Spillover of Hydrogen on Carbon and its Role in Catalytic Hydrocarbon Reforming

Kaoru Fujimoto

Department of Synthetic Chemistry, Faculty of Engineering, University of Tokyo
7-3-1, Hongo, Bunkyo-ku, Tokyo 113

(Received February 6, 1984)

The hydrogen in the gas phase and in the paraffin hydrocarbons become reversible at above 300°C when metal supported active carbon is incorporated in the system. The metal-active carbon promotes the transfer of hydrogen atom by normal and reverse spillover effects. Any material on active carbon which can dissociate molecular hydrogen to atomic hydrogen can be the gate of hydrogen spillover. In the case of catalytic dehydrogenation, paraffins are dehydrogenated by active carbon to form olefins or aromatics and surface hydrogen. The hydrogen atoms on the carbon migrate on its surface until they are transferred onto the metal particles where they combine to form hydrogen molecules which are desorbed into the gas phase. The metal particles on the carbon merely accelerate the desorption of hydrogen. The organo-sulfur compounds incorporated in a paraffin dehydrogenation system react with the hydrogen atoms on the metals to form hydrocarbons and hydrogen sulfide by hydrogenolysis. The hydrogen on the metal can be the hydrogen found in the gas phase and in the paraffin molecules. By regulating the hydrogen pressure (initial pressure 6 atm) and temperature (390°C), the hydrogenolysis of thiophene by decaline with a Mo-active carbon catalyst proceeds without any consumption of gaseous hydrogen.

1. Introduction

Metal catalysts are some of the most popular catalysts in the field of hydrocarbon reforming such as hydrogenation, dehydrogenation, isomerization and oxidation. Metal catalysts are used mostly as supported catalysts which are prepared by dispersing fine metal particles on porous materials (carriers) such as active carbon, alumina, silica gel and zeolites. The carrier of a supported catalyst has been considered as an agent for holding the fine metal particles on the catalyst surface, and the carrier itself has no special effects on the catalyst. Recently, many cases have been found in which catalytic features of supported metals were greatly affected by the carriers indicating that they not only enlarge the surface areas of the active components, but they interact with the components in several ways to affect their catalytic properties.

Interactions between carriers and active components in terms of catalysis are: (1) the electron donor-acceptor effect in the case of carbon or acidic and basic carriers, (2) the coordination effect in the case of a polymer support, (3) the SMSI (Strong Metal Support Interaction) effect, a recently developed concept and (4) the spillover effect, the subject of the present report.

Since the spillover phenomena themselves and some examples of catalytic reactions involving them have been reviewed elsewhere\(^1\),\(^2\) their details will not be repeated here. The present paper will deal only with the normal and reverse spillover of hydrogen on active carbon and the catalytic reforming of hydrocarbons promoted by these spillovers studied by the author.

2. Spillover of Hydrogen on Active Carbon

The first spillover phenomenon reported was the spillover of hydrogen on a Pt/Al\(_2\)O\(_3\)-WO\(_3\) system\(^3\). The spillover of hydrogen on a platinized carbon was also reported in the same year\(^4\). Although the rate and the amount of adsorption of hydrogen on carbon black was quite slow and insignificant as shown in Fig. 1, only 0.2 wt% of the supported platinum significantly promoted the rate and the amount of hydrogen adsorption. It is apparent from the figure that the amount of adsorbed hydrogen on the platinized carbon is more than ten times greater than the amount of platinum on it.
The phenomenon has been interpreted by the model shown in Fig. 2. The hydrogen molecules in the gas phase are adsorbed on the platinum and dissociated to hydrogen atoms. Then they move from the platinum surface to the carbon surface, migrate on it and then finally trapped on special sites on the carbon surface.

The spillover phenomenon on carbon has been studied in more detail by us and other researchers, and the following features were observed: (1) The rate of spillover is extremely slow at room temperature. It reaches an appreciable level at about 150°C and becomes quite high above 400°C. However, in the presence of H₂SO₄, the rate of hydrogen adsorption on the platinized active carbon is fairly high even at room temperature.

