Activity and Selectivity of a Niobia (Nb_2O_5)-supported Nickel Catalyst in CO Hydrogenation

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A nickel catalyst was more active for CO hydrogenation when supported on niobia (Nb_2O_5) than on silica and shifted the product distribution to higher hydrocarbons with appreciable olefin yields at low conversion levels.

Tauster and Fung have recently identified several binary oxides which, as a catalyst support, exhibit strong metal–support interaction.[1] The catalytic properties of Group 8 metals supported on one of these oxides, titania, have since been investigated by many workers.[2] One particularly interesting observation has been the unusual activity and selectivity of these catalysts in CO hydrogenation relative to conventional catalysts.[3,4] We report here qualitatively similar data for a nickel catalyst supported on another interacting oxide, niobia (Nb_2O_5). These results establish the general behaviour to be expected for this group of oxide supports. In addition we will highlight the difference in catalytic behaviour between silica- and niobia-supported nickel catalysts.

Niobia was prepared by following the procedure described by Tauster and Fung,[1] except that the calcination step was done in flowing oxygen (50 ml/min at S.T.P.) at 793 K for 2 h. The calcined product, which showed only a crystalline Nb_2O_5 phase by *X*-ray diffraction, had a Brunauer–Emmett–Teller (BET) surface area of 10 m^2/g. A 10 wt % Ni–Nb_2O_5 catalyst was prepared by the method of incipient wetness impregnation using nickel nitrate hexahydrate as the precursor. The catalyst was dried overnight in an air oven at 400 K, and subsequently reduced in flowing hydrogen (50 ml/min at S.T.P.) *in situ* prior to chemisorption and kinetic studies. During reduction the catalyst was heated with a linear increase of temperature with time from room temperature to 773 K in *ca.* 1 h, and held at that temperature for 1 h. Thermogravimetric data[5] showed that this procedure was sufficient for complete reduction of the metal salt to metallic nickel. The average nickel crystallite size, determined by *X*-ray line broadening measurement on the reduced catalyst, was 9($\pm$1) nm. For comparison, a 30 wt % Ni catalyst supported on silica (Davison, grade 952, BET

Table 1. Selectivity of nickel catalysts in CO hydrogenation.[a]

Catalyst	CH_4 formation, %	Product distribution, mole %					
		C_1	C_2	C_3	C_4	C_5	C_{2+}/CH_4[d]
30 wt % Ni–SiO_2	0.70[b]	70.2	22.0	4.8	3.0	—	0.42
10 wt % Ni–Nb_2O_5	0.73[c]	51.0	31.0	14.7	3.0	0.3	0.96

[a] The reaction was run at a total pressure of 101 kPa, with an H_2/CO ratio of 3/1, and at a total flow-rate of 20 ml/min at S.T.P. [b] Reaction temperature was 473 K. [c] Reaction temperature was 484 K. [d] C_{2+} denotes the sum of hydrocarbon products from C_2 to C_5.

Table 2. Activity and olefin/paraffin ratios of nickel catalysts in CO hydrogenation.

Catalyst	Activation energy/kJ mol^{-1}		Turnover frequency[a]/s^{-1}		Olefin/paraffin ratio[b]		
	$E(CH_4)$	$E(CO)$	$N(CH_4)$	$N(CO)$	C_2	C_3	C_4
30 wt % Ni–SiO_2	112	104	8.6×10^{-3}	1.3×10^{-2}	0	0	0
10 wt % Ni–Nb_2O_5	116	112	1.9×10^{-2}	5.8×10^{-2}	0.02	0.55	1.45

[a] Turnover frequency was calculated, by using the experimentally determined activation energy, at 548 K to allow a direct comparison with literature values (refs. 3, 12). [b] Obtained under experimental conditions identical with those indicated in Table 1.

area = 300 m^2/g) was prepared and treated similarly. For this catalyst an average nickel crystallite size of 10(±2) nm was found.

The amount of hydrogen uptake on the Ni–Nb_2O_5 catalyst, measured by a pulsed chemisorption technique[6] at room temperature, was calculated to be less than 0.05 hydrogen atom per surface nickel atom ($H/M_{surface}$). By contrast, for the Ni–SiO_2 catalyst a value near unity was found for the $H/M_{surface}$ ratio after an identical reduction treatment (the crystallite size determined by *X*-ray diffraction was used in calculating the dispersion). This suppression in hydrogen chemisorption is characteristic of strong metal–support interaction.[7] The adsorption study thus confirmed that niobia was an interacting support for nickel, as well as for iridium as previously reported.[1]

The catalytic behaviour of the two nickel catalysts in CO hydrogenation was studied in a stainless-steel microreactor. The kinetic measurements were made following the procedure described by Vannice.[8] In essence the reactor was operated in a differential mode by limiting the CO conversion to a few percent. Shown in Table 1 are the product distributions of the two catalysts, expressed in mole fraction of hydrocarbons at each carbon number, at comparable conversion levels. It is apparent that the Ni–Nb_2O_5 catalyst produced less methane, and more higher hydrocarbons than the Ni–SiO_2 catalyst. Since the two catalysts had similar crystallite size, this difference was a consequence of metal–support interaction, which had been identified earlier by hydrogen chemisorption.

In addition to the change in selectivity, the Ni–Nb_2O_5 catalyst was also found to be slightly more active for CO hydrogenation. Shown in Table 2 are measured activities, activation energies, and olefin/paraffin ratios for the two catalysts. Our results for the Ni–SiO_2 catalyst are in good agreement with literature data.[3,9] In the calculation of turnover frequency, the number of surface sites was determined from the average crystallite size measured by *X*-ray diffraction. This method was adopted because both H_2 and CO adsorption are suppressed on catalysts with strong metal–support interaction.[7] The use of adsorption data in calculating turnover frequency will lead to an even higher value for the Ni–Nb_2O_5 catalyst.

The increase in CO hydrogenation activity in conjunction with a shift in product distribution observed here has also been reported for Ni–TiO_2 catalysts by several authors[3,9–11] and for Ni–Nb_2O_5 and Ni–Ta_2O_5 catalysts by Kugler and Tauster.[12] However, of particular interest in our results was the finding that the Ni–Nb_2O_5 catalyst produced significant amounts of olefins. The olefin/paraffin ratios are not explicitly reported in previous studies.[9–11] Vannice and Garten[3] and Kugler and Tauster[12] found predominantly paraffinic hydrocarbon products, but their conversion levels and operating conditions are different from ours, preventing a direct comparison. The point remains unchanged that the nickel catalyst produced olefins when supported on niobia but not on silica, with other variables being the same in our study. In fact the olefin/paraffin ratio increased with increasing carbon number, such that for C_3 and C_4 hydrocarbons comparable amounts of olefins and paraffins were produced. This observation represents a unique manifestation of metal–support interaction.

We thank the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. The authors also thank the Sun Company for an equipment grant.

Received, 29th September 1982; Com. 1150

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