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Environmental Chemistry

Catalytic Abatement of Nitrous Oxide Coupled with Selective Production of Hydrogen and Ethylene**

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In the past two decades, global warming caused by anthropogenic emissions of greenhouse gases has become an intensively discussed topic of public and scientific interest. The Kyoto protocol to the United Nations Framework Convention on Climate Change is a practical step to control the emissions of environmentally harmful gases. The protocol obliges participating countries to reduce emission of CO_2 as well as non-CO_2 greenhouse gases. One of the non-CO_2 greenhouse gases is nitrous oxide (N_2O), which has a 310 times greater potential than CO_2 to warm up the atmosphere. Moreover, N_2O contributes to the destruction of ozone in the stratosphere.

One of the anthropogenic sources of N_2O is the production of adipic and nitric acids, both of which are key components in the manufacture of a variety of commercial products. The estimated annual production (without abatement) of N_2O in these processes[1,2] is approximately 1.3 Mton, which corresponds to about 20% of the overall anthropogenic N_2O emissions.[3] There are several commercial N_2O removal technologies[3–6] that are based on catalytic or thermal conversion of N_2O to N_2 and O_2. When N_2O is abated by selective catalytic reduction, the reducing agents, such as natural gas and/or ammonia, are converted into CO_x and N_2, respectively. However, a process that combines N_2O removal with the simultaneous production of important chemical products would be both more sustainable and economically attractive.

In this regard Solutia Inc., in collaboration with the Boreskov Institute of Catalysis (BIC), developed a technology that employs pure N_2O as an oxidant to produce phenol from benzene over Fe-MFI zeolites.[7,8] Fe-MFI zeolites are also promising catalysts for the oxidative dehydrogenation of propane to propene using N_2O as an oxidant.[9,10] These elegant approaches, however, suffer from fast catalyst deactivation and low selectivity when N_2O is contaminated with O_2 and NO_x, which is the case with off-gases from the production of adipic[8] and nitric[3] acids. Unfortunately, the purification of off-gases results in a substantial cost increase of the above processes, which makes them uneconomical. Thus, better catalysts tolerant to O_2 and NO_x are key to allow for the development of green processes using waste N_2O.

Herein, we present a novel process and catalyst for N_2O decomposition to N_2 with simultaneous production of H_2 and C_2H_4 from C_2H_6. Our concept is based on the use of the exothermic N_2O decomposition for the thermal dehydrogenation of ethane. Calcium oxide doped with small amounts of sodium oxide (Na/CaO) was used as a catalyst. To determine whether the procedure for catalyst preparation is reproducible, two catalyst charges were prepared with sodium concentrations of 0.9 and 1.5 at.% ($Na_{0.009}CaO$ and $Na_{0.015}CaO$). It was found that the catalysts are active for direct N_2O decomposition.

For example, a nearly complete (ca. 99%) N_2O conversion was achieved when an N_2O–Ne mixture (40 vol.% N_2O in Ne) was fed over $Na_{0.009}CaO$ at 903 K with a contact time of 0.048 $s\,g_{cat}\,mL^{-1}$. As a result of the exothermicity of N_2O decomposition, the catalyst temperature rose above 1100 K. The N_2O conversion without catalyst did not exceed 5% at 903 K and no temperature increase was detected. However, the catalyst temperature increased above 1100 K when a mixture of N_2O and C_2H_6 ($N_2O/C_2H_6/Ne = 40{:}40{:}20$) was fed over Na/CaO at 903 K with a contact time of 0.048 $s\,g_{cat}\,mL^{-1}$. Moreover, N_2O is almost completely ($X(N_2O) > 99\%$) converted into N_2, while C_2H_6 is converted ($X(C_2H_6) > 50\%$) into C_2H_4 and H_2; CH_4, CO_x, and H_2O were also observed as reaction products. The conversion of N_2O and C_2H_6 did not exceed 10 and 18%, respectively, when the same N_2O–C_2H_6 mixture was fed to the reactor without catalyst (filled with 250–350-μm SiO_2 particles) at 1023 K. Thus, $Na_{0.009}CaO$ and $Na_{0.015}CaO$ catalyze direct N_2O decomposition and N_2O abatement with C_2H_6.

