Effects of Strong Metal–Support Interaction in the Case of Nickel supported on a Silica Surface containing Titanium Ions

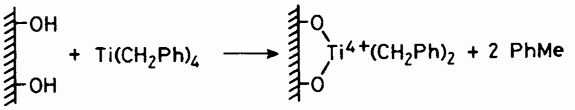
Yurii I. Yermakov, Yurii A. Ryndin, Oleg S. Alekseev, and Maria N. Vassileva
Institute of Catalysis, Novosibirsk 630090, U.S.S.R.

The properties of (Ni + Ti)–SiO_2 catalysts, obtained by anchoring $Ni(\pi\text{-}C_3H_5)_2$ on silica modified by low-valent titanium ions, were shown to be similar to those of Ni–TiO_2 in the hydrogenation of CO; this result is evidence of the direct interaction of metallic nickel particles with low-valent ions of titanium, resulting from the phenomenon of 'strong metal–support interaction.'

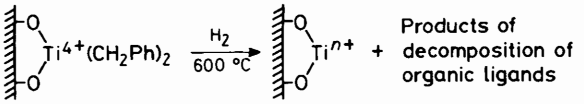
The first publication[1] in which the term 'strong metal–support interaction' (SMSI) was used to describe the specific features of some supported metallic catalysts led to numerous publications in this area and 4 years later an International Symposium was organized on this subject.[2] The interest of researchers in this area is in the hope of developing a new method for controlling the catalytic properties of dispersed metal particles by supporting them on oxides of transition and rare-earth elements. With TiO_2 as a support the following effects of SMSI have been described:[1,2] (1) a decrease in the amount of chemisorbed H_2 and CO on the supported metals and (2) a change in the catalytic properties of the metal particles in the reactions of hydrocarbons and CO with H_2. These effects appear after the high-temperature reduction of the catalysts and disappear after oxidation.

Similar effects were found earlier[3—6] for catalysts obtained by anchoring highly-dispersed particles of active metals on the surface low-valent ions of Mo, W, or Re. This fact allows one to assume that the probable reason for SMSI is the direct interaction of metal particles with low-valent ions of transition elements. To verify this hypothesis, the properties of Ni–TiO_2 were compared with those of (Ni + Ti)–SiO_2 catalysts prepared from organometallic precursors.

Monometallic nickel catalysts (C) and (A) (Figure 1) were prepared by the interaction of diallylnickel in pentane with the hydroxy groups of SiO_2 (250 m^2/g) dehydrated at 600 °C and TiO_2 (60 m^2/g, anatase) dehydrated at 550 °C, respectively, with subsequent reduction with hydrogen at 400 °C in both cases.[3] The preparation of the (Ni + Ti)–SiO_2 catalyst (B) consisted of the following steps: (i) treatment of SiO_2 with a pentane solution of tetrabenzyltitanium and subsequent removal of pentane by evacuation at 25 °C. The attachment of organometallic Ti complexes takes place on the surface of SiO_2[7] [equation (1)]. (ii) Treatment of the sample from (i) with hydrogen at 600 °C to produce surface low-valent ions of titanium [equation (2)]. The average oxidation number of Ti ions (n) in the product from (ii), calculated from the quantity of oxygen consumed for its complete oxidation, was *ca.* 2.6. This result indicates the presence of titanium in low oxidation states on the SiO_2 surface. (iii) Adsorption of diallylnickel from its pentane solution onto the Ti^{n+}–SiO_2 sample. (iv) Reduction of the (Ni + Ti)–SiO_2 catalyst with hydrogen at 400 °C.



(1)



(2)

The hydrogenation of CO was carried out in a differential glass reactor at 250 °C, under atmospheric pressure and using a molar ratio of CO : H_2 of 1 : 2. The reaction products (C_1—C_6) were analysed chromatographically. The use of $Ni(\pi\text{-}C_3H_5)_2$ as a precursor provides the possibility of producing highly-dispersed supported nickel catalysts with particle sizes of less than 10 Å[4] (after treatment with hydrogen at 400 °C).

