

Hydrocarbon reactions on MoS₂ revisited, II: Catalytic properties in alkene hydrogenation, *cis*–*trans* isomerization, and H₂/D₂ exchange

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Received 3 February 2008; revised 10 March 2008; accepted 10 March 2008

Available online 14 April 2008

Abstract

MoS₂ prepared by thermal decomposition of ammonium tetrathiomolybdate in inert gas at temperatures up to 773 K was activated by treatments involving thermoevacuation at 723 K and/or reduction at 573 K. The effect of different activations on the activity in ethylene hydrogenation, *cis*–*trans* isomerization of 2-butene, and H₂/D₂ isotope exchange (all measured at temperatures around 473 K) was compared, taking into account the extent of Mo exposition as measured by oxygen chemisorption. It was found that activation had a widely varying impact on the test reactions, indicating that these proceed on sites with different numbers of vacancies. Hydrogenation activity was boosted by two orders of magnitude when reduction of the catalyst at 573 K was followed by thermoevacuation at 723 K, whereas this change was moderate with H₂/D₂ exchange and negative with *cis*–*trans* isomerization. For the latter reaction, mere thermoevacuation was a suitable activation, and the impact of subsequent catalyst reduction was negative, whereas appreciable activity in the former reactions was obtained only when thermoevacuation was combined with a subsequent reduction. The data suggest that all three reactions proceeded on different sites, probably 3 vacancies per Mo for olefin hydrogenation, 2 vacancies per Mo for H₂/D₂ exchange, and 1 vacancy per Mo for *cis*–*trans* isomerization, with the latter two reactions involving adjacent –SH groups. Sites with greater Mo exposure than stated may be suitable for H₂/D₂ exchange but not for *cis*–*trans* isomerization. With increasing severity of the activation treatments, sites with a small number of vacancies appeared to combine and migrate toward the rims or to escape into the bulk. Therefore, very high hydrogenation activity may be seen on surfaces with an oxygen chemisorption capacity far from the maximum value occurring after less drastic treatments. Our findings imply that a combination of chemisorption studies with test reactions may be a valuable tool for surface characterization of sulfide catalysts.

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Keywords: Molybdenum sulfide; Active sites; Hydrogenation of ethene; *Cis*–*trans* isomerization; H₂/D₂ isotope exchange

1. Introduction

The catalytic properties of MoS₂ have been studied in great detail because of MoS₂'s role in hydrorefining catalysis. Owing to this application, most attention has been paid to reactions of molecules containing S and N in aromatic systems [1–4]. Beyond the cleavage of C–S and C–N bonds, MoS₂ catalyzes a number of hydrocarbon reactions as a hydrogenation or *cis*–*trans* rearrangement of double bonds, which are part of the reaction networks in hydrorefining, and H/D exchange with hydrocarbons or between H₂ and D₂. The latter group of reactions

was studied extensively by Tanaka et al. [5]; some of their experiments are textbook examples today, although some of their conclusions are coming under increasing question. Although it is obvious from Tanaka's work that hydrogenation requires a higher degree of coordinative unsaturation than *cis*–*trans* isomerization, Jalowiecki et al. reported that the latter proceeds on sites both of lower and higher unsaturation than required for the hydrogenation reaction, but most effectively on the most exposed Mo sites [6]. Another serious issue is the doubt about the existence of hydrogen directly bound to Mo sites (i.e., Mo–H) recently raised in theoretical papers [7–12].

The present work was guided by the concept of using the well-studied hydrocarbon reactions as chemical probes for the surface properties of MoS₂ and other chalcogenide phases.

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We report some relevant results obtained with MoS₂ prepared by low-temperature (≤ 773 K) decomposition of ammonium tetrathiomolybdate (ATTM). In Part I of this work [13], we reported that reductive activation of such materials in hydrogen at 573 K (with or without previous thermoevacuation at 773 K) produced appreciable amounts of coordinatively unsaturated Mo sites even though the S/Mo ratio did not fall below 2. With increasing reduction temperature, the extent of coordinative unsaturation (characterized by oxygen chemisorption) passed a maximum, which casts some doubt on attempts to relate the S/Mo stoichiometry to the MoS₂ vacancy structure. Because the properties of MoS₂ batches prepared through the same synthesis route are not well reproducible, catalytic investigations should be performed only on batches that have been well characterized.

Here, in Part II of this work, we report the catalytic properties of a MoS₂ batch that was characterized after different activations in Part I [13]. We found that olefin hydrogenation, *cis*–*trans* isomerization, and H₂/D₂ exchange were affected in different ways by variations in the severity of the activation treatment and hence the site structure on the surface, suggesting that these reactions require different degrees of Mo exposure.

2. Experimental

2.1. Materials

All of the data presented here, with a few exceptions that will be mentioned in the text, were obtained with one MoS₂ batch. The preparation procedure for this batch, labeled MoS₂(A₁), was described in detail in Part I [13]. It is based on the thermal decomposition of ATTM in flowing nitrogen at temperatures up to 773 K. This catalyst was activated by different treatments described in Part I [13] as well: V₇₂₃, evacuation at 723 K for 4 h; V₇₂₃/R₅₇₃, reduction in H₂ (10% in He) for 3 h at 573 K after previous V₇₂₃; R₅₇₃, reduction in H₂ (10% in He) for 3 h at 573 K without previous V₇₂₃. In some cases, thermoevacuation was performed after the reduction step (i.e., R₅₇₃/V₇₂₃). In cases where the activation temperature differed from the standard value, this temperature was included in the designation (e.g., V₇₂₃/R₄₇₃, indicating reduction only at 473 K).

