Catalysis Letters Vol. 104, Nos. 3–4, November 2005 (© 2005)
DOI: 10.1007/s10562-005-7946-8

Highly efficient Fe-silicalite zeolite in direct propane ammoxidation with N_2O and O_2

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Received 22 February 2005; accepted 24 June 2005

A novel process for the direct ammoxidation of propane over steam-activated Fe-silicalite at 723–823 K is reported. Yields of acrylonitrile (ACN) and acetonitrile (AcCN) below 5% were obtained using N_2O or O_2 as the oxidant. Co-feeding N_2O and O_2 boosts the performance of Fe-silicalite compared to the individual oxidants, leading to AcCN yields of 14% and ACN yields of 11% (propane conversions of 40% and products selectivity of 25–30%). The beneficial effect of O_2 on the propane ammoxidation with N_2O contrasts with other N_2O-mediated selective oxidations over iron-containing zeolites (e.g. hydroxylation of benzene and oxidative dehydrogenation of propane), where a small amount of O_2 in the feed dramatically reduces the selectivity to the desired product. It is shown that the productivity of ACN and especially AcCN, expressed as mol product h^{-1} $kg_{cat}{}^{-1}$, is significantly higher over Fe-silicalite than over active propane ammoxidation catalysts reported in the literature. Our results open new perspectives to improve the performance of alkane ammoxidation catalysts.

KEY WORDS: propane; ammoxidation; iron zeolites; N_2O; O_2; acrylonitrile; acetonitrile.

1. Introduction

Acrylonitrile (ACN) is extensively used for the production of acrylic fibers, rubbers, plastics, and adiponitrile. Today, ca. 10 billion pounds of ACN are produced worldwide by the SOHIO/BP process, involving the reaction of propylene, ammonia, and oxygen over complex mixed-metal molybdates at 673–773 K [1]. Despite the high efficiency of this process, with ACN yields >80% on commercial scale, significant research efforts are directed towards developing catalytic systems for the direct ammoxidation of propane, due to the abundance and lower cost of propane relative to propylene, the increasing demand for ACN, and the risk of propylene shortage due to its increasing demand in the petrochemical industry.

Propane ammoxidation represents a technological challenge due to the fact that alkane activation is a more difficult process than alkene activation, and requires more severe operating conditions and very active and selective catalysts. A number of mixed oxide catalysts have been proposed for propane ammoxidation with O_2, including (i) rutile structures with V, Sb, W, and Al as key elements [2–4], (ii) Bi–Mo–V scheelite structures [5–8], (iii) vanadyl pyrophosphates [9], (iv) Ga-antimonate, pure or modified with W, Ni, and P [10], and (v) V–Al oxynitrides [11]. ACN yields in the range of 30–60% have been reported over multicomponent Sb–V–Al–W and Mo–V–Nb–Te oxides [1,4,6,8]. Acetonitrile (AcCN) is obtained as a by-product of propylene/propane ammoxidation, with typical yields $<5\%$. ACN manufacture is today's exclusive industrial source of AcCN, at levels of 2–3 wt% with respect to ACN.

Explorative studies on the performance of metal-containing zeolites in ammoxidation reactions are relatively scarce. Li and Armor [12–14] investigated the ammoxidation of ethane with O_2 over metal-containing zeolites, concluding that Co^{2+} exchanged ZSM-5, beta, and NU-87 showed much higher reaction rate and yield to acetonitrile than most oxide-based catalysts for the ammoxidation reactions [12]. In a related study with various zeolite topologies (MFI, BEA, MOR, FER), Bulánek *et al.* [15] reported Co-beta as the most effective one for ethane ammoxidation with O_2, leading to a conversion of ethane of 11% and a selectivity to acetonitrile of 46% at 723 K. In the same study, it was concluded that the ammoxidation of propane with O_2 over Co-zeolites produces no acrylonitrile, leading to propylene, acetonitrile, and carbon oxides. Adding N_2O to the feed mixture, containing O_2, NH_3, and C_2H_6 (or C_3H_8), had no effect on the products selectivity and slightly lowered the hydrocarbon conversions. Over a different system, Derouane *et al.* [16] indicated that the presence of Brønsted sites in synergy with redox sites in Ga-modified MFI zeolites is responsible for their performance in the direct ammoxidation of propane to acrylonitrile with O_2. These materials showed propane

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1011-372X/05/1100–0163/0

conversions close to 50%, ACN selectivities of 40%, and CO_x yields <1% at 773 K.

