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Promoting Effect of Triglyme on Lean NO_x Reduction Over Ag/Al_2O_3

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Abstract The highly oxygenated hydrocarbon triethylene glycol dimethyl ether or triglyme ($CH_3O–(C_2H_4O–)_3CH_3$) was found to efficiently reduce NO_x under lean conditions over Ag/Al_2O_3, but gave a low NO_x conversion over Cu-ZSM-5. Furthermore, triglyme showed an extraordinary promoting effect when added together with propene as reducing agent for NO_x over Ag/Al_2O_3 at low temperature. This is most likely due to that triglyme promotes the activation of propene.

Keywords Hydrocarbon-SCR · NO_x Reduction · Alumina · Triglyme · Ether · Propene · Ag/Al_2O_3 · Cu-ZSM-5

1 Introduction

Hydrocarbon-based selective catalytic reduction (HC-SCR) is a potential method to remove NO_x under oxygen excess conditions such as diesel engine exhausts. Two of the most extensively researched catalysts in this area are Ag/Al_2O_3 and zeolite Cu-ZSM-5. Most studies using these catalysts have been performed with pure hydrocarbons such as alkanes or alkenes as reducing agents. However, there is an increase in the research and use of alternative fuels to diesel such as e.g. methanol, ethanol, dimethyl ether, and different fatty acid alkyl esters, which often contain considerably higher amounts of oxygen than conventional diesel. Thus, it is becoming increasingly interesting to study oxidized hydrocarbons as reducing agents for NO_x. In the present study, triethylene glycol dimethyl ether or triglyme ($CH_3O–(C_2H_4O–)_3CH_3$), which is a common and readily available solvent, has been investigated as reducing agent over Ag/Al_2O_3 and Cu-ZSM-5 catalysts. Triglyme was selected as it has a high oxygen content through four ether groups. With regard to diesel engine applications it has in some earlier studies been used blended in diesel fuel to reduce soot emissions [1, 2]. Here, we report on a new intriguing promoting effect of triglyme on lean NO_x reduction over Ag/Al_2O_3, when added in small amounts to the hydrocarbon reducing agent propene.

2 Experimental Methods

2.1 Catalysts

Commercial Cu-ZSM-5 and Ag/Al_2O_3-based lean NO_x catalysts (LNC) were used in the experiments. The Cu-ZSM-5-catalyst was from a Cleaire Longview® retrofit HC-SCR system, with a delivery status from spring 2005. The BET surface area of the monolith was 137 m^2/g, and the washcoat molar composition was $SiO_2/Al_2O_3 = 73$ and $Cu/Al = 0.9$.[1] The Ag/Al_2O_3 catalyst was developed as part of another study [3]. The catalyst samples were cut from larger monoliths and had a diameter of 20 mm, a length of 45 mm, and a cell density/wall thickness of 400 cpsi (cells per square inch)/6 mil.

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[1] From own analyses.

2.2 Experimental Equipment

The catalytic activity experiments were performed in a vertically mounted synthetic exhaust gas flow reactor. The metallic reactor tube had a diameter of 20 mm, but had a flow restrictor that reduced the effective sample diameter to 17.5 mm. The inlet gas was heated by a capillary preheater, and the reactor wall was heated by metallic heating coils. Thermocouples were used to measure the temperature before and after the catalyst as well as at the reactor wall. A sintered quartz plate was mounted in the reactor inlet to facilitate an even distribution of the gas over the reactor cross-section. Mass flow controllers for gases (Brooks), distilled water (Brooks 5,881, 2–90 g/h), and liquid triglyme (Bronkhorst High-Tech LIQUI-FLOW®), when present, were used to regulate the flow composition into the reactor. The liquid triglyme was dosed in a low N_2 gas flow to create an aerosol, which was then added to the main gas stream through a capillary just before the reactor inlet. The reactor outlet gas was continuously analyzed with a frequency of 1 Hz using a Gasmet™ FT-IR analyzer for measuring CO and CO_2, and a chemiluminescence instrument (Eco Physics, CLD 700 RE ht) to measure NO and NO_x. High purity gases of N_2, O_2, NO (Air Liquide, ≥99.999%), CO_2, CO (Air Liquide, ≥99%) and propene (Air Liquide, ≥99.4%), and liquid triethylene glycol dimethyl ether (Clariant, ≥99%) were used in the feed stream. In the evaluation of the measured data, the NO_x conversion is defined as $1 - [NO_x]_{out}/[NO_x]_{in}$ and the yields of CO and CO_2 as $[X]_{out}/[C]_{in}$, where X denotes the component in question and $[C]_{in}$ is the total concentration of C-atoms from the reducing agent in the gas feed.