In Part I [13], we reported that the surface of MoS₂(A₁) was initially contaminated by ammonium sulfate species, which could be completely removed by V₇₂₃/R₅₇₃ or R₅₇₃, whereas after V₇₂₃, residual surface Mo(VI) oxide species were observed. The catalytic data reported herein were mostly obtained on surfaces cleaned by V₇₂₃/R₅₇₃ or R₅₇₃. For data obtained after V₇₂₃ or V₇₂₃/R₄₇₃, possible effects of surface impurities also were considered.

All gases and gas mixtures used were provided by Messer GmbH, except for Ar, which was provided by Air Liquide.

2.2. Catalytic measurements

The catalytic data were measured in the setup depicted (in simplified form) in Fig. 1. The catalytic microflow reactor was

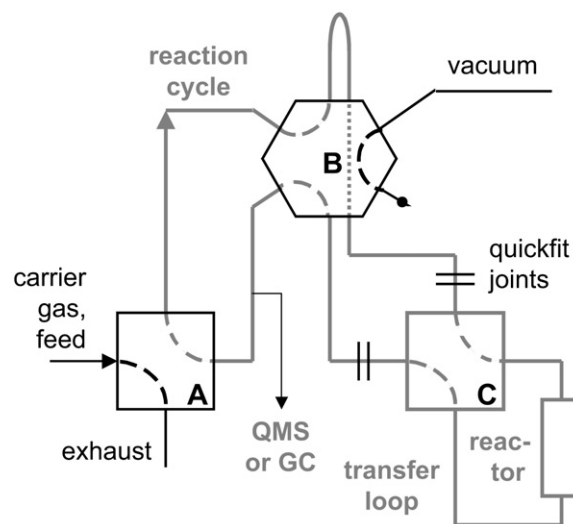


Fig. 1. Scheme of the catalytic setup allowing rapid switch between pulse and flow operation, retrieval of sensitive catalyst states into a glove box, and convenient switch between activation and reaction modes. Cycle pump and dosing valve for pulse chemisorption studies omitted.

included in a reaction cycle (gray lines), which can be opened by valve A to allow operation in flow mode. Valve C allows separation of the reactor from the cycle. The corresponding part can be detached at the joints to transfer a sample to a glove box (or vice versa, to present an air-sensitive catalyst for catalytic investigation). The six-way valve B serves to switch the reactor between the reaction cycle and the vacuum pump, to ensure minimum contamination of the sample surface after thermoevacuation treatments. This setup also was used to measure oxygen chemisorption (OCS) in the pulse regime (flow mode; dosing valve omitted in Fig. 1) or to measure the exchangeable hydrogen on the catalyst (see Part I [13]). After measuring OCS, the catalyst was reactivated for subsequent catalytic studies by reduction (10% H₂/He) at 473 K for 1 h. Exploratory studies [13] have found that this treatment restores the OCS capacity without creating new adsorption sites.

All reactions were studied in the recycle mode to cover a wide range of reaction rates, including very low ones. Only some deactivation tests were performed in the flow mode. The reaction cycle was first evacuated (with the transfer loop under helium) and then filled with the required gases, which were cycled while the reactor was heated to the desired temperature. After switching the transfer loop containing 0.1 g of MoS₂ into the cycle, the kinetic run was started. Mixing effects were seen in the concentration measurements only within the first minute because of the good pump performance.

For the hydrogenation of ethylene, the cycle was filled with 100 mbar of an ethylene/He mixture (30% ethylene) and 100 mbar H₂ (pure or mixed with D₂, 99.7%), subsequently with He, up to a total pressure of 1 bar. After the transfer loop was included, initial concentrations of 2.4 vol% ethylene and 8 vol% H₂ (H₂/D₂) were obtained. The reaction products in the kinetic runs were analyzed continuously by calibrated mass spectrometry. Some earlier runs designed to study the influence of D₂ on the reaction rate involved gas chromatographic

product analyses. The isomerization of *cis*-but-2-ene was performed in the presence of H₂, because it is known that this isomerization is extremely slow without hydrogen [5,14]. First, 100 mbar of a mixture containing 500 ppm *cis*-but-2-ene in He and 100 mbar of H₂ were dosed, resulting in 0.004 vol% butene and 8 vol% H₂ after the addition of He and inclusion of the transfer loop. The products were analyzed by gas chromatography. Analogously, for the study of the H₂/D₂ exchange, 50 mbar of H₂ and of D₂ were dosed, resulting in a concentration of 4 vol% for each. The development of concentrations in the cycle was analyzed by calibrated mass spectrometry. A first-order reaction rate law, as reported by Wilson et al. [15], was suitable for representing the data at conversions up to 20%. A series of experiments also was conducted with a lower initial concentration [0.8 vol% H₂ (D₂)].

3. Results

3.1. Hydrogenation of ethylene

The hydrogenation of ethylene was studied at temperatures of 440–480 K. For samples activated by V₇₂₃, a measurable reaction rate was found only at 450 K. With the other activations, hydrogenation occurred already at room temperature, but strong deactivation was noted. This deactivation most likely was related to the deposition of carbonaceous material, because when the catalyst was treated with 10% H₂/He at 573 K, hydrocarbons of different carbon number (including heavier molecules than ethane) were identified in the desorbing gas by GC. The kinetic data for conversions <20% could be fitted by a rate law (pseudo-) first-order in ethylene.

Fig. 2 summarizes the data obtained in an Arrhenius plot, and Table 1 gives rate constants for $T = 473$ K, initial reaction rates related to the OCS capacity, and activation energies. Measurements after V₇₂₃ were complicated by a parallel activation of the catalyst due to the presence of hydrogen. The final state of this activation (i.e., the activity achieved after reduction of the thermoevuated surface in 10% H₂/He at 473 K for 3 h) are shown in Fig. 2a (dashed line). Because this activation process competes strongly with the rate measurement, data for ethylene hydrogenation after V₇₂₃ are reported only for a single low temperature, 450 K.

