catalyst was cooled to 313 K in hydrogen and evacuated at that temperature for 1 h, catalyst with hydrogen adsorbed at high temperature (CAT–H) was formed.

CAT–H was also prepared in a different way. When distinction between adsorbed hydrogen and deuterium was necessary, after reduction with hydrogen the catalyst was evacuated at 823 K for 1 h, then hydrogen or deuterium at 12.3 kPa pressure was recirculated through it at the same temperature for 10 min. After this the catalyst was cooled to 313 K in the gas and evacuated at the same temperature for 1 h. Experimental results indicated (*9*) that the character of catalysts was identical whether they were cooled directly in hydrogen or were treated again with hydrogen (or deuterium) after evacuation.

Procedures

The greater part of the experiments were carried out in a closed glass recirculation system. Butenes (5×10^{-3} mol) were recirculated through the reactor at 313 K and atmospheric pressure for 30 s. The reaction was terminated by freezing the reaction mixture into a trap cooled with liquid nitrogen. After closing the reactor the reaction mixture was evaporated into the system for analysis. The components of the sample were separated at 293 K on a 3-m-long chromatographic column containing Chromosorb P coated with 20% dibenzylamine; a flame ionization detector was applied.

In order to determine the participation of adsorbed hydrogen (deuterium) in the transformation, butene or a mixture of 90% butene and 10% deuterium was recirculated at 313 K for 1 min through CAT–H containing either hydrogen or deuterium. The reaction was terminated by freezing the reaction mixture with liquid nitrogen. Separation was carried out at 273 K, and a thermal conductivity cell was used as detector. The individual separated compounds were collected at the exit of the gas chromatographic column in traps cooled with liquid nitrogen. Mass spectrometric analysis was carried out with a Varian EM 600 mass spectrometer using a low ionization voltage (15 eV) to minimize fragmentation.

Experiments with *cis*-2-butene-d_0 + -d_8 mixture using 0.015 g CAT–H were carried out in an all-glass microcatalytic pulse system.

RESULTS

Reaction of a Mixture of cis-2-Butene-d_8 and cis-2-Butene-d_0

The reaction was carried out at 333 K over CAT–H reduced for 1 h, in order to determine the participation of metathesis in the *cis–trans* transformation. After the first pulse, the catalyst was contacted with the reaction mixture (initial pressure 26.6 kPa) at 333 K for 10 min. After this treatment the catalyst was flushed with ultra-pure helium for approximately 1 h. The data obtained are collected in Table 1.

Besides *trans*-2- and 1-butene only a trace amount of propene was formed. This and the deuterium distribution in the product *trans*-2-butene (second part of Table 1) indicate that metathesis played no significant role in the *cis–trans* transformation of 2-butenes on CAT–H.

Co-isomerization of 50% 1-Butene and 50% cis-2-Butene (Table 2.)

Metathesis of 1-butene and cross-metathesis of 1-butene with 2-butenes should lead to the formation of ethene + hexene and propene + pentene, as was observed on CAT. On CAT–H no pentene and ethene, and only a negligible amount of pro-

TABLE 1

Product Distribution (%) from Reaction of *cis*-2-C_4H_8 + *cis*-2-C_4D_8 over Molybdena–Alumina[a]

Pulse no.	*cis*-Butene	*trans*-Butene	1-Butene	Propene
1	53.3	43.4	3.1	0.2
2[b]	59.2	38.1	2.6	0.2

Pulse no.	Butene isomers	Deuterium distribution (%)								
		d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8
0	*cis*[c]	45.7	0	0	0	0	0	0.8	7.2	46.3
1	*cis*	26.2	6.7	5.7	5.0	7.1	5.9	6.2	9.5	27.0
	trans	10.2	11.8	10.5	11.6	12.0	11.4	11.1	13.8	8.4
2	*cis*	35.0	2.9	2.9	2.5	2.5	2.5	4.1	10.2	37.2
	trans	13.4	14.7	8.9	7.6	8.4	8.1	10.2	17.8	10.9

[a] 15 mg catalyst (1.25 × 10^{-5} mol MoO_x) reduced at 773 K with hydrogen (60 cm^3/min) for 1 h (the average number of electrons placed in the course of reduction on Mo^{6+} is about 1.3), and flushed with helium at 333 K for 1 h (*6*). Experiment in pulse system at 333 K, He carrier gas 60 cm^3/min, pulse size 1.73 × 10^{-5} mol.

