

Oxidative Dehydrogenation of Ethane over MoVTeNbO Catalyst Prepared by a Slurry Method

HAN Zhisan, YI Xiaodong, XIE Qi, LI Rongchun, LIN Hong, HE Yiming,
CHEN Luqian, WENG Weizheng, WAN Huilin

(Department of Chemistry, State Key Laboratory for Physical Chemistry of Solid Surfaces, Institute of Physical Chemistry, Xiamen University, Xiamen 361005, Fujian, China)

Key words: ethane, oxidative dehydrogenation, ethene, molybdenum oxide, vanadium oxide, tellurium oxide, niobium oxide, mixed metal oxide catalyst

CLC number: O643 **Document code:** A

The oxidative dehydrogenation (ODH) of ethane to ethene has attracted much attention in recent years. López Nieto *et al.*^[1] reported that MoVTeNbO catalysts prepared by hydrothermal synthesis show high activity and selectivity for ODH of ethane, and an ethene yield of 75% was obtained at 400 °C on the best catalysts. In ethane oxidation, the catalytic behavior of MoVTeNbO catalysts can be mainly related to the presence of the multifunctional Te₂M₂₀O₅₇ orthorhombic phase in cooperation with the (V,Nb)-containing Mo₅O₁₄-type phase^[2,3].

In this paper, we report the preparation of the MoVTeNbO catalyst by a slurry method, its characterization and the influence of the calcination atmosphere on the catalyst performance for the ODH of ethane.

The MoVTeNbO catalyst was prepared by a slurry method. Ammonium heptamolybdate, ammonium metavanadate and telluric acid were dissolved upon heating to 80 °C in a flask, and niobium oxalate was dissolved in another flask. The atomic ratio of Mo V Te Nb was 1 0.3 0.23 0.1. The aqueous solution of niobium oxalate was added to the first flask to result in a slurry. The water in this slurry was removed by a rotary evaporator to obtain the precursor solid. After it was dried at 80 °C for 10 h, the precursor solid was calcined at 600 °C for 2 h in a N₂ stream (the sample is denoted as SL-N). For comparison, the same precursor solid was calcined at 600 °C for 2 h in air (denoted as SL-A).

The catalytic performance of the MoVTeNbO catalyst for the ODH of ethane was tested in a fixed-bed quartz tubular reactor at atmospheric pressure. The result is shown in Table 1. SL-N showed good catalytic performance for the ODH of ethane to ethene at reaction temperatures above 400 °C, and ethene was formed as the main product. The ethane conversion increased and the selectivity for ethene decreased with increasing temperature. A maximum ethene yield of 80.9% was achieved at 440 °C on SL-N. However, on SL-A almost no activity for the ODH of ethane was detected.

Table 1 ODH of ethane on MoVTeNbO catalyst samples

Sample	<i>t</i> / °C	<i>X</i> / %	<i>S</i> / %			<i>Y</i> / %
			C ₂ H ₄	CO	CO ₂	
Blank	440	—	—	—	—	—
SL-N	400	59.0	95.4	0.8	3.8	56.3
	420	75.5	93.6	1.4	5.0	70.7
	440	89.6	90.3	1.5	8.2	80.9
	460	95.8	83.4	3.9	12.8	79.9
SL-A	440	—	—	—	—	—

Reaction conditions: 500 mg catalyst, total flow rate 10 ml/min, feed composition 30% C₂H₆/30% O₂/40% N₂.

XRD patterns of the MoVTeNbO catalyst are shown in Fig 1. SL-A was primarily composed of the MoO₃ phase but no MoO₃ was observed in the pattern of SL-N. SL-N gave peaks at $2\theta = 7.7^\circ, 9.0^\circ, 22.1^\circ, 26.2^\circ, 26.8^\circ, 27.3^\circ, 29.2^\circ$ and 35.4° , which were mainly related to an orthorhombic Te₂M₂₀O₅₇ (M = Mo, V and Nb) phase, while peaks

Received date: 2005-01-17. **First author:** HAN Zhisan, male, born in 1979, MS student.

Corresponding author: WAN Huilin. Tel: (0592)2186569; Fax: (0592)2183047; E-mail: hlwan@xmu.edu.cn.

Foundation item: Supported by the National Basic Research Program of China (G1999022408), and the National Natural Science Foundation of China (20433030).

at 7.7° , 8.7° , 14.0° , 22.1° , 23.3° , 24.9° , 29.7° , 31.5° , 32.4° and 33.5° were attributed to $(\text{Mo}_{0.93}\text{V}_{0.07})_5\text{O}_{14}$ [JCPDS, 31-1437] and/or $\text{Nb}_{0.09}\text{Mo}_{0.91}\text{O}_{2.80}$ [JCPDS, 27-1310] or $\text{Mo}_{5-x}(\text{V}/\text{Nb})_x\text{O}_{14}$ -like phases. The peaks at 22.1° , 28.2° , 36.2° , 45.2° and 50.0° were assigned to the $\text{Te}_{0.33}\text{MO}_3$ ($M = \text{Mo}$, V , and Nb) phase^[2~4].

