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Reduced Nickel Hydromolybdate Catalysts: Hydrogen Chemisorption and Activity in Benzene Hydrogenation

It has been shown previously (*1*) that the reduction of a synthesized hydrated nickel molybdate '$NiO,MoO_3,2H_2O$' by hydrogen at a temperature above 250°C leads to a catalyst active in hydrogenation of benzene to cyclohexane at 100°C. The nickel ions in the initial binary compound are not reduced merely into the state of metallic nickel, as evidenced by the fact that its X-ray pattern is absent. The second component (molybdenum oxide) is also reduced and gives with nickel the intermetallic compound $MoNi_4$ (*2*). This reduction at a fairly low temperature (somewhat above 250°C) is not encountered with the anhydrous nickel molybdate ($NiMoO_4$), for which a temperature range of 500–600°C is required (*3*). In the case of ternary HDS catalysts, NiO (3%), MoO_3 (10%) on γ-Al_2O_3, calcined before use at 500°C and therefore containing Ni MoO_4, the reduction at 350°C does not even produce MoO_2 to any significant extent. The subsequent sulfidation of this oxide is difficult, in contrast to MoO_3 (*4*), and the catalysts reduced below 350°C before sulfidation were active in HDS whereas reduction at higher temperatures impaired the catalytic activity.

The intermetallic $MoNi_4$ formed by low-temperature reduction of hydrated nickel molybdate, where the initial surface area (236 m^2/g) drops only very little by reduction (230 m^2/g) is an interesting compound to exploit for catalytic activity. Indeed, recently various intermetallics have been found to be of great interest as catalysts for various reactions. Among them are RE_xNi_y (RE = rare earth or lanthanum) intermetallics which are active in CO hydrogenation, toluene dealkylation, and ethane hydrogenolysis (*5*), while other intermetallics are effective and selective catalysts in CO methanation, ethylene hydrogenation, hydrocarbon isomerization, and ammonia synthesis (*6*). There are also catalyst precursors such as nickel–cerium intermetallics which by oxidation give methanation catalysts (*7*). However, they are usually prepared (*5*) by metallurgical methods (melting) and exhibit very low surface areas. A method enabling their formation with a surface area of the same order of magnitude as that of the parent oxides seems to be provided, at least, for the $MoNi_4$ intermetallic (*1*). For other nickel intermetallics a standard supported nickel catalyst may be derivatized by interaction with Groups IIIA and IVA volatile organometallic compound (*8*).

The catalytic activity in the hydrogenation of benzene of reduced hydrated nickel molybdate (containing $MoNi_4$) was compared with that of pure nickel (*1*). Although it is easy to titrate by chemisorption (H_2 or CO) the surface of pure nickel, no corresponding data exist for the intermetallic $MoNi_4$, so the turnover frequencies are not available for this comparison. In the present study an attempt is made to determine the amount of chemisorbed hydrogen as a function of the extent of reduction of the solid, in order to place the comparison of catalytic activity on a more firm basis than that hitherto based on the supposed surface area of $MoNi_4$ (*1, 2*). Moreover, the composition of the parent hydrated nickel molybdate (Ni/Mo = 1) does not correspond to that of the intermetallic (Ni/Mo = 4), and in the reduced precursor, together with $MoNi_4$, there remains an excess of molybdenum oxide as well as some nonreduced NiO (*1*). Also, an attempt has been

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made to prepare a precursor of the catalyst with a nickel-to-molybdenum ratio Ni/Mo = 4, instead of 1, by using a similar method of preparation as for the previous hydrated nickel molybdate. The catalytic behavior of the reduced resulting sample is then compared with the behavior of the reduced nickel hydromolybdate.

The method of obtaining the hydrated nickel molybdate has been previously described (*1*) and is similar to the one used to prepare hydrated nickel aluminate (*9*). It consists in the elimination of ammonia by boiling an aqueous solution of ammonium molybdate and nickel nitrate ammonia complex.

When the nickel/molybdenum ratio in the solution is 1 the resulting precipitate has the composition MoO_4Ni, 2 H_2O (*1*) and its X-ray diagram corresponds to that (*10*) of a hydrated nickel molybdate of composition MoO_3, y NiO, z H_2O, ε NH_3 with $1 < y < 2$ and $z = 2$ for $y = 1$. Its surface area is 236 m^2/g. Calcination in air gives the anhydrous nickel molybdate easily identified by its X-ray diagram (*3, 11*).

When the nickel/molybdenum ratio in the solution is 4 instead of 1, the precipitation of nickel is not complete because the resulting ratio in the solid is Ni/Mo = 2.7. The X-ray pattern is the same as for the sample for which Ni/Mo = 1 but the intensity of lines is much smaller, indicating that this sample is probably a mixture of hydrated nickel molybdate and an excess of amorphous nickel hydroxide. The surface area is 150 m^2/g. After calcining at 980°C the X-ray diffraction pattern shows that the resulting compound is a mixture of anhydrous nickel molybdate as before and of an excess of nickel oxide NiO. These results show that the preparation in an aqueous medium of hydrated nickel molybdates does not lead to binary compounds with Ni/Mo ratio higher than 2, as already pointed out by Corbet et al. (*10*). In the case of anhydrous nickel molybdate only the phase $NiMoO_4$ is known, any excess of Ni or Mo being in the form of the respective oxide (*12*).

