Effect of alloying on carbon formation during ethane dehydrogenation

Anne Krogh Rovik, Søren K. Klitgaard, Søren Dahl, Claus Hviid Christensen, Ib Chorkendorff

Center for Individual Nanoparticle Functionality CINF, Department of Physics, Technical University of Denmark, DK-2800 Kgs. Lyngby, Denmark
Center for Sustainable and Green Chemistry, Department of Chemistry, Technical University of Denmark, DK-2800 Kgs. Lyngby, Denmark
Haldor Topsøe A/S, Nymøllevej 55, DK-2800 Kgs. Lyngby, Denmark

ABSTRACT

The structure sensitivity of different transition metals in the hydrogenolysis, dehydrogenation, and coking reactions during ethane conversion has been investigated. The investigated metals, Ni, Ru, Rh, and Pd, are co-impregnated with Ag onto an inactive MgAl2O4 spinel support and tested in the conversion of ethane. A tendency is clear for all catalysts: In the first period of time 100% ethane is converted and roughly half of the carbon is converted into coke and deposited on the catalyst. The other half of the carbon is converted into methane. The active sites in the hydrogenolysis are blocked by coke during the initial period where after dehydrogenation of ethane is observed. It has previously been predicted in surface science studies that Ag covers the steps of certain transition metals. Here it is documented that the hydrogenolysis and coking reactions are significantly suppressed by co-impregnation of Ag and Ni. The effect of Ag is limited for Ru since the active sites are self-poisoned by carbon; nor for Rh/spinel is the effect observed, which is possibly due to island formation of Ag on the terraces of the Rh metal. A prolongation of the initial period with hydrogenolysis is observed for Ag/Pd/spinel due to an alloy formation of Ag and Pd at these conditions. From our results it can therefore be concluded that hydrogenolysis mainly takes place on the steps and kinks of the transition metal particles, dehydrogenation reactions mainly takes place on the terraces, and coking is significantly reduced by covering the steps sites by Ag. This important information can be used in designing new catalysts with improved selectivity and stability.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Ethene is an important commodity chemical, which is used as feedstock for many chemicals and polymers. Today ethene is mainly produced by steam cracking of naphta while the non-oxidative dehydrogenation of ethane to ethene is of limited commercial interest due to thermodynamic constraints. Coking of the catalyst in the direct dehydrogenation reaction also leads to relatively short lifetimes of the catalyst. In spite of the limited commercial interest the non-oxidative dehydrogenation of ethane is an interesting reaction for the investigation of the properties of different catalysts. The rather simple reaction can elucidate the role of, e.g. step or kink sites on different transition metals impregnated on an inactive carrier. This important information can be used in designing new catalysts with improved selectivity and stability.

The fact that steps and kinks on a metal surface play a significant role in heterogeneous catalysis has been known for many years. More than 30 years ago Blakely and Somorjai demonstrated that steps and kinks on a well-defined platinum surface enhanced the hydrogenolysis of cyclohexane to hexane whereas the dehydrogenation reaction was unaffected by the step density [1]. Equivalent studies were made by Sinfelt [2,3] where the dehydrogenation of cyclohexane was unaffected by the addition of Cu to Ni or Ru while the hydrogenolysis of ethane was reduced. In contrast to Somorjai, Sinfelt explains the effect with electronic interactions between the metals and geometric effects without mentioning the surface structure of the catalytic metals. Several studies on the role of steps has been made since, see Ref. [4], e.g. on Ru in the ammonia synthesis [5,6], the effect with and without sulphur in the decomposition of methane and CO [7–12], and the effect of step sites in the dehydrogenation of ethane [13]. The hydrogenolysis of ethene on Cu-Ru/SiO2 and Ag-Ru/SiO2 has also been investigated by Smale and King [14–16]. According to their experiments Ag acts as an inert site blocker on the low-coordination sites of the Ru metal. They conclude that the hydrogenolysis reaction indeed is structure sensitive. Smale and King conclude that defects or steps are the most active sites for the desorption of weakly adsorbed hydrogen, while cleaving the carbon–carbon bond mainly takes place on the terraces. Vang et al. [13] investigated the ethane hydrogenolysis reaction on 1 wt% Ni/spinel and 0.1 wt% Ag–0.9 wt% Ni/spinel. By combining scanning...
tunnelling microscopy, density functional theory (DFT) calculations, and integral plug flow reactor experiments Vang et al. was able to elucidate the effect of the step sites. According to Ref. [13] step edges have higher activity for decomposition of ethene compared to the terrace sites and the effect is more pronounced for C–C bond breaking compared to C–H bond breaking. By selectively covering the step sites by Ag atoms the rate constant for ethane hydrogenolysis was reduced by an order of magnitude. This is in contrast to the conclusions of Smale and King [14,15], but this clearly elucidates the role of the step sites in the C–C bond breaking reaction.

