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A new type of selectivity by using bimetallic catalysts

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The results demonstrate a very interesting change in selectivity for the bimolecular reaction between benzophenone and methanol in the presence of hydrogen to produce ether; 1-methoxy-1,1-diphenylmethane by using silica supported bimetallic Ni-Cu (75:25) and Ni-Fe (75:25) catalysts as compared to Ni/SiO_2. However, no suppression of C-O bond hydrogenolysis was observed for bimetallic as well as for TiO_2 supported catalysts.

Keywords: Benzophenone; hydrogenation; hydrogenolysis; Ni-Cu and Ni-Fe bimetallic catalysts

1. Introduction

The activity and selectivity of metallic catalysts are known to be influenced by alloying and by metal support interaction. Sinfelt and coworkers [1] showed that a small addition of copper to nickel produced a large decrease in activity for ethane hydrogenolysis but hardly any change in activity for dehydrogenation of cyclohexane. Ko and Garten [2] more recently demonstrated that a similar change in activity can be achieved in the case of Ni/TiO_2 as compared to Ni/SiO_2. However, there have been very few attempts to exploit the above findings in liquid phase hydrogenations which are frequently encountered in organic syntheses. The present work was primarily undertaken to investigate the effect of alloying and metal support interaction on the activity and selectivity in the hydrogenation of benzophenone, which is known to be accompanied by an undesirable side reaction involving hydrogenolysis of the carbinol.

2. Experimental

Hydrogenation of benzophenone was investigated on Ni, Ni-Cu (75:25) and Ni-Fe (75:25) supported on silica (Aerosil 200) and TiO_2 P25) of Degussa. The

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Table 1
Reaction products of benzophenone in methanol in presence of Ni based catalysts and hydrogen [a]

Catalyst	Time (hrs)	Conversion of benzophenone (%)	Selectivity to products [b] (mol%)		
			I	II [c]	III
Ni/SiO_2	4.5	89.33	68.26	19.67	12.07
Ni/TiO_2(LTR)	2.5	92.6	52.06	37.47	10.47
Ni/TiO_2(HTR)	2.0	87.4	60.72	30.26	9.02
$Ni\text{-}Cu/SiO_2$ [d]	6.0	83.8	46.40	43.68	9.92
$Ni\text{-}Fe/SiO_2$	4.5	85.86	84.47	4.64	10.89
$Ni\text{-}Fe/TiO_2$	2.0	86.7	84.48	1.67	13.85

[a] Benzophenone (0.65 mol) was hydrogenated by using 0.24 gm catalyst in 35.5 ml of methanol at 408 K and 850 psi of hydrogen pressure. The catalysts were pre-reduced and used without exposure to air.

[b] I: Benzhydrol; II: Ether (1-methoxy-1,1-diphenylmethane); III: diphenylmethane.

[c] II was separated by using column chromatography and was identified by IR and NMR.

[d] Catalyst loading = 0.48 gm.

LTR: Low Temperature Reduction.

HTR: High Temperature reduction.

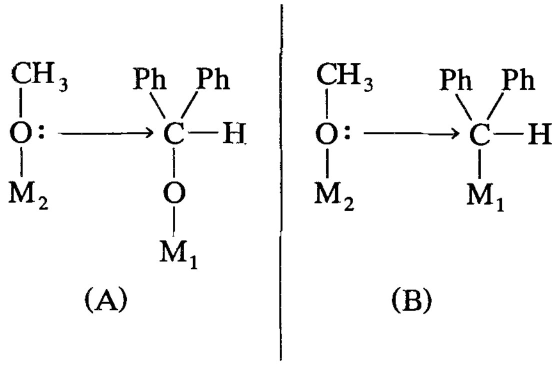
supported catalysts were prepared by impregnation of nitrates in appropriate proportion by incipient wetness technique. The total metal loading on the support was kept constant at 20% by weight. The nitrates were decomposed to corresponding oxides by heating in a flow of air at 723 K for 4 hours. The catalysts were reduced in H_2 at 523 K for 2 hours followed by another 2 hours at 723 K prior to use. The X-ray diffraction patterns of the catalysts showed no presence of oxides. The diffraction patterns showed presence of a single phase for Cu-Ni catalysts while presence of some non-alloyed nickel was observed in the Ni-Fe catalysts. The detailed characterization of the catalysts will be published elsewhere [3]. The hydrogenation of benzophenone in methanol was carried out in a 100 ml Parr autoclave under hydrogen partial pressure of 850 psi at 408 K. The products were analyzed on a gas chromatograph using 2 m × 0.33 cm 10% Carbowax (KOH washed) on a Chromosorb W column using FID.

3. Results and discussion

The results of the investigation are summerized in table 1. The selectivities to different products obtained at a conversion of 85–90% are reported in this table. In addition to the hydrogenation to the carbinol a more predominant side reaction on Ni/SiO_2 and $Ni\text{-}Cu(75:25)/SiO_2$ catalyst is the formation of an ether, 1-methoxy-1,1-diphenylmethane ($C_6H_5CH(OCH_3)C_6H_5$ which involves participation of the solvent, methanol. Formation of ethers from the reactions of alcohols on nickel catalysts has been previously reported [4]. Also formation of ether during hydrogenation of ketone in alcoholic solvents over noble metal catalysts has been reported [5]. In the continuation of the reaction the ether was converted to diphenylmethane. The use of Ni/TiO_2 resulted in an enhancement of the rate of hydrogenation. However, the selectivity to benzhydrol was affected adversely. Contrary to expectations, the reduction at high temperature (HTR-823 K) did not result in a suppression of hydrogenolysis of the carbinol. The activity of the catalyst was reduced considerably by addition of copper. Here again the expected decrease in hydrogenolysis was not observed but the ether formation was enhanced significantly. Addition of iron also did not decrease the hydrogenolysis, however the ether formation was observed to reduce significantly. Ni-Fe/TiO_2 catalyst produced still lower quantities of ether.

