Catalysis Letters 15 (1992) 385–391

Binary spinel cobaltites of nickel, copper and zinc as precursors of catalysts for carbon oxides methanation

D. Klissurski, E. Uzunova and K. Ivanov [1]

Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Sofia 1040, Bulgaria
[1] Department of Chemistry, Agrotechnical University, Plovdiv 4000, Bulgaria

Received 22 January 1992; accepted 29 May 1992.

The hydrogenation of carbon oxides (CO and CO_2) on bimetallic Cu/Co and Ni/Co as well as Co/ZnO catalysts obtained by reduction of the corresponding spinel cobaltites $Me_xCo_{3-x}O_4$ is investigated. The predominant hydrogenation process is methanation and in the case of nickel cobaltite high and stable activity and selectivity are reached, no carbon deposition and carbide formation being observed.

Keywords: Methanation; spinel cobaltites; cobalt; nickel; copper; zinc

1. Introduction

Hydrogenation of CO_x to methane is a special case of the Fischer–Tropsch process. Since the classical works of Sabatier and Senderens [1,2], where nickel and cobalt catalysts are reported, nickel is still the most studied catalyst for methanation due to its high efficiency and relatively low price [3–7]. Methanation is mainly applied for (i) the production of methane-enriched gases (substituents of natural gas) and (ii) the elimination of carbon monoxide admixtures from hydrogen, thus preventing the poisoning of catalysts for ammonia production [8].

Cobalt is the next metal in activity towards the methanation reaction. However, deposition of larger amounts of carbon than in the case of nickel has been established [9]. Various crystal forms of cobalt are found to be active in CO hydrogenation, the highest activity belonging to the structure with a high degree of disorder, which has been established by Hofer and co-workers [10]. In a recent study of Copperthwaite and co-workers [11], formation of a β-Co phase was detected by in situ X-ray diffraction during a CO hydrogenation reaction over different cobalt-containing catalysts.

The regime of reduction plays an important role in the preparation of an active catalyst. It is not necessary to attain complete reduction of the cobalt catalysts [12]. Maximum activity has been observed at reduction degrees of 60–70%. The presence of oxides, that are not reduced, leads to the formation of catalysts with a larger specific surface area and a higher activity.

The hydrogenation of CO_2 to methane has not been investigated to the same extent as that of CO [13,14]. The catalysts used for the two processes are in principle the same, but hydrogenation of CO_2 does not proceed till measurable CO amounts are present in the system. Usually, the hydrogenation of CO_2 to methane takes place with a high selectivity.

The possibility of application of highly dispersed spinel cobaltites of nickel, copper and zinc as precursors of catalysts for the hydrogenation of carbon oxides is studied in the present paper.

2. Experimental

The spinel cobaltites were prepared from coprecipitated hydroxidecarbonates [15–17] by thermal decomposition at 573 K in air. The catalytic process was performed in a fixed bed reactor in the temperature range 473–573 K and pressure 1–10 atm. The spinel cobaltites were reduced in a gas mixture with composition $H_2/CO/CO_2 = 80/15/5$ at 523 K for 4 h. The reaction products were analyzed gas-chromatographically with a Perkin-Elmer apparatus using Porapak Q columns with thermal conductivity and flame ionization detectors. The space velocity (GHSV) was varied in the interval 10^2–(2×10^3) h^{-1}.

3. Results and discussion

The reactivity of the different spinel cobaltites towards hydrogen can be compared by temperature-programmed reduction. The TPR spectrum of copper cobaltite exhibits a single maximum at 583 K, table 1. The spectra of zinc and nickel cobaltite have three peaks each, the third peak of the zinc cobaltite partly overlapping with the second. The spectra are explained assuming successive reduction of Me^{2+}, Co^{3+} and Co^{2+} cations in the spinel lattice. In the case of nickel cobaltite, the sequence of reduction is Ni^{2+}, Co^{3+}, Co^{2+}, while with zinc cobaltite the reduction proceeds in the order Co^{3+}, Co^{2+}, Zn^{2+}. The maxima of reduction of Co^{3+} and Co^{2+} agree with the literature data for Co_3O_4 [18]. The presence of the easily reducible copper ion in the copper cobaltite lattice is the reason for the easier reduction of cobalt. This is also characteristic of other easily reducible oxides, e.g., of silver, and is attributed to the high formation rate of copper atoms or clusters, which act as reduction sites of cobalt oxides.