Activation energies were derived for several activation treatments. There appears to be no relationship between pretreatment and activation energy, E_A , although the scatter in the data measured after the R₅₇₃ treatment casts some doubt on the corresponding E_A value. But for V₇₂₃/R₄₇₃, a similar activation energy of 41 kJ/mol was obtained. Therefore, it appears safe to conclude that the activation energy was 35–40 kJ/mol irrespective of the pretreatment. This suggests that the same type of site was operative after the activations, with only the number of sites changing.

Remarkably, the rate constants at 473 K varied by almost three orders of magnitude depending on the treatment of the catalyst (Table 1). Fig. 2a shows that reduction after previous thermoevacuation (V₇₂₃/R₅₇₃) led to a more active catalyst state compared with mere reduction (R₅₇₃) despite the greater

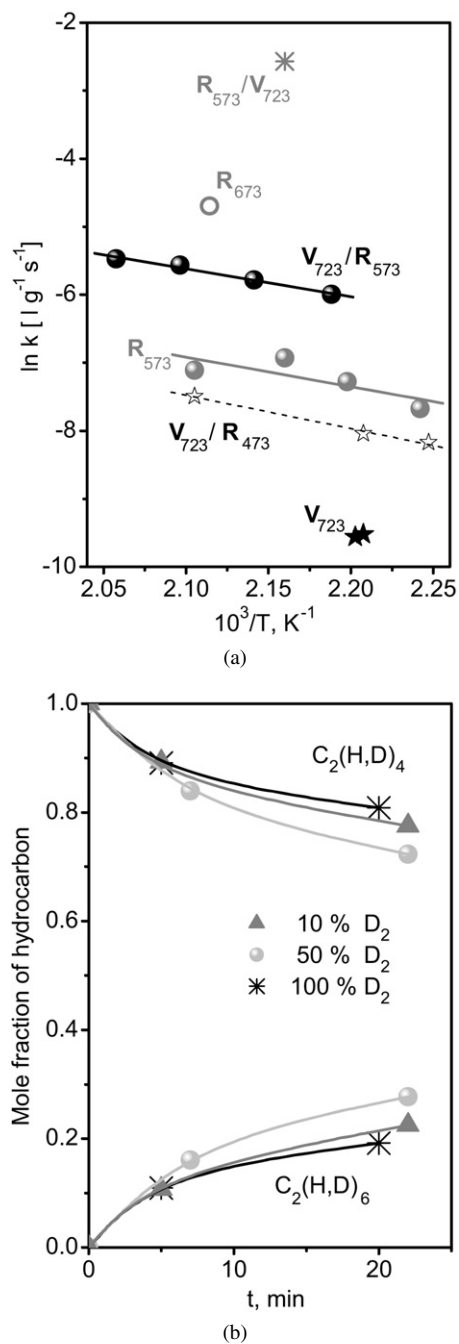


Fig. 2. Ethylene hydrogenation over MoS₂. (a) (Pseudo-) first-order rate constants measured after different activation treatments. V₇₂₃, evacuation (723 K, 4 h); V₇₂₃/R₅₇₃, reduction in H₂ (10% in He, 3 h, 573 K) after previous V₇₂₃; V₇₂₃/R₄₇₃, 3 h reduction H₂ (10% in He) at 473 K after V₇₂₃ (after this the surface may contain residual impurities [13]); R₅₇₃, reduction in H₂ (10% in He, 3 h, 573 K) without previous V₇₂₃; R₅₇₃/V₇₂₃, evacuation (723 K, 4 h) after previous R₅₇₃. MoS₂ batch used—MoS₂(A₁) from Part I [13]. (b) Batch hydrogenation of ethylene with different isotopic composition of hydrogen. $T_R = 463$ K, activation by V₇₂₃/R₅₇₃. MoS₂ batch used—MoS₂(B) from Part I [13].

degree of Mo exposure (i.e., OCS capacity) in the latter case. However, the most striking result is the effect of thermoevacuation subsequent to the reduction treatment (R₅₇₃/V₇₂₃). Such thermoevacuation decreased the degree of coordinative unsaturation while simultaneously the activity was boosted by two

Table 1
Ethylene hydrogenation: summary of kinetic data^a (Fig. 2)

Activation	OCS, $\mu\text{mol g}^{-1}$	$10^4 k$ at 473 K ^a , $1 \text{ g}^{-1} \text{ s}^{-1}$	$10^2 r_0/\text{OCS}$ at 473 K ^b , s^{-1}	E_A , kJ mol^{-1}
V ₇₂₃	6.5	1.1	1.7	n.d.
V ₇₂₃ /R ₄₇₃	11	5.3	4.8	41
V ₇₂₃ /R ₅₇₃	28	34	12	34
R ₅₇₃	60	9.4	1.5	36
R ₅₇₃ /V ₇₂₃	29	770	254	n.d.
R ₆₇₃	42	91	21	n.d.

^a MoS₂ batch used—MoS₂(A₁) from Part I [13].

^b Extrapolated with an activation energy of 35 kJ mol^{-1} (V₇₂₃, R₆₇₃, R₅₇₃/V₇₂₃), or interpolated from Arrhenius curves.

