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Novel Mo/Ga/H-ZSM-5 catalyst in environmentally important reductive transformation of N_2O in presence of CH_4

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ABSTRACT

Direct decomposition of N_2O and the reduction of N_2O with CH_4 over Ga/H-ZSM-5 and Mo/Ga/H-ZSM-5 (Si/Al = 40) catalysts in a plug flow reactor under steady-state conditions as well as by temperature programmed surface reaction (TPSR) have been investigated. Ga ions were ion-exchanged from liquid phase while Mo was deposited onto the Ga/H-ZSM-5 sample using incipient wetness technique. The catalysts were characterized by means of XRF, XPS, TPR, CO chemisorption, TEM and EDS. The N_2O forms redox centers in the Mo/Ga/H-ZSM-5 catalysts at elevated temperatures, which are extremely active in the reaction with CH_4 already at around 373 K. Addition of Mo to the Ga/H-ZSM-5 decreased the T_{50} temperature in the N_2O decomposition and reduction of N_2O with CH_4 from 819 to 787 K and from 755 to 646 K, respectively. The oxidation/reduction of the Mo/Ga/H-ZSM-5 sample is more favoured in the interaction with N_2O/CH_4 as compared to that using O_2/H_2 and the mechanism of the redox reactions might also be different. The reduction of N_2O with CH_4 cannot be described with the Mars–van Krevelen redox mechanism, but by the participation of CH_4 via MoGa–OCH_3 species in a complex oxygen transfer mechanism is proposed at which N_2O does not directly reoxidise the reduced active centers.

1. Introduction

The study of reaction between nitrous oxide and methane is important from several points of view. N_2O and CH_4 are strong greenhouse-effect gases with global warming potential (GWP) per molecule of about 296 and 23 times higher than that of carbon dioxide, respectively [1]. N_2O and CH_4 are also identified as a contributor to the destruction of ozone in the stratosphere. Their transformation into harmless compounds is an environmentally important task. The standard enthalpy changes (ΔG^0) at 800 K for N_2O decomposition, CH_4 oxidation with N_2O, and with O_2 are -142, -343, -405 kJ/mol, respectively. Because of the kinetic reasons there are active heterogeneous catalysts performing higher CH_4 conversion at low temperature in the reaction with N_2O than with O_2 [2,3] without decomposition of N_2O. These catalysts are exclusively H-ZSM-5 based catalysts modified by iron. On Fe-ZSM-5 a new form of surface oxygen (α-oxygen) is generated from N_2O, which is different from that obtained from O_2, and readily reacts with CH_4 to produce CH_3OH even at room temperature [2,4].

There are numerous studies reported on the mechanism of N_2O decomposition on Fe modified MFI (ZSM-5) or BEA type zeolites in the presence or absence of reducing agent [3,5–8]. The high activity of the Fe containing ZSM-5 catalysts could not yet be reached by other catalysts. From environmental point of view the development of novel, improved catalysts for the reduction of N_2O by methane as well as the study of the molecular and atomic mechanism of the process are actual problems. Our investigations are based on the Ga modified H-ZSM-5, on which promising results have been obtained in the non-oxidative activation of methane by hydrogen-transfer applying alkenes on H-GaAlMFI below 873 K. According to Choudhary et al. [9] the co-existence of strong acidity and the extra framework Ga-oxide species in the catalyst provides the strong dehydrogenation function. Also the effect of reductive and oxidative atmospheres on the propane aromatization activity and selectivity of Ga/H-ZSM-5 was already discussed [10]. Hydrogen pretreatment clearly increase the dispersion of the gallium, thereby generating more active sites combining intimately gallium species (Ga^{3+}, O^{2-}) ion pairs and Brøensted sites from the zeolite, enhancing overall catalytic performance, and dispersed gallium species acting as portholes to release dihydrogen.

Regarding the methane activation in the $N_2O + CH_4$ reaction the formation of CH_x surface intermedier species on the catalyst are relevant. PtCoNaY, $PtCoAl_2O_3$ [11–13] and monometallic M/H-ZSM-5 (Ag, Mo, In, Fe, Ga, etc.) [14] catalysts show good performance in this process.

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It can be concluded that the Mo bonded to the strongly acidic Ga/H-ZSM-5 has strong affinity to methane, and can be a promising novel catalyst in N_2O reduction with methane.

In the present work we aim at investigating the reaction between N_2O and CH_4 over the Mo/Ga/H-ZSM-5 catalyst by using steady-state flow system technique, temperature programmed surface reaction (TPSR) with MS detection, and in situ XPS. We expect to elucidate the main components of the reaction mechanism in the Mo/Ga/H-ZSM-5–N_2O–CH_4 catalytic system and decrease the temperature of N_2O decomposition (both direct and reductive ones with methane).

