# $Ni/TiO_2$ Catalysts. The Role of the Titania in providing Active Sites

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*Summary* Data are presented which show that the role of titanium dioxide in promoting nickel catalysts is reaction-specific, and may not require a metal–support interaction.

TITANIA-SUPPORTED nickel catalysts exhibit anomalous hydrogen and carbon monoxide chemisorption capacities, and have very high activities for methanation.[1] Since the nickel particles are large (> 20,000 atoms per particle) it is unlikely that the titania support could materially affect the nickel surface, the source of the catalytic properties.

10% $Ni/TiO_2$ and 10% $Ni/SiO_2$ catalysts (prepared by impregnation) have been tested in the hydrogenolysis of n-hexane and the hydrogenation of CO to methane in a flow reactor, after reduction at 723 K. Hydrogen chemisorption isotherms have been determined in a static system, and specific metal surface areas evaluated by extrapolation to zero hydrogen pressure, and by plotting a Langmuir isotherm. Reduction experiments have shown that the titania is reduced during the pretreatment of the catalyst.

TABLE. Specific activities of nickel catalysts in n-hexane hydrogenolysis, and in methanation.

| | Hydrogenolysis | | Methanation | |
|---|---|---|---|---|
| Catalyst | $C_0$[a] | $C_L$[b] | $C_0$[a] | $C_L$[b] |
| 10% $Ni/SiO_2$ | 0·68 | 0·59 | 0·007 | 0·006 |
| 10% $Ni/TiO_2$ | 0·84 | 0·72 | 0·15 | 0·13 |

[a] Specific activity based on hydrogen adsorption at zero pressure. [b] Specific activity based on hydrogen adsorption, extrapolated from Langmuir isotherm.

The rate of hydrogenolysis is very sensitive to the surface morphology of the metal[2] and should readily expose differences due to support interactions. The Table lists the specific activities for both reactions studied. The specific activities of both catalysts for n-hexane hydrogenolysis were very similar, and the product distributions (not given here) were identical. We conclude, since this reaction is very sensitive to surface effects, that the two catalysts have very similar Ni surfaces. For methanation, however, the titania-supported catalyst was more than 20 times more active than the silica-supported catalyst. Furthermore, as the Figure shows, the $Ni/TiO_2$ catalyst produced quite large amounts of ethane, whereas none was found with the silica catalyst.

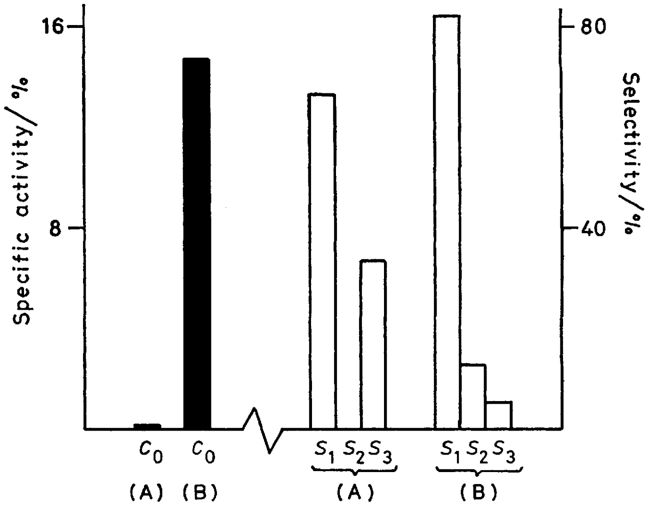

FIGURE. Specific activity and product selectivity for the reaction of carbon monoxide and hydrogen over nickel catalysts. (A), 10% $Ni/SiO_2$; (B), 10% $Ni/TiO_2$; $C_0$, specific activity based on hydrogen adsorption at zero pressure. $S_1$, $S_2$, $S_3$, selectivities for the formation of methane, ethane, and carbon dioxide, respectively.

Similar effects in methanation reported by Vannice and Garten[1] have been attributed to metal–support interactions. Our evidence is that the promotion of the nickel by the titania is reaction-specific. Furthermore, since no promotional effect was observed in the hydrogenolysis reaction, the promotion in methanation cannot necessarily be explained on the basis of a modified nickel surface. We postulate that it is the adsorption of CO, under reaction conditions, on to partially reduced titania ($Ti_4O_7$ shear phase) which is responsible for raising the activity in methanation.

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[2] G. A. Martin and J. A. Dalmon, *C. R. Hebd. Seances Acad. Sci., Ser. C*, 1978, **286**, 127.