Production of Higher Alcohols from Synthesis Gas on Nickel Oxide-based Catalysts

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Nickel-containing catalysts, coprecipitated with titanium or manganese and promoted by copper and sodium, effectively produced higher alcohols such as ethanol and propanol from synthesis gas.

The reactions of CO and H_2 on various coprecipitated nickel catalysts have been studied, and nickel catalysts are usually used in industry for the production of hydrocarbons, especially methane. Though there are many reports on the hydrogenation of CO catalysed by Ni, Pt, or Rh supported on metal oxides, we were unaware of any reports concerning the production of alcohols on nickel-based catalysts until our recent discovery that higher alcohols such as ethanol and propanol were efficiently produced from CO and H_2 on nickel-containing catalysts.[1] We now report studies on the characteristic behaviour of coprecipitated nickel oxide-containing catalysts.

Table 1. Production of higher alcohols from synthesis gas (H_2 : CO, 2 : 1).[a]

Catalyst	Cu : Ni : M : Na[b] (molar ratio)	Reaction temp./K	CO conversion[c] /mol %	Selectivity for alcohols/mol %	Wt. % of C_{2+} alcohols
NiO/TiO_2[d]		630	20	9	57
		630	1[e]	0	0
$NiO–Al_2O_3$	1 : 1	632	20	7	23
$NiO–SiO_2$	1 : 1	631	20	<1	0
NiO–MnO	1 : 1	574	20	40	51
$NiO–TiO_2$	1 : 1	565	19	44	54
$NiO–TiO_2–Na_2O$	1 : 1 : 0.48	568	20	40	46
$CuO–TiO_2$	1 : 1	623	9[f]	65	7
$CuO–TiO_2–Na_2O$	1 : 1 : 0.48	617	12	79	6
CuO–NiO	1 : 1	593	20	48	13
$CuO–NiO–Na_2O$	1 : 1 : 0.48	599	21	48	36
$CuO–NiO–TiO_2$	1 : 1 : 1	587	18	39	20
$CuO–NiO–TiO_2–Na_2O$	1 : 1 : 1 : 0.32	572	21	65	49

[a] Pressure 6 MPa; gas space velocity 4000 h^{-1}. [b] M = Al, Si, Mn, or Ti. [c] CO converted into CO_2 is excluded. [d] 10 wt% NiO supported on titania. [e] After 20 h on stream. [f] CO conversion was only 10 mol% at 660 K.

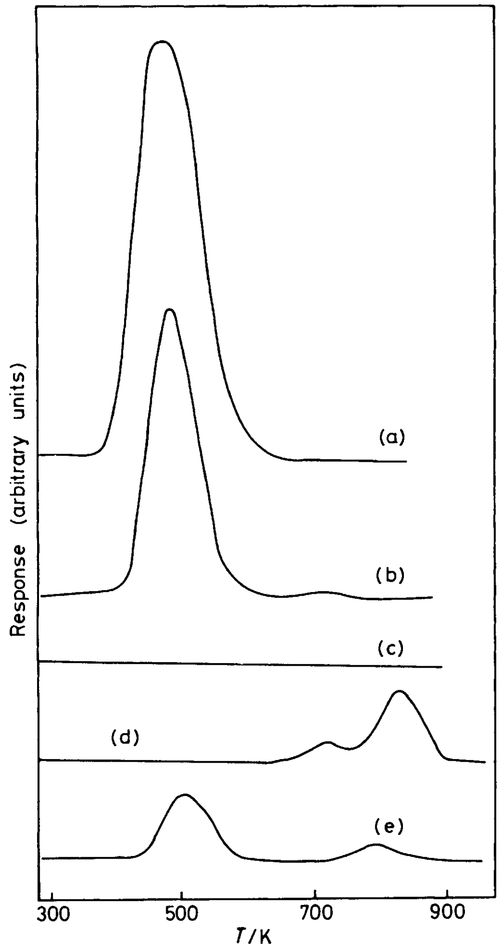

Figure 1. Effect of sodium on CO T.P.D. from coprecipitated Cu, Ni-containing catalysts following adsorption at 373 K; CO exposure 100 Torr: (a) CuO–NiO–TiO_2–Na_2O; (b) CuO–TiO_2–Na_2O; (c) CuO–TiO_2; (d) NiO–TiO_2–Na_2O; (e) NiO–TiO_2.