(2) Any material which can adsorb hydrogen dissociatively can be effective as the “gate” of hydrogen spillover. Examples of such gate materials are platinum group metals, nickel, cobalt, iron, copper, molybdenum, tungsten, vanadium, chromium and their sulfides.

(3) Transfer of hydrogen from the “gate” to carbon needs a “bridge” material such as carbon or carbonaceous materials.

(4) The rate of hydrogen spillover increases with increasing metal content whereas the equilibrium amount of adsorbed hydrogen is affected neither by the amount nor the kind of metal used.

(5) The equilibrium amount of hydrogen decreases with increasing adsorption temperature indicating positive heat of adsorption.

(6) The nature of the site of hydrogen acceptation is still not clear. The following facts strongly suggest that the surface radical site acts for accepting the spillover hydrogen atom. That is, the spin concentration of active carbon increases by evacuation at high temperatures and decreases with adsorption of hydrogen. The facts are most reasonably interpreted by the reaction shown below.

\[ X\cdot H \rightleftharpoons X-H \]  

3. Dehydrogenation and Transfer Dehydrogenation of Aliphatic Paraffins Catalyzed by Active Carbon

Active carbon catalyzes the dehydrogenation of aliphatic and alicyclic paraffins above 400°C. Products are mixtures of aliphatic mono-olefins and di-olefins having the same molecular structures as those of the feed hydrocarbons. In the case of paraffins whose main carbon skeleton consists of more than six carbon atoms, they form aromatic hydrocarbons as well as aliphatic olefins. For example, n-octane forms ethyl benzene and o-xylene with a mixture of C₈ olefines. It is apparent that active carbon is catalytically active for dehydrogenation and dehydrocyclization. However, its activity drops quickly with process time to reach, within one hour, a steady state value which is about one tenth or less of the initial value. The activity loss is not attributable to the covering of the active sites by carbonaceous materials. It should be noted that when the reaction is conducted in an inert carrier, hydrogen gas evolves from the catalyst bed long after the feeding of paraffin is stopped and the original level of catalytic activity is recovered. It strongly suggests that the activity loss can be attributed to the covering of the active sites by hydrogen and that the desorption of hydrogen from active carbon is slow compared to the dehydrogenation of paraffin molecules; thus, it must be the rate determining step. Therefore, any method which promotes the desorption of hydrogen on the carbon surface can be expected to enhance the catalytic activity of the carbon.

To verify the concept, an attempt was made to transfer hydrogen from isopentane to ethylene catalyzed by active carbon. The reaction is expressed as
\[ C_2H_4 + 2X \rightarrow C_2H_6 + 2X-H \]  
(2)

\[ 2X-H + C_2H_4 \rightarrow 2X + C_2H_6 \]  
(3)

where, \( X \) means the active site on carbon. Because the equilibrium of ethane dehydrogenation is more favorable to ethane than isopentane, the equilibrium of reaction (4) is more to the right. As shown in

\[ C_2H_4 + C_2H_6 \rightarrow C_2H_{10} + C_2H_4 \]  
(4)

**Fig. 3** the dynamic transient response to the pulse-wise addition of \( C_2H_4 \) in the system of isopentane and active carbon the dehydrogen of isopentane is promoted whereas the generation of hydrogenation gas decreased. The same phenomenon was observed for the steady state reaction, where, the yield of isopentens increased and that of hydrogen gas decreased with increased \( C_2H_4 \) concentration in the feed (Fig. 4). These data lead to the conclusion that the hydrogen atom on the carbon surface is picked up by ethylene as ethane to accelerate the removal of the hydrogen to promote the overall rate. An effective hydrogen acceptor can not only be ethylene but also any other material such as oxygen, nitrogen oxides, sulfur dioxide and butadiene which can react with hydrogen atom.

