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On the Strong Metal–Support Interactions Effects in the Reactions of Hydrocarbons

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Selectivity and activity in reactions of *n*-hexane, neohexane (2,2-dimethylbutane), and methylcyclopentane have been measured with Rh/TiO_2 and Rh/SiO_2 catalysts. A comparison is made between the effects of poisoning by carbon(aceous) layers and the Strong Metal–Support Interactions (SMSI) state. The changes in activity and selectivity lead to the conclusion that in the SMSI state the surface is covered by a blocking layer of a titanium oxide.

INTRODUCTION

The first observations of SMSI (Strong Metal–Support Interaction) effects did not attract particular attention (*1, 2*). However, when the Exxon group published their papers showing that the effect is quite general and can be quite pronounced, interest increased sharply (*3–5*). The results obtained since then on the SMSI effect have been exhaustively reviewed by Bond (*6*) at a recent symposium devoted to this topic and by Bond and Burch elsewhere (*7*).

Phenomenologically, one speaks of a SMSI effect when with a supported metal, a high-temperature reduction by hydrogen, followed by a high-temperature evacuation, suppresses appreciably the subsequently measured H_2 or CO adsorption. The region of reduction temperatures in which the SMSI effects are pronounced depends mainly on the oxide on which the metal is mounted (*3–5*). Another important feature is that a mild oxidation followed by low-temperature reduction almost restores the original adsorption capacity. There is at the moment quite extended information on the SMSI effects on chemisorption but the data on SMSI effects in catalysis are rather scarce (*7, 8*). This situation has led us to the study described by this paper. We expected that information on the effects caused by SMSI in the selectivity of metals might throw some light on the nature of SMSI.

There are essentially three types of explanation suggested in the literature for the SMSI effects:

1. During the high-temperature reduction, the metal or the support become loaded with strongly bound hydrogen (*2, 9*) which cannot be removed by evacuation and which prevents the subsequent low-temperature hydrogen—or CO—adsorption.

2. During the high-temperature reduction, the oxide is partially reduced so that its cations then possess unpaired *d*-electrons. It is proposed that in this state the lower oxide can influence the electronic and physical (e.g., shape of the particles) structure of the supported metal. Many authors speculate on an electron transfer from the oxide to the metal (*3–7*) although this is a much less obvious effect than usually expected (*10, 11*).

3. During the initial steps of the catalyst preparation or during the high-temperature reduction the support material encroaches on the outer metal surface (lower oxides evidently adhere better to the metal than oxides in their highest valency) (*4, 5*) and blocks it against the subsequent adsorption of H_2 or CO; admitted oxygen or water can cause a recrystallization of the spread material and regeneration of the adsorption ca-

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pacity of the metal after a repeated low-temperature reduction (*11–15*). Some oxides can probably be reduced to the metallic state and the element from the oxide can alloy with the metal supported by the oxide (*1, 16, 17*).

Since the selectivity of metals in hydrocarbon reactions can be influenced by the hydrogen surface concentration (for reviews see Refs. (*18, 19*)) one would expect that if the explanation of the SMSI effects as described in **1** above is correct, SMSI should lead to pronounced selectivity changes. These changes could be then similar to those caused by an increased hydrogen surface concentration.

The selectivity of various metals is different due to their different electronic structures. One would expect that the effects described in **2** above would cause similar changes in the selectivity to those observed when going in the Periodic Table from left to right (*6*).

The selectivity changes due to the effects in **3** above would depend on the way in which the oxide would be spread over the metal. When the oxide covers the metal by a more or less continuous layer, leaving only some patches of metal surface uncovered, then the selectivity changes should be much less pronounced than the drop in the activity. When the oxide is spread in such a way that it leaves on the metal surface ensembles of active sites smaller than on the oxide-free surface, the selectivity changes in the hydrocarbon reaction should be rather pronounced and should be reminiscent of those evoked by alloying Group VIII metals with the much less active Group IB metals.

Thus a selectivity study can be helpful in elucidating the problem of the SMSI effects. We have chosen the reactions of C_6 hydrocarbons to examine this.