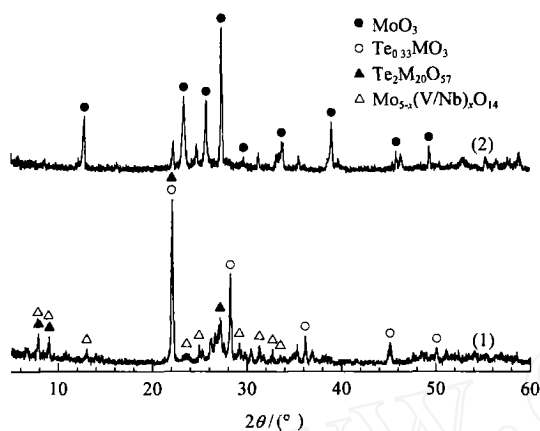


Fig 1 XRD patterns of solid MoVTeNbO catalyst samples
(1) SL-N, (2) SL-A

The difference in the surface morphology of the two samples was revealed by SEM, as shown in Fig 2. SL-A has plate-like structure with fairly smooth surfaces, while SL-N has a porous surface morphology with some fine structure, which was in good agreement with the surface area measurements. The BET specific surface area of SL-N was $6.92 \text{ m}^2/\text{g}$, while that of SL-A was only $0.31 \text{ m}^2/\text{g}$. This result also agreed with the finding by Watanabe *et al*^[5] that a higher surface area of the catalyst correlated well with a higher catalytic activity.

In conclusion, the MoVTeNbO catalyst prepared by the slurry method and calcined at 600 in a N_2 stream exhibits an ethane conversion of 90% and an ethene selectivity of 90% at 440. A highly crys-

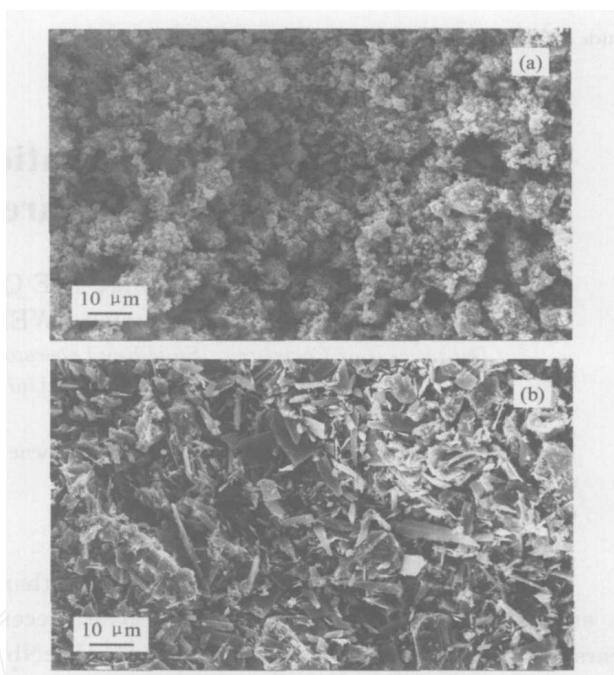


Fig 2 SEM images of MoVTeNbO catalyst samples
(a) SL-N, (b) SL-A

talline MoVTeNbO catalyst may be one of the most effective catalysts for ethene production using low cost ethane.

References

- 1 L ópez Nieto J M, Botella P, V áquez M I, Dejoz A. *Chem Commun*, 2002, (17): 1906
- 2 L ópez Nieto J M, Botella P, Concepci ón P, Dejoz A, V áquez M I. *Catal Today*, 1999, **91-92**: 241
- 3 Botella P, Garc ía Gonz ález E, Dejoz A, L ópez Nieto J M, V áquez M I, Gonz ález-Calbet J. *J Catal*, 2004, **225**(2): 428
- 4 Millet J M M, Roussel H, Pigamo A, Dubois J L, Jumas J C. *Appl Catal A*, 2002, **232**(1-2): 77
- 5 Watanabe H, Koyasu Y. *Appl Catal A*, 2000, **194-195**: 479

浆态法制备的 MoVTeNbO 催化剂上的乙烷氧化脱氢

韩智三, 伊晓东, 谢 棋, 李荣春, 林 洪, 何益明,
陈陆千, 翁维正, 万惠霖*

(厦门大学化学系, 固体表面物理化学国家重点实验室, 物理化学研究所, 福建厦门 361005)

摘要: 采用浆态法在 N_2 气氛下焙烧制得了 $\text{MoV}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.1}\text{O}_x$ 催化剂。在以该催化剂催化的乙烷氧化脱氢制乙烯的反应中, 440 下乙烷的转化率和乙烯的选择性均在 90% 左右, 乙烯产率达 80.9%。但在空气气氛下焙烧得到的催化剂几乎没有催化活性。用 XRD 和 SEM 等方法考察了催化剂的结构。

关键词: 乙烷, 氧化脱氢, 乙烯, 氧化钼, 氧化钒, 氧化铌, 混合金属氧化物催化剂

(Ed L YX)