Effect of the Basic Function in Co,MgO/C Catalysts on the Selective Oxidation of Methane by Carbon Dioxide

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Magnesium oxide prevents deactivation of cobalt catalysts during the CH_4 + CO_2 reaction, probably owing to a change in the structure and reactivity of chemisorbed intermediates.

Transformation of methane and carbon dioxide, the cheapest carbon-containing materials, into more valuable compounds is an important objective in the current research in catalysis. Methane can be partially oxidized to methanol and/or formaldehyde, or dimerized to ethane and ethylene *via* oxidative dehydrogenation. Unfortunately, both reactions have hitherto only been achieved with low yields. Carbon dioxide can be used to obtain a number of compounds, such as carbon monoxide, methanol and methane *via* hydrogenation, or oxalate and organic acids by coupling with organic substrates. However, in these cases hydrogen or expensive reactants are used, which may limit the economical use of such methods. Recently, the reaction between both reactants to produce synthesis gas ($CO_2 + CH_4 \rightarrow 2CO + 2H_2$) has been considered. Several catalysts are effective for this reaction, including Ni/SiO_2,[1] Rh/Al_2O_3,[2] $Ln_2Ru_2O_7$[3] (Ln = lanthanoid element), Pt/Al_2O_3,[4] Ru or Ir supported on Eu_2O_3,[5] and Ni, Pd, Ru, Rh or Ir supported on Al_2O_3.[6,7] In general the active phase is a Group VIII metal (mainly noble metals) to which, in some cases, basic ingredients such as Ln or Eu are added. This communication reports the catalytic behaviour of the Co,MgO/C system in the partial oxidation of methane with carbon dioxide. In order to increase the catalytically active surface area, cobalt and magnesium oxide were dispersed on an inert high-purity activated carbon. The interaction of CH_4 and CO_2 with the catalyst was studied by temperature programmed desorption (TPD).

The support was a commercial activated carbon (from Merck). It was treated with HCl and HF solutions in order to remove inorganic materials and, after washing and drying, was heated to 1223 K in a N_2 flow. The resultant support had a Brunauer–Emmett–Teller (BET) surface area of 1100 $m^2 g^{-1}$ (N_2, 77 K). Catalysts were prepared by consecutive impregnation with ethanolic solutions of cobalt and magnesium nitrates.[8] Before reaction and TPD experiments, samples were reduced in a hydrogen flow at 673 K for 12 h. The catalytic activity was examined over a range of temperatures (673–923 K) at atmospheric pressure, using a CH_4–CO_2–He (10:10:80) flow (100 $cm^3 min^{-1}$). Individual flows of reactants (CH_4, CO_2) and diluent (He) were controlled by mass flowmeters, and the effluents from the reactor were analysed by gas chromatography. The desorbed gases (CH_4, CO, CO_2 *etc.*) during the TPD measurements were analysed by an on-line mass quadrupole system with the capacity to follow simultaneously sixteen masses (*m/z*).

The catalytic performance of the catalysts at three reaction temperatures and for several times on stream is reported in Table 1. As expected, synthesis gas formation becomes more efficient at higher temperatures, with CO yields of 16% at 773 K and 60% at 923 K for the Co,MgO/C catalyst. These values are near the equilibrium conversions calculated from the equilibrium constants.[1] It is worth noting that whereas the Co,MgO/C catalyst is stable during the reaction times at all the temperatures studied, the Co/C sample is gradually deactivated and suddenly becomes inactive at the highest reaction temperature (923 K) studied. In contrast to noble metal samples including Ir,[5,7] Ru,[3,5] Rh[2,4,6] or Ru on activated carbon,[9] which maintain a very high performance for many hours on stream, non-noble metals such as Ni,[7] or Co in our case, rapidly decline in conversions and selectivities. This deactivation seems to be due to carbon deposition over the metal, as these latter catalysts are efficient for the Boudouard reaction ($2CO \rightarrow CO_2 + C$). The activity of the Co/C sample which was deactivated by the reaction at 923 K was not regenerated by treatment in hydrogen at temperatures as high as 673 K, which indicates the low reactivity of these carbon species. These results suggest that the role of MgO in the Co,MgO/C system is to avoid the Boudouard reaction. The deactivation by carbon deposition on the Co/C sample more strongly affects the methane than the carbon dioxide activation, since the yield for hydrogen production from CH_4 decreases to a greater extent than the yield for carbon monoxide (Table 1). Other deactivation mechanisms such as sintering of the cobalt particles cannot be excluded. However, this is not considered to be the principle mechanism of deactivation, since studies carried out at reaction tempera-

