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Catalysis Today 24 (1995) 273–275

CATALYSIS TODAY

Oxidative coupling of methane over oxides of alkali earth metals using N_2O as oxidant

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Abstract

Using a CH_4–O_2 and a CH_4–N_2O reaction mixture, N_2O was shown to be a more active and a more selective oxidant then O_2 when CH_4 conversion was similar for both oxidants. It was established that the defect structure of SrO was changed under catalytic conditions. The participation of defects of SrO in the N_2O decomposition was proposed. The presence of hydrogen significantly enhances the decomposition of N_2O and the formation of C_2H_6 over SrO.

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1. Introduction

Earlier, Otsuka and Nakajima [1] have found that the oxidative coupling of methane (OCM) over Sm_2O_3 proceeded with high selectivity but low activity in ethane formation using N_2O as the oxidant. Similar results were obtained by Yamamoto et al. [2] when Li/MgO with a high amount of alkali promoter was used. However, Anshits et al. [3] have also shown that over Li/CaO and Na/CaO catalysts with a low amount of alkali promoter (<2 at.-%) the rates of product formation were greater with N_2O than with O_2 when the oxidants were compared at the same methane conversion.

Thus it was instructive to study the OCM over SrO when N_2O was used as an oxidant. It was of particular interest to investigate the structure of the catalysts after treatment by the reaction mixtures.

2. Experimental

The SrO catalyst was prepared by calcining the high purity $SrCO_3$ with oxygen for 2 hours at $T = 1523$ K to remove the carbonates. Catalytic activity was examined at 1023 K in a microcatalytic quartz fixed-bed reactor using the reaction mixtures: CH_4:O_2:He = 30:15:55 vol.-% or CH_4:N_2O:He = 30:30:40 vol.-%. Gas chromatography was used to analyze the product stream. Separation of the various components was achieved using NaX zeolite and Porapak Q columns. EPR spectra were recorded on a RE 1307 radio-spectrometer at 77 K. Prior to the spectroscopic study the samples were treated under flow conditions at 1023 K, cooled to 77 K and γ-irradiated (3 Mrad).

3. Results and discussion

In this study an attempt was made to compare N_2O and O_2 as oxidants at a nearly equal level of

SSDI 0920-5861(95)00042-9

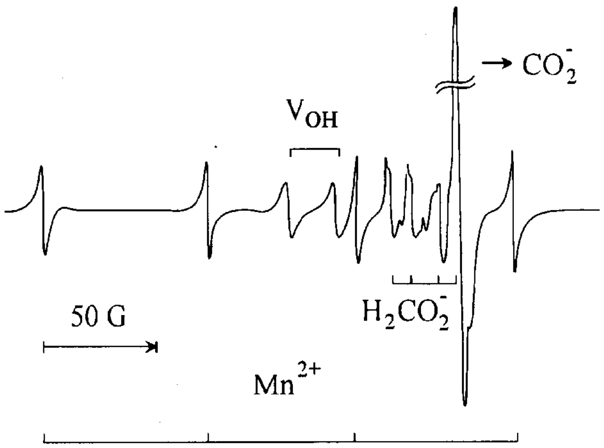

Fig. 1. EPR spectrum of the γ-irradiated SrO after treatment at 1023 K under a CH_4:N_2O = 30:10 vol.-% mixture.

CH_4 conversion over SrO. The results obtained may be summarized as follows:

- N_2O is a more active and selective oxidant when compare with O_2 at 1023 K (the summary activities were $7.0 * 10^{19}$ and $1.2 * 10^{19}$ molecular CH_4 $* s^{-1}$ $* m^{-2}$ for CH_4:N_2O:He = 30:30:40 and CH_4:O_2:He = 30:15:55 vol.-% mixtures, respectively;
- the substitution O_2 by N_2O results in a decreasing rate of CO formation.

It should be noted that the nature of defects in the SrO lattice is the same after the treatment of the catalyst of both reaction mixtures (Fig. 1).