The role of step sites in carbon formation and thereby deactivation of the catalyst has been investigated by several groups. DFT calculations by Bengaard et al. [17] reveal that the nucleation of graphite primarily takes place at the step sites of Ni where after the carbon migrates to the terraces. Covering the step sites by, e.g. Au suppresses graphite formation significantly [18]. Parizotto et al. [19] have strongly suppressed the formation of graphitic carbon in the steam reforming of methane on Ni/Al2O3 by co-impregnation of Ag which is expected to act very similar to Au. Production of whisks is observed by transmission electron microscopy (TEM) on Ni/Al2O3 whereas the amount of carbon filaments was negligible on the Ag catalysts. Coke formation can therefore be suppressed by co-impregnation of Ag on the Ni catalyst leading to longer lifetimes of the catalyst.

In literature there seems to be an agreement that the step sites play a significant role in catalysis [5–10]. But apparently there is also some disagreement to which sites are active in the C–C bond scission reaction (hydrogenolysis) and which sites are the most active in the C–H scission (dehydrogenation) [13–15].

Here we wish to elucidate the role of steps and terraces in the conversion of ethane on a number of transition metals that displays very different behaviour which can be explained in terms of their alloy and segregation towards Ag. This is done by co-impregnation of Ag on Ni, Ru, Rh, and Pd onto the inactive MgAl2O4 spinel support and investigating the effect on activity, selectivity, and coking of the catalysts.

2. Materials and methods

2.1. Catalyst preparation

The catalysts were prepared by incipient wetness impregnation. The carrier MgAl2O₄ spinel was crushed and sieved to the desired particle size of 212–355 μm and afterwards dried overnight at 393 K. The metals were introduced by incipient wetness impregnation of aqueous solutions of Pd(NO₃)₂•2H₂O, Rh(NO₃)₃•xH₂O, Ni(NO₃)₂•6H₂O or Ru(NO)(NO₃). The Ag was introduced by co-impregnation of aqueous solutions of AgNO₃ and the respective metal nitrate. The impregnated samples were dried at 393 K over night and calcined at 673 K for 4 h. The samples all have the same molar metal content of 3.4 × 10⁻⁴ mol/g catalyst and a metal to silver molar ratio of 5:1.

2.2. Catalytic tests

The catalytic tests were carried out in a plug flow reactor. Prior to the tests 400 mg of the catalysts were diluted with 400 mg of quartz of the same sieve fraction. The quartz reactor tube had an inner diameter of 3.7 mm and the length of the catalyst bed was 60 mm. The catalysts were activated for 2 h in a flow of hydrogen (675 mL(SATP)/h) at 823 K. Hereby the metal oxides were reduced to the metallic state.

The catalytic tests were carried out at atmospheric pressure at 823 K. The ethane was diluted in Ar (9.7 vol% ethane in Ar) and the total ethane/Ar flow was 1000 mL(SATP)/h. These gases were sent to an on-line coupled HP6890A gas chromatograph, separated by a HP-PLOT Q and a HP-PLOT Mole Sieve column, and analyzed by a Thermal Conductivity Detector (TCD) and a Flame Ionization Detector (FID) in series. All piping and valves were heated to around 473 K to avoid condensation, even though the only products observed are methane and ethane.

The conversions (X) are calculated from the TCD results due to the internal standard, which is only observed in the TCD. The selectivities (S) are calculated from the FID results. The calculations are shown in Eqs. (1) and (2):

\[ X = \frac{100\% \cdot \left( F_{\text{ethane},0} - F_{\text{ethane},t} \right)}{F_{\text{ethane},0}} \]

\[ S = \frac{100\% \cdot \sum_{\text{products}} \frac{RF_{\text{product}}}{RF_{\text{ethane},0}}}{RF_{\text{ethane},0}} \]

The coke deposition on the catalysts (C) at a specific time on stream (TOS) is calculated from the TCD results, since the TCD detects the internal standard Ar:

\[ C = \frac{100\% \cdot \left( \frac{2 \cdot F_{\text{ethane},0} - \sum_{\text{products}} X_{\text{C, compound}} \cdot RF_{\text{compound}}}{RF_{\text{ethane},0}} \right)}{RF_{\text{ethane},0}} \]

F<sub>ethane,0</sub> is the molar flow of ethane into the reactor. RF<sub>ethane</sub> is the response factor for ethane compared to Ar. A<sub>ethane</sub> is the area of ethane in the TCD. F<sub>Ar</sub> is the molar flow of Ar. A<sub>Ar</sub> is the area of Ar in the TCD. A<sub>product</sub> is the area of a compound in TCD or FID. RF<sub>product</sub> is the response factor for a product compared to Ar. X<sub>C, compound</sub> is the number of carbon atoms in a compound. RF<sub>compound</sub> is the response factor for a compound compared to Ar. A<sub>compound</sub> is the area of a compound in the TCD.