EXPERIMENTAL

Apparatus, reaction conditions, and data evaluation. An open-flow system has been used to test the catalysts at atmospheric pressure. The reactor was operated at pseudo-differential conditions, wherever possible. The total flow rate (except in those experiments when it was intentionally varied) was 15 ml/min with the following feed ratios: H_2/*n*-hexane = 16; H_2/methylcyclopentane (MCP) = 17; H_2/2,2 dimethylbutane (neohexane) = 18. Hydrocarbons were obtained from Fluka (puriss.). When necessary corrections for impurities were made. Analysis of the products were performed by GLC. The following parameters were evaluated:

$$\text{conversion } \alpha = 100 \frac{\sum_{i=1}^{6} \sum_{j,j\neq k} iC_i^{(j)}}{6C_6^{(k)} + \sum_{i=1}^{6} \sum_{j,j\neq k} iC_i^{(j)}}$$

and

$$\text{selectivity } S_i^{(j)} = 100 \frac{iC_i^{(j)}}{\sum_{i=1}^{6} \sum_{j,j\neq k} iC_i^{(j)}},$$

where i = products with i carbon atoms
j = various isomers
k = hydrocarbon in the feed.

Other details of the data evaluation were the same as in our previous papers (*20, 21*). By the use of an "after-hydrogenation" reactor all alkenes were converted into alkanes and most of benzene was detected as cyclohexane.

Catalyst preparation. The catalysts have been prepared by impregnating the supports with small volumes of solutions of the required concentration of the metal precursor. As metal precursor a water solution of $RhCl_3 \cdot 3H_2O$ was used to prepare 2% Rh/SiO_2, 3% Rh/SiO_2, and 3% Rh/TiO_2 catalysts.

After drying overnight at 393 K in air, the catalysts were prereduced for several hours by H_2 (30 ml/min) at 525 K. TiO_2 used as a support was a Degussa product, containing both anatase and rutile. SiO_2 used was Kieselgel 60, from Merck, in 70–230 mesh (ASTM) fraction.

A weighed amount of the prereduced catalyst was introduced into a quartz reactor and reduced in situ for 14 h with H_2 (15 ml/min) at standard reduction temperature (573 K for TiO_2 supported catalysts, 723 K for SiO_2-supported catalysts). The activity and selectivity of the catalysts were then measured. Subsequently the titania-supported catalysts were subjected to reduction at elevated temperatures (933 and 1183 K), so that an SMSI effect was achieved (of probably varying degree) and activity and selectivity were redetermined. The catalysts were then oxidized *in situ* (1 h, 673 K) and the whole procedure was repeated.

For measurements with different hydrocarbons, fresh catalysts were always used. The metal particle size of the Rh/SiO_2 catalysts was checked by X-ray line broadening. Catalysts 2% Rh/SiO_2 and 3% Rh/SiO_2 reduced at 723 K showed particles of about 4.5 nm. After high-temperature reduction at 1138 K, TiO_2 was converted to a pure rutile structure, as judged by X-ray diffraction. With 3% Rh/TiO_2 the rhodium particle size was checked by high-resolution electron microscopy after low- and high-temperature reduction.

After low-temperature reduction (at 573 K) the average rhodium particle size was about 2 nm. After high-temperature reduction (1138 K) the average metal particle size had not increased. Thus sintering of the rhodium particles cannot explain the drop in activity accompanying the SMSI state. Although the average size of the Rh particles was unaffected by high-temperature reduction, the average size of the TiO_2 carrier particles increased by a factor of 4–5.

Since from the start of this study we suspected (and this suspicion was gaining successively more support as the work progressed) that the SMSI effect is mainly due to the blocking of the metal surface, we decided to compare the SMSI effects with those achieved by deposition of a (blocking) carbon(aceous) layer. In these experiments, the 2% Rh/SiO_2 was first reduced in a standard (723 K) way and tested in catalytic reactions. Thereafter, a mixture of N_2/*n*-pentane (ratio 5/1) was led over the catalyst at 723 K for 15 h. Then the catalyst was briefly rereduced at 470 K, for $\frac{1}{2}$ h, to remove the most reactive and volatile fragments. After that the standard catalytic test was performed.

