LEAD CONTAINING ZEOLITES AS CATALYSTS
FOR OXIDATIVE CONVERSION OF METHANE

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Dedicated to Dr Miloš Kraus on the occasion of his 65th birthday.

The oxidative conversion of methane was studied over lead containing zeolites of type X, silicalite and ALPO-5 in the temperature range 750 – 850 °C. An impregnation of catalysts in the range 3 – 7 wt.% lead was found optimum for the conversion and C_2 selectivity. The 6.4 wt.% lead-containing zeolite showed the best C_2 hydrocarbon yield. Higher reaction temperatures caused higher C_2H_4/C_2H_6 ratios. The catalysts did not deactivate in 10 h time-on-stream. PbO and zeolitic basic sites play role in the reaction.

In recent years numerous investigations on the oxidative conversion of methane have appeared in the literature. Different oxide systems have been used as catalysts for this reaction[1 – 3]. We have directed our attention to investigation of controlled structure basic catalytic systems, such as hydrotalcite[4] and in the present case, zeolites. Zeolites have both acid and basic sites. Basicity is one of the most important requirements of catalysts for methane oxidative coupling reaction[5].

In this work we describe the reaction of methane with oxygen in the presence of lead-containing zeolites, in order to understand the role of lead content and zeolite support on the conversion and selectivity to C_2 hydrocarbons.

EXPERIMENTAL

The catalysts were prepared by the incipient wetness method, using aqueous solutions of lead nitrate to be adsorbed on the zeolite support. The starting zeolite was NaX (SiO_2/Al_2O_3 = 2.5). The impregnation was followed by drying at 120 °C and calcination at 850 °C for 2 h. Samples were prepared with lead content of 3.3, 6.4, 12.2, and 22 wt.%. ALPO-5 and silicalite were impregnated with 6.4 wt.% lead in the same way. The samples were characterized by X-ray powder diffraction and IR spectroscopy before and after calcination, and after methane conversion as well.

The catalytic experiments were conducted in a fixed-bed, flow-type reactor, at atmospheric pressure. The reactor was a quartz tube (i. d. 8 mm) packed with 1 g of the catalyst, held in place with two quartz

wool plugs. The samples were activated in flowing air at the reaction temperature for 2 h before use. Then a feed consisting of methane and air at a total flow rate of 60 ml/min and CH_4 to O_2 ratio of 4.5 : 1 was admitted to the reactor at temperatures of 750, 800 and 850 °C. The compositions of the reaction products were analysed with an on-line gas chromatograph. Two columns, operated in parallel were used for separation – Porapak QS and Molecular Sieve 5A.

The methane conversion was calculated as moles C in the reaction products per mole C in the effluent gas. The selectivity to C_2 hydrocarbons was defined as 2X moles C_2 hydrocarbons produced per mole of the methane converted. Blank experiments, conducted with methane and air in the range of conditions employed, indicated that uncatalyzed reaction played no role, it was negligible. However, homogeneous gas phase reactions of the reaction products cannot be excluded.

RESULTS AND DISCUSSION

The major products of methane conversion were CO_2, C_2H_4 and C_2H_6. It was rare to observe a trace of CO in the reaction product, and no C_3 hydrocarbons were observed in any experiment. The catalysts retained their full activity and selectivity in 10 h runs.

Figure 1 shows the catalytic performance of Pb/NaX catalysts with various content of lead, added to NaX zeolite. In addition, Fig. 1 also includes the results obtained in the presence of NaX zeolite without lead. The impregnation to only 3.3 wt.% lead on NaX increased conversion from 4 to 9% and C_2 selectivity from 37% to 68%. But with increasing lead content, the methane conversion hardly changes. C_2 selectivity is positively influenced by lead content, maximizing at 6.4 wt.% lead. The more lead in the sample reduces slightly the C_2 selectivity but to the level higher than that of the initial NaX.

