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Comparison of O_2 and N_2O as oxidants for the oxidative coupling of methane over Bi-containing oxide catalysts

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Abstract

The comparative study of the oxidative coupling of methane has been carried out over Bi_2O_3, 20 at.% Er/Bi_2O_3 and 0.2 at.% Li/Bi_2O_3 using O_2 and N_2O as oxidants. It was shown that the rate of C_2 production was higher in the presence of N_2O as compared with O_2 for undoped and Er doped Bi_2O_3 catalysts at the same level of methane conversion. For Li/Bi_2O_3 the rates of C_2 production were similar for both oxidants. Different mechanisms for N_2O decomposition were suggested over doped and undoped Bi_2O_3.

1. Introduction

A number of authors have carried out a comparative study of the oxidative coupling of methane (OCM) over irreducible oxides using O_2 and N_2O as oxidants [1–4]. The feature of all catalysts studied is a high selectivity for C_2 products at a lower temperature using CH_4–N_2O mixture in comparison with the CH_4–O_2 mixture. In most studies it has been shown that N_2O is the less efficient oxidant as compared with O_2. Nevertheless, it was found [3] that N_2O reactivity in C_2-product formation exceeded the reactivity for oxygen over Li/CaO ($0 < Li < 3$ at.%) at a comparable level of CH_4 conversion. Such studies with N_2O for reducible oxides have not been done yet. The present work is aimed to compare the OCM catalyst performance using O_2 and N_2O as oxidants over reducible oxides based on Bi_2O_3.

2. Experimental

Catalysts 0.2 at.% Li/Bi_2O_3, 20 at.% Er/Bi_2O_3 were prepared by impregnation followed by calcination in air at 1053 K for 3–5 hours. We have chosen so different promoter concentrations because of the solid solutions are formed in these systems at such dopant concentration. The flow microcatalytic set-up with fixed bed catalyst and GC analysis was used. Catalyst activity was examined at 1023–1053 K using reaction mixtures: $CH_4{:}O_2{:}He = 30{:}15{:}55$ vol.% and $CH_4{:}N_2O{:}He = 30{:}30{:}40$ vol.%. To perform the study on mechanism of N_2O decomposition a gaseous oxygen (0–15 vol.%) was added to the reaction mixture $CH_4{:}N_2O{:}He = 30{:}10{:}(60 - x)$ vol.%, where x – oxygen concentration. The rates of product formation were determined at methane conversion less than 3%.

3. Results and discussion

The essential differences were found in methane conversion routes when O_2 was replaced by N_2O over all catalysts studied. Ethane and CO_2

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were observed as primary products using O_2 and the only ethane was a primary product using N_2O. Therefore, only one kind of active species is likely to form from N_2O and just these species are responsible for ethane formation from methane. CO_2 was suggested to produce by following oxidation of the coupling products when a molecular oxygen formed by N_2O decomposition and unaccommodated on the surface began to evolve to gas phase. Probably, this is one of the important reason of high selectivity with N_2O as oxidant.

As seen from the Table, Bi_2O_3 and Er/Bi_2O_3 displayed more high activity in C_2 product formation when O_2 was substituted by N_2O. For Li/Bi_2O_3 the rates of C_2 production were approximately equal for both oxidants. The rate of N_2O decomposition was 2–5 times higher than the rate of CH_4 conversion, but both rates have the values of the same order and are comparable with each other.

Two mechanisms for N_2O decomposition have been suggested [5, 6]:

a) N_2O decomposition over oxygen vacancies [5]:

$$N_2O + () \rightarrow N_2 + (O) \tag{1}$$

$$(O) \rightleftharpoons () + 1/2\, O_2 \tag{2}$$

() – anion vacancy.

Since the stage (2) is limiting, the increase of oxygen concentration leads to the decrease of the rate of N_2O decomposition.

b) N_2O decomposition over active centres, including impure transition metal ions [6]:

$$N_2O + () \rightarrow N_2 + (O) \tag{3}$$

$$N_2O + (O) \rightarrow N_2 + O_2 + () \tag{4}$$

() – active centre.

Here, the stage (4) is limiting and the rate of N_2O decomposition is independent on O_2 concentration.