The hydrogen acceptor added lowers the activation energy of the transfer dehydrogenation as well as accelerates it. For example, the apparent activation energy of isopentane dehydrogenation decreased from 25 kcal/mol to 15 kcal/mol by adding oxygen gas, and the decrease was accompanied with three hold increase in the rate at 450°C. Taking into considerations of the promotional effects of a hydrogen acceptor suggests a reaction diagram as shown in **Fig. 5**, which indicates that the activation enthalpy of the second step (desorption of hydrogen from carbon surface) is lowered by the reaction of surface hydrogen with the acceptor molecule, and that when the reaction is fully accelerated the apparent activation energy approaches the activation enthalpy of the hydrogen transfer step from isopentane to the carbon surface. The above consideration has been theorized as follows: The apparent activation energy is expressed as equation (5) from its definition

\[ \Delta E_a = -R \frac{\partial \ln \nu}{\partial (1/T)} = RT \frac{\partial \ln \nu}{\partial T} \]  
(5)
Where $E_a$ is the apparent activation energy, $R$ is the gas constant, $\nu$ is the reaction rate and $T$ is the absolute reaction temperature. On the assumption that the steady state is attained between reactions (2) and (3) the rate $\nu$ is expressed by equation (6).

$$\nu = \frac{k_2 f_2(P_{RH}) f_3(P_A)}{k_2 f_2(P_{RH}) + k_3 f_3(P_A)}$$  \hspace{1cm} (6)

where $k_2$ and $f_2(P)$ and $k_3$ and $f_3(P)$ are the rate constants and rate equations of reaction (2) and reaction (3), respectively. Thus, $E_a$ is derived from equations (5) and (6) as equation (7) which can be rewritten as equation (8).

$$AE_a = \frac{AE_k f_3(P_A) + AE_k f_3(P_{RH})}{k_2 f_2(P_{RH}) + k_3 f_3(P_A)}$$ \hspace{1cm} (7)

$$AE_a = AE_k + \frac{AE_k - AE_3}{k_2 f_2(P_{RH}) + k_3 f_3(P_A)} k_3 f_3(P_{RH})$$ \hspace{1cm} (8)

Where $AE_a$ and $AE_k$ are the activation enthalpies of reaction (2) and (3), respectively. It is apparent from equation (8) that when reaction (3) is fully accelerated by adding a suitable hydrogen acceptor, the value of $k_3 f_3(P_A)$ is increased substantially to allow the value of $AE_a$ approach $AE_k$.

4. Reverse Spillover of Hydrogen and Catalytic Dehydrogenation of Paraffins

As was pointed out the slowest step in the paraffin dehydrogenation on a carbon catalyst is the desorption of hydrogen from the carbon surface. Thus the most effective way for promoting its catalytic activity is to accelerated the rate of hydrogen desorption from the surface. Figs. 6 and 7 show catalytic activities of metal-supported active carbon catalysts for isopentane and cyclohexane dehydrogenation as a function of metal loading. For both cases the catalytic activities are markedly enhanced by the supported metals. The findings can be reasonably interpreted in two ways. The first is that a supported metal or some metal-carbon complex which might be formed by the supported metal on the carbon surface may have catalytic activity. The second is that the supported metal may have some accelerative effect on hydrogen desorption. It should be noted that activities of fully promoted active carbon catalysts lie on some levels which depend neither on the amount nor the species of the supported metals. Furthermore, the data in Fig. 7 show that even sulfided metals, which were prepared by treating reduced catalysts with hydrogen sulfide at 400°C, exhibit sufficiently high promoting effects on catalytic activity even though the metal sulfides themselves show little activity when they are supported on silica gel.