2.3 Experimental Design

All catalytic tests were initiated by a conditioning of the catalyst at 550 °C for 30 min in 10% O_2, 5% H_2O, and a balance of N_2. The catalytic activity was then evaluated under steady-state conditions at temperatures between 550 and 200 °C at an interval of 50 °C in a gas consisting of 800 ppm NO, 10% O_2, 5% H_2O, and 1,067 or 2,134 ppm propene and/or 100, 200, 400 or 800 ppm triglyme, and with N_2 balance. The total gas flow was 6,000 mL/min, giving a space velocity of 33,300 h^{-1}. At each temperature measurements were made after conditions had stabilized, which typically required around 15–30 min (depending on temperature and reductant mixture used).

A test was also performed where the influence of the amount of triglyme was analyzed in more detail at temperatures of 250, 300, and 350 °C. The concentration of triglyme was varied between 0 and 400 ppm in a gas consisting of 1,067 ppm propene, 800 ppm NO, 10% O_2, 5% H_2O, and N_2 balance.

3 Results and Discussion

3.1 Catalytic Activity with Triglyme as Reducing Agent

The efficiency of triglyme as reducing agent for NO_x under lean conditions was evaluated in steady-state experiments on the two catalysts. The results from the tests of the Cu-ZSM-5 catalyst at temperatures between 200 and 500 °C are shown in Fig. 1. The maximum NO_x conversion reached was about 25% between 350 and 500 °C and at an HC_1/NO_x molar ratio of eight. The NO_x conversion and conversion of triglyme to CO and CO_2 started to increase at about the same temperature. It is evident that triglyme is not an efficient reducing agent for NO_x over Cu-ZSM-5 and is mostly consumed by oxidation by O_2. These results are in accordance with earlier studies of reducing agents with related structures, which showed that dimethyl ether

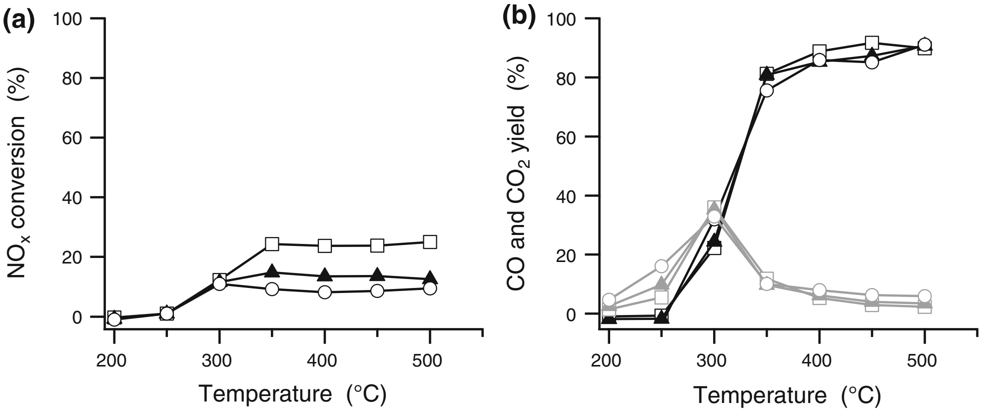

Fig. 1 Steady-state experiments showing the NO_x conversion (**a**), and CO– (*grey symbols*) and CO_2 yield (*black symbols*) (**b**) over Cu-ZSM-5 with triglyme as reducing agent at temperatures between 200 and 500 °C. Conditions: 800 ppm NO, 5% H_2O, 10% O_2, and either 200 (*open circle*), 400 (*filled triangle*) or 800 (*open square*) ppm triglyme, and with N_2 balance. Space velocity = 33,300 h^{-1}

gave practically no NO_x conversion over Cu-ZSM-5, highly oxygenated ethylene glycol gave low conversion, whereas higher ethers like dibutyl ether gave considerable NO_x conversion [4, 5].