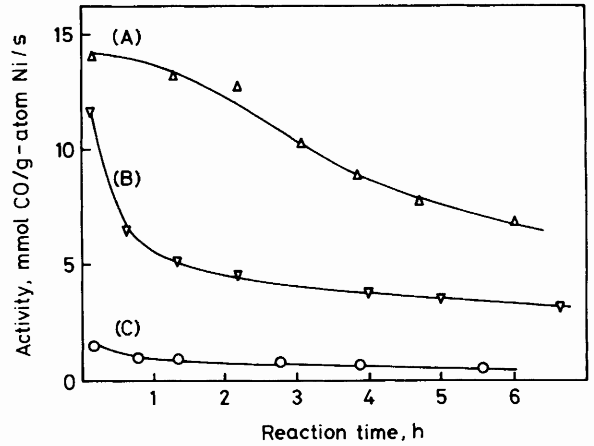


Figure 1. Activity of nickel catalysts in the hydrogenation of CO *vs.* reaction time. (A) 0.47% Ni–TiO_2, (B) (0.70% Ni + 1.06% Ti)–SiO_2, (C) 0.72% Ni–SiO_2.

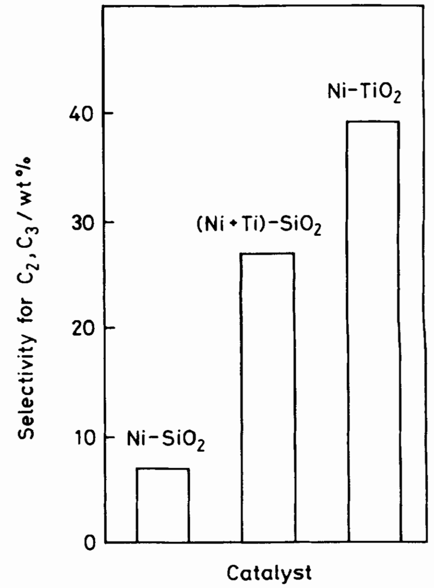


Figure 2. Selectivity for the formation of C_2, C_3 hydrocarbons after 6 h of catalysis.

The dependence of the activity of the nickel catalysts on reaction time is shown in Figure 1 and the relative yields of the ethane–propane fraction are given in Figure 2. The Ni–TiO_2 catalyst is about one order of magnitude more active and is more selective for the formation of C_2, C_3 hydrocarbons than Ni–SiO_2. This result is similar to those in the literature data,[2] but it was obtained for a catalyst with a higher dispersion of nickel.

The initial activity and the C_2, C_3 hydrocarbon selectivity of the (Ni + Ti)–SiO_2 catalyst are close to those of the Ni–TiO_2 catalyst. The decrease in the activity with reaction time was followed by coke deposition.

The evident difference in properties of (Ni + Ti)–SiO_2 and Ni–SiO_2 catalysts in the hydrogenation of CO is due to the interaction of nickel with the titanium ions (Ti–SiO_2 samples were inactive under these conditions). The similarity in the properties of (Ni + Ti)–SiO_2 and Ni–TiO_2 catalysts in the hydrogenation of CO allows us to propose that the reason for SMSI is a direct interaction of nickel atoms with low-valent titanium ions.

If this is the main reason for SMSI effects, the SMSI phenomenon is one of the cases of previously reported phenomena[3—6] of stabilization of dispersed metal particles and the change in their catalytic properties in the presence of low-valent ions [systems (M + E^{n+})–SiO_2, where M = Ni, Pd, or Pt and E^{n+} = ions of Mo, W, Re, or Sn]. Modification of the properties of dispersed metal particles by their interaction with surface low-valent ions is an effective way to regulate the catalytic activity of supported metallic catalysts.[3—6]

Received, 2nd July 1984; Com. 927

References

1 S. J. Tauster, S. C. Fung, and R. L. Garten, *J. Am. Chem. Soc.*, 1978, **100**, 170.
2 R. Burch and A. R. Flambard, *Stud. Surf. Sci. Catal.*, 1982, **11**, 193.
3 Yu. I. Yermakov, *Catal. Rev. Sci. Eng.*, 1977, **12**, 93.
4 Yu. A. Ryndin, A. P. Chernyshev, V. I. Zaikovskii, E. N. Yurchenko, and Yu. I. Yermakov, *React. Kinet. Catal. Lett.*, 1982, **21**, 125.
5 M. S. Ioffe, B. N. Kuznetsov, Yu. A. Ryndin, and Yu. I. Yermakov, The VIth International Congress on Catalysis, London, 1976, A5.
6 Yu. I. Yermakov, The VIIth International Congress on Catalysis, Tokyo, 1980, P5.
7 N. G. Maksimov, G. A. Nesterov, V. A. Zakharov, P. V. Stchastnev, V. F. Anufrienko, and Yu. I. Yermakov, *J. Mol. Catal.*, 1978, **4**, 167.