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Oxidation of propane with oxygen, nitrous oxide and oxygen/nitrous oxide mixture over Co- and Fe-zeolites

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Abstract

Oxygen, nitrous oxide and their mixture was used in oxidation of propane over CoH(Fe)–BEA and parent H(Fe)-zeolites (containing trace concentrations of Fe) of beta and ZSM-5 structures. CoH(Fe)–BEA zeolite exhibited a substantial increase in propene yield (from 2.0 to 6.8%), if together with molecular oxygen, nitrous oxide was used. No other oxygenates were detected. With increasing concentration of molecular oxygen in the propane/nitrous oxide/oxygen mixture, a synergetic effect of oxygen and nitrous oxide resulting in nearly threefold increase in propene yield was observed. At the reaction conditions studied, the highest propane conversion (15.8%) with 61.9% selectivity to propene and propene yield of 9.8%, and the sum of selectivities to oxygenates of 10.3% (foremost propyl alcohol and propanal) was achieved with the steamed H(Fe)–MFI zeolite when a mixture of nitrous oxide and oxygen was used. It is concluded that, the oxidation activity of nitrous oxide originates from specific Fe species, present in CoH(Fe)–BEA and H(Fe)-zeolites, exhibiting extra-ordinary activity in hydroxylation of propane to propyl alcohol (dehydrated to propene) and its further oxidation to propanal, whereas Co ions contribute only to propane oxidation to propene and carbon oxides.

Keywords: Propane oxidation; Propene; Nitrous oxide; Hydroxylation of hydrocarbons; Co-beta; Fe–ZSM-5

1. Introduction

Conversion of low alkanes, so far consumed mostly in energy production, to alkenes, alcohol, aldehydes and organic acids is a great challenge in catalysis, as these products are more reactive than the corresponding alkanes. In spite of the effort devoted for several decades to development of mixed metal oxides as catalysts for selective paraffin oxidations, no industrial process converting low paraffins to olefins by oxidative dehydrogenation is on stream.

In recent decade, metal ion species exchanged in zeolites have been discovered as very active and selective oxidation catalysts. Li and Armor [1–3] disclosed high activity of Co ions in ZSM-5 and beta zeolites in ammoxidation of ethane to acetonitrile with ethene as an intermediate. The ammoxidation activity of Co-zeolites was much higher as compared to that of Nb–Sb–Al mixed oxides [4]. Also specific Fe species formed in ZSM-5 zeolites have been revealed as extremely active and selective in oxidation of benzene to phenol with nitrous oxide. The atomic oxygen formed from nitrous oxide decomposition did not recombine to molecular oxygen, but it was trapped by Fe species and transferred into benzene molecule [5,6]. The catalyst based on Fe–ZSM-5 for benzene transformation to phenol is developed up to the stage of the industrial process.

Very recently, Fe–ZSM-5 zeolites were reported to be active in propane oxidation to propene with nitrous oxide [7–9]. Like with benzene oxidation to phenol, the Fe species have been shown to exhibit extreme activity, while Broensted and Al–Lewis acid sites themselves have not possessed significant activity [10]. We have reported that propane oxidation with nitrous oxide over steamed Fe–ZSM-5 led at propane conversion (44%) to high selectivity of requested propene (56%) as well as to C_1–C_3 oxygenates, phenol and aromatics. The yield of propene was comparable to that one achieved with the most active

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mixed metal oxides for propane oxidative dehydrogenation [9].

In our previous works we reported high activity of Co-beta zeolites in oxidative dehydrogenation of propane to propene [11,12] and the observation that addition of N_2O increases substantially the propene yield [13]. In the present paper, we studied the role of the Co ions and Fe species in zeolites in the oxidation of propane with molecular oxygen, nitrous oxide and their mixture to analyze the contribution of the Co and Fe species in the individual reactions.

2. Experimental

NH_4–MFI zeolite with Si/Al 12.5 (190 ppm Fe) was provided by the Research Institute of Inorganic Chemistry Inc., CZ; denoted as H(Fe)–MFI. A part of NH_4–MFI was heated in a stream of oxygen containing 30% water vapour at temperature of 600 °C for 6 h; denoted as H(Fe)–MFI-HT. NH_4–BEA with Si/Al 12.4 (400 ppm Fe), denoted as H(Fe)–BEA and purchased from PQ Corporation, was exchanged with Co ions from 0.01 M $Co(acetate)_2$ solution. The solid was then thoroughly washed with distilled water, filtered and dried on air. The content of Co was 1.8 wt.%, Co/Al molar ratio 0.25, and the Fe content in the zeolite increased to 450 ppm; denoted as CoH(Fe)–BEA. The elemental analysis of zeolites was done by X-ray fluorescence spectroscopy (XRF) and inductively coupled plasma emission spectrometry (ICP-OES). XRD of all zeolites revealed well crystalline samples, with the crystal size ranging from 0.1–0.25 μm and from 0.5 to 1.5 μm for BEA and MFI zeolites, respectively, as estimated from scanning electron microscopy.