Table 1 CH_4 + CO_2 reaction over Co/C and Co,MgO/C at several temperatures and times on stream[a]

Catalyst	Reaction temp./K	Time on stream/min	CH_4 converted (%)	CO_2 converted (%)	Yield[b] of H_2 (%)	Yield[c] of CO (%)
Co/C	773	5	12.1	19.5	8.1	14.2
	773	40	10.4	17.6	6.5	12.5
	873	5	33.2	46.6	24.4	35.1
	873	50	26.2	39.5	17.6	28.5
	873	120	15.2	33.4	9.3	25.9
	923	5	0.6	4.1	0.0	3.5
	923	40	0.1	1.1	0.0	0.8
Co,MgO/C	773	5	14.2	21.6	9.5	15.7
	773	30	14.1	22.1	9.9	16.2
	873	5	49.0	60.5	37.9	46.6
	873	50	47.1	58.9	36.0	45.2
	873	120	46.1	58.3	35.0	44.3
	923	5	66.1	77.1	52.1	60.4
	923	40	64.1	76.1	50.2	59.1

[a] Reactant gas mixture: CH_4–CO_2–He (10:10:80); total flow: 100 $cm^3 min^{-1}$; total pressure, 0.1 MPa. [b] Yield = (amount of H_2 in products)/(2 × amount of CH_4 in reactants). [c] Yield = (amount of CO in products)/[amount of (CO_2 + CH_4) in reactants].

tures of 773 K also show a significant deactivation for the Co/C sample compared to the Co,MgO/C sample. In a previous study on these catalysts[8] it has been shown by TPD of CO that carbon-supported magnesium oxide is able to form carbonate-like structures by the interaction of CO with adsorbed oxygen and/or lattice O^{2-} ions. Also, it has been proved that the addition of MgO to Co/C induces a shift of the high temperature TPD peaks associated with CO bridged species on Co towards higher temperatures (from 680 K in Co/C to 750 K in Co,MgO/C). Thus, the basic function (MgO) stabilizes the chemisorbed CO at higher temperatures and, in this way, prevents the Boudouard reaction.

TPD spectra of adsorbed CO_2 have been recorded, analysing both the desorbed CO_2 and the CO produced. Some points arise from the comparison of TPD spectra obtained for Co/C, MgO/C and Co,MgO/C samples. CO_2 chemisorption takes place mainly on MgO (desorption peaks at 570 and 890 K), and the decomposition of adsorbed CO_2 to CO, which is observed at temperatures higher than 673 K, is carried out on metallic cobalt. Therefore, a new type of cooperative effect is identified. On the other hand, TPD spectra of adsorbed CH_4 show that together with physically adsorbed CH_4 and weakly chemisorbed species (TPD peaks at 373 and 473 K), a high temperature peak, near 800 K, appears for samples containing cobalt. In this case the presence of MgO in the catalyst does not seem to be as important as for CO or CO_2 chemisorption.

In conclusion, the role of basic function (MgO) on the activities and selectivities of cobalt catalysts in the partial oxidation of methane with carbon dioxide to yield synthesis gas is to prevent the deactivation of the catalyst. By studying the interaction of reactants (CO_2, CH_4) and products (CO) on the catalyst surfaces (TPD) it can be inferred that the presence of MgO changes the nature of CO_2 and CO chemisorbed species, this avoiding carbon deposition by the Boudouard reaction on the working catalyst, and the subsequent deactivation.

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