The corresponding results from the steady-state activity tests of the Ag/Al_2O_3 catalyst with triglyme as reducing agent at temperatures between 200 and 550 °C are shown in Fig. 2. The maximum NO_x conversion of 80%, at an HC_1/NO_x molar ratio of eight, was achieved already at 300 °C. The yields of CO and CO_2 also show that the conversion of triglyme started at a lower temperature over Ag/Al_2O_3 compared to Cu-ZSM-5. In fact some NO_x conversion was achieved already at 200 °C over Ag/Al_2O_3. Thus, triglyme is considerably more efficient as reducing agent for NO_x over Ag/Al_2O_3 compared to Cu-ZSM-5.

A previous study of the same catalysts with different biodiesels as reducing agents showed that the oxygenated fuel RME gave a lower maximum NO_x conversion and at a higher temperature over the Ag/Al_2O_3 catalyst than over Cu-ZSM-5 [6]. In general, Ag/Al_2O_3 was there found active at a higher temperature and shown to be more sensitive to the fuel used as reducing agent than Cu-ZSM-5. However, other studies have found that oxygenated hydrocarbons such as alcohols are efficient reductants at lower temperatures over Ag/Al_2O_3 [7–10]. One study showed that primary alcohols gave a higher NO_x conversion at low temperature than ethyl acetate and acetone [11]. Yu et al. [10] found that partially oxidized hydrocarbons such as C_2H_5OH and CH_3CHO were extremely efficient for NO_x reduction, while highly oxidized hydrocarbons such as CH_3COOH gave lower NO_x conversion. They showed with DRIFT studies that enolic species (CH_2=CH–O^-) were the main surface species present during the partial oxidation of C_2H_5OH or CH_3CHO over Ag/Al_2O_3, whereas acetate (CH_3COO^-) was the main surface species with C_3H_6 or CH_3COOH. The enolic species were found more reactive than the acetate species toward NO + O_2, to yield intermediate –NCO species, which explained the difference in NO_x conversion for the different reducing agents. The higher reactivity of the enolic species formed from ethanol was also used to explain why ethanol was much more efficient for NO_x reduction than dimethyl ether, which gave formate species over Ag/Al_2O_3 [12]. Comparing these studies with the results obtained here it is probable that the –CH_2–CH_2–O– entities of triglyme will form similar species as ethanol on the catalyst surface [13]. Thus, it is likely that triglyme would partly behave similar to ethanol in the NO_x reduction reaction over Ag/Al_2O_3.

3.2 Promoting Effect of Triglyme for NO_x Reduction with Propene

The remarkably high NO_x conversion with triglyme over Ag/Al_2O_3 already at 250–300 °C suggests that triglyme might be efficient as an additive to a conventional hydrocarbon reducing agent to increase the NO_x conversion at lower temperatures. With the addition of triglyme to the reductant, the Ag/Al_2O_3 catalyst would thus exhibit a high NO_x conversion activity over a wider temperature window. This effect was investigated using propene as a representative hydrocarbon reductant.

Figure 3a–h shows the NO_x conversion over Ag/Al_2O_3 between 200 and 550 °C using either propene or triglyme separately or in combination as reducing agents at varying concentrations as indicated in each graph. With pure propene as reducing agent, the NO_x conversion was negligible until the temperature reached about 400 °C, and the maximum in NO_x conversion of 45–60%, depending on propene concentration, was not achieved until 500 °C. With pure triglyme on the other hand, the maximum NO_x conversion was achieved at 300 °C as has already been shown. However, it is clear that under all conditions tested here,