The catalytic performance of Na/CaO materials in N_2O removal with simultaneous generation of C_2H_4 and H_2 from C_2H_6 is shown in Table 1. The N_2O conversion (X) to N_2 was above 99%. No significant difference in the catalytic performance of $Na_{0.009}CaO$ and $Na_{0.015}CaO$ was observed, which indicates the good reproducibility of the method of catalyst preparation. Ethane is converted into ethylene with approximately 50% yield (Y) and 63% selectivity (S). Other C-

Table 1: Catalysts and their performance in N_2O removal with simultaneous C_2H_4 and H_2 production from C_2H_6.[a]

Catalyst	C balance [%]	$X(C_2H_6)$ [%]	$X(N_2O)$ [%]	$S(C_2H_4)$ [%]	$Y(C_2H_4)$ [%]
$Na_{0.009}CaO$	99	79	100	60	47
$Na_{0.015}CaO$	99	78	99	64	51

[a] $T_{oven} = 903$ K, $W/F^{[a]} = 0.048$ $s\,g_{cat}\,mL^{-1}$, $C_2H_6/N_2O/Ne = 40{:}40{:}20$. W/F: contact time, where W = weight of catalyst and F = total gas flow rate.

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containing reaction products were CO, CO_2, and CH_4 with $S(CH_4)/S(CO_x) \approx 1$. The carbon balance was above 98%, which indicates that coke or higher hydrocarbons are minor products. Low coke deposition may be explained by the temperature-driven coke removal by H_2O and/or CO_2 to yield CO and H_2. The ethylene yield is comparable to that reported for industrial steam cracking of ethane[11] and for short-contact-time ethane oxidation with oxygen over Pt-based catalysts[12,13] and over rare-earth or alkaline-earth-metal oxides.[14]

Figure 1 exemplifies concentration profiles of C_2H_6, C_2H_4, H_2, and N_2O as a function of time-on-stream over $Na_{0.015}CaO$ catalyst using a C_2H_6–N_2O feed with a contact time of $0.048\ s\,g_{cat}\,mL^{-1}$. The C_2H_4 outlet concentration was circa 15 vol.%. Any noticeable catalyst deactivation was not detected during 180 min on stream. Similar behavior was also observed for the $Na_{0.009}CaO$ catalyst. The H_2/C_2H_4 ratio was about 1:1 (Figure 1) and is similar to the industrial steam cracking of ethane.[11] This high production of hydrogen is remarkable as no hydrogen was observed during ethane,[15] benzene,[7] or propane[9,10] oxidation with N_2O over Fe-MFI zeolites. Notably, the space–time yields of C_2H_4 and N_2 were rather high: 17 and 27 $kg(product)\,kg(cat)^{-1}\,h^{-1}$, respectively, with the latter being considerably higher than that reported for processes catalyzed by Fe-ZSM-5.

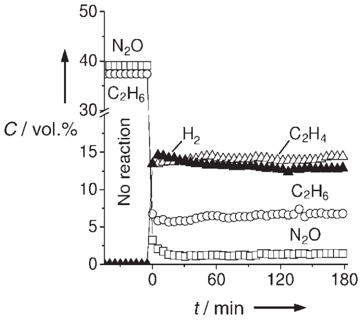

Figure 1. Time-on-stream profiles of outlet concentrations (*C*) of feed components and reaction products after water condensation upon C_2H_6 oxidation with N_2O over $Na_{0.015}CaO$. Reaction conditions: $T_{oven} = 903$ K, $W/F = 0.048\ s\,g_{cat}\,mL^{-1}$, $C_2H_6/N_2O/Ne = 40:40:20$.