2.3. TPO

Immediately after the test, TPO was carried out in the same setup by flowing 2 vol% O<sub>2</sub> in Ar through the catalyst and ramping the temperature by 0.5 K/min from 473 to 1073 K. The flow of O₂/Ar was 6400 mL/h(SATP) for all catalysts except Pd/spinel and Ag-Pd/spinel. Here the flow was 9000 mL/h to ensure a complete combustion of the large coke deposits on the catalysts. The amount of CO<sub>2</sub> was analyzed by the same GC setup as in the tests. No CO was detected due to a complete combustion of the carbonaceous species in a surplus of oxygen. No H₂O was observed from oxidation of hydrocarbons since the HP-PLOT Mole Sieve column, used for separation of Ar and CO, absorbs any humidity from the gas stream.

The total carbon deposition is determined by temperature programmed oxidation. The area under the TPO curve (CO₂ signal vs. time) is proportional to the total amount of carbon deposited.

2.4. TEM

The catalysts were also investigated by TEM using a JEM 2000FX microscope operated at an accelerating voltage of 300 kV. The ground samples were suspended in ethanol and put on a 300 mesh copper grid coated with a holey carbon film.

2.5. TPR

Temperature programmed reduction is performed on a Micromeritics Autochem II 2920 equipped with a TCD detector. The temperature ramp and the hydrogen flow used are exactly as in the pretreatment of the catalysts. That is, heating from ambient temperature to 823 K by 20 K/min. The temperature is kept constant for 2 h and the hydrogen flow is 675 mL(SATP)/h.
3. Results

3.1. TPR

Temperature programmed reductions of the catalysts were performed in order to verify the total reduction of the catalysts during the pretreatments. As can be seen from Fig. 1 all catalysts are reduced during the pretreatment since the TCD signal returns to baseline after approximately 20 min at 823 K.

3.2. TEM

Transmission electron microscopy images are shown in Fig. 2. These images are representative for the samples.

The average diameters of the metal particles are summarized in Table 1.

As can be seen from Table 1 and Fig. 2 the particles are evenly distributed on the support and the diameters of the metal particles are of the same order of magnitude. The effect on the particle size of co-impregnating Ag is negligible. The Rh particles (3 nm) are somewhat smaller than Ni, Ru, and Pd (6–8 nm), but the estimated number of total surface atoms in each sample is in the same order of magnitude for all the catalysts. The total number of surface metal atoms on Ru/spinel, which has the largest particles, is less than a factor of 3 lower than Rh, which has the smallest particles according to TEM. The number of surface atoms in Ni/spinel, Ag-Ni/spinel, Pd/spinel, and Ag-Pd/spinel are in between. This is estimated by taking the average diameter of a metal particle obtained from TEM and calculating the number of particles assuming an average diameter for all particles. The surface area of a sphere with the given diameter is calculated along with the number of atoms on this surface given a crystal structure of CCP. It is noted that the calculations are only very rough estimations of the total number of surface atoms.

3.3. Catalytic tests

The catalysts were tested in the conversion of ethane at 823 K. The results are shown in Fig. 3.

Similar for all catalysts is an initial period of 100% conversion of ethane. In this period ethane is converted solely into methane and coke. The time of this period depends on the metal impregnated onto the spinel. After the initial period the conversion of ethane drops dramatically to 1.8–9%. Ethane is now converted into ethene, methane, and coke.

The first period of total conversion is shown in more detail in Fig. 4.

Rh/spinel and Pd/spinel reveal a relatively long period of hydrogenolysis and coking of the catalyst, i.e. 74 and 90 min, respectively. Ni/spinel hydrogenolyze the ethane for 37 min whereas Ru/spinel only hydrogenolyze for a couple of minutes. Ag is expected to influence the conversion of ethane as described previously. Ru/spinel does not have a long initial period of hydrogenolysis and coking and co-impregnating Ag onto Ru/spinel does not change the time of the initial period significantly.