The above results clearly indicate that–as anticipated earlier–alloying as well as high temperature reduction of Ni/TiO_2 catalyst do not suppress the C-O hydrogenolysis suggesting that the hydrogenolysis of C-O bond probably involves sites different from those required for C-C bond hydrogenolysis. However, the result demonstrates a very interesting change in selectivity of ether formation as a result of alloying. The reaction was further investigated by using pure benzhydrol as substrate on Ni, Ni-Fe and Ni-Cu on silica catalysts. The results are shown in fig. 1 and clearly show remarkable difference in the yield of ether by addition of copper and iron.

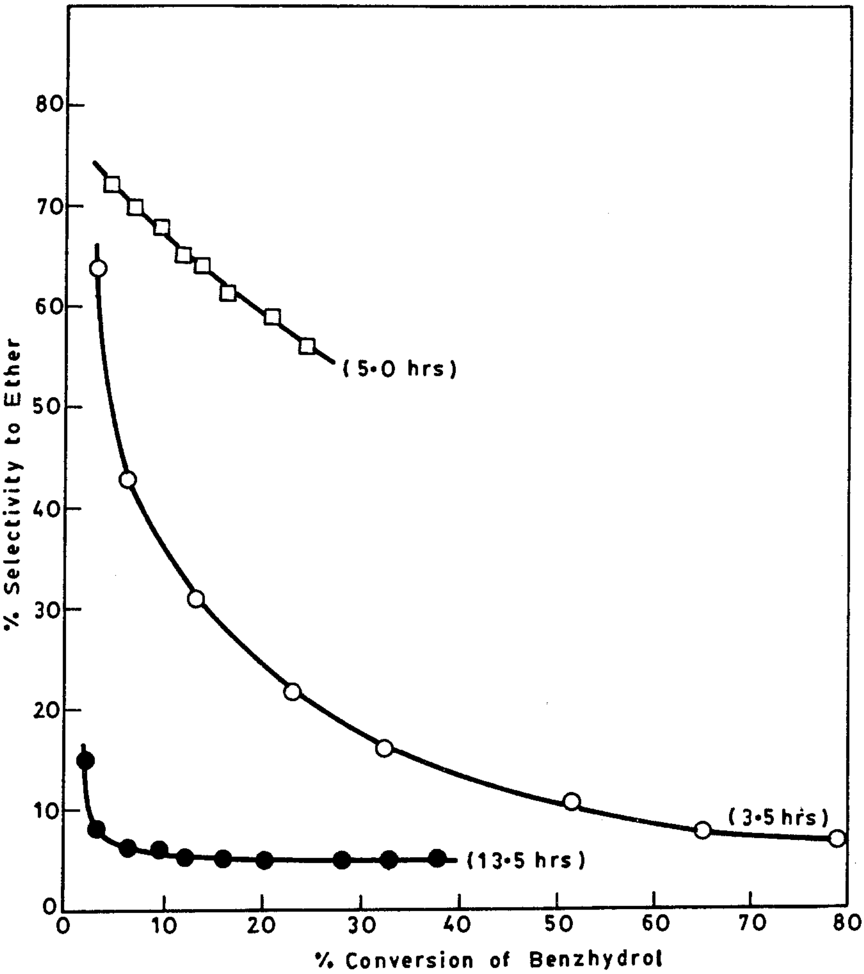
Formation of methoxy species by dissociation of methanol on Fe, Ni and Cu single crystal surfaces has been demonstrated by Madix [6]. The ether formation is also enhanced by the presence of electron withdrawing substituents on the carbinol carbon (e.g. no ether formation occurs with phenyl methyl carbinol under similar conditions). Hence ether formation is very likely to occur by nucleophilic attack of a methoxy species on carbinol carbon either prior to or after hydrogenolysis of the C-O bond as shown respectively in (A) and (B) below:



(A) (B)

M_1, M_2: Metal sites

In Ni-Cu and Ni-Fe catalysts the surface is known to be enriched by copper [7] and iron [8]. Thus on the bimetallic catalysts the nickel atoms will be



○——○: Ni/SiO$_2$, 0.24 gm, □——□: Ni-Cu/SiO$_2$, 0.48 gm, ●——●: Ni-Fe/SiO$_2$, 0.48 gm

Fig. 1. Variation of selectivity to ether (1-methoxy-1,1-diphenylmethane) with conversion of benzhydrol over various catalysts. The figures in parentheses indicate the reaction time. *Reaction conditions*: Benzhydrol, 8 gm; Methanol, 35.5 ml; Temperature, 408 K; Hydrogen pressure, 850 psi.

preferentially surrounded by copper or iron atoms on the surface. Hence the above bimolecular reaction is likely to involve methoxy species bonded to iron or copper on the bimetallic catalysts. Madix [6] has reported heats of adsorption of the methoxy species on these metals, which are as follows: Fe: −87, Ni: −60, Cu: −8 kJ/mol. These heats of adsorption suggest that the ease of addition of the methoxy species adsorbed on these metals is likely to be in the order Cu > Ni > Fe, which indeed agrees with the order in which the yield of ether varies on Ni-Cu, Ni and Ni-Fe catalysts.

4. Conclusions

The present communication shows that in the hydrogenation of benzophenone the hydrogenolysis of the C-O bond cannot be suppressed by using high temperature reduced nickel on titania or bimetallic catalysts. The results however demonstrate a new type of selectivity which can be achieved using bimetallic catalysts. It is shown that the selectivity of bimolecular reactions can be modified remarkably by choosing an alloy component with appropriate strength of adsorption for the reactants.

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