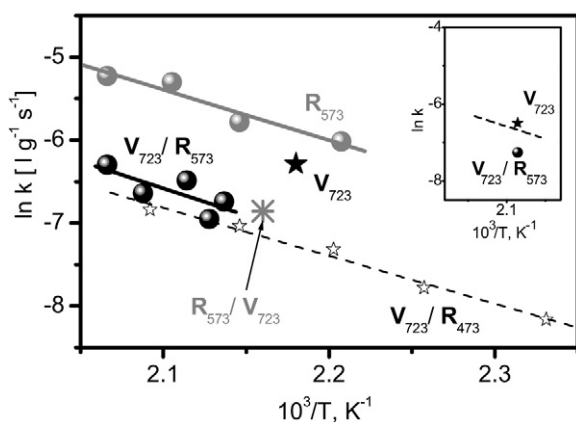


Fig. 3. *Cis-trans* isomerization of 2-butene over MoS₂. First-order rate constants measured after different activation treatments. MoS₂ batch used—MoS₂(A₁) from Part I [13]. For explanation of labels see Fig. 2a. Inset: Experiments with a different MoS₂ batch (MoS₂(A^{*})) from [13] with initially clean surface; dashed line, V₇₂₃/R₅₇₃ regression curve from main panel.

orders of magnitude. For the same OCS capacity, the rate constant after R₅₇₃/V₇₂₃ was as much as 30-fold that obtained with the reverse order of treatment (V₇₂₃/R₅₇₃). The effect was markedly larger than the change resulting from simply an increase in reduction temperature (R₆₇₃), which also led to enhanced hydrogenation activity with a diminished OCS capacity.

The ethylene hydrogenation was checked for a kinetic isotope effect by performing the reaction in H₂/D₂ mixtures of different H₂/D₂ ratios (using a MoS₂ batch labeled “MoS₂(B)” in Part I [13]). The results of the experiments performed at 463 K are displayed in Fig. 2b. It is obvious that the presence of D₂ did not change the reaction rate, because the curves for 100% D₂ and 10% D₂ are identical; the slight deviation with the 1:1 mixture is due to experimental reasons rather than to a kinetic isotope effect.

3.2. Isomerization of *cis-but-2-ene*

Cis-trans isomerization of *cis-but-2-ene* was studied at 423–473 K (Fig. 3, Table 2). Deactivation phenomena were weak under the conditions used here, and a 1-h treatment in 10% H₂/He at 473 K was sufficient to restore standard activity after each run. For this reaction, the reduction activation (R₅₇₃) yielded the highest catalytic activity, as opposed to ethylene hydrogenation. Again in strong contrast to hydrogenation, the

Table 2
Isomerization of *cis-but-2-ene*: summary of kinetic data^a (Fig. 3)

Activation	OCS, $\mu\text{mol g}^{-1}$	$10^3 k$ at 473 K ^a , $1 \text{ g}^{-1} \text{ s}^{-1}$	$10^4 r_0/\text{OCS}$ at 473 K ^b , s^{-1}	E_A , kJ mol^{-1}
V ₇₂₃	6.5	2.8	7	n.d.
V ₇₂₃ /R ₄₇₃	11	1.0	1.5	48
V ₇₂₃ /R ₅₇₃	28	1.3	0.75	54
R ₅₇₃	60	4.1	1.1	51
R ₅₇₃ /V ₇₂₃	29	1.3	0.75	n.d.

^a MoS₂ batch used—MoS₂(A₁) from Part I [13].

^b Extrapolated with an activation energy of 52 kJ mol^{-1} (V₇₂₃, R₅₇₃/V₇₂₃), or interpolated from Arrhenius curve.

activity decreased when thermoevacuation was applied after the reduction treatment (R₅₇₃/V₇₂₃), which boosted the hydrogenation activity dramatically. In *cis-trans* isomerization, the activity levels after V₇₂₃/R₅₇₃ and R₅₇₃/V₇₂₃ treatments were comparable (Fig. 3).

It is remarkable that the rate constant at 473 K obtained after different activation treatments differed only slightly (Table 2). Indeed, mere thermoevacuation V₇₂₃ led to an even higher activity compared with the same V₇₂₃ treatment followed by reduction. Correspondingly, the activity related to the OCS capacity (i.e., the rater per vacancy) was highest after thermoevacuation. Because the initial contaminations on the MoS₂ batch used were not completely removed by the V₇₂₃ treatment, with Mo(VI) oxide species retained on the surface [13], this experiment was repeated with a different MoS₂ batch for which a clean surface had been demonstrated by XPS (MoS₂(A₂) in [13]). The result of the catalytic test is shown in the inset of Fig. 3. Again, the isomerization activity was higher after mere thermoevacuation and decreased on subsequent reduction. The dashed line in the inset is the regression line for the activities measured after V₇₂₃/R₅₇₃ on our standard MoS₂ (obtained from the main panel). Obviously, this was somewhat more active than MoS₂(A₂) (by a factor of ≈2), but the response to the activation condition was the same and thus was not determined by oxide impurities remaining on the standard MoS₂ after V₇₂₃.

As shown in Fig. 3, the activation energy of *cis-trans* isomerization did not depend on the activation procedure and amounted to 51–54 kJ mol^{-1} . As for ethylene hydrogenation, this finding suggests that the isomerization site was the same on all surfaces.

3.3. H₂/D₂ isotope exchange

The kinetic data of the H₂/D₂ isotope exchange are summarized in Fig. 4 and Table 3. During the experiments, which were conducted mainly at 423–473 K, no deactivation was noted. The comparison between different activation procedures is shown in Fig. 4a. The ranking of rates achieved after the activations differed from that of the other two reactions. Whereas mere thermoevacuation rendered the least active surface as in the case of ethylene hydrogenation, the activities achieved after reduction at 573 K were virtually identical without or with previous thermoevacuation (Fig. 4a). Thermoevacuation after R₅₇₃, yielding a dramatic activity gain in hydrogenation, re-