The catalytic activity in the hydrogenation of benzene has been measured in a dynamic differential reactor (conversion of the order of 3%) at 100°C, the partial pressure of benzene being 60 Torr, the total pressure 760 Torr, and the total flow rate 30 cm^3/min.

The surface areas (BET) of reduced samples and the volumes of chemisorbed hydrogen at 25°C and 600 Torr have been measured *in situ* after reduction of the precursor at various temperatures under the same conditions as for the catalytic tests: 2 · 5 h in flowing hydrogen (30 cm^3/min).

The activity of the two samples (Ni/Mo = 1 and Ni/Mo = 2.7) as a function of the reduction temperature is shown in Fig. 1. As is the case for the sample in which Ni/Mo = 1 (curve a), the sample with Ni/Mo = 2.7 (curve b) is not active for reduction temperatures lower than 250°C. The activity is a maximum for a reduction temperature of 270°C and decreases when the reduction temperature increases.

The X-ray diffraction patterns have been recorded in hydrogen in a heating chamber with a heating rate of 2.5°C/min. The patterns of the initial nickel hydromolybdate disappear in both cases between 250 and

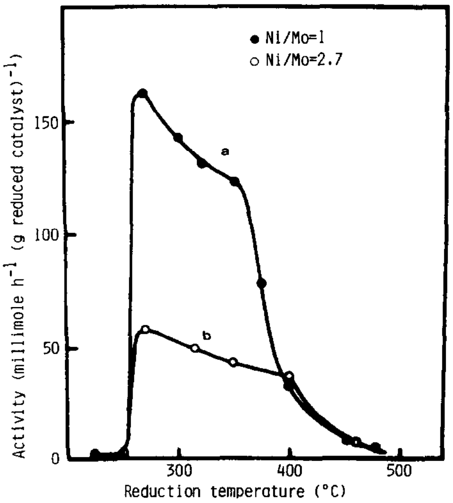

FIG. 1. Catalytic activity for hydrogenation of benzene at 100°C as a function of the reduction temperature. Time of reduction = 2 · 5 h.

TABLE 1

Characterization of the Precursor (Ni/Mo = 1) Reduced at Increasing Temperatures and Catalytic Activity in the Hydrogenation of Benzene

Reduction temp. (°C)	Weight loss (%)	BET surface area (m^2 g^{-1})	V_{H_2},total (cm^3 g^{-1})	V_{H_2},irrev. (cm^3 g^{-1})	*a*/at H irrev. (molecule C_6H_6 h^{-1})
270	12	230	14.1	6.1	26
350	15	180	23.0	16.0	31
400	21	148	26.0	16.0	27
462	35	70	38.0	23.5	3

260°C. Above these temperatures the diagram of the first sample (Ni/Mo = 1) shows the pattern of the intermetallic compound $MoNi_4$ together with the pattern of a poorly crystallized nickel oxide. No patterns which could be related to MoO_3 or MoO_2 (or Mo) in excess are recorded. For the second sample (Ni/Mo = 2.7) the main line which is attributed to Ni is gradually shifted toward the position of the main line of $MoNi_4$. As the precursor contains an excess of NiO (or $Ni(OH)_2$, see above) with respect to the composition of hydrated nickel molybdate, it is not surprising that this excess is easily reduced to Ni. At temperatures above 390°C the diagram is that of $MoNi_4$. It should be pointed out that the reduction of anhydrous nickel molybdate, which is possible at 500–600°C, gives Ni–Mo solid solution (alloy, and not the intermetallic $MoNi_4$) and amorphous and crystallized MoO_2 (*3*).

The amount of adsorbed hydrogen is measured at room temperature at 600 Torr after reduction at various temperatures, followed by outgassing at the same temperature for 2 · 5 h. After this first adsorption giving the total adsorbed volume (V_{H_2},total), the sample is outgassed at room temperature during 14 h and the volume of adsorbed hydrogen is measured again, the difference giving the volume of hydrogen adsorbed irreversibly (V_{H_2},irrev.). The volumes, V_{H_2},irrev., can be used to calculate the activity per site by assuming one metallic site for Ni, or one adsorption site in the case of $MoNi_4$, per hydrogen atom. The results are summarized in Table 1 (Ni/Mo = 1) and Table 2 (Ni/Mo = 2.7) which also give the weight losses and surface areas (BET) as a function of the temperature of reduction.

