

## Selective Oxidation of Methane to Methanol Using Molecular Oxygen on $\text{MoO}_x/(\text{LaCoO}_3+\text{Co}_3\text{O}_4)$ Catalysts

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**Abstract:** Comparatively high  $\text{CH}_3\text{OH}$  selectivity (60.0%) and yield (6.7%) were obtained on  $\text{MoO}_x/(\text{LaCoO}_3+\text{Co}_3\text{O}_4)$  catalysts in selective oxidation of methane to methanol using molecular oxygen as oxidant. The interaction between  $\text{MoO}_x$  and La-Co-oxide modified the molecular structure of molybdenum oxide and the ratio of  $\text{O}/\text{O}^{2-}$  on the catalyst surface, which controlled the catalytic performance of  $\text{MoO}_x/(\text{LaCoO}_3+\text{Co}_3\text{O}_4)$  catalysts.

**Keywords:** Methane, selective oxidation, methanol, molybdenum oxide species,  $\text{O}/\text{O}^{2-}$  ratio.

Direct and selective oxidation of methane to methanol (SOM) using molecular oxygen on solid-state oxide catalysts is one of the most attractive and challenging tasks in catalysis and chemical engineering<sup>1</sup>. Generally speaking, higher  $\text{CH}_3\text{OH}$  selectivity and yield could be obtained when using  $\text{N}_2\text{O}$  as oxidant instead of  $\text{O}_2$ . It is reasoned that peroxide species ( $\text{O}^\cdot$ ) easily producing from  $\text{N}_2\text{O}$  was more reactive species responsible for the formation of oxygenates than lattice oxygen species ( $\text{O}^{2-}$ )<sup>1</sup>. However,  $\text{N}_2\text{O}$  is too expensive and corrosive to be used as oxidant in the industrial process of the SOM. Therefore, it is necessary to further develop effective catalysts using  $\text{O}_2$  as oxidant.

The pervosikite type oxide has high ability to activate molecular oxygen, due to its lattice deficient sites. To our knowledge, the pervosikite oxide catalysts show good activity in combustion of methane, partial oxidation of methane to syngas and oxidative coupling of methane *etc.*<sup>2</sup> Few research works on the SOM using pervosikite oxide catalysts have been reported so far. Here, well-dispersed  $\text{MoO}_x/\text{La-Co-oxide}$  catalysts are investigated and found to have excellent performance in selective oxidation of methane to methanol using  $\text{O}_2$  as oxidant.

The La-Co-oxide was prepared by using citric acid sol-gel method as described in reference<sup>3</sup>. The  $\text{MoO}_x/\text{La-Co-oxide}$  catalysts with Mo loading 3–10wt% (described as n-MLC, in which n express wt% of Mo) were prepared by impregnation of La-Co-oxide powder with different amount of  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$  (Tianjing Chemical Co. Ltd., A.R.) aqueous solution. The catalyst precursor was dried at 383 K for 8 h, and then calcinated at 773 K for 8 h.

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**Table 1** Catalytic performance of the catalysts in the SOM to methanol

Catalysts	$S_{\text{BET}}$ /m <sup>2</sup> ·g <sup>-1</sup>	Conv CH <sub>4</sub> %	Selectivity %			Yield % CH <sub>3</sub> OH
			CH <sub>3</sub> OH	CO	CO <sub>2</sub>	
Reactor	-	0.9	4.9	43.1	51.8	0.04
La-Co-O	10.8	4.2	-	8.6	91.4	-
3-MLC	10.8	8.9	33.2	31.7	34.8	3.0
7-MLC	11.2	11.2	60.0	21.8	18.2	6.7
10-MLC	11.8	11.6	28.8	11.2	60.0	3.3
MoO <sub>3</sub>	44.5	1.6	6.9(HCHO)	40.8	52.2	0.1(HCHO)

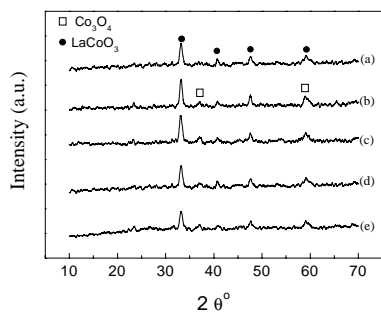
Reaction conditions: 420 °C, 4.2 MPa, CH<sub>4</sub>/O<sub>2</sub>/N<sub>2</sub>=10/1/1, 14400 mL/(g-cat)·h<sup>-1</sup>.