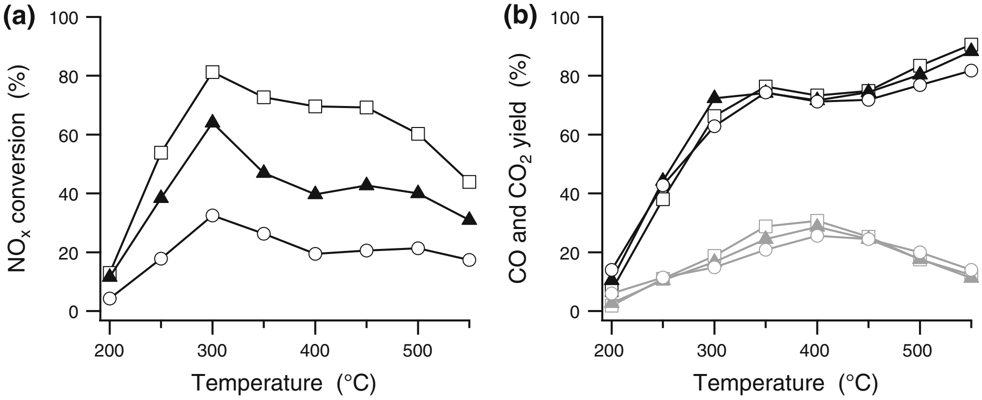

Fig. 2 Steady-state experiments showing the NO_x conversion (**a**), and CO– (*grey symbols*) and CO_2 yield (*black symbols*) (**b**) over Ag/Al_2O_3 with triglyme as reducing agent at temperatures between 200 and 550 °C. Conditions: 800 ppm NO, 5% H_2O, 10% O_2, and either 200 (*open circle*), 400 (*filled triangle*) or 800 (*open square*) ppm triglyme, and with N_2 balance. Space velocity = 33,300 h^{-1}

the combination of propene and triglyme gave a higher NO_x conversion than the sum of the two NO_x conversions achieved with the reducing agents separately at temperatures between 300 and 450 °C. At 200 and 250 °C the NO_x conversion was similar for pure triglyme and the combination of triglyme and propene, which shows that at these temperatures propene could not be activated on the catalyst and was not contributing to the NO_x reduction. At a temperature of 500 °C and above, the NO_x conversion for the combination of reducing agents was lower than the sum of the conversions achieved using propene and triglyme separately, but still higher than the conversion reached with either component alone. At 550 °C for the highest propene concentration (Fig. 3c, d), the NO_x conversion was similar for the combination of triglyme and propene as for pure propene, showing that triglyme was not contributing to NO_x reduction. At these temperatures triglyme was consumed by oxidation with oxygen to a high extent and not available for NO_x reduction. In the intermediate temperature range, between 300 and 450 °C, triglyme dramatically promoted the NO_x reduction reaction. The overall highest NO_x conversion of about 80% was achieved between 350 and 450 °C with the highest triglyme concentration (400 ppm) in combination with 1,067 ppm propene (Fig. 3b). Similarly, the lowest triglyme concentration (100 ppm) gave the lowest NO_x conversion although the propene concentration was doubled (2,134 ppm). When the triglyme concentration was intermediate i.e. 200 ppm the influence of the propene concentration of either 1,067 or 2,134 ppm was low.

The CO formation when using the combination of triglyme and propene was about the same as the sum of the CO formation for propene and triglyme separately. However, regarding the conversion of the reducing agent to CO_2, it is interesting to note that the CO_2 formation for the combination of the reducing agents between 300 and 450 °C was higher than the sum of the CO_2 formed for them separately. Thus, triglyme appears to contribute to an increased oxidation of propene in this temperature interval. Below 300 °C, the CO_2 formation for the combination was the same as the CO_2 formation when using only triglyme, whereas above 450 °C it was about equal to the sum of the CO_2 formed for triglyme and propene separately.

To investigate in more detail the influence of the triglyme concentration on the NO_x reduction over Ag/Al_2O_3, with a combination of propene and triglyme as reducing agents, an experiment was performed where the propene concentration was kept at 1,067 ppm and the triglyme concentration was varied between 0 and 400 ppm. This was performed at lower temperatures where the effect of triglyme is particularly interesting and evident, i.e. at 250, 300 and 350 °C. Figure 4 shows the results from this experiment. In the temperature interval investigated, the NO_x conversion was virtually zero with only propene added as shown at 0 ppm triglyme concentration in Fig. 4. With gradually increasing concentration of triglyme up to 400 ppm, a steady, but not proportional, increase in NO_x conversion was achieved. Out of the three temperatures investigated the effect of adding triglyme was largest at 350 °C.

The results presented in Figs. 3 and 4 show that at low temperatures propene was not contributing to the reduction of NO_x, whereas at high temperatures triglyme was not contributing. Consequently, for the combined use of triglyme and a hydrocarbon as reducing agents in a practical application, the amount of the two needs to be varied with temperature to optimize the NO_x conversion relative to the fuel penalty or cost associated with the addition of the reducing agents.

With respect to the promoting effect of triglyme on NO_x reduction with propene there are two possible explanations; either the reaction proceeds through the same mechanism as without triglyme, but the adsorbed species on the catalyst surface have been modified, or the reaction proceeds through a new reaction path in the presence of triglyme.