2. Experimental

2.1. Catalyst preparation

H-ZSM-5 (Si/Al = 40) was synthesized as in [15] by using of tetrapropyl ammonium bromide as template. Ga/H-ZSM-5 containing 0.4 wt% Ga was prepared by the conventional liquid phase ion-exchange using 0.1 molar $Ga(NO_3)_3 \times H_2O$ solution and stirring overnight followed by centrifugation. The procedure was repeated three times using wet cake and fresh solutions. The solid material was subsequently washed nitrate free with double distilled water and dried in a dessicator at ambient temperature. Mo/Ga/H-ZSM-5 catalyst containing 3.0 wt% Mo was prepared by incipient wetness technique on the base of Ga/H-ZSM-5 using solution of $(NH_4)_6Mo_7O_{24} \times 4H_2O$ in bidestilled water. Sample was dried for 24 h at 383 K.

2.2. Catalyst characterization and temperature programmed reaction studies

The samples were characterized by X-ray fluorescence method (XRF), X-ray photoelectron spectroscopy (XPS), temperature programmed reduction (TPR), CO chemisorption and transmission electron spectroscopy (TEM).

X-ray photoelectron spectroscopy (XPS) of the samples were performed on the as received, reduced and spent catalyst samples using an in situ catalytic reactor attached to an XSAM-800 photoelectron spectrometer manufactured by KRATOS. Mg Kα characteristic X-ray line, 40 eV pass energy and FAT mode were applied for recording the XPS lines of Mo 3d, Ga 2p, O 1s, C 1s, and Si 2p. The sequence of in situ treatments is given in Table 2. The Si 2p peak at 103.3 eV BE was used as internal reference for charge compensation.

Temperature programmed surface reaction (TPSR), temperature programmed reduction (TPR) and CO adsorption measurements were performed in a flow reactor. The Ga/H-ZSM-5 and Mo/Ga/H-ZSM-5 samples were first treated in oxygen at 573 K for 1 h then cooled to room temperature. The samples were characterized by TPR using 1 vol.% hydrogen/argon mixture with 20 K min^{-1} temperature ramp rate. The gases applied in the TPSR experiments, He (5.0), 1% N_2O(5.0)/He(5.0), and 1% CH_4(5.5)/He(5.0) were used without additional purification (in parenthesis the purity of gases are shown). The feed components and reaction products were analyzed qualitatively by means of a quadrupole mass spectrometer type Hiden HAL 02/100 on the basis of related components atomic mass units (AMUs): 44 (N_2O, CO_2), 32 (O_2), 30 (N_2O, C_2H_6), 28 (N_2, N_2O, CO, CO_2, C_2H_6), 27 (C_2H_4), 16 (O_2), 2 (H_2).

Two types of the TPSR were performed by using of MS:

- reaction of CH_4 with oxygen species formed by decomposition of N_2O. In this case the catalysts were treated in 1%N_2O/He at different temperatures, purged and cooled to room temperature in He and started a temperature ramp of 20 K/min in 1%CH_4/He;
- reaction of N_2O with surface CH_x species formed by non–oxidative CH_4 chemisorption. In this case the catalysts were pulsed 15 times with 100 μl CH_4 at different temperatures and cooled to room temperature in He followed by a temperature ramp of 20 K/min in 1%N_2O/He.

2.3. Steady-state catalytic studies

Direct N_2O decomposition and reduction of N_2O with CH_4 was investigated in a steady-state flow system mode. 100 mg catalyst was packed between two layers of quartz wool in the quartz microreactor (6 mm ID). N_2O/He = 19.8%/80.2%, or stoichiometric N_2O/CH_4/He = 19.8%/4.9%/75.3% mixtures were introduced into the system with flow rate 25 $cm^3\ min^{-1}$ at atmospheric pressure. The inlet gases and the products of reactions CH_4, N_2O, N_2, O_2, CO_2, C_{2+} hydrocarbons were analyzed by means of a gas chromatograph type CHROMPACK CP 9002 using a 50 m long plot fused silica column (0.53 mm ID) with stationary phase of CP-Al_2O_3/KCl for hydrocarbons (FID detector), and a 30 m long Carboxen 1006 PLOT column (0.53 ID) in a temperature programmed mode for the permanent gases (TC detector). Conversions of N_2O and CH_4 were calculated from the difference between the feed and effluent concentrations. Only CO_2 and N_2 were detected as products.

3. Results

3.1. Surface and bulk structure of Mo/Ga/H-ZSM-5 catalyst as a function of conditions

XRD proved that the structure of the zeolite was not destroyed in the impregnation followed by the calcination. The physical characterization of the catalysts is given in Table 1.

The H_2 consumption in TPR of Ga/H-ZSM-5 treated by O_2 and N_2O is higher than that calculated assuming total reduction of Ga^{3+} to Ga^0, by a factor of 3.6 and 1.4, respectively. The respective hydrogen uptake for the O_2 and N_2O treated Mo/Ga/H-ZSM-5 catalysts was 0.6 and 0.3 times smaller than those assuming the total reduction of Ga^{3+} and Mo^{6+} into metallic Ga and Mo. The CO chemisorption is just the reverse, as five times more CO is chemisorbed after reduction in hydrogen on Ga/H-ZSM-5 calcined

Table 1
Metal loading, TPR and CO chemisorption data of the samples.