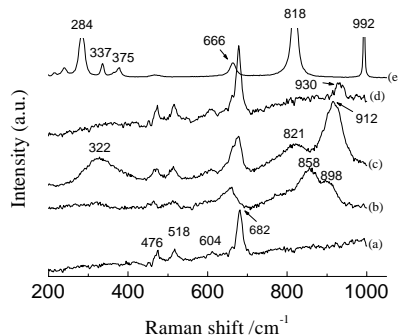
The catalytic test was carried out in a continuous vertical-flow fixed-bed reactor, which was a 460 mm long quartz line tube (6.7 mm *i.d.*) tightly fixed in a stainless steel tube. The effluent kept at 423 K was analyzed by on-line gas-chromatograph (SHIMADZU, GC-8A, TCD) equipped with two columns: GDX-403 for separating CH<sub>3</sub>OH, HCHO, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, H<sub>2</sub>O, CO<sub>2</sub>, and TDX-01 for N<sub>2</sub>, O<sub>2</sub>, CH<sub>4</sub>, CO. The N<sub>2</sub> in feed gas acted as both diluent and internal standard.

XRD measurement was carried out on BRUKER D8 Advanced X-rays powder diffractometer with Cu K $\alpha$  ( $\lambda=0.15046$  nm). LR spectra were recorded on RENISHAW RM1000 Raman spectrometer equipped with He<sup>+</sup>/Ne<sup>+</sup> laser ( $\lambda=514$  nm, W=15 mW). XPS measurements were performed by PE PHI-5300 ESCA spectrometer, Al K $\alpha$  (1486.6 eV, 10.1 kV).

Firstly, the effect of gas-phase homogeneous oxidation of methane on the formation of CH<sub>3</sub>OH was investigated (**Table 1**). 4.9% CH<sub>3</sub>OH selectivity and very low CH<sub>4</sub> conversion were obtained in the reactor packed with quartz wool (its volume was equal to that of catalyst bed), indicating that the gas-phase homogeneous oxidation of methane had no great contribution to the formation of CH<sub>3</sub>OH. In order to minimize the contribution of any gas-phase reaction, the space of up and down catalyst bed (0.5 g, 20~40 mesh) was filled with quartz wool. La-Co-oxide mainly demonstrated the activity in combustion of methane. MoO<sub>3</sub> showed 6.9% HCHO selectivity with 1.6% CH<sub>4</sub> conversion. CH<sub>3</sub>OH, CO and CO<sub>2</sub> were main products in the SOM on MLC catalysts. Catalytic performance strongly depended on Mo-loading. The highest CH<sub>3</sub>OH selectivity (*ca.* 60%) and yield (*ca.* 6.7%) were achieved on 7-MLC catalyst. These results suggest that the synergetic effect between molybdenum oxide and La-Co-oxide took place.

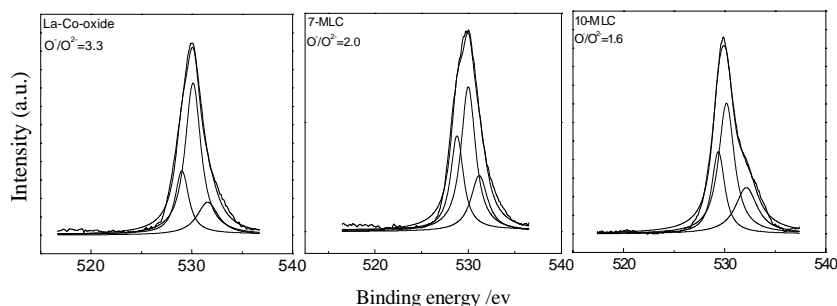
XRD results show that La-Co-oxide was mainly composed of LaCoO<sub>3</sub> and Co<sub>3</sub>O<sub>4</sub> (**Figure 1**). When Mo loading on La-Co-oxide, only LaCoO<sub>3</sub> and Co<sub>3</sub>O<sub>4</sub> peaks were detected in XRD. It is deduced that amorphous and well-dispersed molybdenum oxide formed on La-Co-oxide surface. La-Co-oxide possessed Raman bands at 682, 604, 518 and 476 cm<sup>-1</sup>, which were assigned to LaCoO<sub>3</sub> (604, 518 and 476 cm<sup>-1</sup>) and Co<sub>3</sub>O<sub>4</sub> (682 cm<sup>-1</sup>), respectively (**Figure 2**)<sup>4</sup>. 3-MLC catalysts gave new Raman bands appearing at 889 and 858 cm<sup>-1</sup>, due to  $\nu\text{Mo}=\text{O}$  and  $\nu\text{Mo}-\text{O}-\text{Mo}$  in the isolated [MoO<sub>4</sub>]<sup>2-</sup> species<sup>5</sup>. Likewise, Raman bands near 912, 821 and 322 cm<sup>-1</sup> were detected on 7-MLC catalysts. These bands were assigned to  $\nu\text{Mo}=\text{O}$ ,  $\nu\text{Mo}-\text{O}-\text{Mo}$  and  $\delta\text{Mo}=\text{O}$  in the isolated and distorted [MoO<sub>4</sub>]<sup>2-</sup> species<sup>5</sup>. 10-MLC catalyst presented Raman bands at 930 cm<sup>-1</sup>