In more detail, the behavior of hydrogen on the free and metal-supported carbon surface is illustrated as follows: In the case of metal-free active carbon the hydrogen atom which is transferred from a paraffin molecule by the catalytic action of active carbon moves onto its surface with a fairly low speed. Therefore, the chances of two hydrogen atoms colliding to form a hydrogen molecule are
quite small, when the concentration of hydrogen atoms on the carbon surface is rather small (ca $4 \times 10^{12}$ atoms/cm$^2$). However, on active carbon, which metal particles, which can adsorb hydrogen molecules dissociatively, the hydrogen atoms migrate on it can be transferred to the metal surface. Because of the high affinity of hydrogen atoms with the metal surface they can concentrated on the surface. The rate of hydrogen transfer from a metal to carbon was shown to be high$^5$; thus, the rate of the reverse process could be sufficiently rapid. Since the rate of recombination of hydrogen atoms into hydrogen molecules and the rate of desorption into the gas phase is quite high at reaction temperature, the desorption rate of hydrogen on the metal-supported carbon is effectively accelerated, that enables high catalytic activity. The phenomenon is just the reverse of spillover which has been described in the first chapter; thus, it is named by the author "revers spillover".

A reaction model of paraffin dehydrogenation promoted by the reverse spillover effect is illustrated by equations from (9) to (11).

$$C_nH_{2n+2} + 2X \rightarrow C_nH_{2n+2}X - H \quad (9)$$
$$2X - H + 2M \rightarrow 2X + 2M - H \quad (10)$$
$$2M - H \rightarrow 2M + H_2 \quad (11)$$

Where $X$ and $M$ mean the active site on the carbon and the supported metal particles, respectively. The energy diagram of the system is illustrated in Fig. 9. The promotional effect of the reverse spillover phenomenon is most suitably interpreted by the divide of the high activation enthalpy of direct hydrogen desorption from carbon into two steps with relatively low enthalpy as well as by the concentration of hydrogen on the metal surface. Thus, it could be concluded that the rate determining step on the fully promoted catalyst could shift from the hydrogen desorption step to the hydrogen transfer step (reaction (9)), whose rate should not be affected by the amount nor the species of the supported metal that coincided well with the experimental findings shown in Figs. 6 and 7.

The apparent activation energy shifts from 26 kcal/mol to 16 kcal/mol through the reverse spillover promotional effect, irrelevant to the metal species (Table 1), is also well explained by the shift of the rate determining step mentioned above. The value of 16 kcal/mol is very close to the value 15 kcal/mol, which was obtained by full promotion with the added oxygen for the transfer dehydrogenation of isopentane on metal-free active carbon.

Promotion by the reverse spillover effect is also supported by the following examples:

1. The catalytic activity of active carbon catalysts has an excellent relationship with the initial rate of hydrogen adsorption at 400°C (Fig. 10)$^5$. Since the initial rate of hydrogen adsorption is the rate of hydrogen transfer from a metal particle to the carbon surface, it should have a direct relationship to the rate of hydrogen transfer from carbon to metal particles. On the catalyst, where the hydrogen transfer from metal to carbon is rapid, the reverse process must also be rapid and, thus, the catalytic activity is high.

2. The catalytic activity of metal supported active carbon is suppressed by hydrogen molecule in the gas phase, proportionally to its pressure, whereas that of unsupported active carbon is not affected by hydrogen. This effect is explained by the normal spillover effect. That is, molecular hy-
hydrogen in the gas phase transfers to the carbon surface through the supported metal particles as hydrogen atoms, and cover its active sites to suppress activity. 

(3) The Temperature Programmed Desorption (TPD) spectrum of adsorbed hydrogen on active carbon shifts to lower temperature by the supported metals and by the increase in their content (Fig. 11). The last finding is a direct proof of the promotional effect of supported metals for hydrogen desorption, that is, the reverse spillover effect. The analysis of TPD spectra gives a range of activation energy distribution extending from 39 kcal/mol (at full coverage) to 49 kcal/mol (at zero coverage)^7). These values are almost independent of the species and the amount of supported metals. The increase in the metal loading shows a linear relationship to the frequency factor of the rate equation for hydrogen desorption. It indicates that the increase in the metal loading means the increase in the site of hydrogen desorption. The value of activation energy agreed well with that of hydrogen migration on the carbon surface (39 kcal/mol), as shown by other workers^9). Another important finding is that even supported metal sulfide can be the gates of normal and reverse spillovers of hydrogen when they are supported on the active carbon. It means that active carbon catalysts are sulfur tolerant.