The C_2H_4 and C_2H_6 dependence on lead content is shown in Fig. 2. With lead content increasing to 3 – 6 wt.% the C_2H_4/C_2H_6 ratio increases. Above 3 – 6 wt.% lead C_2H_4/C_2H_6 ratio decreases.
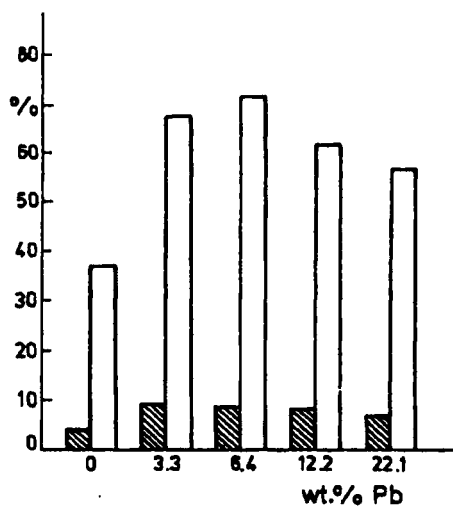

FIG. 1
Conversion (hatched bar) and C_2 selectivity (open bar) over lead containing X zeolite at 750 °C

These results show that the optimal catalyst at which the best conversion, C_2 selectivity and C_2H_4/C_2H_6 ratio were produced under the experimental conditions is that containing no more than 6.4 wt.% lead. Therefore, changes in the nature and production of catalytic centers depend on the lead content.

Methane conversion is only weakly increased by temperature. But the higher temperature leads to the higher C_2H_4/C_2H_6 ratios. This is shown in Fig. 3 for the sample containing 6.4 wt.% lead and it is valid for all the catalysts at higher temperatures. However, homogeneous gas phase reactions of the coupling products are also possible.

The trend of the yields of C_2 hydrocarbons and CO_2 for the samples with increasing lead content at 800 °C is shown in Fig. 4. It can be concluded again that 6.4 wt.% lead-containing zeolite gives the best C_2 yield (8%). The higher lead content is not preferable.

To get some insight into the importance of catalytic structure and the state of lead, the catalysts were characterized by X-ray diffraction and IR spectroscopy. Following the assumption for the redox cycle $Pb^{2+}-Pb^0$ (refs[4,6]), PbO and Pb^0 (metallic lead) should be present in the samples. In diffractograms of lead-containing NaX zeolite, the peaks of PbO with d-spacings of 3.07, 2.97 and 2.71 Å were partly overlapped with these of the zeolite. In diffractograms of the same samples after the reaction, the peaks of Pb^0 were overlapped with these of the zeolite (d-spacing of 2.88 Å) and of the PbO (d-spacing of 2.49 Å). This is shown in Fig. 5 and does not disprove an assumption that the oxidative dimerization of methane proceeds via redox cycle between Pb^{2+} and Pb^0.
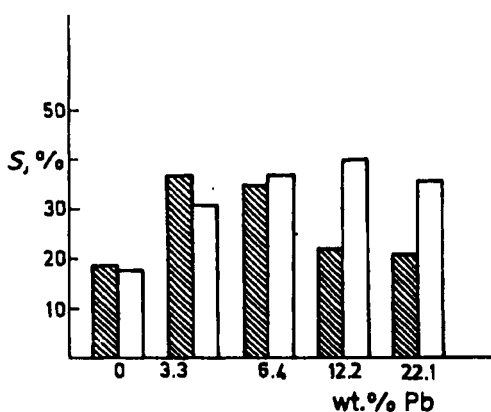

FIG. 2
C_2H_4 selectivity (hatched bar) and C_2H_6 selectivity (open bar) S over lead containing X zeolite at 750 °C
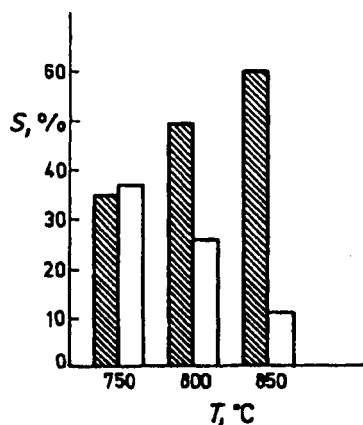
FIG. 3
Temperature dependence of C_2H_4 selectivity (hatched bar) and C_2H_6 selectivity (open bar) S over 6.4 wt.% lead containing X zeolite