To our knowledge there is little published research on the combined use of different reducing agents and an effect such as the one presented here has not previously been reported. Zhu et al. [14] showed in a study over Ag/Al_2O_3 that NO_x reduction took place in a wider temperature range when combining methanol or ethanol with propene or propane as reducing agents. The NO_x conversion and temperature window achieved were approximately the sum of that achieved with the two reducing agents separately, which indicates that they work relatively independently of each other. However, the effect of combining triglyme with propene evidenced in this study is more pronounced, showing a more than additive effect when using both reducing agents.

In order to understand the promoting effect of triglyme on NO_x reduction with propene the reaction mechanism must be considered. Numerous mechanistic studies have been performed over Ag/Al_2O_3 and commonly with propene as reducing agent. However, the detailed mechanism involved is still not completely understood. Nevertheless, a general overview of the most important steps during the reaction can be discerned [8, 15–17]. In a first step NO and hydrocarbon are oxidized to yield nitrates or nitrites and partially oxidized hydrocarbon species (e.g. enolic or acetate). The reaction between these species leads to the formation of reduced nitrogen species such as –NCO, –CN, and NH_3 either directly or via organo-nitrogen compounds (R–ONO and R–NO_2). Subsequently, the reduced forms of nitrogen react with NO + O_2 or nitrates to yield N_2. The formation of the organo-nitrogen species from reaction between nitrates and oxygenates is likely to be the rate-determining step of the reaction [8, 15]. As mentioned

