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PARTIAL OXIDATION OF METHANE OVER PHOSPHATE

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Partial oxidation of methane over unpromoted and promoted iron phosphate catalysts was investigated in the temperature range of 873-953 K in a flow reactor. Using XRD and IR techniques, the bulk and surface structure of the given catalysts have been studied. The modification functions of lanthanum phosphate for partial oxidation of methane were also examined.

Парциальное окисление метана на промотированном и непромотированном фосфатном катализаторе железа исследовали в интервале температур 873-953 К и в проточном реакторе. Поверхностная и блочная структура катализатора исследована с помощью рентгено-дифракционной и ИК-спектроскопий. Проверяли влияние модифицирования фосфатом лантана на частичное окисление метана.

INTRODUCTION

As is well known, the methane molecule is very stable. In the recent few decades chemists have focused on finding ways to selectively break part of the four C-H bonds in methane in order to obtain more useful oxygen-containing organic compounds, such as formaldehyde, methanol and formic acid.

Based on achievements in homogeneous catalytic investigations, some heterogeneous catalytic systems for carrying out partial oxidation of methane have been developed. A great number of solid catalysts have been performed for this reaction, based on e.g. aluminium silicate [1], metal oxide [2], precious metal [3], complex oxide [4], solid acid [5] and phosphate [6].

We now report on some catalytic properties of iron phosphate for partial oxidation of methane and the effect of lanthanum on the reaction mentioned above.

EXPERIMENTAL

Iron phosphate (unpromoted and promoted) were prepared by precipitation and co-precipitation methods in solution with certain pH values. Catalyst cakes were dried at 383 K in air for 4 h, followed by a calcination procedure at 873 K in air for 6 h. The La-promoted catalysts were obtained by using La_2O_3 dissolved in nitric acid. Crystal structure of the catalysts was determined by XRD technique with a Shimadzu XD-3 type diffractometer (Cu K_α target and Ni filter). The IR technique was used to examine adsorption states of methane on iron phosphate (Nicolet 50-X type FT IR spectrometer). A fixed bed reactor and a continuous flow manifold were used. Reactant from the manifold and water vapor from a steam boiler were adjusted to the desired composition and passed through the catalyst bed at a total flow rate of 108 cm^3/min. Typically, a molar composition of about 5% methane at 1 atm was employed for all experiments. The entire manifold was heated at 393 K to prevent condensation of water vapor. A stainless steel tube was used as a reactor, (i.d. 9 mm, length 200 mm). For each run 1 cm^3 catalyst was loaded and fixed on asbestos. Reaction temperature was controlled and monitored with a thermocouple embedded in the catalyst bed. The temperature range used was 873-953 K. A certain period of time was needed for the system to reach a steady state and be ready for sampling for analysis. An in-line 2305-E type gas chromatograph equipped with a six-port sampling valve, a thermal conductivity detector and two analytical columns were used. One of the columns was packed with 60-80 mesh TDX-01 for separating and determining air, CO, CO_2 and CH_4; the other one was packed with 60-80 mesh Apieson-201 for HCHO, CH_3OH and higher hydrocarbon analysis.

RESULTS AND DISCUSSION

a) Temperature dependence of catalytic properties of unpromoted iron phosphate

As is shown in Table 1, in the given temperature range methane conversion obviously increased with temperature, for example, from 0.7 % at 873 K to 3.7 % at 953 K. However, the total selectivity to HCHO and HCOOH declined as the temperature increased, for instance, at temperatures lower than 873 K CO did not form at all, while at higher temperatures the selectivity to CO was near 40 % and at 953 K a selectivity of 57 % for CO was obtained. Methane was not converted below 873 K on the given catalysts. It is interesting that no methanol was detected in any run. Evaluated apparent activation energies for HCHO, HCOOH and CO were 34.5, 6.8 and 48.8 kcal/mol, respectively.

Table 1

Temperature dependence of catalytic properties

T (K)	$r \times 10^6$ (mol/cm^3 min)				Select. (%)				CH_4
	HCHO	HCOOH	CO	CO_2	HCHO	HCOOH	CO	CO_2	conv.(%)
873	0.44	1.05	0	0	29.5	70.5	0	0	0.7
893	0.74	1.14	0	0	39.4	60.6	0	0	0.8
913	1.18	1.21	1.55	0	29.9	30.7	39.3	0	1.8
933	1.65	1.38	2.18	0	31.7	26.5	41.8	0	2.3
953	2.05	1.46	4.65	0	25.1	17.9	57.0	0	3.7

Total flow rate: 108 cm^3, cat. 1 cm^3, CH_4 4.6 %
Apparent contact time: 0.56 s

b) Apparent contact time dependence of the catalytic properties of unpromoted iron phosphate

The effect of the apparent contact time on the activity and selectivity of unpromoted iron phosphate for the partial oxidation of methane is shown in Fig. 1. This experiment was performed at 933 K. It is easy to see that the longer the contact time, the lower the selectivity of the oxygen-containing organic compounds. This fact means that there exist some secondary reactions of the intermediates produced.