What happens with the zeolite support is clear not only from the diffractograms but from the IR spectra as well. Although the crystal structures of calcined NaX and of NaX after the reaction are partly destroyed, as judged from diminished intensities of

TABLE I
Oxidative conversion of methane at 800 °C

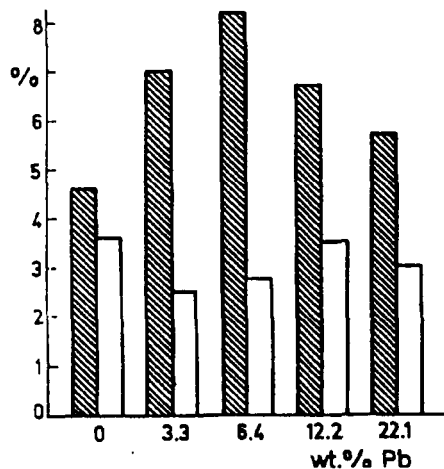| Catalyst	CH_4 conv. %	Selectivities, %			C_2 yield %
		CO_2	C_2H_4	C_2H_6	
6.4% Pb / NaX	11.0	25	49	26	8.2
6.4% Pb / Silicalite	5.6	51	25	24	2.6
6.4% Pb / ALPO-5	6.0	23	46	31	4.5

FIG. 4
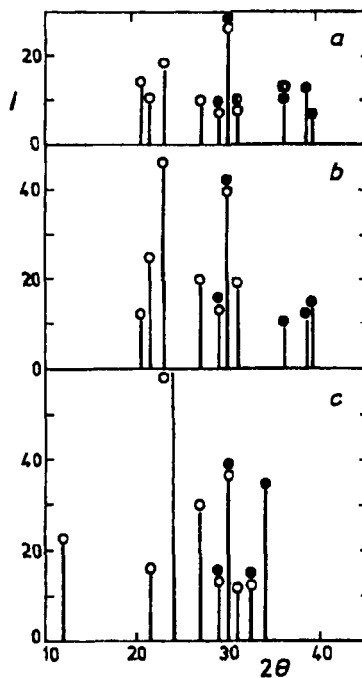C_2 hydrocarbon (hatched bar) and CO_2 (open bar) yields over lead containing X zeolite at 800 °C

FIG. 5
X-Ray diffraction spectra of 6.4% Pb/NaX (I stands for intensity): (O) zeolite, (●) PbO, (◐) Pb^0. a Uncalcined; b calcined, 850 °C, 2 h; c after reaction

structure sensitive bands at 575 and 1 075 cm^{-1} in the IR spectra[7], the catalysts prepared on NaX have activities comparable with of the catalysts prepared on other conventional supports[8]. This suggests that other factors (e.g. basicity) besides the structure and surface are also important for the reaction.

The crystal structures of silicalite and ALPO-5 after calcination and after the reaction decompose to the lesser extent compared to NaX, although the latter catalyst is more active (see Table I). Methane conversion in the presence of 6.4 wt.% lead-containing NaX is 11.0%, whereas on the corresponding lead-containing ALPO-5 and silicalite methane conversions are 5.6% and 6.0%, respectively. In the same time, the C_2 selectivities of 6.4% Pb/ALPO-5 and 6.4% Pb/NaX are similar – 77% and 75%, respectively. Hence, the crystal structure cannot be fully responsible for variations in the catalytic activity and selectivity.

Summarizing, the data on the activity and selectivity of the lead-containing zeolites examined suggest that some role in the reaction is played by zeolitic basic sites. The importance of basic properties of the catalyst is postulated for the oxidative conversion of methane[9]. The nature of zeolitic basic sites is still unclear but probably they could be the oxygen atoms from the zeolite lattice, acting as hydrogen acceptors. Ultimately, these basic sites are in some way associated with the lead oxide present on the surface, both affecting conversion and C_2 selectivity to varying degrees. Further studies are under way to determine the basicity of zeolites and its role in the reaction of oxidative conversion of methane.

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