This paper introduces a novel process for direct ammoxidation of propane over steam-activated Fe-silicalite zeolite using N_2O and O_2 as the oxidant. Our strategy consisted in combining the reported properties of Fe-MFI zeolites in the O_2-mediated oxidation of ammonia [17] and the N_2O-mediated oxidative dehydrogenation of propane [18] in order to develop efficient catalysts for propane ammoxidation. Fe-silicalite exhibits notable performances when mixtures of N_2O and O_2 are co-added in the feed, displaying higher ACN and AcCN productivities than other reported zeolites and mixed oxide catalysts.

2. Experimental

The preparation and characterization of Fe-silicalite (Si/Al$\sim\infty$ and 0.68 wt% Fe) has been described in detail elsewhere [19, 20]. Briefly, the preparation of isomorphously substituted zeolite by hydrothermal synthesis was followed by calcination in static air at 823 K for 10 h and activation in steam (30 vol% H_2O in 30 ml STP min^{-1} of N_2 flow) at 873 K for 5 h.

The ammoxidation of propane was studied at 723 and 823 K in a fixed-bed quartz reactor (6 mm id), using ca. 80 mg of catalyst diluted with 120 mg of SiO_2 (both 125–200 μm) and a total gas flow of 100 ml STP min^{-1} at atmospheric pressure (GHSV = 150,000 ml h^{-1} g^{-1}). The space time was $W/F^o(C_3H_8)$ = 6 g_{cat} h mol^{-1}, where W is the catalyst mass and $F^o(C_3H_8)$ is the molar flow of propane at the reactor inlet. Feed mixtures of C_3H_8:NH_3:N_2O:O_2:He = 5:5:5:0:85, 5:5:0:5:85, and 5:5:5:5:80 were used and are referred to hereafter as N_2O, O_2, and N_2O + O_2, respectively. Product gases were analyzed on-line by GC (HP 5890) equipped with FID and TCD detectors and QMS (Balzers Thermostar). Conversions (X), selectivities (S), and yields (Y) were calculated on the basis of moles of propane converted.

3. Results and discussion

The steady-state performance of steam-activated Fe-silicalite zeolite in propane ammoxidation is shown in table 1 and figures 1 and 2. In all our tests, ACN, AcCN, and CO_x were the main reaction products. Traces of propylene were analyzed, while N_2, NO_x, HCN, or oxygenated hydrocarbons were not detected at the reactor outlet. Despite the markedly different nature of the oxidant, the C_3H_8 conversion and ACN selectivity over Fe-silicalite at 823 K were rather similar with N_2O or O_2 (16–19% and 27–30%, respectively), resulting in ACN yields of ca. 5%. This result contrasts with absence of ACN during the ammoxidation of propane over Co-exchanged zeolites with O_2 [15]. The selectivity to AcCN over Fe-silicalite with N_2O (20%) is double than that with O_2 (10%), obtaining AcCN yields of 4.8% and 1.6%, respectively. A lower CO_x production is thus obtained using N_2O as the oxidant. Detrimental of the reaction with N_2O as the oxidant is the catalyst deactivation, observable in a 2 h-test. Attending to the black colour of the spent catalyst, the decreased activity is probably due to coke formation, as can be also expected from previous deactivation studies of the propane oxidative dehydrogenation with N_2O over these materials [21]. Contrarily, Fe-silicalite displayed stable ammoxidation performance O_2 or $N_2O + O_2$ mixtures.

