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Oxidative coupling of methane over sodium doped V–Mo–O–SiO_2 honeycomb catalysts

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Abstract

Sodium doped V–Mo–O–SiO_2 honeycomb catalysts prepared by mixing and extrusion through the unique die. Catalytic activity of this honeycombs in oxidative coupling of methane (OCM) was investigated.

1. Introduction

Honeycomb monolithic catalysts possess a number of unique characteristics as to be very attractive for the oxidative coupling of methane (OCM) allowing both basic studies on the heterogenous–homogeneous reactions and industrial process design.

It is generally considered that OCM reaction proceeds via formation of CH_3 radicals on the surface of the catalyst and subsequent coupling in the 'gas phase' to form a molecule of ethane. The contribution of 'gas phase reaction' in the OCM is still matter of debate. Kalenik and Wolf proposed and demonstrated that void volume between catalyst particles and mainly post catalyst free volume are the place for homogeneous reactions [1]. Van der Wiele et al. claimed that 'the gas phase reaction' occurs mainly in a diffusive layer near the catalyst surface [2]. McCarty et al. [3] argued that 'gas phase reaction' mainly proceeds in the pores of catalyst particles.

Honeycomb catalyst could have application in the industrial OCM process due to the possibility of very accurate regulation and optimization of the single channel diameter, thickness of walls (S/V, void volume), length of catalyst bed and assembling mode of honeycomb layers inside the reactor. Also the well known low pressure drop of honeycomb reactor allows to operate at low residence time in the OCM process.

2. Experimental

Catalyst preparation. Sodium doped V–Mo–SiO_2 monolithic honeycomb catalysts K-2, K-4 were prepared by mixing powders of oxides of Al, Si, $(NH_4)_6Mo_7O_{24} \times 4H_2O$ and $VOSO_4 \times 3H_2O$ with water and methylcellose as plasticizer. Sample K-3 was prepared from pure oxides of V and Mo. Honeycomb structure was formed by extrusion through the unique die. After drying and calcination honeycomb cylinders with diameter – 10

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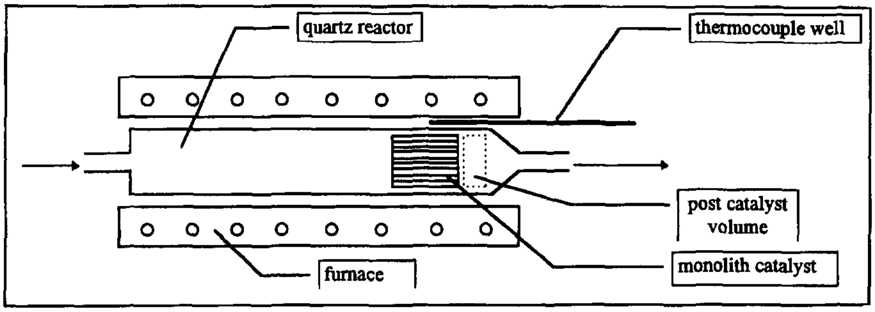

Fig. 1. Reactor.

mm; cell size – 1.2 × 1.2 mm; wall thickness – 0.2 mm; wall thickness – 0.2 mm, number of cells per cm^2 – 49 were obtained. Sodium was introduced into the catalyst in composition of methylcellose (MC) containing sodium chlorate. Sodium content in MC was about 18 wt%. BET surface area of monoliths was measured by argon thermal desorption. Vanadium content was determined by plasma spectrovac BAIRD apparatus, molybdenum content was obtained by atomic absorption spectrometer AAS1N, sodium content was determined by FLAPHOKOL apparatus. X-ray powder diffraction patterns were recorded using CuK_α radiation. The samples and their main features are listed in the Table .

Catalyst testing. A continuous flow apparatus with quartz tube reactor (ID 10 mm) has been used [4]. Gas analysis was provided with a HP 5890 A gas chromatograph. The influences of reaction temperature, gas flow rate, length of honeycomb, position of honeycomb in the reactor (as depicted in Fig. 1), post catalyst reaction volume, pore structure of monolith and CH_4:O_2 ratio on the catalyst ratio on the catalyst activity and product distribution have been ascertained.