X-band ESR spectra of Fe^{3+} ions were monitored at room temperature (RT) by ESR spectrometer (ERS-220, Germany). The zeolites were pre-treated in an oxygen stream at 450 °C for 2 h, cooled to 150 °C and evacuated for 30 min at 10^{-2} Pa. Then the samples were transferred under vacuum to a quartz cell. Mn^{2+} ions were used as an internal standard.

Oxidation of propane was carried out in a fixed bed through flow-micro-reactor at atmospheric pressure. The catalyst (0.2 g) was mixed with 1.5 cm^3 of inert silicon carbide. The compositions of the reaction $C_3H_8/O_2/N_2O$ mixtures (total flow rate 100 ml/min) were in the range 5/0–22.5/0–10 vol.%, in the helium as carrier gas. Catalyst was pre-treated in an oxygen stream at 450 °C for 1 h before each run. Gas chromatographic (CHROM 5, CZ) on-line analysis was carried out using Porapak Q column enabling separation of N_2O, CO_2, hydrocarbons, alcohols and aromatics, and molecular sieve 5A for analysis of permanent gases (i.e. O_2, N_2, CO).

3. Results

The results of propane oxidation over CoH(Fe)- and parent H(Fe)-beta zeolites containing trace Fe concentration (450 and 400 ppm, respectively) with oxygen, nitrous oxide and using both oxidants at 450 °C are summarized in Table 1. Oxidation of propane with molecular oxygen over CoH(Fe)–BEA catalyst exhibited similar values of selectivity to carbon mono- and dioxide and the selectivity to propene reached 33.6% at propane conversion of 5.9%. The substitution of oxygen by nitrous oxide led to a dramatic increase in propene selectivity from 33.6 to 68%. On the other hand, the conversion of propane decreased to 3.8% and the selectivity of carbon monoxide fell down to 2.3%, while that of CO_2 did not change considerably. Using of both

Table 1
Propane oxidation over CoH(Fe)- and H(Fe)-zeolites at 450 °C, total flow = 100 ml/min, catalyst weight = 0.2 g

Catalyst	$C_3H_8/O_2/N_2O$ (vol.%)	$X_{C_3H_8}$ (%)	Selectivity (%)						$Y_{C_3H_6}$ (%)
			CO	CO_2	C_2H_4	C_3H_6	C_1–C_3, C_7 oxygenates[a]	Aromatics[b]	
CoH(Fe)–BEA 450 ppm Fe 1.8 wt.% Co	5/6.5/0	5.9	32.3	34.1	nd	33.6	nd	nd	2.0
	5/0/10	3.8	2.3	29.7	nd	68.0	nd	nd	2.6
	5/6.5/10	13.9	22.0	40.5	nd	37.5	nd	nd	5.2
	5/22.5/0	9.7	39.2	27.7	7.4	25.7	nd	nd	2.5
	5/22.5/10	27.9	33.1	39.6	3.0	24.3	nd	nd	6.8
H(Fe)–BEA 400 ppm Fe	5/6.5/0	2.1	29.1	21.6	nd	49.3	nd	nd	1.0
	5/0/10	2.8	1.8	2.3	nd	95.9	nd	nd	2.7
	5/6.5/10	8.7	15.7	23.7	nd	60.6	nd	nd	5.2
H(Fe)–MFI 190 ppm Fe	5/6.5/0	1.2	26.5	14.6	1.6	57.3	nd	nd	0.7
	5/0/10	3.8	5.6	65.7	2.0	26.7	nd	nd	1.0
	5/6.5/10	6.8	8.7	63.7	0.3	27.3	nd	nd	1.9
H(Fe)–MFI-HT 190 ppm Fe	5/6.5/0	1.6	26.4	14.1	nd	59.4	nd	nd	0.9
	5/0/10	10.2	0.9	1.5	2.5	83.3	7.1	1.7	8.5
	5/6.5/10	15.8	10.5	9.8	4.0	61.9	12.5	1.5	9.8

nd, not detected.
[a] Sum of selectivities to propanal, ethanol, *i*-propanol, acetone, acetaldehyde and phenol.
[b] Sum of selectivities to benzene, toluene and xylenes.

oxidizing agents resulted in a dramatic increase in conversion of propane (13.9%), and the selectivity to propene also slightly increased compared to propane oxidation with both molecular oxygen and nitrous oxide. Therefore, the yield of propene increased up to 5.2% that is two and a half times higher than that with molecular oxygen and two times, if only nitrous oxide was applied.