**Figure 1** XRD patterns of the catalysts

 (a) LaCoO<sub>3</sub>, (b) La-Co-O, (c) 3-MLC, (d) 7-MLC, (e) 10-MLC

**Figure 2** LR spectra of the catalysts

 (a) La-Co-O, (b) 3-MLC, (c) 7-MLC, (d) 10-MLC (e) MoO<sub>3</sub>

attributing to  $\nu\text{Mo}=\text{O}$  in  $[\text{Mo}_7\text{O}_{24}]^{6-}$  species<sup>5</sup>. The results of LRS further indicated that molybdenum oxide was amorphous, and molecular structure of molybdenum oxide was closely relative to Mo-loading. Combined with the results of catalytic test, these studies also reveal that the isolated and distorted  $[\text{MoO}_4]^{2-}$  species enhanced the formation of CH<sub>3</sub>OH. The reason is that Mo-OCH<sub>3</sub> intermediate easily generated and transferred to CH<sub>3</sub>OH on  $[\text{MoO}_4]^{2-}$  species<sup>1</sup>.

XPS studies were carried out to know ion oxidation state on these catalysts. The MLC catalysts showed Co<sub>2p<sub>3/2</sub></sub> was at *ca.* 779.6±0.3 eV, La<sub>3d<sub>5/2</sub></sub> at 833.4±0.2 eV and Mo<sub>3d<sub>5/2</sub></sub> at 233.2±0.2 eV, respectively, for Co<sup>3+</sup>, La<sup>3+</sup> and Mo<sup>6+</sup> on the catalysts surface. Moreover, the increase of Co<sub>2p</sub> with the increase of Mo-loading was observed, likewise, both La<sub>3d</sub> and Mo<sub>3d</sub> ascended as Mo-loading. These results imply that O<sup>2-</sup> deficient sites gradually decreased in these catalysts with Mo-loading leading weakened the electron shield for the nucleus of ions, so the Co<sub>2p</sub>, La<sub>3d</sub> and Mo<sub>3d</sub> all increased. **Figure 3** presented O<sub>1s</sub> XPS spectra recorded on MLC catalysts. Detailed analysis and Lorentzian curve fitting of these O<sub>1s</sub> XPS spectra revealed the existence of oxygen species in mixed value state on these catalysts: O<sup>2-</sup><sub>1s</sub> at 528.8~529.0 eV, O<sup>1-</sup><sub>1s</sub> at 530.1~530.2 eV and OH/CO<sub>3</sub><sup>2-</sup> at 532.1~532.5 eV. The O<sup>1-</sup>/O<sup>2-</sup> ratio can be estimated according to the area of these sub-peaks. It is worth of noticing, the O<sup>1-</sup>/O<sup>2-</sup> ratio gradually reduced with the increase of Mo-loading. It is well known that the O<sup>2-</sup> deficient sites act as sites for activation of molecular oxygen. The above results show that the O<sup>2-</sup> deficient sites in MLC catalyst reduced with the Mo loading, resulting in the

**Figure 3** O<sub>1s</sub> XPS spectra of the catalysts


continuous decrease of O<sup>-</sup> species. The O<sup>-</sup> species were more active for the selective oxidation of methane to methanol. However, more O<sup>-</sup> species on the catalysts can induce total combustion of methane to be dominative reaction. The proper ratio of O<sup>-</sup>/O<sup>2-</sup> species existing on the oxide catalysts, such as on 7-MLC catalysts, could improve CH<sub>3</sub>OH selectivity and yield. More recently, Ostuka *et al.*<sup>5</sup> claimed that Fe<sup>3+</sup> sites in several catalysts enhanced the formation of O<sup>-</sup> species, leading to high CH<sub>3</sub>OH selectivity and yield. In summary, the interaction between MoO<sub>x</sub> species and La-Co-oxide modified the structure of molybdenum oxides and the O<sup>-</sup>/O<sup>2-</sup> ratio on the catalysts surface, determining the catalytic performance in the SOM of MLC catalysts.

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