As seen from Fig. 1a, for undoped Bi_2O_3 the addition of oxygen to the reaction mixture with N_2O did not influence on the rate of N_2O decomposition. Therefore, N_2O decomposition occurs according to the mechanism b), i.e. there was no competition between O_2 and N_2O for the activation sites. Apparently, the number of oxygen species required for methane activation increases with the rise of oxygen concentration. On account of that the rates of C_2H_6 and CO_2 formation increased.

For Li/Bi_2O_3 (Fig. 1b), as well as for Er/Bi_2O_3, the decomposition of N_2O was suppressed by addition of oxygen. In this case N_2O decomposition is suggested to proceed according to mechanism a). Apparently, added oxygen and

Table.
The comparison of OCM performance of oxide catalysts using O_2 and N_2O as oxidant ($T = 1053$ K, $CH_4:O_2:He = 30:15:55$ and $CH_4:N_2O:He = 30:30:40$ vol.%, flow rates of 40-60 ml/min, $X_{CH4} = (0.5\text{-}1\ \%)$).

Catalyst	Oxidant	Rate of product formation, μmol/m^2·s			Selectivity C_2^+, %
		C_2^+	CO_2	N_2	
Bi_2O_3	O_2	0.2	0.1	-	67
	N_2O	0.5	0.02	1.0	97
20 at.% Er/Bi_2O_3	O_2	1.7	4.9	-	28
	N_2O	4.6	0.4	26.	92
0.2 at.% Li/Bi_2O_3	O_2	3.2	2.5	-	58
	N_2O	2.8	0.08	6.6	97

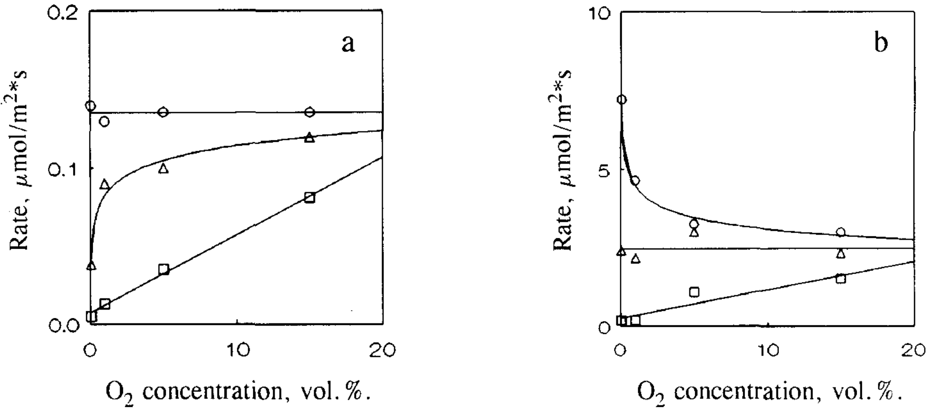

Fig. 1. The rates of formation of C_2H_6 (△), CO_2 (□) and N_2O decomposition (○) versus O_2 concentration; a – Bi_2O_3; b – Li/Bi_2O_3 (T = 1053 K, CH_4:N_2O:O_2:He = 30:10:X:(60 – X)).

N_2O competed for the activation centres. Since there is limited amount of sites for oxidant activation over each catalyst, the rate of C_2H_6 formation was not changed with the addition of oxygen. The rate of CO_2 formation increased over both catalysts due to the oxidation of methane and coupling products by molecular oxygen.

It is known [7] that the introduction of Li or Er into the Bi_2O_3 lattice causes the increase of concentration of oxygen vacancies within a range of solid solution formation. That is why, the oxygen vacancies may serve as active sites for N_2O decomposition over latter catalysts. As for undoped Bi_2O_3, here the N_2O activation may proceed over coordinately unsaturated cation ions due to their redox properties.

4. Conclusion

The comparative study of the oxidative coupling of methane has been carried out over undoped and Li or Er doped Bi_2O_3 using O_2 and N_2O as oxidants. It has been shown that there is a competition between molecular oxygen and N_2O for the activation sites over doped Bi_2O_3 catalysts and no such competition has been found over undoped Bi_2O_3. Oxygen vacancies were suggested to be the sites for oxidant activation over former catalysts while a host cation ions are likely to serve as such sites over latter catalyst.

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6. References

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