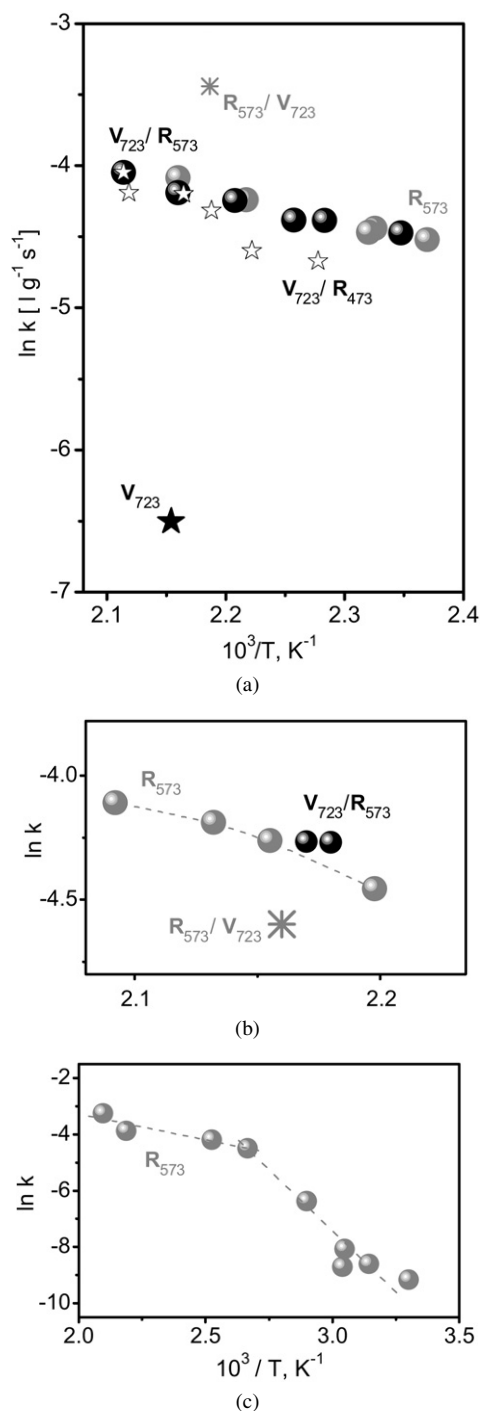


Fig. 4. H_2/D_2 isotope exchange over MoS_2 . First-order rate constants measured after different activation treatments. MoS_2 batch used— $\text{MoS}_2(\text{A}_1)$ from Part I [13]. (a) $c_0(\text{H}_2) = c_0(\text{D}_2) = 4 \text{ vol}\%$; (b) $c_0(\text{H}_2) = c_0(\text{D}_2) = 0.8 \text{ vol}\%$; (c) study of wide temperature range, $c_0(\text{H}_2) = c_0(\text{D}_2) = 4 \text{ vol}\%$. For explanation of labels see Fig. 2a.

sulted in only a moderate increase in H_2/D_2 scrambling activity compared with $\text{V}_{723}/\text{R}_{573}$ and R_{573} .

The results for H_2/D_2 exchange differed from those of the other reactions also in terms of divergence of activation energies after different treatments. Whereas rather low activation energies (15–18 kJ mol^{-1}) were found after the R_{573} and $\text{V}_{723}/\text{R}_{573}$ treatments, the data measured after $\text{V}_{723}/\text{R}_{473}$ ex-

Table 3
 H_2/D_2 scrambling: summary of kinetic data^a (Fig. 4)

Activation	OCS, $\mu\text{mol g}^{-1}$	$10^3 k$ at 473 K ^a , $\text{g}^{-1} \text{s}^{-1}$	r_0/OCS at 473 K ^b , s^{-1}	E_A , kJ mol^{-1}
V_{723}	6.5	1.5	0.4	n.d.
$\text{V}_{723}/\text{R}_{473}$	11	16.8	2.8	31
$\text{V}_{723}/\text{R}_{573}$	28	18.8 [15.8]	1.25	15
R_{573}	60	18.3 [≈ 16]	0.55	17.5 ^c [28]
$\text{R}_{573}/\text{V}_{723}$	29	34.5 [12]	2.1	n.d.

Measurements with $c_0(\text{H}_2) = c_0(\text{D}_2) = 4 \text{ vol}\%$, in brackets data for $c_0(\text{H}_2) = c_0(\text{D}_2) = 0.8 \text{ vol}\%$. For mass transfer influence on data—see text.

^a MoS_2 batch used— $\text{MoS}_2(\text{A}_1)$ from Part I [13].

^b Extrapolated with an activation energy of 15 kJ mol^{-1} or interpolated from Arrhenius curves, in brackets data from Fig. 4b, extrapolated with an activation energy of 28 kJ mol^{-1} .

^c 63 kJ mol^{-1} for 303 K < T < 373 K (Fig. 4c).

hibited a clearly greater increase of the rate constant with temperature and an activation energy of $\approx 30 \text{ kJ mol}^{-1}$. This may suggest the presence of mass transport limitations. Because the standard procedures used to identify such effects (i.e., decreased catalyst particle size for pore diffusion limitations, increased linear gas velocity for external mass transport limitations) could not be readily performed under the present experimental conditions, the problem was tackled by decreasing the intrinsic reaction rates; experiments were performed with lower H_2 (D_2) pressure (Fig. 4b) or over a very wide temperature range (Fig. 4c). With reduced H_2 (D_2) pressure, a higher activation energy of 30 kJ mol^{-1} indeed was observed (Fig. 4b, Table 3) in a series performed after R_{573} activation. A comparison between activation procedures also was made under these conditions. Whereas the identity of activities achieved by R_{573} and $\text{V}_{723}/\text{R}_{573}$ was fully reproduced, an unexpected behavior was observed with the $\text{R}_{573}/\text{V}_{723}$ sequence; the resulting reaction rates were once larger, once smaller than those found after R_{573} and $\text{V}_{723}/\text{R}_{573}$. These differences were moderate but clearly significant (Figs. 4a, 4b).