RESULTS

3% Rh/TiO_2, *n*-Hexane

The results obtained with this system (146 mg catalyst used under standard measuring conditions), are presented in Table 1. It can be seen from a comparison of results at the same (or nearly the same) measuring temperature, that only the highest reduction temperature decreases the activity of the catalyst appreciably. The changes of selectivity parameters caused by the SMSI effect are only marginal and also the spectrum of products does not show any pronounced change (see Fig. 1).

2% Rh/SiO_2, *n*-Hexane

Results obtained with this system are in Table 2 (in the experiment the results of which are shown, 12 mg of the catalyst was used). It should be noted that this catalyst

TABLE 1

Influence of the Reduction Temperature of 3% Rh/TiO_2 on *n*-Hexane Reactions

Catalyst	T_{red} (K)	T_{meas} (K)	Conv. (%)	S_{cr} (%)	S_{iso} (%)	S_{cycl} (%)
3% Rh/TiO_2	573	470	7.6	97.9	1.5	0.6
	573	521	61.3	98.6	1.4	0.0
	573	574	60.4	96.3	3.0	0.7
3% Rh/TiO_2	933	475	10.5	99.4	0.6	0.0
	933	525	68.0	98.8	1.1	0.1
	933	576	60.9	97.6	2.5	0.9
3% Rh/TiO_2	1138	482	0.7	98.5	1.5	0.0
	1138	520	4.5	96.9	1.0	2.1
	1138	571	8.0	94.6	3.3	3.1

Note. T_{red}, reduction temperature (reduction time was 14 h); T_{meas}, measurement temperature; Conv., conversion; S_{cr}, selectivity for hydrogenolysis (cracking); S_{iso}, selectivity for isomerization; S_{cycl}, selectivity for dehydrocyclization.

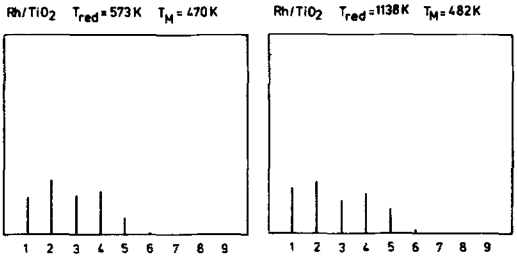


FIG. 1. Product distributions of the reaction of *n*-hexane on the 3% Rh/TiO_2 catalyst. (1–5) C_1–C_5, (6) 2MP, (7) 3MP, (8) MCP, (9) cyclohexane.

TABLE 2

Selectivity of 2% Rh/SiO_2 in *n*-Hexane Reactions

Catalyst	T_{red} (K)	T_{meas} (K)	Conv. (%)	S_{cr} (%)	S_{iso} (%)	S_{cycl} (%)
2% Rh/SiO_2	723	523	0.12	89.6	9.1	2.3
	723	578	0.45	77.6	8.6	13.8
	723	626	1.78	60.8	12.8	26.4

Note. For symbols see Table 1.

showed a more severe self-poisoning than the Rh/TiO_2 catalyst. Due to lower overall conversions (see Discussion) the selectivity in nondestructive reactions is higher.

2% Rh/SiO_2 and 3% Rh/TiO_2 in Methylcyclopentane Reactions

Results obtained with the two catalysts and MCP are compared in Table 3. The main reaction followed here is the ring opening. As can be seen, Rh catalysts reveal a strong preference for the "selective" mechanism (using the terminology introduced by Gault (*28*)). This means that there is a strong suppression of hexane formation leading to a selective deviation from the statistical thermodynamic ratio 2MP : 3MP : *n*-Hex = 1 : 0.5 : 1. This preference is only slightly suppressed and hexane formation enhanced when a SMSI effect is evoked. Again, the SMSI effect suppresses the overall activity but the selectivity changes are not very pronounced. It is re-