[b] After the first pulse the catalyst was soaked with the reactant (initial pressure 2.6 kPa, 8 cm^3 NTP) for 10 min at 333 K, and flushed with helium at the same temperature for 1 h.

[c] Deuterium distribution in initial *cis*-2-butene.

pene were formed. Considering that much more *trans*-2-butene was formed than over CAT, the contribution of the metathesis to the transformation of butenes on CAT–H can be neglected.

H/D Exchange between Butene and D_2 or Adsorbed Deuterium over CAT–H (Table 3)

In the experiments the reaction conditions were chosen so as to obtain isomerization conversions not too close to equilibrium. Under these conditions the ratio of H atoms adsorbed on the surface to the butene molecules in the system was approx 0.01 : 1.0 [6.3 × 10^{-5} mol MoO_x on the catalyst; 0.24 mol H_2/mol MoO_x (*10*) → 1.5 × 10^{-5} mol H_2, 5 × 10^{-3} mol butene]. On catalyst treated with deuterium 0.8–1.0% butene-d_1 was formed; this is in good agreement with the value expected if all the adsorbed hydrogen was exchanged with butene. Zero concentration of butane in *cis*-2-butene and low concentration of it in 1-butene indicates that the adsorbed hydrogen could be removed by exchange rather than by hydrogenation.

TABLE 2

Co-isomerization of 50% 1-C_4H_8, 50% *cis*-2-C_4H_8 over Molybdena–Alumina Reduced for 2 h[a]

Catalyst sample	Products (%)				
	trans-C_4H_8	C_3H_6	C_5H_{10}	C_2H_4[b]	*n*-C_4H_{10}
CAT	0.70	4 × 10^{-2}	3 × 10^{-2}	2 × 10^{-3}	8 × 10^{-3}
CAT–H	10.57	2 × 10^{-3}	—	—	4 × 10^{-2}

[a] Recirculation system. 0.1 g catalyst reduced with hydrogen at 823 K and evacuated at the given temperature for 1 h. Isomerization of 5 × 10^{-3} mol mixture at 313 K, atmospheric pressure for 30 s.

[b] Hexenes were not determined quantitatively.

Transformation of cis-2-Butene over CAT and CAT–H Catalysts Reduced for Different Times

Two series of experiments were carried out over both types of catalysts. In one series 100% butene was used, whereas in the other the butene contained 1% of hydrogen. The data obtained are summarized in Fig. 1. Curves in Fig. 1a indicate the percentage of *trans*-2-butene, and in Fig. 1b that of *n*-

TABLE 3

Isomerization of *cis*-2-Butene and 1-Butene in the Absence or Presence of D_2 over CAT–H Holding Deuterium or Hydrogen[a]

Expt. no.	Adsorbed at 823 K	Reagent	Butane (mol%)	Butene isomers (mol%)		Deuterium distribution (%)		
						d_0	d_1	d_2–d_8
1	D_2	100% *cis*-Butene	0	cis	60.5	99.3	0.7	—
				trans	36.5	99.1	0.9	—
				1-b	3.0			
2	D_2	90% *cis*-Butene 10% D_2	7.2	cis	42.0	91.0	9.0	—
				trans	53.9	87.9	12.1	—
				1-b	4.1			
3	H_2	90% *cis*-Butene 10% D_2	7.7	cis	43.9	91.9	8.8	—
				trans	51.0	88.8	11.2	—
				1-b	5.1			
4	D_2	100% 1-Butene	0.2	1-b	51.2	99.1	0.9	
				cis	14.3	98.9	1.1	
				trans	34.5	98.9	1.1	
5	D_2	90% 1-Butene 10% D_2	8.5	1-b	23.1	90.2	9.8	—
				cis	23.8	88.2	11.8	—
				trans	53.1	88.3	11.7	—
6	H_2	90% 1-Butene 10% D_2	8.8	1-b	26.8	90.2	9.8	—
				cis	22.6	87.4	12.6	—
				trans	50.6	87.2	12.8	