As shown in table 1 and figure 1, co-feeding of N_2O and O_2 induces the best catalytic performance, doubling the conversion of propane as compared to the experiments with the individual oxidants. The selectivity to ACN at 823 K is very similar in the three cases (25–30%), while the selectivity to AcCN significantly increased from 10% and 20.5% in O_2 and N_2O, respectively, to 32% in N_2O + O_2. Consequently, ACN/AcCN ratios <1 in mixtures of both oxidants. Largely improved yields of ACN (10.5%) and AcCN (13.4%) were attained in N_2O + O_2 mixtures over Fe-silicalite at 823 K. To the best of our knowledge, this AcCN yield is the highest reported so far over propane ammoxidation catalysts (see performance of reported active catalysts in table 1). It is clearly superior to values obtained during ethane and propane ammoxidation over Co-zeolites, where AcCN selectivities of 37% and conversion of hydrocarbons up to 14% lead to maximum AcCN yields of 5%.

The ammonia conversion over Fe-silicalite was influenced by the nature of the oxidant (figure 1). At 823 K, the NH_3 conversion in N_2O + O_2 (45%) was significantly lower than in N_2O (60%) and O_2 (72%). However, the conversion of N_2O (ca. 95% at 823 K) was not affected by the presence or absence of O_2 in the feed mixture. The influence of the temperature on the ammoxidation performance of Fe-silicalite in N_2O + O_2 is shown in table 1 and figure 2. The conversions of C_3H_8 and N_2O considerably increase with temperature, while the conversion of NH_3 decreases from 70% to 40%. The yields of products were substantially higher at 823 K (10.5% for ACN and 13.4% for AcCN) compared to 723 K (2.7% for ACN and 5.4% for AcCN).

As shown in table 1, previous studies have reported multicomponent mixed oxide catalysts for propane ammoxidation displaying ACN yields up to 60% [1]. Within zeolitic materials, the highest ACN yield reported so far was close to 20% over Ga-ZSM-5 [16]. A common denominator of these studies is the use of O_2 as the oxidant. These yields are evidently superior to those obtained over the steam-activated Fe-silicalite introduced here. However, the experimental conditions strongly differ from study to study, making difficult a rigorous simile between the different systems. In order to accomplish so, one could compare the catalysts

Table 1
Steady-state performance of steam-activated FeMFI zeolites in propane ammoxidation and comparison with catalysts in the literature

Catalyst	Oxidant	T/K	$W/F^o(C_3H_8)$/ g_{cat} h mol^{-1}	$X(C_3H_8)$/%	S/%		Y/%		P^a/ mol h kg_{cat}^{-1}		Ref
					ACN	AcCN	ACN	AcCN	ACN	AcCN	
Fe-silicalite	N_2O	823	6	19	27	20.5	5.1	3.9	17	13	This work
	O_2	823	6	16	30	10	4.8	1.6	16	5.3	This work
	N_2O+O_2	823	6	42	25	32	10.5	13.4	35	45	This work
	N_2O+O_2	723	6	18	15	30	2.7	5.4	9	18	This work
Co-beta	O_2	723	15	7.3	0	36.6	0	2.7	0	1.8	[15]
Co-ZSM-5	O_2	723	15	14	0	27.9	0	3.9	0	2.6	[15]
Ga-ZSM-5	O_2	773	163	48	40	n.s.[b]	19.2	-	1.2	-	[16]
V–Sb–O	O_2	698	2036	30	26.6	10	8	3	0.04	0.01	[2]
Fe–Sb–O	O_2	773	740	22	23	n.s.	5	–	0.07	–	[3]
V–Sb–W–Al–O	O_2	773	53	77	48	13	37	9.2	7	1.7	[4]
Ca–Bi–Mo–O	O_2	783	12	15	63	7	9.5	1	7.9	0.9	[5]
Mo–V–Nb–Te–O	O_2	713	31.2	89.1	60	n.s.	53.5	–	1.4	–	[7]
V–Al oxynitride	O_2	773	8	59	50	5	29.5	2.9	37	3.7	[11]

