The Excellent Performance of TiO_2-Supported Li-Mn-W Oxide Catalyst for Oxidative Dehydrogenation of Ethane to Ethylene

Yu Liu,* Yudong Zhang, Xuxia Liu, Jinzhen Xue, and Shuben Li
State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics,
Chinese Academy of Sciences, Lanzhou 730000, P.R.China

(Received June 22, 1998; CL-980468)

Novel alkali metal promoted TiO_2-supported Mn-W catalysts are shown to be highly selective for oxidative dehydrogenation of ethane. 96.8% selectivity to ethylene with the 56.2% ethane conversion is achieved over 2.2 wt%Li-2.1 wt%W-1.7 wt%Mn/TiO_2 catalyst at 620 °C. Moreover, the results of 200 h stability test and being performed at elevated pressures indicate that this Li-promoted catalyst can be used both under atmospheric pressure and elevated pressures.

The selective oxidation of light alkanes to alkene is always desirable and has attracted much attention. The oxidative dehydrogenation of ethane (OXDE) has been extensively investigated over various kinds of oxide catalysts. Moreover, as the secondary reaction of oxidative coupling of methane, many catalysts for oxidative coupling of methane were also used to study their performance of OXDE, such as Li/MgO[1-3] and rare earth oxides.[4] So far, great effort has been making to seek more effective catalysts, especially with high selectivity to ethylene and good stability for this approach. In our previous paper[5], we reported the performance of Na_2WO_4-Mn/SiO_2 catalyst for OXDE, which is also a good catalyst for oxidative coupling of methane. W and Mn are considered to be necessary for methane activation.[6] Since the oxidative dehydrogenation of ethane is the secondary reaction of OCM, based on the above results, the present paper designs a new class of TiO_2-supported manganese-tungsten oxides promoted by different alkali metal ions for OXDE, the Li-Mn-W/TiO_2 oxide catalyst exhibits 96.8% selectivity to ethylene with the 56.2% ethane conversion at 620 °C.

The TiO_2-supported Mn-W catalysts were prepared by slurry mixing method from the solutions with an appropriate concentration of $Mn(NO_3)_2$ (A.R., Shanghai Reagent Factory) and $(NH_4)_5H_5[H_2(WO_4)_6{\cdot}H_2O]$ (A.R. Beijing Reagent Factory) and TiO_2(Rutile, A.R., Shenyang Reagent Factory). The resulting slurry was dried at 120 °C overnight. The alkali metals promoted catalysts were obtained through a wet impregnation of the TiO_2-supported Mn-W with an alkali-metal nitrate solution. After drying at 120 °C overnight , the promoted catalysts were caclined at 650 °C for 6 h. The catalytic runs were carried out in a fixed-bed continuous flow reactor loaded with 0.5 g catalyst which could be used under both atmospheric and elevated pressures, and was described elsewhere.[7,8]

In all experiments, the reactant gas, 20% ethane, 10% oxygen and 70% nitrogen were co-fed and their flow rates were controlled by mass flow controller(Model D07-11/ZM, Beijing Jianzhong Machinery Factory). The products were analyzed by on-line gas chromatography, using a Porapak Q column for C_2H_6, C_2H_4, CO_2, CH_4 and a 5A column for O_2, N_2, CH_4 and CO. The carbon and oxygen balances in all runs were generally >96% and >95% respectively. Almost no hydrogen was detected in the experiments and no carbon deposited on the surface of the catalyst.

Table 1. The performance of unpromoted and alkali metal promoted TiO_2-supported W-Mn catalyst for OXDE

Catalyst	C_2H_6 Conversion /%	Selectivity /%			
		C_2H_4	CO	CO_2	CH_4
2.1 wt%W-1.7 wt%Mn/TiO_2	69.8	75.5	9.7	14.5	0.8
2.2 wt%Li-2.1 wt%W-1.7 wt%Mn/TiO_2	56.2	96.8	1.0	2.2	0
2.2 wt%Na-2.1 wt%W-1.7 wt%Mn/TiO_2	47.6	91.9	2.9	5.9	0.3
2.2 wt%K-2.1 wt%W-1.7 wt%Mn/TiO_2	45.9	86.1	4.9	8.5	0.5

Reaction conditions: T=620 °C, GHSV=12000 h^{-1}, catalyst charge: 0.5 g

Table 2. The effect of temperature on the performance of Li-promoted TiO_2 supported W-Mn catalyst for OXDE

T /°C	Conversion /%		Selectivity /%			
	C_2H_6	O_2	C_2H_4	CO	CO_2	CH_4
540	23.5	26.7	88.9	4.2	6.9	0
560	32.7	-	92.3	2.5	5.2	0
580	40.9	42.3	94.5	1.8	3.7	0
600	48.7	-	96.1	1.2	2.7	0
620	56.2	59.0	96.8	1.0	2.2	0
620*	0.8	-	66.5	17.8	15.7	0
640	62.3	65.1	95.2	1.0	3.6	0.2
640*	2.0	-	59.4	21.5	19.0	0.1
660	65.9	69.6	93.1	0.6	6.0	0.3
660*	3.4	-	52.6	24.8	22.4	0.2
680	69.2	75.8	91.5	0.2	7.6	0.7
680*	6.7	-	47.3	26.9	25.3	0.5

Reaction conditions: GHSV=12000 h^{-1}, catalyst charge: 0.5 g
*The results of blank reaction of OXDE, total flow rate: 100 ml/min