[a] 0.1 g catalyst (6.3×10^{-5} mol MoO_x) reduced at 823 K with hydrogen (initial pressure 100 kPa) for 1 h and evacuated at the same temperature for 1 h; 13.3 kPa D_2 or H_2 was recirculated at 823 K for 10 min and the catalyst was evacuated at 313 K for 15 min; 100 kPa (5×10^{-3} mol) reagent was recirculated at 313 K for 1 min.

butane formed; the ratio *trans*-2-butene/1-butene obtained in the same experiments is represented by Fig. 1c. Both over CAT and CAT–H catalysts isomerization was significantly enhanced by 1% H_2 in the gas phase.

The ratio *trans*-2-butene/1-butene over CAT (Fig. 1c) varied with the degree of catalyst reduction, and at least at lower extents of reduction is influenced significantly by hydrogen in the gas phase. We have to emphasize again that over CAT catalysts *cis*-2-butene was transformed to *trans*-2-butene to a greater or less extent via metathesis (*5*), and the fraction of *trans*-2-butene formed via metathesis depended on the degree of catalyst reduction. Over CAT–H the ratio of *trans*-2-butene/1-butene (Fig. 1c) was not influenced by the extent of catalyst reduction or by the presence or absence of hydrogen in the gas phase. This indicates that the same isomerization mechanism was effective over CAT–H independently of the extent of reduction.

In the absence of hydrogen there was no significant difference between the amount of *n*-butane formed over CAT and CAT–H (Fig. 1b). Formation of considerably more butane could be expected over CAT–H presuming that the hydrogen adsorbed at high temperature is able to hydrogenate butene. In the presence of hydrogen in the gas phase, however, a much higher hydrogenation rate was observed over CAT–H than over CAT.

Isomerization of Each of the n-Butene Isomers over CAT–H

In order to avoid external mass transfer limitations during continuous experiments in the recirculation system, the butene had