In the Arrhenius plot measured after R_{573} with 0.8 vol% H_2 (D_2) (Fig. 4b), a curvature can be seen; however, this is not significant at the given level of experimental scatter. Rate constants covering a wide temperature range of 303–473 K [activation R_{573} , 4 vol% H_2 (D_2)] are presented in Fig. 4c. The increased activation energy at low temperatures, and consequently the effect of mass transport at high temperatures, are quite obvious; the activation energy in the low-temperature range was on the order of 60 kJ mol^{-1} .

The uncertainty about the actual activation energy may have caused some error in the extrapolation of the rate constants to 473 K for the compilation in Table 3. But this error is not large, because the temperature differences encountered are small.

4. Discussion

The discussion in this section includes the characterization results reported in Part I [13]. As mentioned in the Introduction, XPS demonstrated that the surface of the MoS_2 batch used here ($\text{MoS}_2(\text{A}_1)$ from Part I [13]) was clean only after activations including reduction at 573 K (e.g., $\text{V}_{723}/\text{R}_{573}$, R_{573}),

whereas after V_{723} , some Mo(VI) oxide remained in the near-surface region, with sulfur present exclusively as sulfide. After V_{723}/R_{473} , the purity of the surface was not checked; however, the rather small OCS capacity may suggest that residual oxide species might have interfered with vacancy formation. However, because all reactions discussed here require coordinatively unsaturated Mo sites and do not proceed on nonactivated MoS_2 [14], we include data from the V_{723} and V_{723}/R_{473} activations in the discussion.

The edge planes of MoS_2 are capable of exposing Mo ions in various site structures, which are differentiated by, for example, the degree of coordinative unsaturation (1, 2, or 3 vacancies per Mo— 1M , 2M , or 3M sites). It has been proposed that the reactions studied here require sites of different Mo exposure, based on product distributions in tracer experiments combined with plausibility arguments [5]. According to these studies, olefin hydrogenation proceeds on 3M sites, H_2/D_2 exchange requires 3MH sites (i.e., 3M sites with one vacancy already occupied by adsorbed H), and *cis-trans* isomerization requires 2MH sites.

Reactions that use a different number of vacancies per Mo also should be distinguishable by their response to the variation of the degree of Mo exposure. This approach was used in a previous study [6], where the degree of Mo exposure was assessed by model calculations on the basis of the experimental S/Mo stoichiometry, and it was concluded that olefin hydrogenation requires triply unsaturated Mo ions (3M), whereas (*cis-trans*) isomerization proceeds on twofold or fourfold unsaturated Mo.

Our studies followed the same approach. Because of significant oxygen chemisorption and catalytic activity with MoS_2 that is not sulfur-deficient (Part I [13]), we believe that oxygen chemisorption cannot be disregarded as a measure of coordinative unsaturation. The problems caused by this are illustrated by comparing hydrogenation activities after V_{723}/R_{573} and R_{573}/V_{723} (Fig. 2, Table 1). It is obvious that both activations led to completely different site structures, even though the overall degree of Mo exposure (as measured by OCS) was identical. A detailed explanation for the drastic difference in the site structure after the treatments requires additional investigation; however, the pronounced differences in the catalytic activity patterns after the activations suggest some conclusions about the site structures and the active-site requirements of the test reactions.

Obviously, olefin hydrogenation was the reaction with the largest space requirement at the Mo site, with a rate constant exhibiting the most dramatic variation among the reactions studied, even without considering the R_{573}/V_{723} activation. Therefore, it is plausible to identify the hydrogenation site as a 3M center, as has been proposed earlier [5,6] and as also suggested by the rim site concept [16]. According to this concept, Mo ions capable of acquiring the required coordinative unsaturation are located at the rims of MoS_2 stacks. When the reaction rates measured in this study are related to the OCS capacity, this “turnover frequency” varies by two orders of magnitude. Because the invariability of the activation energy suggests the presence of only one type of active site, this indicates that other sites counted by OCS also may be converted into hydrogenation sites. The increased hydrogenation activity with the severity of

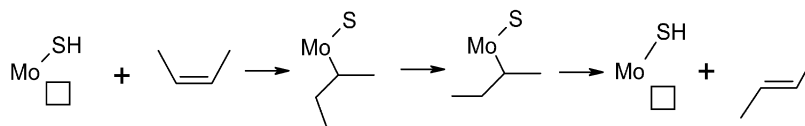
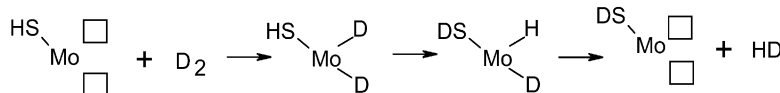
treatments (R_{673} , R_{573}/V_{723}) despite decreasing OCS capacity indicates a role of defect diffusion as well. Likely, smaller defects combine to form larger ones and migrate to the rim; other defects may escape into the bulk crystallite.

Cis-trans isomerization exhibited the least effect of activation treatment on the rate constant; it varied by a factor of ca. 3 (Table 2), compared with a factor of 700 in ethylene hydrogenation and a factor of 12 in H_2/D_2 scrambling (Tables 1 and 3). The response to the reductive activations differed from that with ethylene hydrogenation; whereas thermoevacuation before reduction (V_{723}/R_{573}) favored high hydrogenation activity, this treatment led to a less active state in *cis-trans* isomerization. The most remarkable feature was the high activity after V_{723} , which produced inferior activities in the other reactions. For the *cis-trans* isomerization, the rate constant after V_{723} was well within the range observed for the other activation treatments. The rate decreased with subsequent catalyst reduction; that is, the new vacancies formed hindered the isomerization reaction (Table 2).