It may be caused by formation of similar oxygen active species when O_2 and N_2O are activated. We found that oxygen was poison for the decomposition of N_2O under OCM conditions. It testifies that the adsorption of O_2 yields the same surface oxygen species which are formed from N_2O. For a more detailed understanding of the role of defects formed under OCM reaction, the composition of defects into SrO lattice and rates of N_2O decomposition were compared. Experimental data are presented in Table 1. One can see that the growth of partial pressure of O_2 results in a decreasing rate of N_2O decomposition and a concentration of V_{OH} defects (OH groups stabilized near the cation vacancy). The decomposition of these defects in CaO is accompanied by the formation of anion vacancies [4].

$$([OH]^-)_s + ([OH]^-)_s \rightarrow (O_2^{2-})_s + H_2 \qquad (1)$$

$$(O_2^{2-})_s \rightarrow O + (O_2-)_s + ([\ ])_s \qquad (2)$$

where index ‘s’ means surface; [ ] anion vacancy.

In our case, such a situation seems to be realized, because $T_d(Sr(OH)_2)$ is 500°C. Therefore, the higher the concentration of hydroxyl groups in SrO, the higher the concentration of anion vacancies, which are necessary for N_2O decomposition. For all this the concentration of H_2CO_2 defects increased when the concentration of V_{OH} centres decreased.

To verify our proposition concerning the role of hydroxyl defects or anion vacancies for N_2O decomposition over SrO, the influence of hydrogen on the rate of N_2O decomposition was studied. It is well known that water or hydrogen can dissociatively be trapped in oxide lattice to form OH defects. Experiments on varying quantities (0–10 vol.-%) of hydrogen added to N_2O and CH_4–N_2O

Table 1
The rate of N_2O decomposition versus V_{OH} and $H_2CO_2^-$ defects concentration.

Reaction mixture, vol. %	W, 10^{18} molecula $N_2O*s^{-1}*m^{-2}$	Concentration of defects, au	
		V_{OH}	$H_2CO_2^-$
CH_4:N_2O=30:10	50	4.7	1.1
CH_4:N_2O:O_2=30:10:2	36	2.7	1.4
CH_4:N_2O:O_2=30:10:15	16	0.1	3.0

Table 2
The rates of ethane formation (C_2H_6) and N_2O decomposition (N_2O) over SrO versus partial pressure of hydrogen (T = 1023 K)

Reaction mixtures, vol. %.	W, 10^{18} molecula CH_4 or $N_2O*s^{-1}*m^{-2}$		
	C_2H_6	CO_2	N_2
N_2O:He = 10:90	-	-	57
N_2O:H_2:He = 10:1:89	-	-	150
N_2O:H_2:He = 10:10:80	-	-	300
CH_4:N_2O:He = 30:10:60	35	1	75
CH_4:N_2O:H_2:He = 30:10:2:58	140	1	150

reaction mixtures were carried out (Table 2). The addition of hydrogen to the CH_4–N_2O reaction mixture resulted in increasing the rates of N_2O decomposition and C_2H_6 formation, but did not influenced the rate of CO_2 formation. Strontium oxide is partially converted to $SrCO_3$ under the reaction conditions. In the OCM condition, hydrogen can give oxygen vacancies through the reaction of the reduction of strontium carbonate.

4. Conclusion

It was established that replacement of O_2 with N_2O resulted in increasing the selectivity and activity of formation of C_2 products when CH_4 conversion was similar for both oxidants. The reaction mixture (CH_4–O_2 and CH_4–N_2O) influenced the defect structure of SrO. The catalytic effect of hydrogen on the OCM reaction was established when N_2O was used as oxidant.

5. Acknowledgement

The research described in this publication was made possible in part by Grant No. RKM000 from the International Science Foundation.

6. References

[1] K. Otsuka and T. Nakajima, Inorg. Chim. Acta, 120 (1986) L27.

[2] H.Y. Yamamoto, H.Y. Chu, M. Xu, C. Shi and J.H. Lunsford, J.Catal., 142 (1993) 325.

[3] A.G. Anshits, V.G. Roguleva and E.V. Kondratenko, in V. Corberan and S. Belon (Editors), (Studies in Surface Science and Catalysis, Vol. 82), Elsevier, Amsterdam, 1994, pp. 337–334.

[4] F. Freund, Phys. Chem. Miner., 15 (1987) 1.