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Oxidative coupling of methane at 600°C on CaNiK oxide catalysts

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We are herewith reporting new data which modifies, explains and extends our earlier work on this subject. Previous observations of low CH_4 conversion and high selectivity to C_2 hydrocarbons were erroneous due to the formation of bulk $CaCO_3$ in the catalyst. The carbonate was detected by powder X-ray diffraction and was shown to accumulate during the reaction and decompose during regeneration. Catalytic runs which incorporated an internal standard revealed a deficit in the C balance consistent with carbonate formation. Actual CH_4 conversions were $\approx 20\%$ with $\approx 15\%$ selectivity to hydrocarbons. The effect of steam in promoting coupling over combustion was affirmed.

Keywords: Catalysts; methane conversion; oxidative coupling; X-ray diffraction; effect of steam

1. Introduction

Calcium–nickel–potassium oxide catalysts for the oxidative coupling of methane have been prepared by the thermal decomposition of the mixed salts. The performance of these catalysts has been previously described [1–3]. X-ray diffraction of the most active of these catalysts showed reflections of CaO and NiO only. Subsequent work using the mixed oxides yielded catalytic results similar to the earlier work, that is, high C_{2+} selectivity was observed initially which rapidly declined after 5 to 9 h on stream. A detailed study using the mixed oxide catalyst was undertaken to observe changes in the catalyst during the time on stream.

2. Experimental results and discussion

Catalysts of the composition $Ca_3NiK_{0.1}O_x$ were made by mixing and grinding CaO, NiO and KNO_3 powders followed by activation in flowing oxygen at 680°C

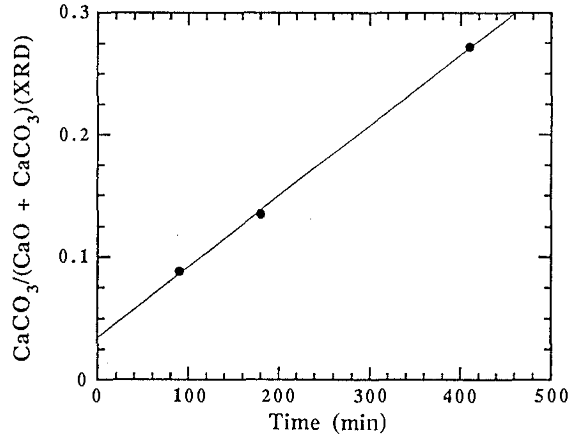

Fig. 1. Carbonate accumulation in $Ca_3NiK_{0.1}O_x$ catalysts X-ray diffraction.

for 18 h. The catalysts were reacted at 600°C in a mixture of methane, oxygen and steam (3:1:6.5 molar ratio) for 1.5, 3.0 and 6.8 h. X-ray diffraction was performed on the used catalyst. The formation of bulk calcium carbonate with the calcite structure was observed, the amount of which grew as the reaction progressed. Fig. 1 shows the amount of $CaCO_3$ in the catalyst as a function of time on stream. This increase must occur through the formation of CO_2 in the gas phase which then reacts with the CaO to form $CaCO_3$. No appreciable $Ca(OH)_2$ was observed in the XRD patterns.

This formation of bulk carbonate was related to the catalyst deactivation described in one of the previous studies [3], which also found that the deactivated catalyst could be reactivated by treatment with oxygen or oxygen plus steam at 680°C. We have now looked to see if the activation and regeneration conditions were sufficient to decompose bulk $CaCO_3$ formed during the reaction. Table 1 shows the decomposition of carbonate as observed by XRD for two used catalysts.

Regeneration in 2.5 cm^3/min oxygen at 680°C overnight (activation conditions) decomposed about half of the carbonate. Regeneration at 680°C in oxygen and steam decomposed essentially all of the carbonate. Treatment at 600°C in oxygen and steam (operating temperature) decomposed just over 10% of the

Table 1
Catalyst regeneration (XRD)

Catalyst	$CaCO_3/(CaO+CaCO_3)$ ratio		%$CaCO_3$ decomposition
deactivated	0.40	0.44	–
regenerated (O_2, 680°C)	–	0.23	48
regenerated (O_2, H_2O, 680°C)	–	0.01	98
regenerated (O_2, H_2O, 600°C)	0.35	–	11

Table 2
Oxidative methane coupling; $Ca_3NiK_{0.1}O_x$ catalyst. Mixed oxides; activation: O_2, 680°C, 18 h. Rxn; $CH_4:O_2:H_2O = 3:1:6.5$, 4.0 mmol CH_4/g cat/h, 600°C