The kinetic data for H_2/D_2 scrambling should be considered carefully, because most of the reaction rates reported in Fig. 4 and Table 3 were affected by mass transport limitations. Unfortunately, the well-characterized $MoS_2(A_1)$ batch was completed after the mass transport influence was clearly identified (Fig. 4c), thus precluding a comparison of activations on low-temperature kinetic measurements. Nevertheless, we can draw some important qualitative conclusions based on the existing data.

Based on the data in Fig. 4 and Table 3, we may infer that the measurements performed around 470 K at the higher H_2/D_2 concentration (Fig. 4a) were in the transition region between the kinetic and the fully mass-transfer controlled regimes, where the activation energy drops to 4–6 kJ mol $^{-1}$ [17]. This indicates that the surface reaction contributed significantly to the experimental rates even under these conditions, and much more so at the lower initial H_2/D_2 concentration (Fig. 4b). As long as a quantitative comparison is avoided, these data can be used to rank the effects of activation procedures, because experimental conditions affecting mass-transfer rates (e.g., gas velocities, particle sizes, bed dimensions) were kept constant during the measurements.

Therefore, we can safely conclude that the intrinsic H_2/D_2 scrambling activities achieved by the V_{723}/R_{573} and R_{573} activations were very close; indeed, their similarity was confirmed under conditions of different mass-transfer impact (Figs. 4a, 4b). This marks a clear difference from hydrogenation, in which activation by V_{723}/R_{573} was much more efficient than by R_{573} , as well as from *cis-trans* isomerization, where the reverse was found. The influence of a reduction subsequent to V_{723} further differentiated H_2/D_2 scrambling from *cis-trans* isomerization; the former was accelerated by R_{573} subsequent to V_{723} , whereas the latter was attenuated. The data related to the comparison between the V_{723}/R_{573} and R_{573}/V_{723} sequences are less clear-cut, with a slight preference for the latter at 4 vol% H_2 (D_2) but for the former at 0.8 vol% H_2 (D_2) (Figs. 4a, 4b). Although we propose a possible reason for this behavior later, these findings clearly demonstrate that these procedures had a

Scheme 1. *Cis-trans* isomerization of 2-butene.Scheme 2. H_2/D_2 exchange, half-cycle. (The analogous reaction with H_2 restores the initial state.)

similar, not different effect on H_2/D_2 scrambling activity. In summary, it can be stated that the response of H_2/D_2 scrambling to the surface modification introduced by the different activation treatments was between that seen for ethylene hydrogenation and *cis-trans* isomerization.

The sometimes drastic differences in the response of the test reactions to the activation treatments suggest that the differences between the active sites proposed in the earlier literature (e.g., ^3M for hydrogenation, ^3MH for H_2/D_2 scrambling, ^2MH for *cis-trans* isomerization [15]) may be too subtle to explain the experimental data obtained here. The formation of sites with greater sulfur deficiencies requires more drastic conditions. Thus, the tendencies for the formation of ^3MH sites and ^3M sites should be parallel at least to some extent; however, the activity patterns in hydrogenation and H_2/D_2 scrambling were clearly divergent. And although the formation of ^2M as well as of ^2MH sites should be favored by a reduction subsequent to the mildest activation (V_{723}), in fact the isomerization activity was suppressed by such a reduction treatment. Indeed, the elimination of active sites for *cis-trans* isomerization by a reductive treatment ($\text{V}_{723}/\text{R}_{573}$ vs V_{723} ; Fig. 3, Table 2) strongly suggests that this reaction proceeds on sites with less Mo exposure than needed for H_2/D_2 scrambling, which was boosted by the same reduction ($\text{V}_{723}/\text{R}_{573}$ vs V_{723} ; Fig. 4a, Table 3). Analogously, a thermoevacuation after reduction at 573 K (i.e., $\text{R}_{573}/\text{V}_{723}$) created new hydrogenation sites (Fig. 2, Table 1) but destroyed sites for *cis-trans* isomerization (Fig. 3, Table 2), whereas it had a moderate and somewhat indistinct effect on H_2/D_2 exchange (Figs. 4a and 4b, Table 3). This indicates that hydrogenation requires Mo sites with higher exposure than H_2/D_2 exchange, which is apparently intermediate in its requirement to the degree of unsaturation in the Mo coordination sphere. Therefore, in agreement with the view that hydrogenation proceeds on ^3M sites [5,6], we believe that ^2M sites are required for H_2/D_2 scrambling and that ^1M sites are required for *cis-trans* isomerization. The hydrogen involved in the latter reactions might be contributed by neighboring SH (or SD) groups instead of Mo-H species, which are viewed skeptically by theoretical chemists [7–12]. Schemes 1 and 2 detail these reactions.

Of course, these models should explain all of our experimental observations as well as the original models proposed by Tanaka did. A relevant fact is that *cis-trans* isomerization is dramatically suppressed in absence of gas-phase hydrogen even when the sample was activated in hydrogen previously.

The explanation for this effect is based on the observation that two-thirds of adsorbed exchangeable hydrogen was desorbed while a sample activated in H_2 at 573 K was cooled to room temperature in inert gas (Part I [13], Fig. 6). We may assume that SH groups adjacent to vacancies were more reactive and thus belonged to those that were removed during this desorption process, so that isomerization required the presence of hydrogen to restore them. Another important observation of the Tanaka group is that (in extrapolation to low conversions) D atoms were not introduced into the butene molecule when *cis-trans* isomerization was performed in D_2 . On a catalyst treated in hydrogen before the reaction (as necessary to create the Mo-H groups required in the earlier mechanism), SH groups also would be available around ^1M sites at the start of the reaction as long as they were not equilibrated with the D_2 -containing gas phase through exchange on adjacent larger Mo_{cus} sites and subsequent spillover.