Catalysts for carbon oxides hydrogenation are obtained by reduction of the spinel cobaltites. The degree of reduction of the oxides ranges from 60 to 80%. Up to 513 K and pressure 10 atm no hydrogenation is observed with all three

Table 1
Temperature-programmed reduction data for different cobaltites

Catalyst	Peak maxima (T (K))	Reduction steps
$Cu_{0.95}Co_{2.05}O_4$	585	
$ZnCo_2O_4$	598	$Co^{3+} \rightarrow Co^{2+}$
	673	$Co^{2+} \rightarrow Co^0$
	720	$Zn^{2+} \rightarrow Zn^0$
$NiCo_2O_4$	530	$Ni^{2+} \rightarrow Ni^0$
	588	$Co^{3+} \rightarrow Co^{2+}$
	640	$Co^{2+} \rightarrow Co^0$
Co_3O_4 [a]	593	$Co^{3+} \rightarrow Co^{2+}$
	663	$Co^{2+} \rightarrow Co^0$

[a] Experimental data from ref. [17].

cobaltites. At 523–553 K the copper–cobalt catalyst shows a higher activity than the other two catalysts. Above 553 K the activity of the three cobaltites sharply increases (fig. 1). In the presence of nickel and zinc cobaltite, the main product of CO hydrogenation is methane (table 2), more than 98% CO conversion being achieved above 573 K. At lower conversion degrees of CO, the CO_2 concentration increases up to two times, due to the reaction [19]

$$2CO + 2H_2 \rightarrow CH_4 + CO_2.$$

Above 573 K, CO_2 is methanated and the conversion reaches 98% (fig. 2). Methanation in presence of copper cobaltite catalyst proceeds with a lower catalyst activity and selectivity. In addition to methane, higher hydrocarbons (up to C_5) are also obtained along with small amounts of oxygen-containing prod-

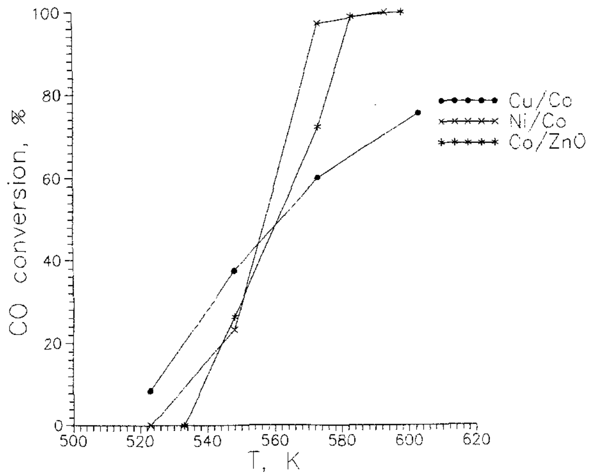

Fig. 1. Carbon oxide conversion on Co/ZnO, Cu/Co and Ni/Co catalysts, depending on temperature at 10 atm and GHSV 2×10^2 h^{-1}.

Table 2
Product distribution and conversion for the zinc–cobalt, copper–cobalt and nickel–cobalt catalysts at 573 K

	ZnO/Co 1 atm	Cu/Co 10 atm	Ni/Co 1 atm
CO conversion (%)	94.0	74.3	96.0
CO_2 conversion (%)	70.6	–	84.6
products composition (%)			
methane	98.6	56.2	99.2
ethane	–	5.4	0.5
ethylene/acetylene	1.0	13.6	0.3
propane	–	9.3	–
methanol	0.27	0.5	–
butane	–	6.0	–
ethanol	0.12	2.9	–
pentane	–	4.0	–
n-propanol	–	2.1	–

ucts (table 2). The phase composition of the reduced catalysts used for 10 h in reaction is shown in the X-ray diagrams (fig. 3). The zinc cobaltite catalyst contains phases of ZnO, cubic Co, α-Co and a Co_2C impurity. In the case of the copper–cobalt catalyst, there is a high content of a Co_2C phase, together with metallic copper and cobalt. Carbidization of copper/cobalt containing catalysts was detected also by Courty et al. [20].