Time (h)	CH_4 conv. (%)	Selectivity (%)			C balance (%)
		C_{2+}	CO_2	undetected in gas phase	
1.5	21	16	1	83	82
2.5	20	15	2	83	83
5.5	20	11	3	86	83
7.5	19	8	33	59	89
11.5	19	7	51	42	92

carbonate. The greater decomposition at the higher temperature can be explained by the higher decomposition pressure of CO_2 over $CaCO_3$ ($\approx$ 16 mm Hg at 680°C versus $\approx$ 2 mm Hg at 600°C). The presence of steam is not expected to affect this equilibrium, as the temperature is above that needed to dehydrate $Ca(OH)_2$, the absence of which is confirmed by XRD. Steam can then act only to enhance the diffusion of bulk carbonate to the surface and/or to help carry the CO_2 away in the effluent. The decomposition of carbonate may then explain the regeneration of catalyst performance upon high temperature treatment.

In order to form the quantity of carbonate observed in the XRD, considerable deficits in both the carbon and oxygen balances must be observed. Upon re-examination of earlier work and of the experimental unit, an error was discovered in the measurement of the reactor effluent which led to erroneous material balances. In order to obtain proper balances, the equipment was modified such that nitrogen could be used as an inert internal standard. The results of a typical run using the internal standard are shown in table 2.

The composition of detectable products in the gas phase (hydrocarbons and CO_x) shows the same ratio as previously observed (80–90% C_{2+}), however, much more methane reacts than can be accounted for in gas phase products. The deficits in the carbon and oxygen balances ($\approx$ 17 and 93%, respectively in the first 6 h) must then reside in those products that are not detected in the outlet stream. The consumption of methane and oxygen for the formation of solid carbonate is in a ratio that is consistent with the deficits in the gas phase C and O balances. However, the formation of coke cannot be entirely excluded. After the first 6 h, the solid can no longer absorb CO_2 as fast as it is created, so the amount of CO_2 detected in the gas phase increases, and the deficits in the material balances decrease, indicating that less CO_2 reacts to form solid carbonate.

When comparing the reaction in the presence and absence of steam, we observed that the methane conversion increased when steam was replaced by helium, but the selectivity to hydrocarbons dropped to zero, and CO was observed in the gas phase (see table 3).

Table 3
Oxidative methane coupling; $Ca_3NiK_{0.1}O_x$ catalyst. Mixed oxides; activation: O_2, 680°C, 18 h. Rxn; $CH_4:O_2:H_2O$ (or He) = 3:1:6.5, 4.0 mmol CH_4/g cat/h, 600°C

Time (h)	Presence of steam					Absence of steam				
	conv. (%)	selectivity (%)			C balance %	conv. (%)	selectivity (%)			C balance %
		C_{2+}	CO_x	undet.			C_{2+}	CO_x	undet.	
1.5	21	16	1	83	82	48	0	10	90	56
2.5	20	15	2	83	83	54	0	7	93	51
5.5	20	11	3	86	83	58	0	43	57	67
7.5	19	8	33	59	89	58	0	48	52	70

The presence of steam must then play some role in the formation of hydrocarbons, possibly by partially hydroxylating the catalyst surface. A more likely explanation is that steam can act as a gas phase radical trap and interrupt the chain reaction of methane combustion to CO_x. This can serve to extend the life of methyl radicals in the gas phase, thus increasing the likelihood that they will couple to form ethane. In the absence of steam, it appears that the NiO is reduced to Ni metal, which then becomes a good catalyst for producing CO from methane. The poor carbon balances can then be attributed to the accumulation of carbon deposits, which is common when methane reacts with Ni in the absence of steam.

If the carbonate CO_2 is included in the outlet stream, the product distribution in the presence of steam falls in line with what is predicted by reaction mechanisms which include gas phase coupling of radicals which are produced by the activation of methane on the catalyst surface [4]. This mechanism also explains the absence of D-substituted hydrocarbons when D_2O was used instead of water in the reaction [2,3].

3. Conclusions

Methane coupling on CaNiK oxide catalysts at relatively low temperatures and in the presence of steam was studied. Previous claims of hydrocarbon selectivities > 90% with no observable loss of carbon were erroneous due to errors in measuring the outlet flow from the reactor. Runs which utilized an internal standard revealed deficits in the C and O balances. These deficits were accounted for in the buildup of solid calcium carbonate on the catalyst, which was observed by X-ray diffraction. While steam is still observed to have a significant effect on the selectivity to hydrocarbons, the yields are considerably below those previously reported.

References

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