Table 1

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Average metal particle diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni/spinel</td>
<td>6</td>
</tr>
<tr>
<td>Ag-Ni/spinel</td>
<td>5</td>
</tr>
<tr>
<td>Pd/spinel</td>
<td>7</td>
</tr>
<tr>
<td>Ag-Pd/spinel</td>
<td>6</td>
</tr>
<tr>
<td>Ru/spinel</td>
<td>8</td>
</tr>
<tr>
<td>Rh/spinel</td>
<td>3</td>
</tr>
</tbody>
</table>

Fig. 1. Temperature programmed reduction of the metal on spinel (grey) and on silver and metal on spinel (black). (a) Ni/spinel and Ag-Ni/spinel, (b) Pd/spinel and Ag-Pd/spinel, (c) Ru/spinel and Ag-Ru/spinel, and (d) Rh/spinel and Ag-Rh/spinel. The hydrogen flow is 28.1 mL(SATP)/min g, the heating ramp is 20 K/min from ambient to 823 K, where after the temperature is kept for 2 h.
The conversion at steady state is slightly higher compared to Ru/spinel. In contrast to this, Ag-Ni/spinel shows a significant decrease of the initial period of hydrogenolysis compared to Ni/spinel. The initial period on Ag-Ni/spinel is 3 min whereas for Ni/spinel it is 37 min. The effect of Ag is not so pronounced for Rh/spinel. The time of the initial period is almost the same with and without Ag. Pd/spinel hydrogenolyzed ethane for a long period of time, i.e. 90 min. Co-impregnation of Ag onto Pd/spinel reveals a slight decrease in the time of the initial period and there is clearly an effect on the transitional period from high conversion to low conversion. The transitional period is prolonged around 20 min by adding Ag.

From the TCD results a carbon balance can be calculated using Ar as a reference. Hereby the carbon depositions on the catalysts are estimated. As can be seen from Fig. 5 around 40–50% of the ingoing carbon is converted into coke and deposited on the catalyst in the initial period. This means that a rather severe coking of the catalysts is observed since roughly half of the carbon is converted into coke and after the initial period the carbon deposition rate falls drastically. In Table 2 the data from the coke depositions are summarized. The rate of the coke deposition in the initial period is merely the same for all catalysts. Only Ru/spinel and Ag-Ru/spinel have higher coking rates but the uncertainties are too high to make an unambiguous conclusion due to only single measurements in the short initial period. As the rate of coking is more or less the same in the initial period the amount of coke is dependent on the time of the initial period. Therefore the Pd catalysts develop more coke than the two Rh catalysts, which again develops more coke.

Fig. 2. TEM images of the catalysts after tests. (a) Pd/spinel, (b) Ag-Pd/spinel, (c) Rh/spinel, (d) Ni/spinel, (e) Ag-Ni/spinel, and (f) Ru/spinel. The black "spots" are the reduced metal particles impregnated onto the spinel support.

Fig. 3. The conversion of ethane at atmospheric pressure and 823 K. The flow of 9.7% ethane/Ar was 1000 mL(SATP)/h. Ag-Pd/spinel ( ), Pd/spinel ( ), Ag-Rh/spinel ( ), Rh/spinel ( ), Ag-Ni/spinel ( ), Ni/spinel ( ), Ag-Ru/spinel ( ), Ru/spinel ( ).

Fig. 4. The conversion of ethane in the initial period where full conversion of ethane is observed. Ag-Pd/spinel ( ), Pd/spinel ( ), Ag-Rh/spinel ( ), Rh/spinel ( ), Ag-Ni/spinel ( ), Ni/spinel ( ), Ag-Ru/spinel ( ), Ru/spinel ( ).
than Ni and Ru. The carbon deposition is clearly minimized in the initial period when co-impregnating Ag on the Pd and Ni catalysts. The total coke deposition in the initial period is reduced 44% for Ag-Pd/spinel and 93% for Ag-Ni/spinel compared to the single metal catalyst. The reason is mainly the reduction of the time of the initial period, but also a decrease in the deposition rate is seen in Fig. 5. The coking of Rh/spinel is almost the same when co-impregnating with Ag while the coking of the Ru catalyst is too low to determine due to the short time of the initial period.

After the initial period the conversions drop to 1.8–9%; here ethane is converted into ethene, methane, and coke.

As can be seen from Figs. 6 and 7 the conversions are significantly reduced compared to the initial period. The conversions on Ni/spinel and Ag-Ni/spinel reach a steady state after 1.5–2 h where after the conversions are constant, around 2%. For the ruthenium catalysts steady state is apparently not reached within 20 h. A continuous deactivation of the catalysts is observed; most likely due to coking. For the rhodium catalysts steady state is reached after around 500 min and the conversion is increased by the addition of Ag. For Ag-Pd/spinel the transitional period is prolonged and no steady state is observed within the time frame studied here when co-impregnating Ag onto Pd/spinel.