[a] Productivity determined as $P = Y/[W/F^o(C_3H_8)]$.
[b] Not specified.

equitably using productivities (mol of product per hour and kilogram of catalyst), which can be defined as the quotient between the yield and the space time $W/F^o(C_3H_8)$. Such parameter corrects the absolute yields for the applied catalyst mass and molar propane flow, giving an indication of the intrinsic catalytic activity. Attending to this performance indicator, table 1 shows that the ACN productivity over Fe-silicalite in N_2O+O_2 (35 mol h^{-1} kg_{cat}^{-1}) is significantly higher than over the most promising catalysts in the literature and very comparable to that of V–Al oxynitrides [11]. Even more notable differences are obtained in the AcCN productivity, amounting up to 45 mol h^{-1} kg_{cat}^{-1} over steam-activated Fe-silicalite, 1–2 orders of magnitude higher than over the other catalysts used in the comparison.

The results presented here clearly show the potential of steam-activated Fe-silicalite for propane and ammonia functionalization via direct ammoxidation, leading to superior productivities of acrylonitrile and particularly acetonitrile. The most striking result over the iron zeolite is the synergetic effect observed in N_2O + O_2 mixtures, leading to both increased propane conversions and products yields. Differently to Fe-MFI, N_2O produced no effect in the ammoxidation of ethane or propane with O_2 over Co-exchanged zeolites [15]. The

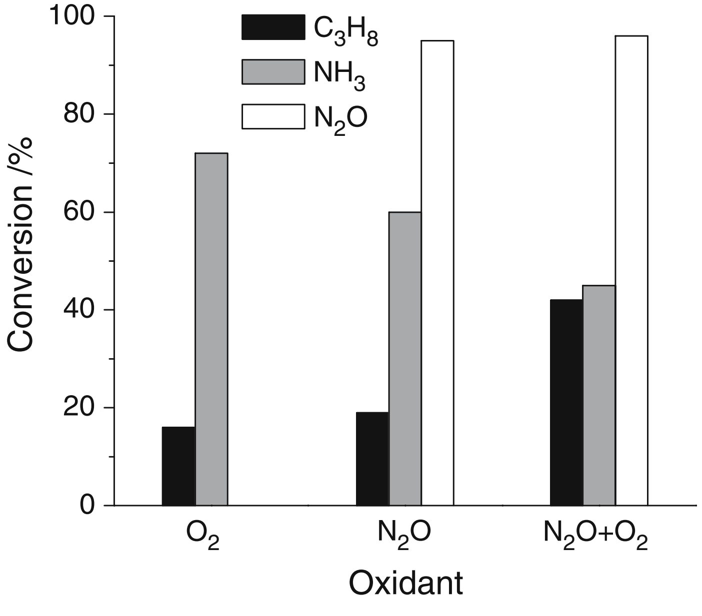

Figure 1. Influence of the oxidant on the conversion of propane, ammonia, and nitrous oxide over Fe-silicalite at 823 K.