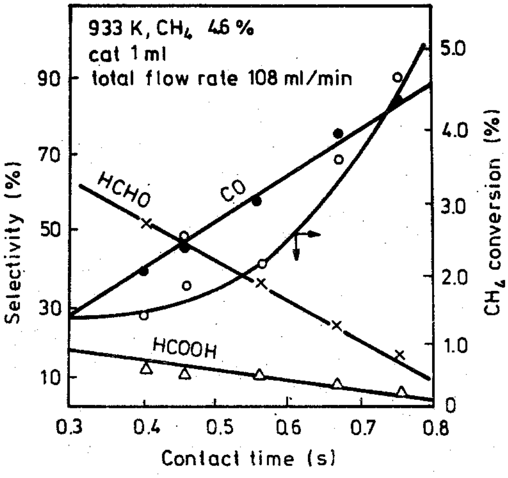

Fig. 1. Contact time dependence

c) Effect of water vapor on catalytic properties

As is shown in Table 2, addition of water vapor may influence both the activity and the selectivity of partial oxida-

Table 2

Effect of water vapor

Water	Total flow rate (cm³ (min)	r×10^6 (mol/cm³ min)			Select. (%)			CH_4 conv. (%)
		HCHO	HCOOH	CO	HCHO	HCOOH	CO	
no	100	0.41	0.19	0	68.4	31.6	0	0.27
yes	108	0.44	1.05	0	29.5	70.5	0	0.67

873 K, cat. 1 cm³, CH_4 4.6 %

tion of methane over iron phosphate. It seems that the modification functions of water vapor may be due to 1) inhibition of formation of CO_2; 2) acceleration of formation of HCOOH from water and CO.

d) Blank test

A blank test was made for the activity of stainless steel and asbestos in methane conversion. The activity and selectivity of these materials for the given reaction are negligible, as shown in Table 3.

Table 3

Blank test

T (K)	Total flow rate	CH_4	methane conv.
873	108 cm^3/min	4.6 %	0.05 %

e) Effect of addition of lanthanum phosphate

As can be seen in Fig. 2, in a wide range of molar percentages, lanthanum phosphate may influence the activity and the selectivity of partial oxidation of methane in different ways. 20 % Lanthanum phosphate can increase the conversion activity of methane and the selectivity to both HCHO and HCOOH. In this case a desired modification function can be expected.

f) XRD measurements

The unpromoted iron phosphate has a fine para-phosphate crystal structure before reaction. However, the bulk structure of the sample subjected to the catalytic reaction of 2 h changed: part of the original para-phosphate transformed into pyrophosphate. We postulate that due to the short reaction time, only a part of the structure change can be detected; as a result, there exist some intermediate crystalline phases which have to be verified in more detail.

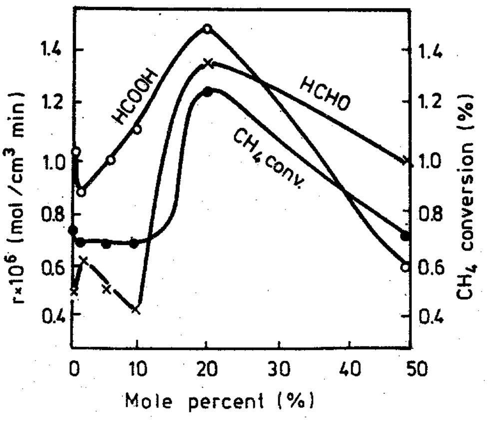

Fig. 2. Effect of La-phosphate on CH_4 oxidation

g) Infrared investigations

The possible chemisorbed species of methane on iron phosphate at 673 K were detected. It can easily be found in Fig. 3 that methyl and methylene radicals formed when methane

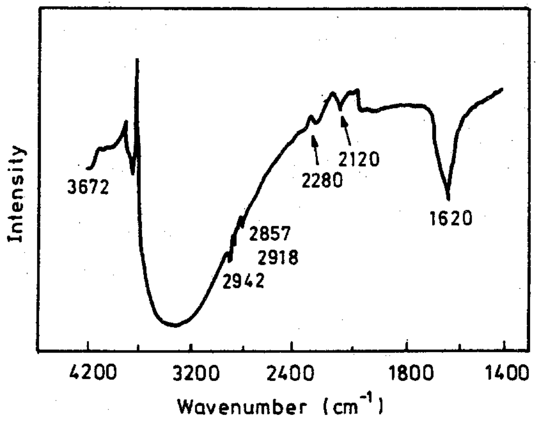

Fig. 3. IR spectrum of chemisorbed species

was chemisorbed on the catalyst surface. Their stretching vibration frequencies are 2857, 2918 and 2942 cm^{-1}, respectively. Besides, an absorption band at 3672 cm^{-1} was detected for hydroxy groups formed. Two more species can also be found for $>$CO (1620 cm^{-1}) and $-$CO (2120 and 2280 cm^{-1}, respectively).

CONCLUDING REMARKS

Based on the infrared experiments, the authors suggest a dissociative chemisorption mechanism for methane on catalyst surface to produce the corresponding methyl and methylene radicals and hydroxy groups. Hydrogen atoms were abstracted by the surface oxygen to form hydroxyls. As no methanol was detected during the experiments, we assume that during the intermediate steps methanol could form, followed by some secondary reactions to afford HCHO and HCOOH.

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