ELSEVIER

Catalysis Today 24 (1995) 263–264

CATALYSIS TODAY

Study on oxidative coupling of methane. Effect of additives on TiO_2-based catalytic performance

M.-C. Gong, X.-H. Xu, Y.-Q. Chen, J.-L. Zhou, Y. Chen

Department of Chemistry and Analytical and Testing Center, Sichuan University, Chengdu 610064, China

Abstract

The effect of Li, La, Mn and W added to TiO_2 on the catalytic performance for the oxidation coupling of methane (OCM) was investigated. The results showed that Li–La–Mn–W/TiO_2 system exhibited high activity and C_2 hydrocarbon selectivity at 770°C with a GHSV of 14400 h^{-1}. The following data were obtained: methane conversion, 41.6%, C_2 selectivity, 61.7% and C_2 yield 25.6%.

1. Introduction

Since 1982, the catalysts involved in the oxidation coupling of methane have been greatly improved [1,2]. In this paper, we will discuss the effect of additives (Li, La, Mn and, W) on the catalytic performance of TiO_2-based catalysts in OCM.

2. Experimental

Catalysts containing different promoters were prepared by impregnation using TiO_2 as support. After being dried and calcinated in air, the catalysts were ground and sieved to 40–60 mesh before use. The experiments were carried out under atmospheric pressure in a conventional flow system with quartz reactor (8 mm i.d.). Product analysis was performed by gas chromatography and calculated with a microcomputer.

3. Results and discussion

The effect of different additives on catalytic properties are shown in Table 1.

3.1. Effect of Li additive on TiO_2-based catalytic performance

The result revealed that the activity of pure TiO_2 (Rutile), i.e. TiO_2(R) is very low using the conditions mentioned below: reaction temperature 770°C, CH_4:O_2 = 1.4:1.0, GHSV = 14400 h^{-1}. When Li salt was added into pure TiO_2(R), the catalyst obtained exhibited no activity, it might be that the compound containing Li covered the relatively inactive centers of pure TiO_2(R). When Li salt was added into Mn/TiO_2, La/TiO_2 and La–Mn/TiO_2, the activity of both catalysts decreased remarkably. However, when Li was added into W/TiO_2, Mn–W/TiO_2, La–W/TiO_2 and La–Mn–W/TiO_2, both the activity and selectivity increased. The results of catalysts 10–15, reveal that all catalysts containing Li exhibited excellent selectivity.

SSDI 0920-5861(95)00039-9

Table 1
The effect of different additives on catalytic properties

No*	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
X_{CH_4}%	0.64	0	20.0	17.3	1.8	0	7.4	32.0	0	3.6	9.8	30.0	2.8	1.96	41.5
S_{C_2}%	100	0	26.8	40.3	26.8	0	78.2	14.5	0	95	75.5	47.2	88.8	100	61.7
Y_{C_2}%	0.64	0	5.3	7.0	0.5	0	5.8	4.6	0	3.4	7.4	14.2	2.4	1.96	25.6

Reaction condition: T=770℃, GHSV=14400h^{-1}, CH_4:O_2=1.4:1.0
*No. 1. TiO_2; 2. Li/TiO 3. La/TiO_2; 4. Mn/TiO_2; 5. W/TiO_2;
6. Li-Mn/TiO_2; 7. Mn-W/TiO_2; 8. La-Mn/TiO_2; 9. Li-La/TiO_2 10. Li-W/TiO_2;
11. Li-Mn-W/TiO_2; 12. La-Mn-W/TiO_2 13. Li-La-Mn/TiO_2 14. Li-La-W/TiO_2 15. Li-La-Mn-W/TiO_2

3.2. Effect of Mn, La additives on TiO_2-based catalysts

When Mn was added to TiO_2(R), the activity increased greatly, showing that the addition of Mn is profitable for methane. While La was added into Mn/TiO_2(R) the activity of the catalyst increased, but the C_2 selectivity decreased. It suggests that the active sites which result in deep oxidation increased after the addition of La. One can see therefore, when Mn and La were added to TiO_2(R), the active sites increased resulting in a higher methane conversion, but also a deep oxidation.

3.3. Effect of W additive on TiO_2-based catalyst

When W was added to TiO_2(R), the activity increased, but when W was added to Mn/TiO_2(R), La/TiO_2 and La–Mn/TiO_2 etc., the activity decreased, while the C_2 selectivity was higher than that of Mn/TiO_2(R) and La–Mn/TiO_2(R), it might be due to the partial covering of the active sites by W.

4. Conclusions

(1) Li is a favorable promoter for La–Mn–W/TiO_2(R).

(2) Catalyst Li–La–Mn–W/TiO_2(R) exhibits high activity and selectivity. It is an excellent catalyst for OCM.

5. References

[1] J. Lunsford, New Frontiers in Catalysis, (1993) 103–126.
[2] C.A. Jones, J.J. Leonard and J.A. Sofranko, J. Catal., 103 (1987) 311.