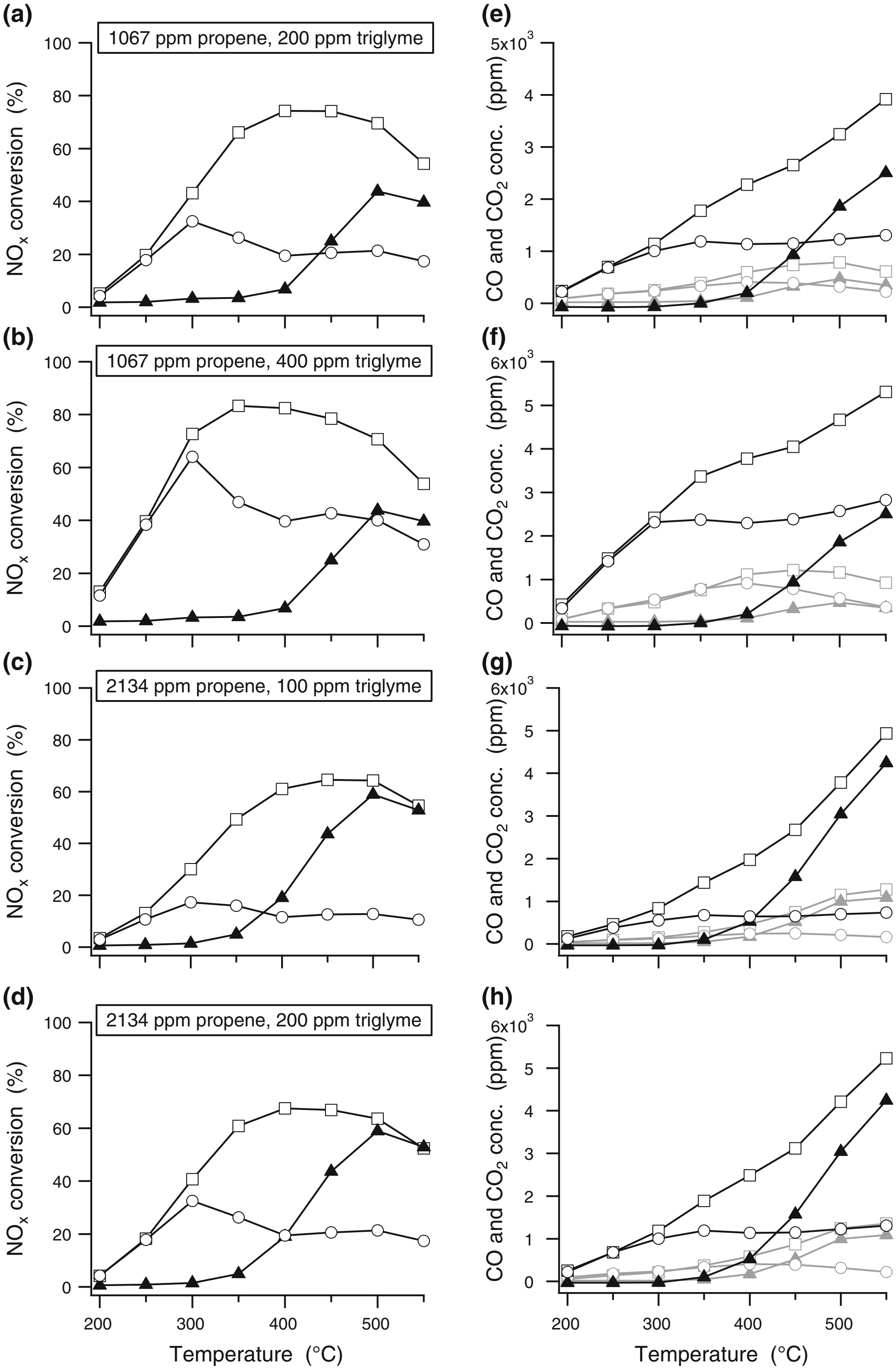

Fig. 3 NO_x conversion and CO– (*grey symbols*) and CO_2 concentration (*black symbols*) over Ag/Al_2O_3 with propene (*filled triangle*), triglyme (*open circle*), or a combination of propene and triglyme (*open square*) as reducing agent at temperatures between 200 and 550 °C. Conditions: 800 ppm NO, 5% H_2O, 10% O_2, and either 100, 200 or 400 ppm triglyme, and 1,067 or 2,134 ppm propene, and with N_2 balance. Space velocity = 33,300 h^{-1}

before, the higher reactivity of enolic species than acetate species toward NO + O_2, to yield intermediate –NCO species, was used by Yu et al. [10] to explain the higher efficiency of ethanol compared to C_3H_6 for NO_x reduction. The suppression of the activity of Ag/Al_2O_3 at low temperature has been assigned to strongly adsorbing nitrates

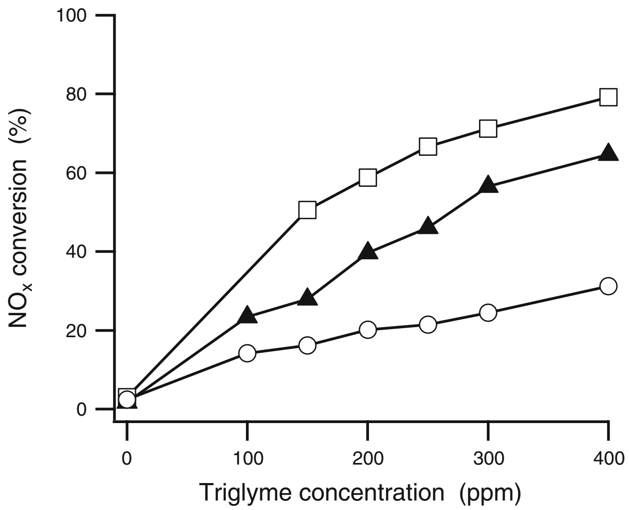

Fig. 4 NO_x conversion as a function of triglyme concentration at 250 (*open circle*), 300 (*filled triangle*) or 350 °C (*open square*). Conditions: 800 ppm NO, 0–400 ppm triglyme, 1,067 ppm propene, 5% H_2O, 10% O_2 and with N_2 balance. Space velocity = 33,300 h^{-1}

and the difficulty of activating propene [16, 18, 19]. This indicates that the promoting effect of triglyme could be associated with the removal of nitrates from the surface and/or the direct activation of propene.

The effect of triglyme could be compared to the effect of hydrogen that has already been proven to reduce the light-off temperature for NO_x reduction over Ag/Al_2O_3 catalysts [20]. However, the reasons for these two effects could clearly be of quite different origin. Although considerable research can be found investigating the hydrogen effect over Ag/Al_2O_3, the mechanisms behind it is still under debate. Besides explanations related to H_2-induced changes in the state and structure of silver during reaction conditions there are other suggestions related to the more direct effect of H_2 in the reaction mechanism that are likely of more relevance to the discussion on the effect of triglyme [19]. Hydrogen has been proposed to promote the activation of the hydrocarbon at lower temperatures through formation of oxygenated intermediates like acetate or enolic species [19, 21, 22]. Hydrogen has also been suggested to promote the formation of nitrate or nitrite species or their reactivity as well as the transformation of cyanide species to isocyanate species [22, 23]. Another suggestion is that the presence of H_2 prevents poisoning of the SCR reaction due to nitrate formation on silver [22].