5. Transfer Hydrodesulfurization with Cycloparaffin Hydrogen Donor

In accordance with the theory of paraffin dehydrogenation promoted by the reverse spillover effect, the hydrogen atoms from paraffin concentrate on the metal particles before they are desorbed into the gas phase. We have tried to utilize the hydrogen for hydrogenolyzing organo-sulfur compounds which exist in petroleum fractions. Since it has already been demonstrated by the present author that even metal sulfides can be the gate of hydrogen reverse spillover, molybdenum sulfides and other metal sulfides were selected as the active species for the hydrodesulfurization.

The reaction was proved to proceed both in the gas phase^15) and in the liquid phase^19). In the solid catalyzed gas phase reaction, several organo-sulfur compounds involving thiol, thioether and thiophenes were decomposed accompanied with de-
The data on thiophene hydrogenolysis as a function of reaction temperature is given in Fig. 12 which shows a material balance with respect to hydrogen. The difference between the amount of hydrogen consumed by hydrogenolysis of thiophene and that of hydrogen supplied by dehydrogenation of methyl cyclohexane to toluene is always surplus for the supply of hydrogen at above 400°C.

In the case of liquid phase reaction, decahydro-naphthalene (decaline) was used as an example of two ring naphthenes which exist in petroleum fractions. Decaline was shown to act as an effective hydrogen donor in the range from 330 to 390°C. It should be noted that several metals other than molybdenum were found to be effective catalysts when they were supported on active carbon and that they exhibited an excellent relationship between the activities of desulfurization and dehydrogenation\(^\text{17}\). As will be explained were in detail below, the hydrogen in the gas phase is reversible with that in decaline in the presence of a catalyst, so the relationship shown in Fig. 13 can reasonably be assigned to the reactions in equation (12).

\[
\text{C}_{16}\text{H}_{18} \leftrightarrow \text{C}_{10}\text{H}_{6} + \text{H}_2 + \text{C}_{6}\text{H}_6 + \text{H}_2\text{S} \quad (12)
\]

That is, when the hydrogen on the catalyst is picked up by thiophene its decrease on the catalyst surface is compensated by the hydrogen supplied from decaline. Reversibility of equation (12) is well supported by the fact that the degree of dehydrogenation is accelerated by three times with thiophene. Thus, it was concluded that the relationship shown in Fig. 13 demonstrated the desulfurizing ability of each metal species. The dehydrogenation of decaline itself proceeded on the carbon surface and its rate was higher than that of desulfurization.

The liquid phase transfer hydrogenolysis is largely affected by gaseous hydrogen as shown in Fig. 13 while the degree of dehydrogenation, which was defined as the g-atom of hydrogen supplied by decaline dehydrogenation divided by g-atom of hydrogen which can be supplied by decaline in the feed when it is completely converted to naphthalene, decreased with increasing hydrogen pressure in the gas phase. At the same time, the extent of thiophene desulfurization increased with increasing hydrogen pressure. These data give a "hydrogen consumption ratio" curve which is defined as the amount of hydrogen supplied by decaline dehydrogenation divided by the amount of hydrogen consumed by hydrogenolysis of thiophene as plotted in Fig. 14 against the initial pressure of hydrogen gas. The ratio decreases from 2.3 (at hydrogen free) to 0.8 (at 11 atm). It means that 2.3 times the amount of hydrogen consumed by thiophene hydrogenolysis was supplied by decaline under the hydrogen free condition. At 6 atm of hydrogen pressure, where the

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Dehydrogenation (mol%)</th>
<th>Desulfurization (mol%)</th>
<th>[C\text{\textsubscript{16}}H\text{\textsubscript{18}}]</th>
<th>[C\text{\textsubscript{10}}H\text{\textsubscript{6}}]</th>
<th>[C\text{\textsubscript{6}}H\text{\textsubscript{6}}]</th>
<th>[H\text{\textsubscript{2}}]</th>
<th>[H\text{\textsubscript{2}}S]</th>
</tr>
</thead>
<tbody>
<tr>
<td>430°C</td>
<td>11.1</td>
<td>6.9</td>
<td>15.0</td>
<td>7.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>450°C</td>
<td>22.0</td>
<td>10.3</td>
<td>34.4</td>
<td>18.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>480°C</td>
<td>41.9</td>
<td>29.2</td>
<td>63.4</td>
<td>45.3</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 2 Hydrogen Transfer Hydrodesulfurization of Organosulfur Compounds**