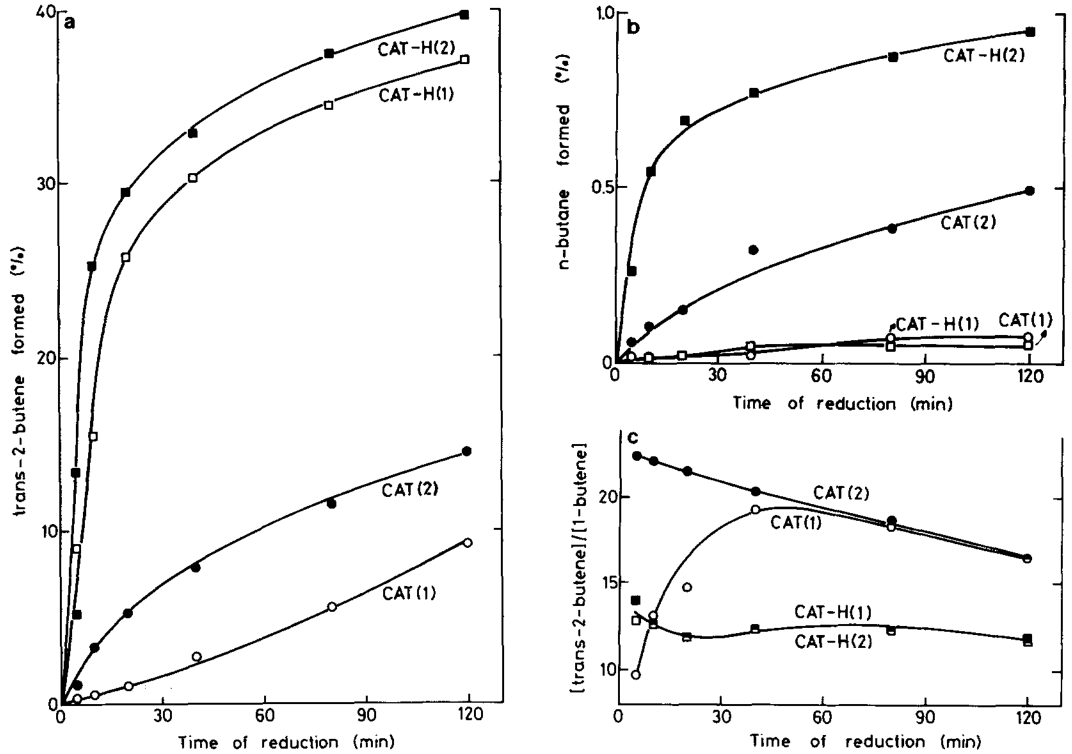


FIG. 1. Concentration of *trans*-2-butene (a) and *n*-butane (b) as well as ratio of *trans*-2-butene/1-butene (c) formed in reaction of 100% *cis*-2-butene (curves 1) and 99% *cis*-2-butene, 1% H_2 (curves 2) over CAT and CAT–H catalysts reduced at 823 K for different times; reaction temperature 313 K.

to be diluted with nitrogen and the amount of catalyst had to be reduced to 5 mg. The results can be seen in Fig. 2. The only products of each of the *n*-butene isomers were the other two isomers. The initial rates were 5.0×10^{-5}, 3.2×10^{-5}, and 1.9×10^{-5} mol g_{cat}^{-1} s^{-1} for isomerization of *cis*-2-, 1-butene, and *trans*-2-butene, respectively.

DISCUSSION

Over freshly oxidized molybdena–alumina, isomerization of *n*-butenes was accompanied by stepwise H/D exchange (*1*). A more extensive hydrogen exchange was obtained over catalyst reduced with hydrogen (*5*) which indicated that multiple exchange takes place besides isomerization. The rate of both isomerization and hydrogen exchange increased as a result of the effect of hydrogen adsorbed at low temperature.

A more considerable increase of isomerization rate resulted if hydrogen had been adsorbed on the catalyst at high temperature (Fig. 1). Together with this, and more significantly, there was an increase in the rate of hydrogen exchange. While over CAT 1.0 H/D atom was exchanged per molecule of *trans*-2-butene formed in isomerization of *cis*-2-butene-d_0 + $-d_8$, the deuterium distribution observed in *trans*-2-butene formed in the same reaction at the same isomerization conversion over CAT–H (Table 1) indicates such an extensive hydrogen scrambling that the results cannot be used to calculate the number of hydrogen exchanged. The extent of hydrogen exchange between deuterium and butenes, however, was identical over CAT and CAT–H at similar isomerization conversion (Table 3).

Over reduced molybdena–alumina it was found (*6*) that the rate of both nonmetathetic isomerization and metathesis

