Mobility of hydrogen species on Ni supported catalysts

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Abstract. A previously developed theoretical model has been used to evaluate metal to support transport rate coefficients of spilt over hydrogen species in case of Ni supported catalysts. Four Ni/oxide (Ni/Cr₂O₃, Ni/ZrO₂, Ni/SiO₂, and Ni/MgO) catalysts were investigated by isotopic transient kinetic method for H/D exchange reaction. A good agreement between experimental data and theoretical ones has been put into evidence, both cases showing an important influence of oxide nature on the quantity of spilt over hydrogen. Fitting the experimental with the calculated theoretical data permitted the evaluation of transport rate coefficients from the spillover initiator (metal) to the acceptor of migrating species (the oxide support).

1. Introduction
Mobility of species on the catalyst surface is a well-known phenomenon in heterogeneous catalysis. These mobile species can be reactants, intermediates as well as reaction products. This mobility is a result of chemisorbed species on a metallic surface that migrate on the support without any loss of activity. This phenomenon is termed spillover and has been observed for several species such as hydrogen, oxygen, nitrogen, carbon monoxide or other small organic species [1, 2].

Ni supported catalysts are known to be very active hydrogenation catalysts. Moreover, hydrogenation catalysts have been demonstrated to be hydrogen spillover initiators due to the presence of even small amounts of metal nanoclusters [3]. In general, hydrogen spillover leads to the formation of new OH groups on the support, as oxygen ions serve as acceptors of hydrogen species (atoms or ions). Thus, the effectiveness of spillover to an oxide support is determined by the hydrogen affinity of the acceptors on the support. However, hydrogen migration from the metal initiator to the support as the acceptor is very difficult to put into evidence as there is a continuous migration of species and oxide supports already contain hydroxyl groups. On the contrary, use of hydrogen isotopes (which present same chemical potentials, but differ in mass) permits ‘marking’ the migrating species. Thus, H/D isotopic exchange reaction is a very relevant solution for the investigation of hydrogen spillover on Ni supported catalysts. Moreover, use of isotopic exchange reaction has been previously reported for hydrogen (H/D) as well as for oxygen (¹⁶O/¹⁸O) as a tool for the study of surface dynamics [4, 5].

2. Experimental
For the purpose of this work, four nickel/oxide catalysts (80 wt % Ni), prepared by co precipitation, were investigated. The characteristics of these Ni supported catalysts are presented in table 1. These catalysts were tested in the H/D exchange reaction by Steady State Isotopic Transient Kinetic Analysis (SSITKA), which implies following up the evolution in time of the involved species until they reach steady state.
The experimental set-up consisted in a gas supply unit, a plug flow reactor and a quadrupole mass spectrometer (QMS) (figure 1). The gas supply unit was able to deliver pure Ar, H\textsubscript{2}, and D\textsubscript{2} or any mixture of these gases. The reactor consisted in a cylindrical furnace, 11 cm of length, into which was placed 1 g of Ni catalyst. The catalyst was first activated in hydrogen, for 10 hours at 350°C, and then the temperature was reduced to the operating temperature (50°C, 100°C, 150°C, 200°C, 250°C and 300°C respectively). A sequence of 3 gas compositions was passed over the catalyst bed. In the first step the gas consisted in a binary mixture of 2 vol% D\textsubscript{2} in Ar, which was maintained until the concentration of D\textsubscript{2} in the effluent gas reached steady state. The second gas switch of pure Ar was maintained until no peak of D\textsubscript{2} or HD was detected. In the third sequence, a binary mixture of 2 vol% H\textsubscript{2} in Ar was passed over the catalyst. The evolution in time of the isotopic species was recorded by the online QMS after switching to the last gas mixture.

![Figure 1. Scheme of the experimental set-up.](image1)

![Figure 2. MS diagram for Ni/MgO at 250°C.](image2)

### 3. Results and discussions

An experimental MS diagram for Ni/MgO at 250°C is presented in figure 2. The last feed switch being H\textsubscript{2} in Ar, one would expect H\textsubscript{2} peak to be the first to appear in the MS diagram. The sequence of hydrogen species may be explained as follows. (a) During the first step (D\textsubscript{2} + Ar), all H chemisorbed on the metal and all H from the oxide surface as OH was replaced with D by H/D exchange. (b) During the second step, when pure Ar is passed over the catalyst, all H from the metal is washed away, while the OD adspecies on the support remain unchanged. (c) Finally, during the third sequence (H\textsubscript{2} + Ar) H is chemisorbed on the free metal surface, after which it spills over the oxide support. H/D exchange between the spilt over H and OD adspecies takes place on the support. D thus liberated from the support passes to the metal by reverse spillover and then desorbs into the gas phase. Because of the increasing probability for D species to get back on the metal, the first species in the effluent gas to be monitored are those containing D (D\textsubscript{2} and HD).