To ascertain whether the catalytic performance of Na/CaO catalysts is influenced by oxygen, we performed tests with different C_2H_6–O_2–N_2O feeds. This knowledge is very important from a practical standpoint, as N_2O-containing off-gases from the industrial production of nitric and adipic acids are usually contaminated with O_2.[3,8] In our experiments, the ratio of ethane molecules to the total number of O atoms in the oxidizing agents (C_2H_6/O) was fixed at one. The latter experimental restriction enables the correct examination of the influence of oxygen on the reaction studied, as the total concentration of oxidant in the reaction mixtures at a fixed contact time is an important parameter that determines the level of hydrocarbon conversion and the resulting temperature in the catalyst bed.

Table 2 shows the catalytic performance of $Na_{0.009}CaO$ using different C_2H_6–O_2–N_2O feeds. No significant effect of O_2 on N_2O conversion was observed. Very low amounts of N_2O (1500 ppm) are also effectively removed ($X(N_2O) > 97\%$) even in a high excess of O_2 ($O_2/N_2O \approx 100$). A lower ethylene yield for the feed with the lowest N_2O concentration is because of lower temperature gradients in the catalyst bed during the course of the reaction.

Table 2: Influence of O_2 on the catalytic reduction of N_2O with simultaneous production of C_2H_4 from C_2H_6 over $Na_{0.009}CaO$.[a]

Reaction mixture [vol.%] N_2O	O_2	C_2H_6	Conversion [%] N_2O	C_2H_6	$S(C_2H_4)$ [%]	$Y(C_2H_4)$ [%]
40	0	40	99.9	79	60	47
24	8	40	99.9	77	63	48
8	16	40	99.8	69	65	45
0.15	20	40	97.8	63	58	36

[a] $T_{oven} = 903$ K, $W/F = 0.048\ s\,g_{cat}\,mL^{-1}$.

Another important question to be answered is whether NO influences the performance of Na/CaO catalysts. To this end, we performed catalytic tests with C_2H_6–N_2O–NO feeds containing 0.06 and 1 vol.% NO. Figure 2 presents time-on-stream concentration profiles of N_2O and C_2H_4 over $Na_{0.009}CaO$ upon switching from an N_2O–C_2H_6 to an N_2O–C_2H_6–NO feed. An NO concentration of 1 vol.% in the latter feed is representative for off-gases from adipic acid production.[8] One can see that NO does not noticeably influence the outlet concentrations of N_2O and C_2H_4. The degree of N_2O conversion was above 99%. This finding is also very important for potential commercial applications, and demonstrates a practical advantage of Na/CaO catalysts over Fe-MFI catalysts.

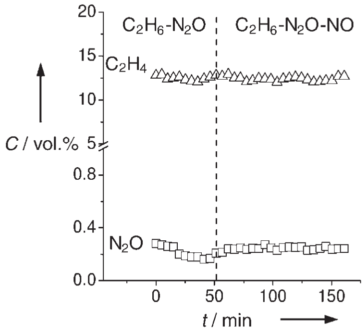

Figure 2. Time-on-stream profiles of outlet concentrations of N_2O and C_2H_4 after water condensation upon C_2H_6 oxidation with N_2O over $Na_{0.009}CaO$. Reaction conditions: $T_{oven} = 903$ K, $W/F = 0.048\ s\,g_{cat}\,mL^{-1}$, $N_2O/C_2H_6/Ne = 40:40:20$, $N_2O/C_2H_6/NO/Ne = 40:40:1:19$.