<table>
<thead>
<tr>
<th>Major Desulfurization Product</th>
<th>n-Pentane</th>
<th>Benzene</th>
<th>n-Butane</th>
<th>Ethylbenzene</th>
</tr>
</thead>
</table>

Catalyst: Mo-Active carbon, Contact time (W/F): 24 g-hr/mol, \(P_{H_2}=4/6\text{ atm}, \quad P_{MCH}=3/12\text{ atm}, \quad P_{prog.}=1/12\text{ atm from Ref. 15} \)

---

The liquid phase transfer hydrogenolysis is largely affected by gaseous hydrogen as shown in Fig. 13 while the degree of dehydrogenation, which was defined as the g-atom of hydrogen supplied by decaline dehydrogenation divided by g-atom of hydrogen which can be supplied by decaline in the feed when it is completely converted to naphthalene, decreased with increasing hydrogen pressure in the gas phase. At the same time, the extent of thiophene desulfurization increased with increasing hydrogen pressure. These data give a "hydrogen consumption ratio" curve which is defined as the amount of hydrogen supplied by decaline dehydrogenation divided by the amount of hydrogen consumed by hydrogenolysis of thiophene as plotted in Fig. 14 against the initial pressure of hydrogen gas. The ratio decreases from 2.3 (at hydrogen free) to 0.8 (at 11 atm). It means that 2.3 times the amount of hydrogen consumed by thiophene hydrogenolysis was supplied by decaline under the hydrogen free condition. At 6 atm of hydrogen pressure, where the
consumption ratio is about unity, the amount of hydrogen consumed equals to that of hydrogen supplied indicating that apparently no gaseous hydrogen was consumed during the reaction. This observation was also supported by the material balance of hydrogen during the reaction, as shown in Table 3. While the amount of hydrogen gas fed was, naturally, proportional to the initial hydrogen pressure, the amount of recovered hydrogen was almost the same independent of the hydrogen pressure. The amount of hydrogen gas recovered was in excess over the amount of hydrogen fed at below 6 atm whereas it was less than the hydrogen fed at 11 atm. The data in Table 3 agree well with the results in Fig. 14, a strongly supporting the reversible processes shown in reaction (12). It is confirmed by the data that on metal-supported active carbon catalysts a series of reactions, which are shown in equations from (13) to (16) proceed during the transfer hydrogenolysis of thiophene by decaline.

\[ C_{10}H_{18} + X \rightarrow C_{10}H_8 + (C_{10}H_{14}) + X-H \] (13)
\[ X-H + M \rightarrow X + M-H \] (14)
\[ M-H \rightarrow M + \frac{1}{2}H_2 \] (15)
\[ M-H + C_2H_5S \rightarrow M + C_2H_6(6-10) + H_2S \] (16)

Where, \( X \) and \( M \) mean the active site of carbon and metal, respectively. The reactions are illustrated in Fig. 15. As shown there it is possible, in the present system, to utilize both hydrogen gas and decaline as hydrogen sources by simply adjusting the reaction temperature and hydrogen pressure. It should be noted that to utilize decaline as a hydrogen source, the reverse spillover of hydrogen is essential.

6. Concluding Remarks

The present authors have succeeded in the reversible transfer of hydrogen between hydrocarbons and gas by utilizing the normal and reverse spillover effects on the metal-supported active carbon catalysts. The clarification of hydrogen behavior on the carbon during the reaction and that of the utilization of hydrogen atoms in the spillover process have successfully been presented.