The selectivities are calculated from the FID results since the FID is the most sensitive detector towards hydrocarbons of low concentrations and therefore the most precise selectivity is obtained this way. The disadvantage is, that the selectivities do not take the carbon deposits into account. The ethene selectivities for the gaseous compounds detected by the GC are observed in Fig. 8. Ethene and methane are the only gaseous compounds produced during the reaction. Therefore the selectivities for ethene are complementary to the methane selectivities. In the initial period 0% ethene and 100% methane are produced. As the conversion drops to steady state the selectivities are changed in favor of the ethene production for all catalysts. The ethene selectivities for both Ru- and both Ni catalysts are 97% or more at

### Table 2

Calculations of coke depositions and conversions from the tests, temperature for the TPO maxima, and types of carbon depositions determined by TEM.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Time of initial period (min)</th>
<th>Coke deposition in initial period (mg/h)</th>
<th>Total coke deposition in initial period (mg)</th>
<th>Conversion at steady state (%)</th>
<th>Coke deposition at steady state (mg/h)</th>
<th>Total coke deposition from TPO (mg)</th>
<th>Equivalent number of monolayers of graphene</th>
<th>Temp for TPO peak maximum (K)</th>
<th>Type of carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd/spinel</td>
<td>90</td>
<td>42</td>
<td>63</td>
<td>8</td>
<td>5</td>
<td>179</td>
<td>25</td>
<td>730</td>
<td>Whiskers</td>
</tr>
<tr>
<td>Ag-Pd/spinel</td>
<td>65</td>
<td>33</td>
<td>35</td>
<td>9</td>
<td>6</td>
<td>215</td>
<td>26</td>
<td>695</td>
<td>Whiskers</td>
</tr>
<tr>
<td>Rh/spinel</td>
<td>64</td>
<td>40</td>
<td>42</td>
<td>2</td>
<td>1</td>
<td>59</td>
<td>4</td>
<td>635</td>
<td>Graphene and few MWNT</td>
</tr>
<tr>
<td>Ag-Rh/spinel</td>
<td>68</td>
<td>40</td>
<td>45</td>
<td>4</td>
<td>3</td>
<td>65</td>
<td>–</td>
<td>600</td>
<td>–</td>
</tr>
<tr>
<td>Ni/spinel</td>
<td>37</td>
<td>49</td>
<td>29</td>
<td>2</td>
<td>&lt;1</td>
<td>49</td>
<td>8</td>
<td>770</td>
<td>Whiskers</td>
</tr>
<tr>
<td>Ag-Ni/spinel</td>
<td>3</td>
<td>42</td>
<td>2</td>
<td>2</td>
<td>&lt;1</td>
<td>9</td>
<td>1</td>
<td>650</td>
<td>Graphene and MWNT</td>
</tr>
<tr>
<td>Ru/spinel</td>
<td>1</td>
<td>81</td>
<td>&lt;1</td>
<td>3</td>
<td>&lt;1</td>
<td>4</td>
<td>1</td>
<td>620</td>
<td>Graphene and few MWNT</td>
</tr>
<tr>
<td>Ag-Ru/spinel</td>
<td>&lt;1</td>
<td>54</td>
<td>&lt;1</td>
<td>4</td>
<td>2</td>
<td>8</td>
<td>–</td>
<td>590</td>
<td>–</td>
</tr>
</tbody>
</table>

![Fig. 5.](image1) The carbon depositions in the initial period calculated from the carbon balances from tests for Ag-Pd/spinel (△), Pd/spinel (○), Ag-Rh/spinel (▲), Rh/spinel (▲), Ag-Ni/spinel (▲), Ni/spinel (○), Ag-Ru/spinel (△), and Ru/spinel ( ○).

![Fig. 6.](image2) Conversion of ethane on Ni/spinel (○), Ag-Ni/spinel (▲), Ru/spinel ( ○), and Ag-Ru/spinel (△).

![Fig. 7.](image3) Conversion of ethane on Rh/spinel (△), Ag-Rh/spinel (▲), Pd/spinel (○), and Ag-Pd/spinel (△).
steady state. For both Rh catalysts the ethene selectivities are around 90% at steady state whereas the selectivities for the two Pd catalysts have not reached a steady state but are still increasing after 20 h on stream.

The carbon depositions have also been calculated for the steady state periods. Unfortunately, the rates of carbon depositions are much more uncertain at steady state compared to the initial period due to the rather low conversions. The rates are shown in Table 2 and range from less than 1–6 mg/h. The carbon depositions are shown in percentage of the ingoing carbon, where they vary from ~0 to 9% at steady state (see Fig. 9). The carbon deposition rates decrease as the ethene conversions decrease. In spite of the severe coking, the catalysts are all still active after 20 h on stream, though quite deactivated. One could imagine that the high carbon depositions would fully deactivate the catalysts. This is apparently not the case since ethene is still converted. The low conversion of ethene after the initial period could be due to non-catalytic thermal cracking of ethene on a completely deactivated catalyst. This is however ruled out since a pure spinel is tested and no conversion of ethane is observed. Another possible explanation could be that carbon deposits possess intrinsic catalytic properties whereby the conversion of ethane is not totally diminished despite the severe coking.