TABLE 3

Selectivity in Ring-opening of MCP as a Function of the Catalyst and the Reduction Temperature

Catalyst	Cat. weight (mg)	T_{red} (K)	T_{meas} (K)	Conv. (%)	S_{cr} (%)	2MP	3MP	Hex	$\frac{Hex}{2MP}$	$\frac{2MP}{3MP}$	$\frac{Hex}{3MP}$
2% Rh/SiO_2	11	723	480	7.0	0.3	74.5	23.8	1.7	0.02	3.13	0.06
		723	521	11.9	3.4	66.5	28.7	4.8	0.07	2.31	0.16
	7	723	527	4.6	6.2	63.1	31.6	5.3	0.08	1.99	0.16
		723	570	4.7	22.0	55.4	34.5	10.1	0.18	1.60	0.29
3% Rh/TiO_2	152	573	473	37.1	6.0	70.9	25.0	4.1	0.06	2.84	0.17
		573	523	44.9	26.0	65.9	27.9	6.2	0.09	2.36	0.21
3% Rh/TiO_2	101	573	473	1.7	1.7	70.6	24.2	5.2	0.07	2.92	0.20
diluted 25×		573	522	1.5	12.0	65.5	30.3	4.3	0.06	2.17	0.13
with TiO_2		573	571	1.1	29.0	54.8	39.0	6.2	0.11	1.41	0.16
3% Rh/TiO_2	152	933	474	4.3	2.0	68.8	27.6	3.6	0.05	2.49	0.12
		933	522	7.5	9.0	62.2	31.5	6.3	0.10	1.97	0.20
		933	571	7.6	27.0	53.3	35.7	11.0	0.21	1.49	0.31
3% Rh/TiO_2	152	1138	474	0.1	6.0	64.7	29.7	5.5	0.09	2.18	0.20
		1138	526	0.2	7.5	58.0	34.5	7.5	0.13	1.68	0.22
		1138	577	0.7	23.0	51.7	37.0	11.3	0.22	1.40	0.31

Note. 2MP, percentage of 2-methylpentane of the total ring-opening products; 3MP, percentage of 3-methylpentane of the total ring-opening products; Hex, percentage of *n*-hexane of the total ring-opening products. Other symbols as in Table 1.

TABLE 4

Selectivity in Ring-opening of MCP as a Function of the Catalyst Treatment

Catalyst and pretreatment	Cat. weight (mg)	T_{meas} (K)	Conv. (%)	S_{cr} (%)	2MP	3MP	Hex	$\frac{Hex}{2MP}$	$\frac{2MP}{3MP}$	$\frac{Hex}{3MP}$
2% Rh/SiO_2	7	544	5.3	12.0	59.5	33.3	7.2	0.12	1.79	0.22
		570	4.7	22.0	55.4	34.5	10.1	0.18	1.60	0.29
		601	3.2	46.0	53.6	37.7	8.7	0.16	1.42	0.23
2% Rh/SiO_2	171	539	2.2	50.0	47.5	40.3	12.2	0.26	1.18	0.30
after standard		570	8.4	40.0	49.2	37.3	13.5	0.28	1.32	0.36
poisoning		603	18.2	72.0	48.3	37.0	14.7	0.30	1.31	0.40

Note. Symbols as in Tables 1 and 3.

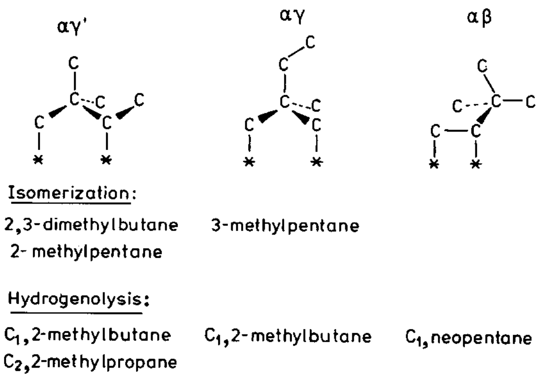
markable that comparable or even higher Hex/2MP ratios can be achieved by deposition on the surface of carbon(aceous) layers (see Table 4).