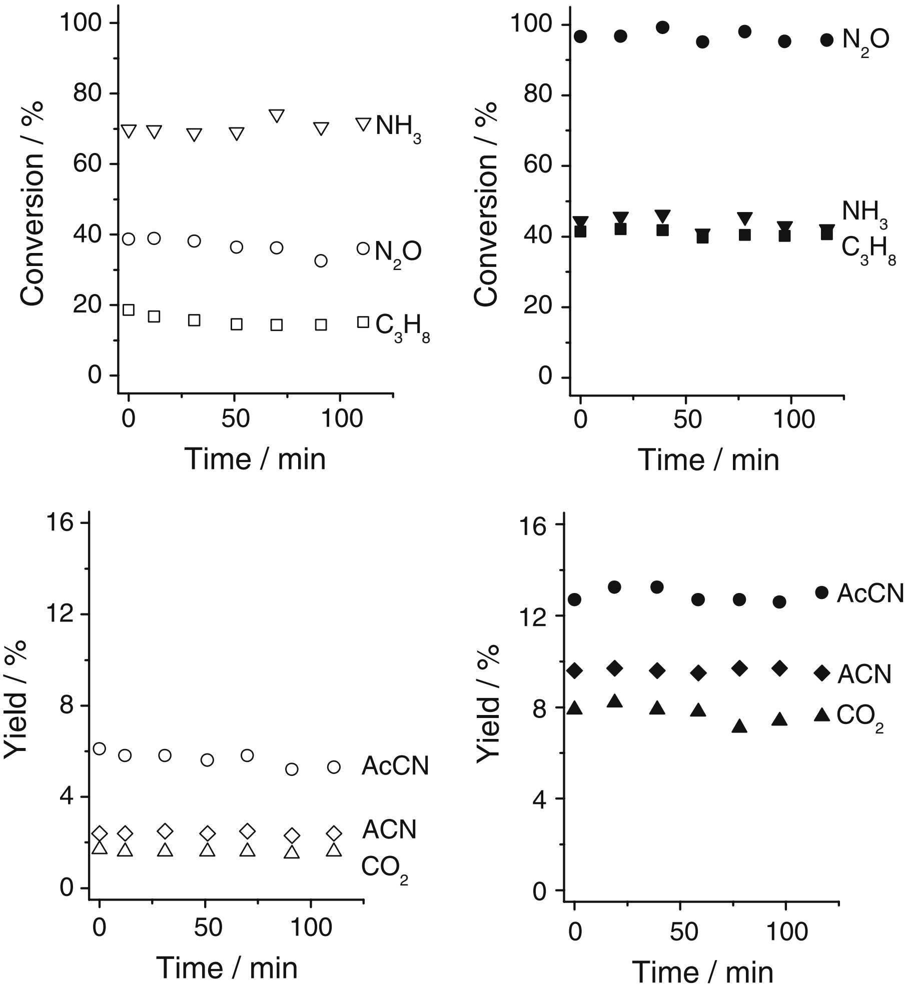

Figure 2. Performance of steam-activated Fe-silicalite vs time on stream in a mixture of C_3H_8:NH_3:N_2O:O_2:Ne = 5:5:5:5:80 at 723 K (open symbols) and 823 K (solid symbols).

cause(s) for the cooperative effect using mixtures of both oxidants cannot be ascertained at this stage and requires detailed mechanistic investigations. It can be postulated that in a mixture of oxidants, the oxidation state of the active iron sites can be varied to achieve higher ACN and AcCN yields. A similar concept has been proposed to explain the positive effect of N_2O in the oxidative dehydrogenation of propane with O_2 over nickel molybdate catalysts [22]. In any case, the positive effect of O_2 in the N_2O-mediated propane ammoxidation over Fe-silicalite is exceptional attending to selective oxidations over iron zeolites. In reactions like the hydroxylation of benzene or the oxidative dehydrogenation of propane, the use of O_2 instead of N_2O or co-addition of small O_2 amounts to the feed mixture severely decreases the selectivity to phenol or propylene, respectively, in favour of the formation of carbon oxides [23–25]. This fact seriously limits the utilization of N_2O in tail-gases (e.g. of adipic acid plants like in the AlphOx process [23]), where significant O_2 amounts are also present, thus involving prohibitive costs for conditioning of the N_2O-containing stream. The ammoxidation of propane over Fe-silicalite reported here provides the first example of a process where mixtures of N_2O and O_2 improve the catalytic performance with respect to the individual oxidants, thus posing less restrictions on the purity of the tail-gas. The present results could be also useful for other catalytic systems typically applied in the ammoxidation of propane.

Our current studies focus on understanding the synergetic effect of N_2O and O_2, tuning reaction conditions, and testing iron-containing zeolites with a modified matrix composition and iron consitution as a basis to further improve the catalytic performance of Fe-silicalite.

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