### 3.4. TPO

After the tests a temperature programmed oxidation (TPO) is performed and the results are shown in Figs. 10 and 11. The amount of carbon on the catalysts is calculated by determining the areas of the CO2 peaks. These amounts are given in Table 2. No CO or H2O is observed. The amount of coke on Ag-Pd/spinel is relatively large (215 mg); therefore the TPO curve is rather flat at the maximum and the TPO curve is slightly elongated since a surplus of oxygen is not available. Nevertheless, the oxidation reaction is not incomplete since no CO is observed and the result is reproducible. Two TPO maxima are observed for Pd/spinel indicating two different coke types being oxidized. These results are confirmed when repeating the TPO experiment. A close-up of the TPOs for the Ru and Ni catalysts is shown in Fig. 11. The deposition of coke on Ni/spinel has definitely decreased significantly when co-impregnating Ag onto the catalyst. The amount of coke is around 5 times higher on Ni/spinel than on Ag-Ni/spinel. The TPO of Ni/spinel has a maximum at 770 K and maximum is 650 K for Ag-Ni/spinel. Twice the amount of coke is deposited on Ag-Ru/spinel compared to Ru/spinel while the maximum is decreased from 620 to 590 K. In general, all the maxima of the TPOs are lowered when Ag is present.
Enthalpy of formation, segregation energies, and the second derivative of the surface energy of Ag on Pd, Rh, Ru, and Ni [20,21]. Phases at 823 K from experimental and theoretical phase diagrams [22,23].

<table>
<thead>
<tr>
<th>Metal</th>
<th>Pd</th>
<th>Rh</th>
<th>Ru</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Enthalpy of formation (eV/atom)</td>
<td>$\Delta H$</td>
<td>0.30</td>
<td>0.54</td>
<td>0.25</td>
</tr>
<tr>
<td>Segregation energy (eV/atom)</td>
<td>$\Delta S$</td>
<td>-0.37</td>
<td>-0.92</td>
<td>-1.74</td>
</tr>
<tr>
<td>Second derivative (eV/atom)</td>
<td>$\Delta S''$</td>
<td>-0.37</td>
<td>-0.79</td>
<td>-1.11</td>
</tr>
<tr>
<td>Phases in phase diagram</td>
<td>Solid</td>
<td>Ag + Rh</td>
<td>Ag + Ru</td>
<td>Ag + Ni</td>
</tr>
<tr>
<td>below 823 K</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3

Fig. 12. TPO of the Pd/spinel after 20 h on stream and immediately after the initial period, i.e. after 90 min on stream.

TPO is also carried out immediately after the initial period for Pd/spinel (see Fig. 12).

The amount of carbon deposited during the whole testing period is more than twice as big as the amount of carbon deposited in the initial period. This is also what is calculated from test (see Table 2). The first TPO maximum is observed after the initial period as well as after the whole testing period. The second TPO maximum is not as clearly seen after the initial period but an indication of it is calculated from test (see Fig. 12).

The type of coke deposited on the catalyst during the reaction is characterized by transmission electron microscopy (see Fig. 13).

On Pd/spinel tested for 20 h large amounts of whiskers are produced during the catalytic reaction and minor amounts of graphitic carbon is observed. On Pd/spinel tested for 90 min the spinel support is visible and only a few whiskers are observed. TEM images of Ag-Pd/spinel reveal a deposition of mainly whiskers but also minor amounts of graphitic carbon. Apparently, the same types of carbon are produced on Pd/spinel and Ag-Pd/spinel in a period of 20 h while mainly whiskers are produced in the initial period. On Ni/spinel mainly graphene sheets encapsulating the Ni particles are observed. A multiwalled carbon nanotubes (MWCNTs) and a few whiskers are also produced. When introducing Ag less graphene sheets are observed, a few carbon nanotubes, and no whiskers. This indicates that graphene is the main carbon type deposited in the initial period since the length of the initial periods is the main deviation between the two catalysts. Ru/spinel mainly produce graphitic carbon although a few multiwalled carbon nanotubes (MWNTs) are observed. Rh/spinel produces the same types of carbon; mainly graphitic carbon, but also a few MWNTs.

4. Discussion

In order to understand how the binary metal catalysts perform during the tests, the alloying tendencies are predicted. The enthalpy of formation predicts the formation of bulk alloys of the binary compounds. The enthalpies are obtained from Ref. [20]. The data are the lower estimate of the enthalpy of formation calculated for a number of different compounds and are shown in the first row of Table 3. The data are in good agreement with the experimental data as given in row 4, where a solid solution is predicted for Ag and Pd while the rest of the binary compounds phase separate in the bulk.