To analyze the contribution of the activity of parent H(Fe)–BEA zeolite, containing trace concentration of iron (400 ppm), to that of CoH(Fe)–BEA, the H(Fe)–BEA zeolite was tested in the above reactions. Propane conversion with the C_3H_8/O_2 reaction was lower compared to the CoH(Fe)–BEA sample, but exhibited lower CO/CO_2 selectivity and higher selectivity to propene (49.3%). Nevertheless, the propene yield was low (1%). Compared to CoH(Fe)–BEA, the C_3H_8/N_2O reaction over H(Fe)–BEA resulted in a similar propane conversion and in a dramatic decrease in selectivity to CO_x from 50.7 to 4.1%. Selectivity to propene reached nearly 96%. The observed positive effect of nitrous oxide addition to the C_3H_8/O_2 mixture on propane conversion was accompanied by a higher propene yield, although the selectivity was lower. The propene yield exhibited the same value as that of CoH(Fe)–BEA zeolite.

Because of the positive response of propane oxidation to propene on the simultaneous presence of oxygen and nitrous oxide with both catalysts, the effect of oxygen concentration over CoH(Fe)–BEA was investigated (see Fig. 1). The yield of propene at the C_3H_8/O_2 reaction increased with increasing concentration of oxygen being 2.0% at 6.5% O_2 and 2.5% at 22.5% O_2 with the change in the selectivity to CO from 32.3 to 39.2%, and the selectivity to CO_2 from 34.1 to 27.7% (see Fig. 1 and Table 1). On the other hand, the propene yield in the $C_3H_8/O_2/N_2O$ reaction, which increased with increasing oxygen concentration, reached a maximum value of 6.8%. With increasing concentration of oxygen in the $C_3H_8/O_2/N_2O$ mixture increased substantially propane conversion (from 13.9 to 27.9%) and slightly propene yield (from 5.2 to 6.8%). The selectivity to CO_2 was nearly the same, but that of CO increased substantially. Moreover, in the products ethene appeared on the account of propene.

The results on propane oxidation in the reactant mixtures given above over H(Fe)–MFI and steamed H(Fe)–MFI-HT (Table 1), showed that lower concentration of Fe in the H(Fe)–MFI zeolite (190 ppm) yields lower propene yields in all the reactions investigated compared to H(Fe)–BEA. A dramatic increase in propane conversion and yield of propene was found for the steamed H(Fe)–MFI-HT zeolite with the reactions where N_2O participated, but not with the C_3H_8/O_2 mixture. In the C_3H_8/N_2O and $C_3H_8/O_2/N_2O$ reactions high selectivity and yield of propene was achieved; the highest propene yield of about 10% with the $C_3H_8/O_2/N_2O$ reaction. Besides propene, the selectivity to ethene (4.0%) and oxygenates, i.e. C_1–C_3 alcohols (2.7%), acetone (2.2%) and propanal (6.3%) was monitored after 400 min time-on-stream (TOS). At shorter TOS values, aromatics and phenol (selectivity at about 10 and 2% after 30 min TOS, respectively) appeared in the products. It is to be pointed out that the selectivity to CO_x was much lower with the C_3H_8/N_2O reaction, while the simultaneous presence of oxygen and N_2O increased the selectivity to CO_x.

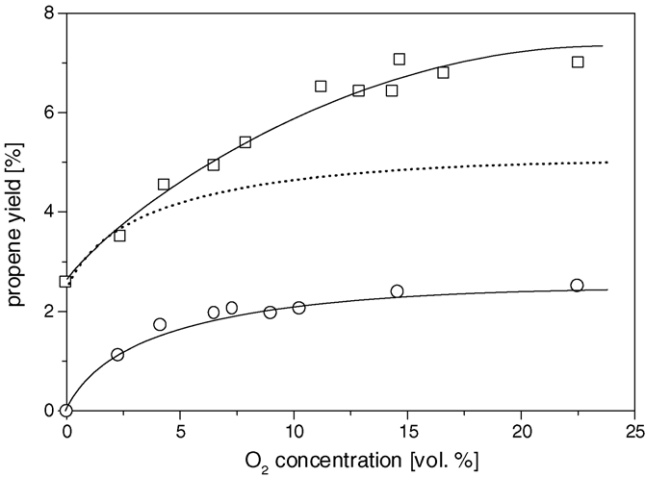

Fig. 1. Effect of oxygen on propane oxidation over CoH(Fe)–BEA expressed as propene as a function of oxygen concentration at 450 °C, F = 100 ml/min, (○) C_3H_8/O_2, (···) (C_3H_8/O_2) + (C_3H_8/N_2O), i.e. theoretical contribution of the individual oxidants to propane oxidation, (□) $C_3H_8/O_2/N_2O$.