The catalyst samples were prepared by coprecipitation with sodium carbonate. The precipitates were aged at 353 K for 2 h, then washed thoroughly with distilled water, dried at 393 K for 5 h, and calcined at 623 K for 2 h in air. Sodium-impregnated catalysts and titania-supported nickel catalyst were prepared by conventional wet impregnation using aqueous solutions of sodium carbonate and nickel nitrate. The nickel-containing catalysts thus obtained were reduced in a hydrogen stream at 513 K for 7 h prior to use. The synthesis reactions over the catalysts (*ca.* 1.0 g) were carried out using an isothermal type micro-reactor at 6.0 MPa (H_2/CO molar ratio 2) and at a space velocity of 4000 h^{-1}. The conversion of CO into alcohols and hydrocarbons (but not CO_2) was maintained at around 20% by controlling the temperature of the catalyst bed. All products were analysed by on-line gas chromatography. The behaviour of chemisorbed CO was studied by temperature-programmed desorption (T.P.D.). Fresh catalysts were reduced in a hydrogen stream (200 cm^3/min) at 773 K for 1 h, and then evacuated for 1 h at the same temperature. After cooling to room temperature, the samples were exposed to CO at 100 Torr (1 Torr = 133.3 Pa) at 373 K for 1 h. After degassing to remove the residual gas, the CO adsorbed on the catalysts was desorbed by increasing the temperature linearly (18 K/min) in a helium stream and the amount of CO in the helium was detected by T.P.D.

Table 1 shows the results of the synthesis reactions. Two types of catalyst, NiO–TiO_2 and NiO–MnO, prepared by coprecipitation showed a comparatively high selectivity for alcohol production and a higher proportion of C_{2+} alcohols. The major by-product was methane. In contrast, the other titania-supported nickel catalyst (NiO/TiO_2 in Table 1) showed poor activity and was deactivated rapidly. On the coprecipitated CuO–TiO_2 catalyst, methanol was mainly produced. Coprecipitated NiO–Al_2O_3 and NiO–SiO_2 catalysts showed high selectivity for hydrocarbon production, mostly methane. The coprecipitated CuO–NiO–TiO_2 catalyst showed poor activity for alcohol production, but both the selectivity for alcohol production and the proportion of C_{2+} alcohols were significantly improved by impregnating this catalyst with sodium. The NiO–TiO_2 catalyst modified by sodium showed a lower selectivity for alcohol production but enhanced hydrocarbon production. Further, the activity of the CuO–TiO_2 catalyst was increased by sodium impregnation.

Thus, higher alcohols are mainly produced on NiO supported on an oxide such as TiO_2 or MnO, and both copper and sodium increase selectivity for alcohol formation. The effect of added sodium was studied by T.P.D., and the results (Figure 1) indicate the desorption of chemisorbed CO. The amount of CO associatively adsorbed on copper markedly increased when sodium was added to the catalysts, and the CO desorption peaks on NiO were shifted to higher temperature. These results suggest the electronic state of both copper and nickel is controlled by the added sodium. Praliaud *et al.*[2] presented evidence for an increase in electron density of metallic nickel due to the presence of potassium and they concluded that the potassium was mainly present as K^+ and located on the support. Further they suggested that an Ni–O–K surface complex was formed. So we think that the sodium is present as Na^+, which forms an Ni–O–Na surface complex, and is mainly located on titania in this case. According to Kiskinova,[3] high-temperature CO desorption peaks result from the recombination of C(ads.) and O(ads.) species derived from dissociatively adsorbed CO. Consequently, CO adsorbed on the NiO–TiO_2–Na_2O catalyst is more strongly bonded to nickel because of the added sodium and the amount of dissociatively adsorbed CO increases. If molecular CO adsorbed on the catalysts contributes to carbon-chain growth,[4] the fact that the NiO–TiO_2–Na_2O catalyst led to a lower proportion of C_{2+} alcohols than that on the NiO–TiO_2 catalyst can be explained by the increase in the amount of dissociatively adsorbed CO.

CO adsorbed on CuO is easily desorbed at room temperature because it is weakly adsorbed, but addition of sodium to catalysts containing CuO leads to strong adsorption of molecular CO (Figure 1). So the activity of the CuO–TiO_2–Na_2O catalyst would be more stabilized than that of the CuO–TiO_2 catalyst. On addition of copper and sodium to the NiO–TiO_2 catalyst, the molecular CO adsorbed on the copper leads to an increase in selectivity for alcohol formation, with the proportion of C_{2+} alcohols being maintained. The performance of these catalysts can be correlated with the T.P.D. results in this way.

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