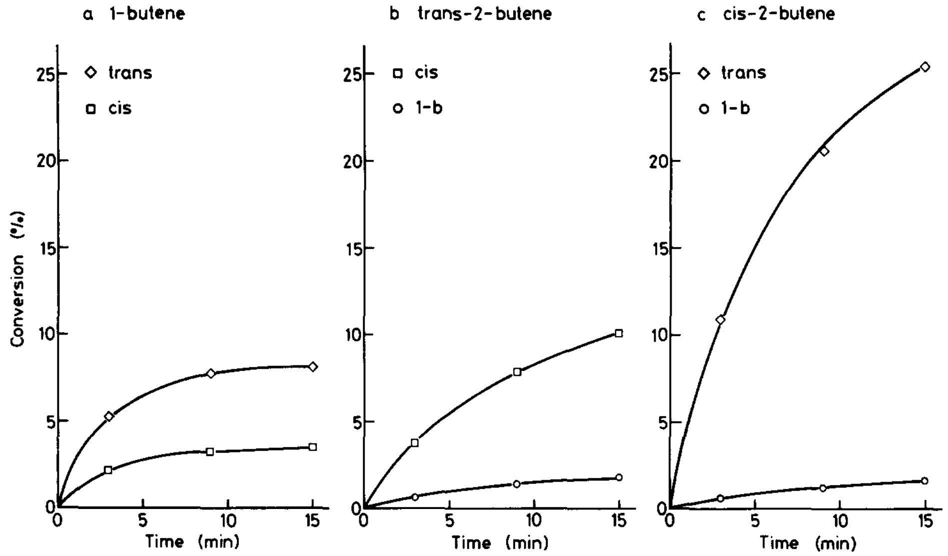


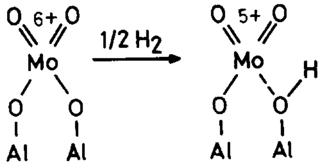
FIG. 2. Isomerization of butenes in the recirculation system at 313 K over 5-mg CAT–H reduced for 1 h; 1.4 kPa butenes, 98.6 kPa N_2.

is proportional to the number of coordinatively unsaturated sites formed during catalyst reduction. From this and other characteristics it was assumed that nonmetathetic isomerization proceeds by hydride insertion via Mo-2-butyl intermediates. First nonmetathetic isomerization then metathesis was accelerated by hydrogen in the gas phase. Similarly, by poisoning with NO first the rate of isomerization, and later that of metathesis, decreased. From this it was concluded that alkylidene intermediates of metathesis were formed by hydrogen abstraction from alkyl intermediates of isomerization.

The main difference between CAT and CAT–H is the almost total lack of metathesis on CAT–H. Presumably nonmetathetic isomerization, which is significantly faster on CAT–H than on CAT, proceeds over both catalysts via Mo-2-butyl intermediates. The observation that hydrogen (deuterium) in the gas phase increased the isomerization rate further (Fig. 1) supports this assumption. Because of the almost total lack of metathesis, formation of Mo-alkylidene intermediates should be hindered by hydrogen adsorbed at high temperature.

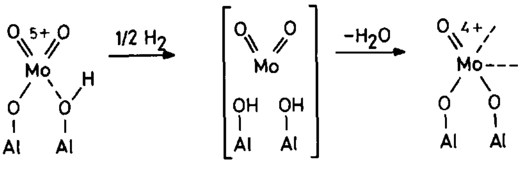
Let us now try to depict the formation of such surface sites which satisfy the requirements given by experimental data.

The infrared spectra in the OH region of reduced molybdena–alumina in the presence and absence of hydrogen adsorbed at high temperature (H_R) reported by Millman *et al.* (*11*) showed the same OH bands, but their intensities were larger in the presence of H_R. No new bands were detected by them which were not also found in the spectrum of the alumina support. They assumed that on reduction it is not the oxygens in the uppermost layer which are attacked by hydrogen, but the bond between Mo and the surface oxygen:



(1)

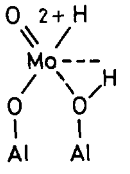
As the reduction proceeds, further formation of OH groups in the sublayer and removal of H_2O was expected by them:



I

(2)

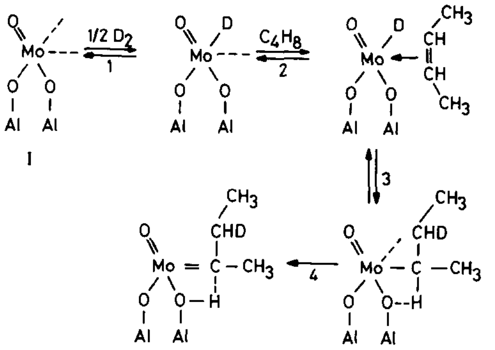
As the intensities of OH bands in the infrared spectra of reduced molybdena–alumina were higher in the presence of H_R, it may be assumed that a certain part of the hydrogen connected to the oxygen in the sublayer can be removed only by evacuation at high temperature. This is possible, if sites like **II** are present on the surface before evacuation.