The MS diagrams were integrated in order to evaluate the quantity of deuterium desorbed from the support (table 1). For each of the four catalysts taken into account, an increase in operating temperature leads to a decrease of desorbed deuterium from the oxide support.

The experimental data were compared with theoretical curves calculated by means of an analytical model previously developed [6]. This theoretical model considers that in the catalyst bed hydrogen can be present in three phases: (i) in gas phase; (ii) chemisorbed on metal; and (iii) as OH/OD on the support. This analytical model based on mass balance equations for hydrogen species in the 3 phases was implemented and solved in MATLAB using the finite difference method. A good agreement between experimental and theoretical data was revealed, for each of the four Ni/oxide catalysts, and at each operating temperature. An example of such an agreement is presented in figure 3.
Table 1. Specific volume of desorbed deuterium.

| Temperature (°C) | \( V_{\text{des}} \) (cm\(^3\) D/m\(^2\) support) | Ni/Cr\(_2\)O\(_3\) | Ni/ZrO\(_2\) | Ni/SiO\(_2\) | Ni/MgO |
|-----------------|---------------------------------|----------------|-------------|-------------|--------|
|                 | \( S_{\text{Ni}} \) = 29.7 m\(^2\)/g | \( S_{\text{Ni}} \) = 19.4 m\(^2\)/g | \( S_{\text{Ni}} \) = 61.9 m\(^2\)/g | \( S_{\text{Ni}} \) = 41.4 m\(^2\)/g |
| 50              | 0.191                           | 0.386          | 0.209       | 0.426       |
| 100             | 0.186                           | 0.329          | 0.161       | 0.408       |
| 150             | 0.170                           | 0.310          | 0.136       | 0.389       |
| 200             | 0.166                           | 0.295          | 0.109       | 0.259       |
| 250             | 0.152                           | 0.196          | 0.094       | 0.293       |
| 300             | 0.130                           | 0.162          | 0.110       | 0.294       |

\( a \) Ni surface area; \( b \) B.E.T. surface area.

Figure 3. Comparison of experimental data with the analytical model for Ni/ZrO\(_2\) at 250°C.

Fitting the experimental data with the calculated curves, for each catalyst and at each operating temperature, permitted the determination of rate coefficients for the transport of hydrogen species from metal to support and vice versa. This rate coefficient is actually a resistance opposed to transport of species from one phase to the other, meaning that a greater value of the rate coefficient leads to a lower quantity of hydrogen which migrates between the metal and the support in either way. Except for the Ni/SiO\(_2\) catalyst, the calculated transport rate coefficients are in agreement with the calculated volumes of desorbed deuterium from the oxide support (figure 4 and figure 5).

The low rate coefficient in case of Ni/MgO could be accounted for the basic character of the oxide, that is O\(^2\)) from its structure easily bonds to hydrogen species present in the catalyst space. This means that a greater quantity of hydrogen spills over onto MgO, the support being thus able to desorb a larger volume of deuterium afterwards (for the case of the experiment described before). Cr\(_2\)O\(_3\) and ZrO\(_2\) present an amphoteric character, which means that the electronic properties of the oxides do not easily permit the formation of OH or OD species on the surface. Larger transport rate coefficients in case of Ni/Cr\(_2\)O\(_3\) and Ni/ZrO\(_2\) catalysts, leading to smaller volumes of desorbed deuterium might be thus explained. The exception recorded in case of Ni/SiO\(_2\) might be caused by the fact that Si is a
semimetal, while $\text{SiO}_2$ presents an acid character. Moreover, virtual immobility of silanol groups ($\text{Si-O-H}$) was previously reported [4].

![Figure 4. Metal to support transport rate coefficients at 250°C.](image)

![Figure 5. Specific volume of desorbed deuterium from the oxide support at 250°C.](image)

### 4. Conclusions
Investigations on spillover of hydrogen species in Ni/oxide catalysts have shown that both temperature and nature of oxide support influence the mobility of species. Metal nanoclusters in the catalysts initiate hydrogen spillover, while the oxide support acts as the acceptor of these species. The quantity of spilt over hydrogen on the oxides differs significantly in case of the four catalysts taken into account. Experimental data as well as theoretically calculated ones have proven this fact as the magnitude of transport rate coefficients for hydrogen migrating from metal to support and vice versa are correlated with the volumes of desorbed deuterium from the oxide supports. Thus, the physico-chemical properties of the support are of great importance in the design of efficient heterogeneous catalysts. Further investigations on hydrogen spillover considering the electronic interactions between the activated species and the support, as well as those between the metal and support are needed.

### References
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