The results in Fig. 3 of the present study showed that the oxidation of propene was increased at lower temperatures in the presence of triglyme. Furthermore, as mentioned above the oxidative activation of the hydrocarbon has been identified as limiting the NO_x reduction reaction at low temperature. Consequently, a likely explanation to the combined effect observed here is that triglyme contributes to the partial oxidation and activation of propene, possibly giving an increased formation of surface enolic species, thus resulting in an increased NO_x conversion at lower temperatures, where propene by itself is not active as reductant. However, it cannot be excluded that triglyme also acts on other parts of the reaction mechanism, e.g. affecting the concentration of surface nitrate species. Further studies are encouraged to elucidate the detailed mechanism of the promoting effect of triglyme on NO_x conversion with propene.

4 Conclusions

The highly oxygenated hydrocarbon triethylene glycol dimethyl ether or triglyme ($CH_3O–(C_2H_4O–)_3CH_3$) was found to give a high NO_x reduction efficiency over a Ag/Al_2O_3 catalyst, but a low NO_x conversion over Cu-ZSM-5. In addition, by adding a low amount of triglyme to propene as reducing agents the NO_x conversion over Ag/Al_2O_3 between 300 and 450 °C could be drastically promoted. The promoting effect of triglyme is likely due to that it activates propene, but it may also affect other parts of the reaction mechanism e.g. by influencing the concentration of surface nitrates.

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References

1. Stoner M, Litzinger T (1999) Soc Automot Eng SP-1461:55–66
2. Hess HS, Boehman AL, Tijm PJA, Waller FJ (2000) Soc Automot Eng SP-1563:91–98
3. Cider L, Jobson E, Preis M, Krutzsch B, Bandl-Konrad B, Burch R, Fricke R, Captain D, Moral N, Gilot P, Martens J, Habermacher D, Lindfors LE, Klingstedt F, Eränen K, Gottschling M, Webster D, Ilkenhans T, Tissler A, Smedler G (2004) Results from Knownox—A European Cooperation Project, Paper No. F2004V184, FISITA World Automotive Congress, Barcelona
4. Erkfeldt S, Palmqvist A, Jobson E (2007) Top Catal 42–43:149–152
5. Erkfeldt S, Palmqvist A, Petersson M (2011) Appl Catal B 102:547–554
6. Erkfeldt S, Palmqvist A, Petersson M (2011) Top Catal 54:1219–1223
7. Miyadera T (1993) Appl Catal B 2:199–205
8. Burch R, Breen JP, Meunier FC (2002) Appl Catal B 39:283–303
9. Kameoka S, Ukisu Y, Miyadera T (2000) Phys Chem Chem Phys 2:367–372
10. Yu Y, He H, Feng Q, Gao H, Yang X (2004) Appl Catal B 49:159–171
11. Thomas JF, Lewis SA Sr, Bunting BG, Storey JM, Graves RL, Park PW (2005) Soc Automot Eng SP-1942:199–209

12. Wu Q, Yu YB, He H (2006) Chin J Catal 27:993–998
13. Dömök M, Tóth M, Raskó J, Erdohelyi A (2007) Appl Catal B 69:262–272
14. Zhu T, Hao J, Fu L, Li J, Liu Z (2005) React Kinet Catal Lett 84:61–67
15. Satsuma A, Shimizu K (2003) Prog Energy Combust Sci 29:71–84
16. Li J, Ke R, Li W, Hao J (2008) Catal Today 139:49–58
17. Tamm S, Ingelsten HH, Palmqvist AEC (2008) J Catal 255:304–312
18. Shimizu K, Satsuma A, Hattori T (2000) Catal Surv Jpn 4: 115–123
19. Satokawa S, Shibata J, Shimizu K-i, Satsuma A, Hattori T, Kojima T (2007) Chem Eng Sci 62:5335–5337
20. Satokawa S (2000) Chem Lett 29:294–295
21. Zhang XL, Yu YB, He H (2007) Appl Catal B 76:241–247
22. Burch R, Breen JP, Hill CJ, Krutzsch B, Konrad B, Jobson E, Cider L, Eranen K, Klingstedt F, Lindfors LE (2004) Top Catal 30–31:19–25
23. Korhonen ST, Beale AM, Newton MA, Weckhuysen BM (2011) J Phys Chem C 115:885–896