A possible mechanism of N_2O abatement with simultaneous production of C_2H_4 and H_2 from C_2H_6 over Na/CaO catalysts should include purely catalytic and purely homogeneous reactions, and should be similar to short-contact-time ethane oxidation with oxygen. Figure 3 shows a schematic representation of the main heterogeneous reaction pathways. As the presence of catalyst is an essential requirement, it is suggested that the reaction is initiated by catalytic N_2O

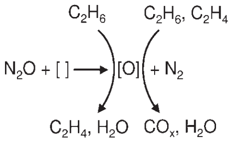

Figure 3. Heterogeneous reaction pathways of N_2O reduction with C_2H_6. [ ]: free surface active site, [O]: surface oxygen species formed from N_2O.

decomposition to yield active surface oxygen species. The generated oxygen species participate in heterogeneous selective (C_2H_4 formation from C_2H_6) and nonselective reactions (C_2H_6/C_2H_4 oxidation to CO_x). It should also be stressed that no H_2 was formed by pure heterogeneous reactions when C_2H_6 or a mixture of C_2H_6 and O_2 were fed to Na/CaO catalysts at 923 K.[16,17] Therefore, reactions leading to H_2 must be occurring through gas-phase reactions.

We suggest the following mechanistic concept to explain the high production of H_2 and C_2H_4 upon N_2O reduction with C_2H_6. The heterogeneous reaction steps in Figure 3 should prevail in the front section of the catalyst bed. As a result of the high exothermicity of N_2O decomposition ($\Delta H = -82\,\mathrm{kJ\,mol^{-1}}(N_2)$ at 900 K) and CO_x formation ($\Delta H = -400\,\mathrm{kJ\,mol^{-1}}(CO)$ and $-700\,\mathrm{kJ\,mol^{-1}}(CO_2)$ at 900 K), the catalyst temperature rises and drives the endothermic ($\Delta H = 144\,\mathrm{kJ\,mol^{-1}}(C_2H_4)$) gas-phase dehydrogenation of C_2H_6 to C_2H_4 and H_2. Its contribution to the overall production of C_2H_4 will depend on the temperature profile in the catalyst bed. However, the operating temperature should not be too high to avoid further pyrolysis reactions that lead finally to carbon and hydrogen. The production of ethylene can be tuned by varying the N_2O/C_2H_6 ratio, contact time, and preheating temperature. The overall process can also operate under autothermal conditions by an efficient coupling of the exothermic and endothermic reactions.

In summary, the high production of C_2H_4 and H_2 with simultaneous near 100% removal of N_2O in a broad range of concentrations (0.15 to 40 vol.%) can be achieved by combining fast catalytic oxidation reactions with gas-phase ethane thermal dehydrogenation. As CO_x, H_2O, NO_x, and O_2 do not noticeably influence the catalytic performance, the suggested process scheme has potential for N_2O abatement technologies in the production of adipic or/and nitric acids.

Experimental Section

For catalyst preparation, CaO was impregnated with an aqueous solution of $NaHCO_3$ at 300 K, then the catalyst precursor was calcined at 1073 K for 3 h. The sodium concentration was kept in a range favorable for the formation of a solid solution in the calcium oxide lattice, as such a structure contains anion vacancies[12] that function as active sites for N_2O decomposition. Catalytic tests were performed in a fixed-bed quartz reactor (internal diameter 6 mm) at atmospheric pressure using catalyst (200 mg) without any dilution by inert materials. The contact time was set to $0.048\,\mathrm{s\,g_{cat}\,mL^{-1}}$. The reaction feeds contained C_2H_6, N_2O, and Ne (40:40:20, v/v). Additionally, catalytic tests were performed with C_2H_6–N_2O feeds containing oxygen and nitric oxide. The feed and the products were analyzed by online mass spectrometry (Balzer Omnistar QSD 200) and online micro gas chromatograph (Chrompack 2000) equipped with Poraplot Q and Molsieve 5 columns; Ar carrier gas was used for H_2 analysis. The reactor temperature was set at 903 K, but because of the exothermic nature of N_2O decomposition and CO_x formation, the temperature of the catalyst bed increased to about 1200 K during the course of the reaction.

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