The increased selectivity for hydrogenolysis (cracking) is apparent, the fragments deposited continue to desorb (mainly as CH_4) during these measurements. When the catalyst is self-poisoned by using a *n*-pentane/H_2 mixture instead of *n*-pentane/N_2 mixture, this phenomenon does not occur, but also the highest Hex/2MP ratio achieved is lower. This shows that (a) Rh is not easily self-poisoned, like, e.g., Pt, (b) the amount of carbon(aceous) species needed to change the selectivity is rather high, and (c) hydrogen prevents a high "carbon" deposition from *n*-pentane on Rh catalysts.

3% Rh/TiO$_2$; 2,2-Dimethylbutane (Neohexane)

As shown in other papers (see Refs. (*22*, *23*)), reactions of this molecule allow us to draw conclusions about the way in which the molecule is adsorbed on the metal surface. The presence of certain products at lowest possible conversions (low conversion is essential to exclude consecutive reactions after readsorption) indicates adsorption in the various forms shown in Scheme 1. C_1 stands for CH_4 and C_2 for C_2H_6.

The amount of propane and butane among the products give us an idea of the extent of multiple (consecutive) reactions. At low conversions these multiple reactions take place during one sojourn of the mole-



SCHEME 1

cules on the surface. The results obtained with neohexane and the 3% Rh/TiO_2 and 2% Rh/SiO_2 catalysts are presented in Table 5. We observe here a clear selectivity effect of the SMSI; the $\alpha\beta$-hydrogenolysis is appreciably suppressed when the catalyst is brought into the SMSI state. Next to it, the usual suppression of the overall activity is also observed. Remarkably, the overall ($\alpha\gamma + \alpha\gamma'$)-selectivity is enhanced by SMSI but not the ($\alpha\gamma + \alpha\gamma'$)-isomerization relative to the ($\alpha\gamma + \alpha\gamma'$)-hydrogenolysis.

DISCUSSION

In the region of reduction temperatures where the SMSI manifests itself by a suppression of the H_2 and CO adsorptions (*3*, *7*), also the activity in hydrocarbon reactions is strongly affected by the high-temperature reduction (see above). For all molecules tested the activity of a catalyst in the SMSI state is lower (electron microscopy shows that the fall in activity is not caused by sintering of the rhodium particles).

In contrast to the activity changes, the selectivity changes by SMSI are not very pronounced and they are different for different molecules. The most pronounced shift in selectivity is that observed with neohexane, where the $\alpha\beta$ adsorption mode is suppressed and the $\alpha\gamma$ mode is relatively enhanced. It is worthwhile mentioning that also with regard to other changes, such as those evoked by alloying or by particle size variations, the $\alpha\beta$ adsorption mode reveals the highest sensitivity (*27*).

Not very pronounced but observable changes are also found with MCP. The carbon(aceous) layer and to a somewhat lesser extent the SMSI state, cause the same shift (in comparison with fresh surfaces of metals reduced at lower temperatures) in the product pattern; relatively more *n*-hexane and less 2MP is formed upon ring-opening, the ratio Hex/2MP and Hex/3MP increase and the ratio 2MP/3MP decreases.

TABLE 5

Selectivity in Neohexane Reactions as a Function of the Catalyst and the Reduction Temperature