These results show that for the two samples the amount of adsorbed hydrogen (V_{H_2},total and V_{H_2},irrev.) increases with the reduction temperature. This result is in

TABLE 2

Characterization of the Precursor (Ni/Mo = 2.7) Reduced at Increasing Temperatures and Catalytic Activity in the Hydrogenation of Benzene

Reduction temp. (°C)	Weight loss (%)	BET surface area (m^2 g^{-1})	V_{H_2},total (cm^3 g^{-1})	V_{H_2},irrev. (cm^3 g^{-1})	*a*/at H irrev. (molecule C_6H_6 h^{-1})
270	18	147	11.3	7.1	259
305	20	125	12.9	10.1	159
350	21	107	14.0	10.8	127
455	25	28	19.2	16.2	6

agreement with the weight loss but seems to be in contradiction with the decrease of the catalytic activity *a* either expressed per gram of catalyst (Fig. 1) or per irreversibly adsorbed H atom (last column of Tables 1 and 2). Indeed, for a hydrogenation reaction, this activity usually increases with the extent of reduction (or the weight loss). The results in Table 1 show that for reduction temperatures in the range 270 to 350°C the activity of the reduced hydromolybdate (Ni/Mo = 1) per adsorbed hydrogen atom is nearly constant (26–31 molecules h^{-1}). The only metallic phase which is detected in this temperature range being the intermetallic compound $MoNi_4$ (together with some NiO but in the absence of Ni, even for the reduction at 500°C), it is possible to conclude that this activity is characteristic of the intermetallic compound. It is not clear, however, whether one hydrogen atom is adsorbed on one $MoNi_4$ surface intermetallic site, or whether it is adsorbed on every Ni atom of the intermetallic.

In the case of the sample in which Ni/Mo = 2.7 the activities per irreversibly adsorbed hydrogen atom (last column of Table 2) are in the same range as the activities for metallic nickel which can be calculated from the data of Aben *et al.* (*13*), viz., 150 molecules h^{-1} Ni at^{-1}, and of van Meerten and Coenen (*14*), viz., 215 molecules h^{-1} Ni at^{-1}. The decrease of the activity per irreversibly adsorbed hydrogen atom observed for this sample when the temperature of reduction increases (Table 2) can therefore be interpreted as the result of the transformation of the metallic nickel into the intermetallic compound $MoNi_4$ (see above for the results of X-ray diffraction).

For the highest reduction temperature the activity per adsorbed hydrogen atom becomes very low (3 molecules C_6H_6 h^{-1} at 462°C for Ni/Mo = 1 and 6 for Ni/Mo = 2.7 at 455°C). It is also low on the basis of unit weight (Fig.1). It can be noted that when the reduction temperature exceeds 400°C the weight loss of the sample with Ni/Mo = 1 is higher (35%) than the loss expected for a dehydration of nickel hydromolybdate and its full reduction in the form of $MoNi_4$ supported on an excess of MoO_2 (30%). This result indicates that a further reduction of MoO_2 into Mo is taking place at these temperatures. Mo is known to chemisorb hydrogen (*15*) but not to be active in the hydrogenation of benzene (*16*). Therefore when metallic molybdenum is present the activity per irreversibly adsorbed hydrogen atom is decreased. The further reduction of MoO_2 into Mo does also apply to the sample with Ni/Mo = 2.7 but it must be recalled that the bulk reduction of MoO_3 or MoO_2 (even amorphous) into Mo is very slow below 500°C and it is only at 600°C that this reduction proceeds to a considerable extent (*3*).

The change of chemisorptive behavior of the samples is illustrated by Fig. 2 showing (above 400°C) an abrupt increase of the amount of irreversibly adsorbed hydrogen per unit of surface area (BET) of the reduced samples. However, the decrease of the catalytic activity on the unit weight basis (Fig. 1) cannot be correlated with hydrogen adsorption capacity. A possible interpretation for both samples would involve a type of SMSI effect in which the reduced molybdenum (from the surface reduction of amorphous MoO_3 or MoO_2) gradually covers the active sites, either $MoNi_4$ or Ni.

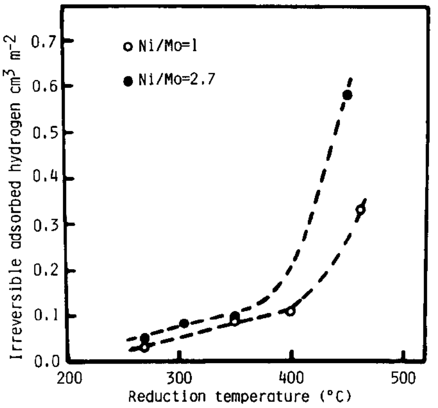

FIG. 2. Volume of irreversibly adsorbed hydrogen per unit surface area (BET) of the catalyst as a function of the reduction temperature.

The conclusions are as follows. The hydrated nickel molybdate is easily reduced by hydrogen at temperatures above 250°C giving the intermetallic compound $MoNi_4$ supported on an amorphous molybdenum oxide phase. The anhydrous nickel molybdate requires a reduction temperature above 450°C and gives Ni–Mo solid solution with an excess of amorphous molybdenum oxide (*3*). The intermetallic compound $MoNi_4$ is 5–7 times less active in the hydrogenation of benzene at 100°C than free metallic nickel on the basis of hydrogen titration of active sites. For the highest reduction temperatures the evaluation of the specific activity or the turnover frequency is perturbed by the reduction of the MoO_2 support into Mo, which chemisorbs hydrogen but is not active in hydrogenation of benzene and which seems to cover the existing active sites, Ni and $MoNi_4$.

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