3. Results and discussion

The temperature dependence of CH_4 conversion and product distribution for the K-2 catalyst are presented in Fig. 2 and for K-3 catalyst in Fig. 3.

In special experiments the post catalyst volume (PCV) was varied. Enlarging of PCV from zero to 1 cm^3 leads to increasing of conversion in OCM reaction (30%) and C_2 selectivity (20%).

This study is aimed to emphasize that conversion–selectivity patterns of such Si–Mo–V oxide catalyst in OCM reaction might be considered very promising according to the activity index recently proposed by Maitra [5]. The activity of the honeycomb catalysts will be compared with those of 'bare' cordierite honeycomb and crushed honeycomb catalysts.

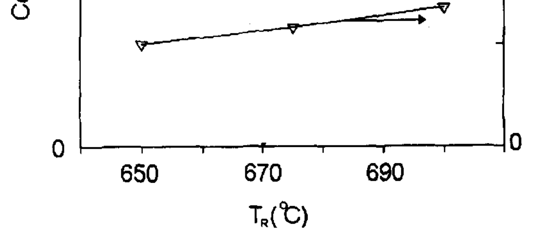

Fig. 2. Oxidative coupling of methane on K-2 honeycomb catalyst. Effect of reaction temperature on CH_4 conversion (◆) and product distribution (▿ – C_2H_4, △ – C_2H_6, ▲ – $C_2H_4+C_2H_6$). $W_{cat}=1.97$ g. Reaction mixture flow 50 cm^3/min ($He/N_2/CH_4/O_2=20/3.2/2.25/1$).

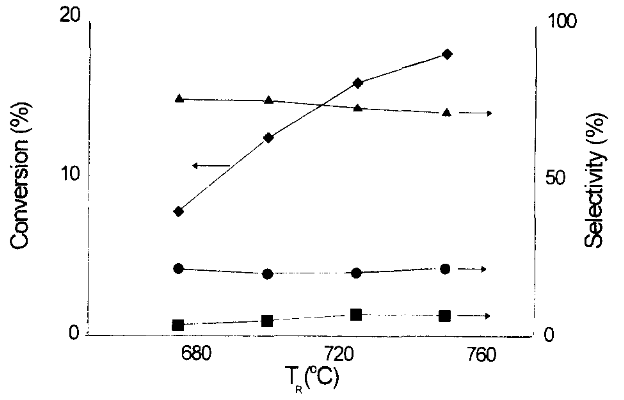

Fig. 3. Oxidative coupling of methane on K-3 honeycomb catalyst. Effect of reaction temperature on CH_4 conversion (◆) and product distribution (● – CO_x, ▲ – $C_2H_4+C_2H_6$, ■ – HCHO). $W_{cat}=1.79$ g. Reaction mixture flow 375 cm^3/min ($He/N_2/CH_4/O_2=20/3.2/6.5/1$).

Table 1

Sample	Composition of initial mixture of row materials	Thermal treatment ,°C Init./Sec.	SBET , m^2/g	Composition, wt%			X-ray analysis
				V	Mo	Na	
K-2 fresh	90 g SiO_2, 6.2 g $(NH_4)_6Mo_7O_{24}\times 4H_2O$, 11.9 g $VOSO_4\times 3H_2O$, 40 g MC	500/700	25	3.5	3.5	7.2	α-cristoballite, NaCl
K-2 used	-//-//-	700/800	4.7	2.2	2.8	6.4	α-cristoballite, NaCl, β-$Na_4V_2O_7$
K-3 fresh	80 g SiO_2, 2.5 V_2O_5, 2.5 MoO_3, 10 g Al_2O_3, 30 g MC	150/500	38	1.3	1.5	6.0	amorphous, NaCl
K-3 used	-//-//-	500/700	2.4	1.2	1.4	5.8	α-cristoballite, β-$Na_4V_2O_7$
K-4 fresh	80 g SiO_2, 1.9 g $(NH_4)_6Mo_7O_{24}\times 4H_2O$, 8.5 g $VOSO_4\times 3H_2O$, 10 g Al_2O_3, 20 g MC	500/500	179	1.8	0.9	3.8	α-cristoballite, NaCl traces
K-4 used	-//-//-	500/800	5.0	2.3	0.8	3.6	α-cristoballite, β-$Na_4V_2O_7$

4. References

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