The surface segregation energy is also considered since this predicts whether Ag segregates from the metal bulk to the surface. All segregation energies are negative (see Table 3) and Ag therefore segregates to the surface. This is in good agreement with the fact, that Ag is the transition metal with the lowest surface energy. Whether Ag alloys when present in the surface is predicted using the second derivative of the surface energy [21]. These are shown in the third row of Table 3. A large positive value indicates that Ag and the metal alloy in the surface, while a negative value indicates a phase separation. It is therefore expected that Ag and Pd alloy in the bulk, that Ag and Ru as well as Rh phase separate in the surface, and that Ag and Ni alloy in the surface. Only Ag-Ni show tendencies like the Au-Ni system regarding alloy formation [17].

The alloying systems are not simple to predict theoretically and the predictions are not fully identical, but the tendency of segregation of Ag to the surface is clear. In conclusion, Ag and Pd are expected to alloy, while Ag on Rh and Ru, are expected to phase separate in the surface. Ag is also expected to alloy in the surface on Ni.

According to theoretical predictions and experimental results Ag covers the steps of the Ni metal [13,19]. It would be very interesting if the exact amount of step and kink sites were known, however, this a general out standing problem in heterogeneous catalysis which have only been clarified in a few incidences like for example the ammonia synthesis over Ruthenium. Here it was estimated to amount to 5% see Ref. [6]. By co-impregnating Ag on Ni the period of severe coking and hydrogenolysis is significantly decreased when testing the bimetallic catalysts. Only 1/5 of the carbon is deposited on Ag-Ni/spinel compared to Ni/spinel. This indicates that the steps are the primary active sites in the hydrogenolysis reaction whereas the dehydrogenation takes place on the terraces and is therefore unaffected by the Ag. The Ag impregnated onto Ni is obviously not entirely blocking the steps since some carbon deposition continues. This is not surprising, since we in this study have only tested an addition of 20% Ag and not attempted to optimize this coverage. Furthermore there might also be a complication of the surface alloy formation competing with the Ag adsorption on the steps making the Ag less efficient than first anticipated. Such arrangement induced by the chemical potential of the reactants has been observed earlier [24].

Co-impregnated Pd and Ag do not show any decrease in the time of hydrogenolysis and coking compared to Pd/spinel. This is due to the fact that Pd and Ag alloy and therefore silver does not preferentially cover the steps and kinks. On the contrary the period of hydrogenolysis and severe coking is actually prolonged leading to growth of carbon whiskers as shall be seen below. The time of the initial period is reduced but the transitional period between initial and steady state is significantly prolonged by Ag. So even though the amount of coke deposited in the initial period is 44% lower for Ag-Pd/spinel, the total amount of coke deposited is 20% larger.

For the system with Ag and Rh there is apparently no positive effect of the silver. The silver segregates to the surface and does not mix with the rhodium, but apparently it does not cover the steps. Possibly because the Ag is present in islands covering parts of the terraces. This does not affect the length of the period with hydrogenolysis significantly as observed in the tests. The conversion at steady state is slightly higher for Ag-Rh/spinel and therefore
Fig. 13. TEM images of the carbonaceous deposits on (a) Pd/spinel after 90 min on stream, (b) Pd/spinel after 20 h on stream, (c) Ag-Pd/spinel, (d) Ni/spinel, (e) Ag-Ni/spinel, (f) Ru/spinel, and (g) Rh/spinel.
10% larger amounts of coke are deposited on the catalyst compared to Rh/spinel.

When Ru is co-impregnated with Ag no significant effect is observed for the initial period of testing. For all catalysts the conversions or coke depositions are influenced by co-impregnation of Ag except for Ru/spinel. Ag and Ru do not mix in the surface and Ag should just as on Ni block the steps. However, since we have evidence that the steps are initially poisoned by carbon on Ru, we do not expect a strong effect of the presence of Ag in this case. In the case of Ni we know that carbon does not efficiently block the surface since carbon forms islands along the steps and the carbon grows into the upper Ni layer [12,25].

During the tests large quantities of coke are deposited on all catalysts. From 4 to 215 mg of carbon is deposited on a 400 mg catalyst with around 3 wt% active metal. On a molar basis 0.3–18 mmol are produced on 0.3 mmol transition metal. Converted into monolayers of carbon this equals 1–26 monolayers if all carbon is present as graphene sheets on the surface of the catalysts (see Table 2).