Catalyst	Cat. weight (mg)	T_{red} (K)	T_{meas} (K)	Conv. (%)	$\alpha\beta_{cr}$ (%)	$\alpha\gamma'_{cr}$ (%)	$\alpha\gamma_{cr}$ (%)	($\alpha\gamma' + \alpha\gamma$) iso (%)	$C_3 + C_4$ (%)
3% Rh/TiO_2	1.3	573	524	1.0	72.2	8.4	7.0	4.6	7.9
		573	564	5.0	77.2	13.7	3.5	1.0	4.6
		573	596	6.2	70.5	20.4	3.1	0.7	5.4
		573	628	8.4	59.7	25.5	3.4	0.8	10.6
		573	673	11.6	53.8	17.9	2.7	6.0	18.9
3% Rh/TiO_2	19.2	1138	524	1.4	87.8	5.4	2.6	2.5	1.8
		1138	564	9.5	79.8	15.0	2.6	0.7	1.9
		1138	599	13.1	62.4	29.2	2.7	0.6	5.1
		1138	621	13.9	53.6	33.2	3.3	0.8	9.2
3% Rh/TiO_2[a]	19.2	1138	565	1.0	72.0	15.8	5.7	2.3	4.3
		1138	600	2.2	56.0	25.4	8.6	2.2	7.8
		1138	620	3.3	43.8	30.1	10.5	3.4	8.0
		1138	673	6.6	16.4	27.5	11.9	13.9	30.4
2% Rh/SiO_2	7	723	561	9.3	78.9	10.7	5.4	1.2	3.9
		723	596	8.2	75.2	16.0	4.6	0.2	4.1
		723	621	21.2	69.0	22.8	2.8	0.1	5.3

Note. For symbols see Table 1 and the text.

[a] This catalyst was reduced for 28 h.

The situation is thus almost similar with Rh (this paper) and Ir (*21*). Our previous paper (*21*) offered some speculations as to why the ring-opening of MCP leading to *n*-hexane might be easier on metal atoms at edges, corners, etc. than on the more flat parts of the metal surface. It is easier to eliminate the activity of atoms on the flat parts by depositing a blocking layer, than to do that with atoms of edges, corners, etc. (*24–27*). Deposition of a blocking layer should then lead to the suppression of the overall activity with a relative enhancement of the selectivity in *n*-hexane formation. It is not yet understood why the formation of 2MP is more suppressed than the formation of 3MP.

The least pronounced selectivity changes are observed with *n*-hexane. Also in this case the overall activity is suppressed. The situation with hexane reminds one of the observations by Sachtler and Somorjai (*26*). These authors found that when Au is spread over the Pt surface by alloying, the selectivity changes, hydrogenolysis is suppressed, and isomerization enhanced (see also Ref. (*27*)) for earlier papers on this subject). On the other hand, when islands of Au are grown epitaxially on Pt, only a nonselective suppression of activity occurs.

Our qualification of selectivity changes as being rather small with *n*-hexane requires one additional remark. In the temperature region applied here, the MCP and benzene concentrations in the products depend rather sharply on the apparent contact time. When the weight/flow rate [g ml^{-1} min] ratio (W/F) is varied between 0.5×10^{-3} and 5×10^{-3} the selectivity of the total dehydrocyclization drops from 20 to 7%. Most of the "missing" dehydrocyclization products appear as products of hydrogenolysis and to a lesser extent as isomerization products (a comparable effect has been observed in Ref. (*25*) with Pt catalysts). When the surface is blocked by an inactive material, such as a carbon(aceous) layer, the effective apparent contact time decreases also with constant W and F. This has to be kept in mind when interpreting some of the (small) changes in selectivity.

Let us now refer back to the Introduction and the three explanations suggested for the SMSI phenomena. If the main effect of SMSI were the storage of additional, strongly bound hydrogen, then provided this hydrogen were active one would expect changes in selectivity by the SMSI (*18*). For lower hydrocarbons up to hexane, a lower hydrogenolysis would be expected. The second explanation of the SMSI, mentioned in the Introduction, speculates on the changes in the electronic structure of (all, or most of) the surface metal atoms by the interaction of the metal particles with the lower oxide made from the supporting oxide upon high-temperature reduction. One speculates on an extended electron transfer from the oxide to the metal (see, for example, Ref. (*6*)).

In the line of these considerations one expects that Rh would simulate Pd when the SMSI state has been evoked. However, selectivity changes found in this study do not support such an idea. It seems that the third explanation, namely that in the SMSI state the metal surface is covered by a blocking layer of an oxide, in the form of islands, can best rationalize the results presented above.

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