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Study on the oxidative coupling of methane: XRD and XPS study of TiO_2-based catalysts promoted by different additives

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Abstract

The catalytic performance of Mn/TiO_2, $La–Mn/TiO_2$, $Li–Mn/TiO_2$ and $Li–La–Mn/TiO_2$ for the oxidative coupling of methane (OCM) was investigated. The catalysts were characterized with XRD and X-ray photoelectron spectroscopy (XPS). The results revealed that catalyst $Li–La–Mn/TiO_2$ exhibited high activity and C_2 selectivity, Ti in this catalyst existed in the Ti(IV) state; Li could promote the formation of lanthanum titanate via the interaction of La and TiO_2, the formed $La_2Ti_2O_7$ and $La_4Ti_9O_{24}$ distributed in the inner surface layer and Mn existed in the outer surface layer in low valence number. The high activity and C_2 selectivity of catalyst $Li–La–Mn/TiO_2$ were intimately related to the valence number of Mn, Li, La and to their distribution on the catalyst surface layer.

1. Introduction

Many researchers devoted a lot of work on oxidative coupling of methane (OCM), especially in the development of catalysts [1–5]. The catalysts containing similar ingredients displayed even obviously different catalytic behavior. That is, besides catalyst components, the physical and chemical properties of catalyst, for instance, crystal form, surface states, surface composition, etc., make an impact on catalytic performance. In this paper, we studied the catalytic performance of TiO_2-based catalysts in OCM and characterized them with XRD and XPS.

2. Experimental

2.1. Preparation of the catalysts

Catalysts containing different promoters were prepared by impregnation using TiO_2 as support. After dried and calcinated in air, the catalysts were ground and sieved through 40–60 mesh before use.

2.2. Activity measurement

The reaction was carried out under atmospheric pressure in a conventional flow system with quartz reactor (8 mm i.d., 0.5 g). The reactants were CH_4 (99.99%) and O_2 (>99.5%). N_2 (>99.5%) was used as diluent. Product analysis was performed by chromatography and a microcomputer.

2.3. XRD and XPS characterization

XRD measurements were carried out on a D/max-rA diffractometer using Cu Kα radiation at 55 kV, 190 mA and 2 kcps. XPS was recorded using Al Kα radiation operating at 13 kV and 28 mA. Binding energies were calculated referring to the C 1S peak at 285.0 eV.

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3. Results and discussion

3.1. *Effect of different additives on catalytic performance*

The properties of the catalysts are shown in Table 1.

3.2. *Surface states of various components in the catalysts*

Data from XRD and XPS analysis are given in Tables 2a and 2b.

The results indicate that the binding energies of Ti $2p_{3/2}$ in different catalysts are a little lower than that in pure TiO_2, it may be due to the formation of titanate. The binding energies of $Mn2p_{1/2}$ are all lower than that in pure MnO_2, and it is clear that the oxidative number of Mn in the catalysts is less than +4. XRD results also show that Mn primarily existed as (Mn_2O_3) 80B, (MnO_2) 8F, $MnCO_3$, MnO, Mn_2TiO_4, i.e., Mn principally existed in the form of Mn(II) and Mn(III). The Li content in catalysts is very low, and then its XPS sensitivity is low, therefore, the XPS spectra of Li were not acquired.

3.3. *Surface distribution of various elements in catalysts*

The surface atom percentages were calculated in times of sensitivity factor and XPS peak area. The average weight loading of the elements and that from XPS results are listed in Table 3.

As for catal. 2, the surface Mn content is twice as high as the average value. It is clear that Mn is enriched in the surface. Combined with related XRD results, it reveals that Mn existed in the form

Table 1
The effect of different additives on catalytic performances

No.	catalyst	X_{CH_4}%	Sc_2%	Yc_2%	$S_{C_2H_4}$%	Yc_2H4%
1	TiO_2	6.3	13.8	0.9	7.5	0.5
2	Mn/TiO_2	17.7	23.0	4.1	11.8	2.1
3	$La-Mn/TiO_2$	16.0	2.8	0.5	0.8	0.1
4	$Li-Mn/TiO_2$	22.1	71.5	15.8	55.2	12.5
5	$Li-La-Mn/TiO_2$	27.5	76.1	20.9	61.2	16.9

Reaction conditions: T=800℃, CHSV=1714 h^{-1} $CH_4:O_2$=3.0:1.0
The results show that Li is an excellent promoter for Mn/TiO_2 and $La-Mn/TiO_2$ catalysts.

Table 2a
The binging energy of the catalysts (eV.)

Catal. No.	Ti $2P_{2/3}$ 458.9 (TiO_2)	Mn $2P_{1/2}$ 643.1 (MnO_2)	La $3d_{2/3}$ 836.2 (La_2O_3)	S 2p
1	458.9			
2	458.6	641.7		
3	458.7	642.3	835.9	
4	458.6	641.9		173.4
5	458.5	642.2	835.7	173.5

Table 2b
The phases of various components existed in the catalysts

Cacal. No.	Phases
1	TiO_2 (R)
2	TiO_2 (R), (Mn_2O_3) 80B
3	TiO_2 (R) (Mn_2O_3) 80B, $La_2Ti_2O_7$, $MnCO_3$, $La_2O_2CO_3$, (MnO) 8F
4	TiO_2 (R), (Mn_2O_3) 80B, Li_2MnO_3, Li_2TiO_3, $Li_2SO_4.H_2O$
5	TiO_2 (R), (Mn_2O_3) 80B Li_2TiO3, $La_2Ti_2O_7$, $La_4Ti_9O_{24}$, La_2O_3, $MnCO_3$, Mn $(OH)_2$, Mn_2TiO_4, $Li_2SO_4 \cdot H_2O$

Table 3.
Contrast between XPS results and average loaded weight of different elements in catalysts

catal.	atom mass percentage (wt. %)					
NO.	Mn		La		Ti	
	XPS	calcul.	XPS	calcul.	XPS	calcul.
1					100	100
2	21.5	11.1			78.5	88.9
3	19.2	10.4	13.8	2.0	67.0	87.6
4	27.5	11.4			72.5	88.6
5	24.4	11.7	2.2	2.2	73.4	86.1

Note: Wt. % = $(M_i / \sum M_i) \times 100\%$, M_i = Mn, La, Ti

of (Mn_2O_3) 80B and enhanced the catalytic activity. As La–Mn/TiO_2 is concerned La content is seven times as high as the average value, so La is even more easily to enrich in the surface than Mn, together with XRD, La in this catalyst existed as $La_2Ti_2O_7$ and $La_2O_3CO_3$, which mainly existed in the upper surface layer. As to catal. 4 and 5, the addition of Li is very favourable for enrichment of Mn in surface, however, La content in catalyst Li–La–Mn/TiO_2 is equal to the average value, in addition, La_2O_3, $La_2Ti_2O_7$ and $La_4Ti_9O_{24}$ were detected by XRD. It suggests that $La_4Ti_9O_{24}$ is predominately dispersed in the inner surface layer.

4. Conclusion

(1) Catalysts Li–Mn/TiO_2 and Li–La–Mn/TiO_2 displayed high activity and C_2 selectivity under the reaction conditions tested.

(2) Among the catalysts studied, element Ti existed in Ti(IV), La in La(III), Mn in Mn(II,III). Li dispersed as Li_2SO_4 in the surface of the catalyst.

(3) The excellent activity and selectivity of Li–La–Mn/TiO_2 originate from the oxidative state of Li, La and Mn, and from their surface distribution.

5. References

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