Methanol from Oxidation of Methane by Nitrous Oxide over FeZSM5 Catalysts

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Under optimum conditions, Cu^{2+}-exchanged FeZSM5 catalyses the oxidation of methane by nitrous oxide with high selectivity for methanol production. H^+-Exchanged FeZSM yields mainly carbon oxides.

At low conversions (0.1—2.7%) the zeolite H-ZSM5 catalyses oxidation of methane by nitrous oxide to appreciable amounts of methanol, formaldehyde, C_2 + C_3 olefins, and C_6—C_{12} aromatic products, although carbon oxides still constitute at least two-thirds of the carbon-containing product.[1,2] Furthermore, methanol is an early product, and olefins and aromatic materials are formed sequentially from it.[2]

Here we describe the oxidation of methane by nitrous oxide over catalysts based on FeZSM, an analogue of ZSM5 with Fe^{3+} in the lattice in place of Al^{3+}. Most attention has been

Table 1. Products from methane oxidation with nitrous oxide over FeZSM5 catalyst.[a]

Catalyst	$CH_4 : N_2O$ molar ratio	Space velocity $\times 10^{-4} (h^{-1})$	Reaction temp. (K)	CH_4 conv. (%)	N_2O conv. (%)	Products (C%)					
						CO_2	CO	MeOH	HCHO	C_2 olef.	C_3 olef.
Cu-FeZSM5	80:20	22.0	615	1.52	16	51	7.2	38	3.8	0.4	0.2
	80:20	43.1	615	1.12	10	35	8.5	50	6.2	0.4	0.4
	80:20	43.1	510	0.25	1.6	19	2.5	78	1.0	—	—
	60:40	42.2	619	[b]	[b]	87	9.7	1.3	2.4	—	—
	18:82	42.2	619	*ca.* 85	*ca.* 50	100	—	—	—	—	—

[a] Data taken after 60 min on stream. [b] Not available.

given to H^+-exchanged FeZSM5 (H-FeZSM5) and to Cu^{2+}-exchanged FeZSM5 (Cu-FeZSM5).

No aromatic products were observed with either of the present catalysts: carbon oxides, methanol (with a trace of formaldehyde), and C_2 + C_3 olefins were obtained. With H-FeZSM5, carbon oxides dominated the products, and amounts of olefins generally exceeded that of methanol. However, over Cu-FeZSM5 the reaction was exceptional in that methanol could be the dominant product, reaching nearly 80% of products under favourable conditions.

The preparative formulation for FeZSM5 was similar to that conventionally used for ZSM5 except that a source of Fe^{3+} was used in place of Al^{3+}, and is generally similar to that since described by Szostak[3] and Chu.[4] The H-FeZSM5 so produced had the composition: SiO_2 90.6, Fe 3.94, Al 0.60 (impurity) Na 0.043 wt. %. The Si : Fe ratio is 21.4.

H-FeZSM5 was a fine crystalline powder, pale tan in colour, with non-euhedral crystals 0.5—1 μm in size. *X*-Ray and electron diffraction patterns were essentially the same as those for normal ZSM5. The measured Na^+ ion exchange capacity was 0.50 mmol g^{-1}.

Leaching (successive treatments with an excess of 1 M-HCl at 373 K; 4 h per treatment) showed that some iron could be removed into solution. After four treatments, the iron content was reduced to 43% of the original value, and after seven treatments, to 30% of the original value; further treatments were ineffectual.

If all the iron and aluminium (impurity) in the as-prepared H-FeZSM5 were in the lattice, the Na^+ exchange capacity would be 0.92 mmol g^{-1} (0.70 mmol g^{-1} from the iron and 0.22 mmol g^{-1} from the aluminium). Comparison with the measured Na^+ exchange capacity shows that the exchange capacity attributable to lattice iron could not have exceeded about 0.3 mmol g^{-1}; that is, about 43% of the total iron was in the lattice. From K^+ exchange data, Szostak[3] also estimated that about 40% of the total iron was in the lattice, and attributed the loss of iron from the lattice to the calcination process (required to decompose the quaternary base).

From these data we conclude that the H-FeZSM5 consisted about 97% of a phase with the ZSM5 skeletal structure containing about 1.7 wt.% iron in the lattice (and about 0.6 wt. % aluminium), together with a separate impurity phase which contributed about 2.2 wt. % to the total iron content. Because of small particle size or lack of crystallinity, this impurity was not detectable by *X*-ray or electron diffraction.

Reactions were carried out in a microreactor† with product analysis by gas chromatography.[2]

Representative data for Cu-FeZSM5 are summarized in Table 1. With both H-FeZSM5 and Cu-FeZSM5, the methane conversion decreased by about 30% during the first 60 min on stream and remained approximately constant thereafter; the data in Table 1 were collected after this initial conversion decrease.

With H-FeZSM5 at 623—670 K, work was restricted to the reactant ratio ($CH_4 : N_2O$) 98 : 2; increasing the N_2O fraction gave 100% CO_2, while at <623 K the CH_4 conversion was too small. Nevertheless, the N_2O conversion was always 100% (from mass balance), and the products were mainly carbon oxides ($CO_2 : CO$ *ca.* 1 : 1 to 3 : 1 depending on temperature and space velocity). The only other products were methanol and C_2 + C_3 olefins, which formed <2 and <3.5C% of products, respectively. That none of this small amount of C_2 + C_3 was converted into aromatic products (unlike reaction over H-ZSM5[2]), we attribute to a lack of sufficiently strong acidic sites, in agreement with ammonia TPD data,[5] butane cracking results,[3] and i.r. data.[4]

Over Cu-FeZSM5 the reaction was quite different. At $CH_4 : N_2O$ 80 : 20 and CH_4 conversion <2%, the proportion of MeOH in the product was in the range 38—78C%, and the reaction was not limited by N_2O conversion. The behaviour was broadly the same in the range $98 : 2 > CH_4 : N_2O > 80 : 20$. However, at $CH_4 : N_2O < 80 : 20$, the methane conversion increased rapidly, as did the fraction of carbon oxides in the products. Clearly Cu-FeZSM5 is a relatively inefficient catalyst for methanol oxidation at low N_2O concentrations. It is also unable to convert methanol into olefins or aromatic products, as would be expected from its non-protonic nature.

Comparative studies were made with a Cu^{2+}-exchanged ZSM5 catalyst (Cu-ZSM5); the results were generally rather similar to those with H-FeZSM5 (products dominated by carbon oxides even at very low conversions, only very small amounts of olefins, aromatic products absent). We conclude therefore that the exceptional behaviour of Cu-FeZSM5 results in some way from a synergism between the copper and iron functions. This is the subject of further study. The propensity of Cu-ZSM5 for total oxidation agrees with observations by Dessau[6] on xylene oxidation. The behaviour of Cu-FeZSM5 reported here suggests that this catalyst may be able, with appropriate reactants, to combine the functions of size–shape selectivity and partial oxidation.

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† Catalyst (0.1 g), temp. range 500—720 K, space velocity 12 000—67 000 h^{-1}, total pressure 1 atm., internal reactor diam. 0.4 cm, catalyst bed length about 1 cm.