Whether *cis-trans* isomerization and H_2/D_2 exchange also can proceed on sites with greater degrees of coordinative unsaturation than required according to Schemes 1 and 2 is relevant aspect of the assignment. The loss of *cis-trans* isomerization activity on further reduction of the V_{723} -activated surface strongly suggests that the higher exposed Mo_{cus} formed contributed little or no activity. A reactivity pattern with very high hydrogenation activity and low activity for H_2/D_2 scrambling but also complete absence of *cis-trans* isomerization was found in a study with mechanochemically activated microcrystalline MoS_2 [14]. This observation can only be explained by a complete inactivity of the highly exposed Mo sites for the latter reaction. Therefore, we can conclude that *cis-trans* isomerization is specific for the ^1M sites. On the other hand, H_2/D_2 scrambling was little affected by the $\text{R}_{573}/\text{V}_{723}$ treatment [enhanced or delayed, depending on the H_2 (D_2) partial pressure], which in turn produced a drastic increase in hydrogenation activity. This suggests that the reaction also may have proceeded on ^3M sites. Indeed, it would be difficult to understand why a reaction involving only hydrogen could not proceed in the presence of an additional vacancy in the Mo coordination sphere, whereas the more specific adsorption of a hydrocarbon moiety may be perturbed to a structure unfavorable for catalysis by the excessive space. The conflicting evidence regarding the effect of $\text{R}_{573}/\text{V}_{723}$ on the H_2/D_2 exchange activities at different partial pressures (Fig. 4, Table 3) may indeed arise from the presence of two types of sites: predominately ^3M sites after $\text{R}_{573}/\text{V}_{723}$ and predominately ^2M sites after R_{573} or $\text{V}_{723}/\text{R}_{573}$.

(*vide supra*), which may respond differently to changes in H₂ (D₂) partial pressure.

Another relevant question concerns the origin of the hydrogen added to the olefin during ethylene hydrogenation. Given the picture developed herein, it is not easy to understand why –SH groups adjacent to Mo_{cus} should not participate in ethylene hydrogenation, whereas they are thought to form the half-hydrogenated state in *cis–trans* isomerization. On the other hand, it is known that no d₁-ethane is formed on reaction in H₂/D₂ mixtures at low conversions [5]; that is, the H/D atoms added originate from the same H₂ (D₂) molecule. In Part I [13], we reported the presence of hydrogenation-active hydrogen on hydrogen-treated surfaces even after cooling in inert gas from 573 K. But its quantities determined after different activation procedures showed no correlation with the hydrogenation activities reported in herein (Table 1). Moreover, comparing the rates of ethane formation from surface hydrogen (data given in Part I [13]) with the initial rates measured in the kinetic runs at the same ethane concentrations demonstrated that the former were much lower than the latter; with strongly bound surface hydrogen (minimum adsorption temperature 473–573 K; cf. [13]), reaction rates between 0.01 (V₇₂₃/R₅₇₃) and 0.06 μmol g⁻¹ s⁻¹ (R₅₇₃/V₇₂₃) were obtained, compared with rates between 0.9 μmol g⁻¹ s⁻¹ (R₅₇₃) and 75 μmol g⁻¹ s⁻¹ (R₅₇₃/V₇₂₃) in the presence of gas-phase hydrogen. Likely, the reaction with this surface hydrogen is a side reaction that is not relevant in the presence of gas-phase hydrogen. The absence of a kinetic isotope effect in olefin hydrogenation (Fig. 2b) implies that all reactions involving H (including adsorption) are rapid. On the other hand, no hydrogen chemisorption could be traced in the pulse mode at temperatures up to 473 K in Part I [13], demonstrating that strong adsorbates were not formed at a sufficient rate under these conditions. But this does not mean that there was no interaction between gas-phase hydrogen and the Mo_{cus} sites; on the contrary, we believe that the whole of our data related to olefin hydrogenation and hydrogen adsorption suggest that the olefin was hydrogenated by a short-lived hydrogen adsorbate on ³M sites.

5. Conclusion

Activation treatments for unsupported MoS₂ consisting of thermoevacuation and hydrogenation steps create widely divergent Mo exposure (as detected by oxygen chemisorption) and have a varied impact on the catalytic activity in ethylene hydrogenation, *cis–trans* isomerization of 2-butene, and isotope exchange between H₂ and D₂. Reduction at 573 K followed by thermoevacuation at 723 K resulted in the highest hydrogenation activity by far, but demonstrated no particular advantage over other treatments for H₂/D₂ exchange and for *cis–trans* isomerization. Mere thermoevacuation at 723 K, resulting in inferior activities for hydrogenation and H₂/D₂ exchange, com-

peted well with the other treatments in *cis–trans* isomerization, and subsequent reduction deteriorated the catalyst performance in this reaction.

Our findings imply that all three reactions proceeded on different sites, with the olefin hydrogenation requiring the highest degree of coordinative unsaturation (i.e., 3 vacancies per Mo). They further suggest that H₂/D₂ exchange could proceed on sites with 2 vacancies per Mo, with adjacent –SH (SD) groups being involved in the mechanism, and that *cis–trans* isomerization requires a single vacancy with an adjacent –SH site. Sites with larger Mo exposure than stated herein may be suitable for H₂/D₂ exchange, but not for *cis–trans* isomerization. With increasing severity of the activation treatments, sites with small numbers of vacancies appear to combine and migrate toward the rims or escape into the bulk. Therefore, very high hydrogenation activities may be observed on surfaces where the oxygen chemisorption capacity is far from the maximum value observed after less vigorous treatments. These conclusions suggest that the combination of chemisorption techniques and test reactions may be a valuable tool for surface characterization for the type of material used in our study.

Acknowledgments

Financial support was provided by the German Science Foundation (Grants Gr 1447-15 and Be-1653/11). The authors thank Thomas Hanft for his help with the experiments.

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