Not only the total amounts of coke are determined by temperature programmed oxidation but also the oxidation profile with the maxima of the TPO peaks are determined. The TPO maximum for Ni/spinel is reduced from 770 to 650 K when Ag is present. The two different temperatures for the TPO indicate that different coke types are present or that the presence of Ag activates the oxidation and thereby lowers the temperature of the TPO maximum. TEM images reveal that mainly graphene sheets are deposited on Ni/spinel but also minor amounts of carbon nanotubes and whiskers are present. On Ag-Ni/spinel graphene sheets and minor amounts of carbon nanotubes are observed but no whiskers are produced. Apparently, the lack of whiskers and the reduced amount of graphene sheets are the reasons for the reduction of the carbon deposits. It can be concluded that the presence of Ag prevents the formation of whiskers; most likely due to Ag covering the step sites where the whiskers are formed. This result is in accordance with Ref. [17] where graphene layers are found to grow from the steps on Ni particles.

The large amounts of carbon on the Pd catalysts are expected since the initial period with 100% ethane conversion and severe coking of the catalyst is much longer compared to the other catalysts. TPO for Pd reveals two maxima at 730 and 765 K, respectively. This could indicate two different kinds of coke deposited. According to the TEM images large amounts of whiskers are deposited on Pd/spinel as well as on Ag-Pd/spinel. Apparently there are not two different coke types. The two maxima could therefore stem from different conditions for the oxidation of the whiskers. One peak from whiskers still connected to metal particle and one peak from the oxidation of whiskers departed from the metal. During the first 90 min on stream severe coking of the catalyst is observed. This is confirmed by TPO after 90 min where around half of the coke is already deposited. The same temperatures for the maxima are observed but the ratio between the first and the second peak is much higher for the short test compared to the long test. This indicates, that some whiskers depart from the metal during the oxidation reaction and therefore are oxidized under different conditions. Ag on Pd does not prevent whiskers from being formed as on Ni since Ag and Pd alloy. This underlines the conclusion that Ag does not cover step sites on the Pd particles, but rather promotes the carbon formation under the condition given here.

There is apparently no significant difference in the test results for Rh/spinel and Ag-Rh/spinel. TPO on the catalysts reveal a significant difference in the maxima, however, i.e. 635 K for Rh/spinel and 600 K for Ag-Rh/spinel. According to TEM large amounts of graphene and very little carbon nanotubes are deposited on Rh/spinel. The lower temperature of the TPO maxima on Ag-Rh/spinel is expected to be caused by either an enhanced activity for the oxidation when Ag is present or a prevention of the carbon nanotubes when Ag covers the step sites of Rh. But since the temperature difference is significant compared to the very small amount of carbon nanotubes the difference in maxima must be due to an enhanced activity for the oxidation when Ag is present.

Ru/spinel has very small amounts of coke deposited since the initial period in the test is very short. Therefore the TPO peak is relatively small with a maximum at 620 K. The TPO peak for Ag-Ru/spinel is twice the size of Ru/spinel and is located around 590 K. Both tests and TPO therefore indicate that more carbon is deposited on Ag-Ru/spinel than on Ru/spinel. This is somewhat surprising since we believe that the steps on the Ru metal particles are self-poisoned by carbon in the initial period where after the Ag-Ru/spinel and the Ru/spinel should perform identically. The effect of the higher coke deposition on Ag-Ru/spinel could be caused by a different size distribution of the Ru metal.

5. Conclusions

The role of the step sites has been elucidated in this study of the ethane hydrogenolysis, dehydrogenation, and coking reactions on Ni/spinel, Pd/spinel, Rh/spinel, and Ru/spinel. Ag and Ni phase separate on the surface of the Ni particles such that Ag covers the steps of the Ni particles. It can therefore be concluded that:

- The initial period of hydrogenolysis and severe coking is significantly reduced by co-impregnating Ag onto Ni/spinel.
- Step sites catalyze the C–C bond scission in ethane hydrogenolysis and the production of whiskers.
- The terraces on the Ni particles catalyze the C–H bond breaking and thus the ethane dehydrogenation reaction.

Since Ag and Pd alloy in the bulk there is no strong tendency to block the steps on the Pd particles. Using Pd as the catalytically active metal reveals nevertheless that the hydrogenolysis and coking reactions are enhanced by the alloy formation. Ru/spinel and Rh/spinel are both rather unaffected by Ag due to the self-poisoning by carbon on the Ru step sites and due to a possible island formation of Ag on the Rh particle surface, i.e. no strong step interaction in the latter case. It can therefore be concluded that hydrogenolysis of ethane is mainly catalyzed by the step sites. Dehydrogenation mainly takes place on the terraces and coking is significantly reduced by covering the step sites by Ag. This important information can beneficially be exploited in designing new catalysts with improved selectivity and stability.

Acknowledgement

This work was supported by the National Research Foundation (CINF and CSG).

References