To obtain some information on the state of Fe ESR spectra of oxidized and dehydrated H(Fe)–MFI and H(Fe)–MFI-HT samples were recorded at RT (Fig. 2). Besides the broad signal at g 2.3 (ΔH ca. 1300 G) of the Fe-oxide-like species, the spectra of both samples showed the signal at g 4.3 (ΔH 50 G), characteristic for tetrahedrally coordinated Fe^{3+} ions. Hydrothermal treatment of H(Fe)–MFI resulted in an increase in the signal of T_d coordinated Fe species and a substantial increase in the intensity of the signals at g 6.0 and 5.6 (ΔH 50 G), reflecting distorted T_d coordinated Fe^{3+} [9]. With the H(Fe)–BEA and CoH(Fe)–BEA samples, the character of the ESR spectra of Fe^{3+} ions was similar to that of H(Fe)–MFI. The intensity of the signal at g 4.3, compared to the H(Fe)–MFI sample, was for H(Fe)–BEA and CoH(Fe)–BEA two times and two and half times higher, in agreement with the Fe concentration (400 and 450 ppm Fe, respectively). No signals, which can be attributed to the presence of trace concentrations of Mn^{2+}, Cu^{2+} and V^{4+} cations were detected.

4. Discussion

4.1. Effect of Fe concentration and zeolite hydrothermal treatment

The results of the activity of Fe-zeolites, regardless of the zeolite structure, obtained in this study and in reference [9,14] indicate that at low iron concentrations of hundreds of ppm the propane conversion in selective oxidation to propene is proportional to Fe ion concentration, like for

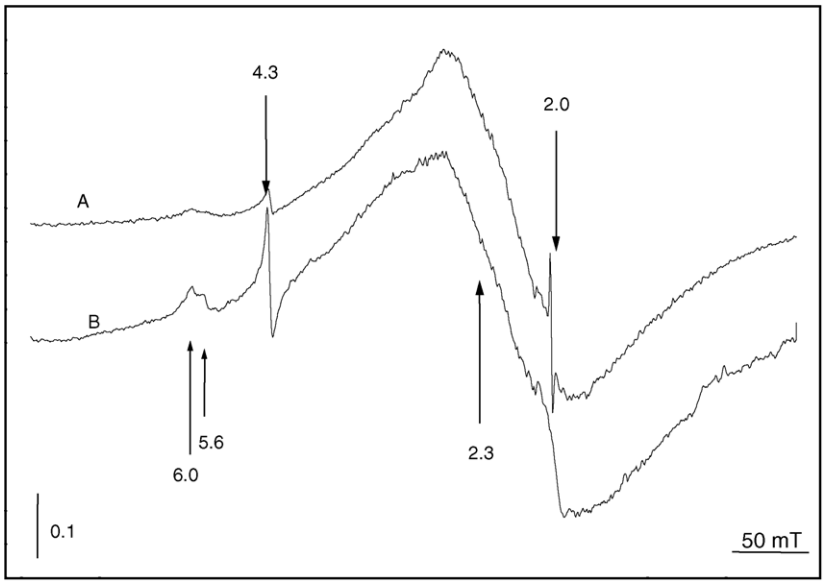

Fig. 2. X-band ESR spectra of dehydrated zeolites monitored at RT: (A) H(Fe)–MFI and (B) H(Fe)–MFI-HT.