The normal spillover phenomenon or that of the reverse spillover has been recognized and studied only since these two decades. Recent studies show that these spillover phenomena occur in extensively. It is expected that new catalyst systems or reaction systems would be developed.

References

白金等の触媒解離能を持つ物質を担持した炭素は比較的高温において一定量の水素を吸着する。吸着される水素量は担持される金属量よりはるかに多く、金属原子1個に1個の水素が吸着すると考えた場合の10倍以上に達し、炭素上に水素がふれ出したことを示す（Fig. 2）。この現象は通常スピローバーの現象と呼ばれるが、活性炭におけるスピローバーの主たる特徴は以下のようになされる。すなわち、(1) 水素の入口となるgate物質は必ずしも金属である必要はなく硫化金属等水素を解離する能力を持っている。すなわちスピローバーに関与するのは水素原子であり300°C以上で顕著となる。2) スピローバーは可逆現象であり高温、低圧の条件下では炭素表面の水素は金属を経由して気相へ脱離する。4) 炭素素面部上の素の受容サイトは表面ラジカルと推定される。

活性炭の表面そのものは400°C以上においてパラフィン炭素化水素から容易に水素を引き抜いてオレフィンあるいは芳香族炭素化水素となるが、活性炭素面での水素原子の再結合、脱離は遅い。しかしこの反応系にエチレンなどの水素受容体を導入すると表面水素は再結合することなくエチレンと反応してエチレンとなり脱離する（Fig. 4）。このため水素の脱離が促進され、その結果反応速度が数倍向上するとともに活性化学エネルギーも約10 kcal/mol低下する。この現象は表面水素とエチレンとの反応の活性化学エネルギーの脱離の活性化学エネルギーより低いとの前提で理論的に解析される。

金属、ミンネラル、ミリブデンあるいはその鉱物を担持した活性炭を触媒としてイソペンタンおよびシクロヘキサンの脱水素反応を行うと450°Cの触媒活性はおのおのの5〜10倍上昇（Table 1, Figs. 6, 7）。興味深いことに触媒活性は金属の担持率とともに上昇がするが、担持率1〜2％程度で頭打ちとなり、その天井値は金属の種類によらなかった。各種触媒の脱水素活性と400°Cにおけるスピローバーの初期速度の間には良好な相関が存在し、水素の移動速度と触媒活性の間に密接な関係が存在することが明らかにされた。これらの事実から金属担持活性炭の高い活性はパラフィン炭素化水素から移動した水素が炭素素面部上を移動して金属表面に移行し、そこで解離され、次いで再結合して分子となり気相へ脱離するというゆるゆる逆スピローバー効果によって水素の脱離が促進されていることが明らかとなった（Fig. 8）。この考察は活性炭表面の水素の昇温脱離ビークが金属の担持によって低温側へシフトする事実によっても支持される。

炭化水素中の水素を用いて脱硫反応を行ういわゆる水素移行脱硫上記の逆スピローバー現象を応用することを試みた。すなわち逆スピローバー効果によって炭化水素から水素を移動し、次いで金属素へ濃縮された水素を硫黄化合物と反応させる方法である。硫黄化合物金属-活性炭触媒によりシクロヘキサン、あるいはデカシシを水素供与体として、気相-液相で350〜450°Cで反応スムーズに進行することが示された。チオフェン-デカシシ系の液相反応において気相に水素が存在しないと390°Cではチオフェンの水素化分解に必要な水素の3.3倍の水素がデカシシの脱水素によって供給された。しかし適当な圧力の水素を共存させるとチオフェンの水素化分解率が一つとして（Fig. 14），反応前に仕込んだ水素とほぼ同量の水素が反応後に回収された（Table 3）。すなわちこの反応系では気相中の水素と炭化水素中の中の水素が触媒を介して可逆関係になり、硫黄化合物によって触媒上上の水素が消費されると逆スピローバー効果により炭化水素から水素が補給される（Fig. 15）。

Keywords
Catalytic dehydrogenation, Hydrodesulfurization, Hydrogen donor solvent, Metal supported carbon, Reverse spillover, Spillover