The nickel–cobalt catalyst, which has the highest activity in the methanation reaction, displays the presence of metallic nickel and cubic cobalt, the lines of

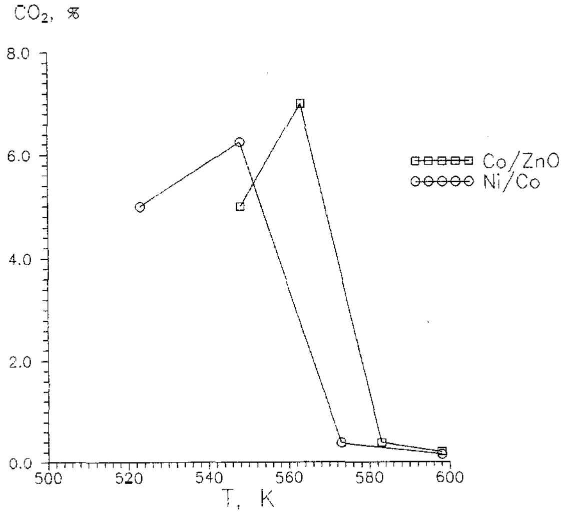

Fig. 2. Change in CO_2 concentration during the methanation reaction at 10 atm and GHSV 2×10^2 h^{-1}.

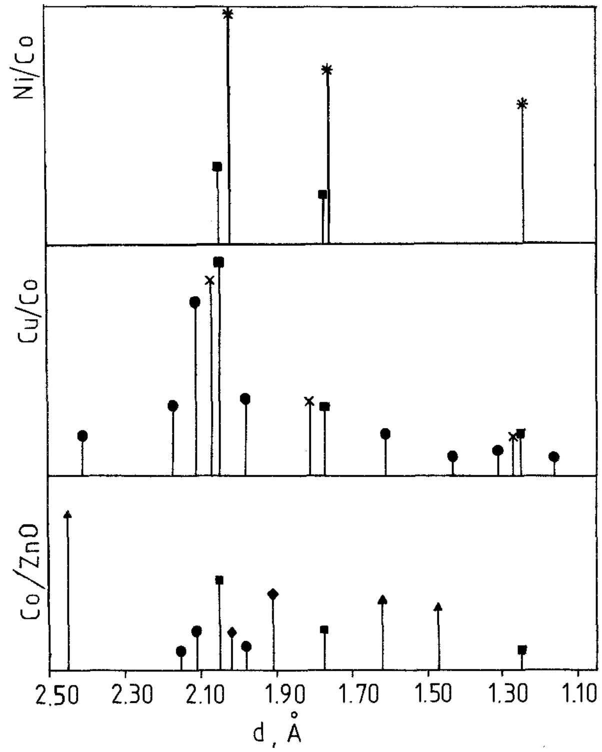

Fig. 3. Phase composition of Co/ZnO, Cu/Co and Ni/Co catalysts after 10 h catalytic test. (▲) ZnO, (♦) α-Co, (■) Co_{cubic}, (●) Co_2C, (×) Cu, (∗) Ni.

cobalt being much less intense than those of nickel (fig. 3). It can be suggested that the reduction of nickel(II) is complete. Regardless of the possibility of formation of solid solutions with unlimited solubility by the nickel–cobalt

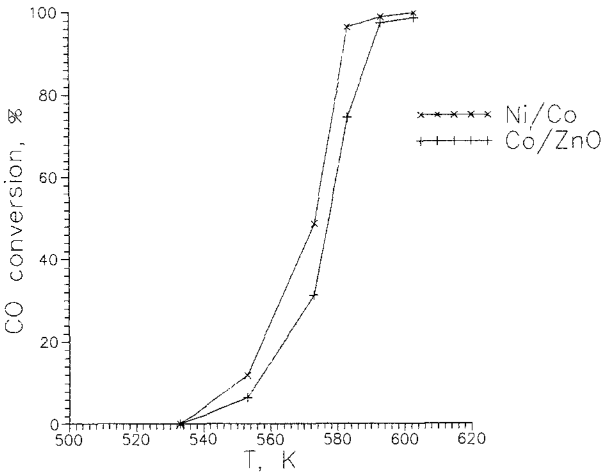

Fig. 4. Carbon oxide conversion on Co/ZnO and Ni/Co catalysts at different temperatures and 1 atm and GHSV 1.8×10^3 h^{-1}.

system, separate metallic nickel and cobalt crystallites are formed during reduction of nickel cobaltite. No carbide phases and carbon deposition are established.