II

According to the results described by Hall and co-workers (*11, 12*), the existence of such sites is more than probable. Their infrared spectroscopic and NMR data indicated the removal of only one OH group from the surface for every H_2 formed in desorption. They assumed that H_R was heterolytically dissociated to form a hydroxyl group and that another hydrogen species, presumably some kind of molybdenum hydride, was unobservable by both NMR and infrared spectroscopy. Species of type **II** meet these requirements; removal of H_2 from them may lead to type **I** species.

Over reduced molybdena–alumina without hydrogen adsorbed at high temperature isomerization of butenes may proceed on sites of type **I** according to Scheme 1. The reaction is accelerated by hydrogen in the gas phase or adsorbed at low temperature (step 1). Steps 1–3 are the heterolytic adsorption of deuterium at the temperature of isomerization, and formation of the half-hydrogenated Mo-butyl species via π-bonded butene as was assumed by Lombardo *et al.* (*13*) in the case of ethylene hydrogenation over reduced molybdena–alumina. The Mo-butyl species are the intermediates for isomerization and hydrogen exchange. Hydrogen in Mo-butyl species close to the molybdenum ion may be attracted by oxygen in the sublayer. If hydrogen abstraction is completed as in step 4, Mo-butylidene species may form, and these can serve as initiators in the chain reaction of metathesis.



SCHEME 1

The possible ways in which alkylidene intermediates may form initially have recently been under investigation. According to Laverty *et al.* (*14*) interaction between coordinatively unsaturated transition metal ions and hydroxy groups of the carrier may give rise to surface metal hydrides. These hydrides isomerize the olefin reversibly to alkylidene complexes via metal–alkyl formation. Over molybdena–alumina reduced with hydrogen, the formation of alkylidene species from alkyl intermediates in the course of hydrogen abstraction by neighboring surface oxygens was suggested by Lombardo *et al.* (*13*). The experimental data that the changes in the rates of nonmetathetic isomerization were observed in the rate of metathesis with some delay (*6*) strongly support the hypothesis that alkylidene intermediates may form from alkyl intermediates.

Scheme 1 can be applied to the isomerization of butenes over CAT–H as well, but in this case type **I** sites are replaced by type **II** sites. Since in these sites there are OH groups in the sublayer, hydrogen abstraction from Mo-butyl intermediates is hindered; consequently only isomerization and hydrogen exchange may proceed, but not metathesis.

Presumably species **I** are dominant on CAT and species **II** on CAT–H. Isomerization and hydrogen exchange of butenes via an associative mechanism may take place on species **I** only after preadsorption of hydrogen, but species **II** are ready for these processes. This may be an explanation for the higher rate of isomerization and hydrogen exchange over CAT–H as well as for their acceleration by hydrogen in the gas phase. Hydrogen exchange between butenes and deuterium gas may take place with nearly equal probability over the two types of sites; therefore the higher rate of hydrogen scrambling between butenes over CAT–H does not involve the higher rate of exchange between butene and deuterium gas.

The rate of *cis–trans* transformation of 2-butenes over CAT was significantly higher than the rate of double bond shift either in 2-butene or in 1-butene (*5*). This can be explained by the observation that metathesis was an additional route for the *cis–trans* transformation. Over CAT–H, where results are insignificantly influenced by metathesis, the rate of double bond shift of 1-butene was similar to the rate of *cis–trans* transformation of 2-butenes (Fig. 2).

The change of the rates of isomerization and metathesis of 2-butenes effected by H_R together with the infrared and NMR data of the catalyst with and without H_R given by Hall and co-workers allowed us to presume the structure of characteristic sites on reduced molybdena–alumina in the presence of H_R. More detailed investigations are required to shed light on the mechanism of isomerization of butenes over such catalysts.

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