oxidation of benzene to phenol with nitrous oxide [10]. The ESR spectra indicate that for all samples investigated most of the iron is located in the Fe-oxide-like species, and only a minor part is in T_d or distorted T_d coordinated environment. Our previous study [10] showed that with the benzene oxidation to phenol the most active Fe sites could be connected with the intensity of the signal at 6.0 and 5.6 reflecting Fe ions in distorted T_d surroundings. However, due to very low concentrations of iron relevant quantitative analysis is not possible. The change in the structure of Fe sites induced by zeolite steaming, is indicated mainly by an increase in the intensity of the signals at *g* 6.0 and 5.6 and it is also accompanied by the changes in concentration of Broensted and Lewis acid sites (for details see reference [10]). This results in a substantial enhancement of the conversion of propane to propene and some oxygenates, if nitrous oxide or the mixture with molecular oxygen is employed. Such enhancement is not found by propane oxidation with molecular oxygen. Thus, some Fe species, formed especially under zeolite steaming, are extra-ordinary active in reactions using atomic oxygen from the decomposed nitrous oxide. On contrary, the results of previous study [9] indicate neither protonic sites nor Lewis sites are active in the oxidation reactions with nitrous oxide. On the other hand, we cannot exclude them particularly Lewis sites from their contribution to the cracking and oligomerization and hydrogen transfer reactions, leading to formation of aromatics and ethene.

4.2. Comparison of the C_3H_8/O_2, C_3H_8/N_2O and $C_3H_8/O_2/N_2O$ reactions

In general, oxidation of propane by molecular oxygen to propene is less selective compared to reactions using nitrous oxide for both Fe- and Co-zeolites. The higher propane conversion and propene yield for CoH(Fe)–BEA compared to H(Fe)–BEA evidences participation of Co ions in propane oxidation to propene. However, the activity of Co ions is much lower compared to Fe species in terms of turn-over-frequency (TOF) values per the corresponding cation (cf. 18,000 ppm Co versus 400 ppm Fe). With the both Co- and Fe-zeolites the selectivity to propene and CO_x is comparable and corresponds to the conversion level. Propane oxidation with N_2O brings generally low selectivity to CO_x, higher propene yield and in the zeolite with highly active Fe species as found with steamed H(Fe)–MFI-HT also formation of oxygenates. Molecular oxygen added to nitrous oxide decreased slightly propene selectivity, but the propane conversion and propene yield is considerably increased as well as the selectivity and yield to oxygenates. From a comparison of the dependence of the propene yield on oxygen concentration in the $C_3H_8/O_2/N_2O$ and C_3H_8/O_2 reactions and of the propene yield in the C_3H_8/N_2O reaction, it implies that there is some synergetic effect between nitrous oxide and molecular oxygen (see Fig. 1). At present we have not enough appropriate data to make serious conclusion.

The mechanism of formation of oxygenates is not completely evidenced by the experiment. It is clear that atomic oxygen formed by nitrous oxide decomposition is via Fe species incorporated into hydrocarbon molecules. During the reaction course aromatics are at first formed, which are in a subsequent step oxidized to phenol. Such reaction is slow down as at longer TOS aromatics are not formed, and oxygen atom participates in the formation of methanol, ethanol, propanol and propanal. Formation of acetaldehyde and acetone might originate also from atomic oxygen or molecular oxygen as well.

4.3. Comparison of the activity of Co and Fe species in propane oxidation

If we accept that the CoH(Fe)–BEA zeolite contains very similar concentration and type of Fe species as the parent H(Fe)–BEA zeolite, then the differences in the activity in the individual reactions between these two samples can be attributed to the Co species. Co ions contribute to higher propane conversion, but the selectivity to propene is lower compared to Fe species. In total the yield of propene is higher with the Co-zeolite in comparison with the Fe-zeolite in the C_3H_8/O_2 reaction. Completely different picture is obtained in the reactions employing nitrous oxide. From Table 1 it is seen that the low selectivity to both CO and CO_2 is obtained with Fe-zeolite, while presence of Co species enhances oxidation to CO_2. With increasing concentration of oxygen increases selectivity to both CO_x and decreases selectivity to propene. But the overall effect is positive as evidenced by the increasing propene yield with increasing oxygen concentration in the $C_3H_8/O_2/N_2O$ mixture.

5. Conclusions

It can be concluded that the iron sites, particularly formed under Fe-zeolite steaming containing trace concentration of Fe incorporated during the zeolite synthesis, are highly active in oxidation of propane with nitrous oxide to alcohols and aldehydes, in which C_3 components prevail, and propene is formed by propyl alcohol dehydration. On the other hand, propane oxidation to propyl alcohol and propanal over Co ions does not occur and only propene is formed. This finding indicates that only specific Fe species, and not Co ions, are able to bind atomic oxygen formed during nitrous oxide decomposition and to transfer it to a hydrocarbon molecule. Therefore, the activity of Co-zeolites in propane oxidation with nitrous oxide should be ascribed to the presence of trace concentrations of iron in Co-zeolites. The role of Co ions is in oxidative dehydrogenation of propane to propene and oxidation of the selective products to carbon oxides.

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