The pressure does not affect substantially the ZnO/Co and the Ni/Co catalysts, but for the Cu/Co catalyst a pressure of 10 atm was needed to achieve measurable conversion. The CO conversion in the temperature interval 523–673 K for ZnO/Co and Ni/Co catalysts at 1 atm is shown in fig. 4. The temperature dependences are similar like those observed at high pressure, fig. 1, where in the range 553–573 K a strong increase in the CO conversion is found. At atmospheric pressure a similar enhancement in the activity of Co/ZnO and Ni/Co catalysts was registered at higher temperature, 563–583 K. The nickel–cobalt catalyst shows the highest activity and selectivity in the methanation reaction. The high degree of carbidization of the Co/ZnO and Cu/Co catalysts suggests that the carbide mechanism of methanation may prevail in these cases.

4. Conclusion

It is shown, that on the basis of spinel cobaltites, active and selective catalysts for CO and CO_2 methanation may be obtained. In the case of nickel cobaltite, the presence of unreduced mixed oxide favors the high dispersity of the active bimetallic phase and prevents sintering. For the Cu/Co and Co/ZnO catalysts, a higher degree of reduction of cobalt was reached, but carbidization of the catalysts was observed. The higher degree of cobalt reduction leads to carbide phase formation.

References

[1] P. Sabatier and J.B. Senderens, Compt. Rend. Acad. Sci. (Paris) 134 (1902) 514.
[2] P. Sabatier and J.B. Senderens, J. Soc. Chem. Ind. 21 (1902) 504.
[3] H. Vandrell and M. Bowker, Appl. Catal. 30 (1987) 151.
[4] K. Bailey, G. Chai and J. Falconer, *Proc. 9th Int. Congress on Catalysis*, Vol. 3 (1988) p. 1090.
[5] K. Kester, E. Zagli and J. Falconer, Appl. Catal. 22 (1986) 311.
[6] B. Chen, J. Falconer, K. Bailey and B. Sen, Appl. Catal. 66 (1990) 283.
[7] G. Somorjai, Catal. Rev. Sci. Eng. 23 (1981) 189.
[8] G. Mills and F. Steffgen, Catal. Rev. 8 (1973) 159.
[9] M. Schlesinger, J. Demeter and M. Greyson, Ind. Chem. Eng. 48 (1956) 68.
[10] R. Anderson, W. Hall and L. Hofer, J. Am. Chem. Soc. 70 (1948) 2465.
[11] S.E. Colley, R.G. Copperthwaite and G.J. Hutchings, Catal. Today 9 (1991) 203.
[12] L. Hofer, in: *Catalysis. Hydrocarbon Synthesis, Hydrogenation and Cyclization*, Vol. 4, ed. P. Emmett (Reinhold, New York, 1956) p. 373.
[13] D. Darensbourg, Chr. Bauch and C. Ovalles, Rev. Inorg. Chem. 7 (1985) 315.
[14] A. Rehmat and S. Randhava, Ind. Eng. Chem. Prod. Res. Develop. 9 (1970) 512.
[15] D. Klissurski and E. Uzunova, J. Mater. Sci. Lett. 9 (1990) 576.
[16] D. Klissurski and E. Uzunova, J. Mater. Sci. Lett. 9 (1990) 1255.

[17] D. Klissurski and E. Uzunova, Chem. Mater. 3 (1991) 1060.
[18] S. Bhatia, J. Beltramini and D.D. Do, Catal. Today 7 (1990) 360.
[19] M. Greyson, in: *Catalysis. Hydrocarbon Synthesis, Hydrogenation and Cyclization*, Vol. 4, ed. P. Emmett (Reinhold, New York, 1956) ch. 6, p. 473.
[20] Ph. Courty, D. Durand, Ed. Freund and A. Sugier, J. Mol. Catal. 17 (1982) 241.