Table 1 shows the performance of OXDE over a series of alkali metal promoted TiO_2 supported W-Mn catalyst. The reaction was carried out at 620 °C with a GHSV of 12000h^{-1}. As maybe seen, only 75.5% selectivity to C_2H_4 with 69.8% conversion of C_2H_6 is obtained. However, the selectivity to ethylene is remarkably improved by the addition of alkali metal to TiO_2-supported W-Mn catalyst, especially in the case of 2.2 wt%Li-2.1 wt%W-1.7 wt%Mn/TiO_2, a 96.8% selectivity to C_2H_4 with 56.2% C_2H_6 conversion is attained. For the Na- and K-promoted catalysts, the conversion of C_2H_6 is almost the same and selectivity to C_2H_4 also increases significantly. The Na-promoted catalyst exhibits nearly 92% selectivity to C_2H_4 with a 47.6% ethane conversion. The selectivity to ethylene and the conversion of ethane over Li- and Na-promoted catalysts are distinctly higher than that observed over K-promoted catalyst. It is aslo noticeable that no methane was detectable only in the case of Li-promoted catalyst and the lowest selectivities to CO and CO_2 are achieved. It seems that the performance of alkali metal promoted TiO_2-supported W-Mn catalysts for OXDE decreases in the order of Li>Na>K.

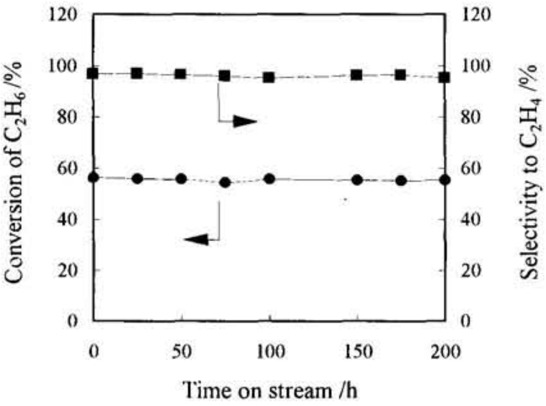

Figure 1. Ethane oxidative dehydrogenation as a function of time on stream over Li-promoted catalyst (T=620 °C, GHSV=12000 h^{-1}, catalyst charge: 0.5 g).

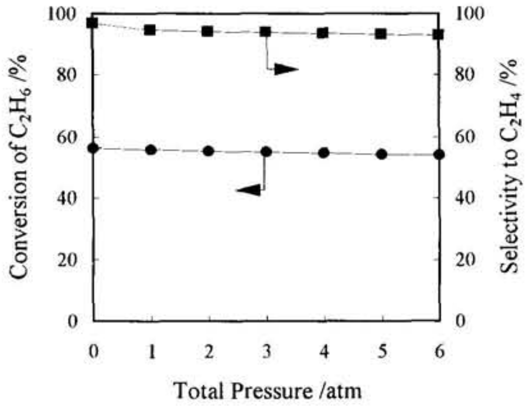

Figure 2. Effect of total reaction pressure on ethane oxidative dehydrogenation over Li-promoted catalyst (T=620 °C, contact time=0.30 s, catalyst charge: 0.5 g).

Table 2 illustrates the effect of reaction temperature on the performance of Li-promoted catalyst for OXDE. It is noted that the conversion of ethane increases significantly with increasing temperature, whereas, the selectivity to ethylene, after reaching a maximum of 96.8% at 620 °C, gradually decreases. The selectivity to ethylene maintains above 92% in the range of 560–660 °C. Obviously, the Li-promoted catalyst is highly selective to ethylene over a quite wide temperature range.

Considering the commercial applications of the Li-promoted catalyst, 200 h stability test and the experiment of effect of pressure on OXDE were performed. As shown in Figure 1, the conversion of ethane and selectivity to ethylene almost remains 55% and 96% respectively during the 200 h test. Figure 2 depicts the performance of the Li-promoted catalyst at elevated pressures. It is apparent that under conditions of constant contact time (τ=0.30s) and at reaction temperature of 620 °C, both conversion and selectivity decreases only slightly with increasing reactant pressure over the Li-promoted catalyst. A C_2H_6 conversion of 53~55% and with a C_2H_4 selectivity of 93% is attained at a pressure of 6 atm, indicating that this catalyst can be effectively used at elevated pressures. To our knowledge, this is only one example of favorable OXDE behavior being achieved at such high pressures.

Based on the above results, it is believed that the Li-promoted TiO_2-supported W-Mn catalyst exhibits high catalytic activity with excellent selectivity to ethylene both under atmospheric pressure and elevated pressures, which opens a promising field in catalyst investigation. Now further work is in progress not only to carry out the reaction on large experimental scales, but also to elucidate the nature of the Li-promoted catalyst.

References

1 S.J.Conway and J.H.Lunsford, *J. Catal.*, **131**, 513 (1991).
2 D.Wang, M.Xu, C.Shi, and J.H.Lunsford, *Catal. Lett.*, **18**, 323(1993).
3 D.Wang, M.P.Rosynek, and J.H.Lunsford, *J. Catal*, **151**, 155(1995).
4 S.Bernal, G.A.Martin, P.Moral, and V.Perrichon, *Catal. Lett.*, **6**, 231(1990).
5 Y.Liu, X.X.Liu, and S.B.Li, *J. Mol. Catal. (China)*, **10**, 401(1996)
6 Z.C.Jiang, C.J.Yu, X.P.Fang, S.B.Li, and H.L.Wang, *J. Phys. Chem.*, **97**, 12870(1993)
7 Y.Liu, C.C.Yu, X.X.Liu, B.Zhang, and S.S.Kong, *Chem. Lett.*, **1996**, 1127
8 Y.Liu, X.X.Liu, J.Z.Xue, R.L.Hou, B.Zhang, C.C.Yu, and S.K.Shen, *Appl. Catal.*, **168**, 139(1998)