Sample	Metal loading[a] (wt.%)		TPR[b] (μmol H_2/g)			CO chemisorption[c] (μmol/g)	
	Ga	Mo	Calculated	Pretreatment at 973 K in		Pretreatment at 973 K in	
				O_2	N_2O	O_2	N_2O
Ga/H-ZSM-5	0.4 (100)	–	86	306	122	1.5	7.5
Mo/Ga/H-ZSM-5	0.4 (9)	3.0 (91)	1025	600	269	11	12.5

[a] In parentheses the relative metal compositions are shown.
[b] 1% H_2/Ar mixture, temperature ramp rate 20 K min^{-1}.
[c] CO pulses at room temperature in He after TPR.

Table 2
XPS data of Mo/Ga/H-ZSM-5 (XSAM-800 by KRATOS, Mg Kα characteristic X-ray line, 40 eV pass energy and FAT mode, Si 2p at 103.3 eV BE were used as internal references for charge compensation).

Pretreatment (in the sequence of in situ treatments)	Conditions	$\frac{Ga^0}{Ga^{3+}}$	$\frac{Mo^0}{\Sigma Mo}$	$\frac{Mo^{4+}}{\Sigma Mo}$	$\frac{Mo^{6+}}{\Sigma Mo}$	$\frac{Ga}{Mo}$	$\frac{Ga}{Si}$	$\frac{Mo}{Si}$
As prepared	383 K, air, 24 h	0.0	0.0	0.0	1.0	21	0.33	0.016
Calcination in air	973 K, air	0.0	0.0	0.0	1.0	7.7	0.08	0.040
Reduction with H_2	973 K, 100% H_2	1.2	0.57	0.43	0.0	5.4	0.18	0.033
Oxidation by N_2O	423 K, 1% N_2O/He	0.91	0.55	0.45	0.0	7.7	0.26	0.034
Oxidation by N_2O	698 K, 1% N_2O/He	0.77	0.0	0.0	1.0	3.4	0.20	0.060
Reduction with CH_4	423 K, 1% CH_4/He	1.04	0.0	0.0	1.0	3.7	0.26	0.061
Reduction with CH_4	698 K, 1% CH_4/He	1.6	0.45	0.42	0.13	2.9	0.22	0.076

in N_2O than in O_2. There is no change in the CO chemisorption on the MoGa catalyst resulting in 12.5 and 11 μmol CO/g for N_2O and O_2 calcination, respectively.

The XPS results given in Table 2 show, that upon calcination in air at 923 K the Ga/Mo ratio decreased from 21 to 7.7, while the Ga/Si ratio changed from 0.33 to 0.084. The migration of Ga into the zeolite structure or inside the supercage is assumed as a possible explanation. Migration of Mo onto Ga might also be an explanation.

The high mobility of gallium upon reduction is believed to be connected to the formation of unstable gaseous Ga_2O oxide [16,17]. Subsequently, the oxide can react with Brøenstead sites in the zeolite micropores and create ZO^- and Ga^+ species. The possible role of Ga^+ is discussed in [18,19]. In our XPS studies (Fig. 1 and Table 2) no Ga^+ was detected due to its instability [20,21]. Ga^0 is formed in reduction in H_2 at 973 K while CH_4 reduces Ga^{3+} already at 423 K. CH_4 is also an efficient reducing agent for Mo^{6+}. It is important to note that H_2 is less effective in the reduction of Mo than CH_4. Ga^0 is only partially oxidised by N_2O even at 698 K while the Mo is fully oxidised. These results suggest that the N_2O/CH_4 redox pair is more effective in the Mo/Ga/H-ZSM-5 system than the O_2/H_2 one. The fresh and calcined catalysts contain Mo^{6+} only, while on reduction in H_2 Mo^{6+} disappears and Mo^{4+} as well as Mo^0 forms. There is no change on treatment with N_2O at 423 K but at 698 K Mo is fully oxidised. CH_4 proved to be a stronger reducing agent than H_2, as it reduces Mo to the same extent at 698 K as H_2 does at 973 K. This suggests that the $N_2O + CH_4$ redox pair might have advantages against the $H_2 + O_2$ one and the mechanism of the redox reactions might also be different.

TEM studies have shown that there are MoGa containing particles of 1–2 nm inside the pores of the zeolite but no larger ones were detected as shown in Fig. 2. This is in accordance with the XRD results of calcined samples showing no other crystalline phases except zeolite itself. The formation of high dispersion of Mo is reasonable if we suppose that Mo is anchored preferentially on the strong acidic sites, which are in large excess compared to Mo (1171 μmol/g strong acidic sites of the parent Ga/H-ZSM-5 [22] vs. 313 μmol/g Mo).

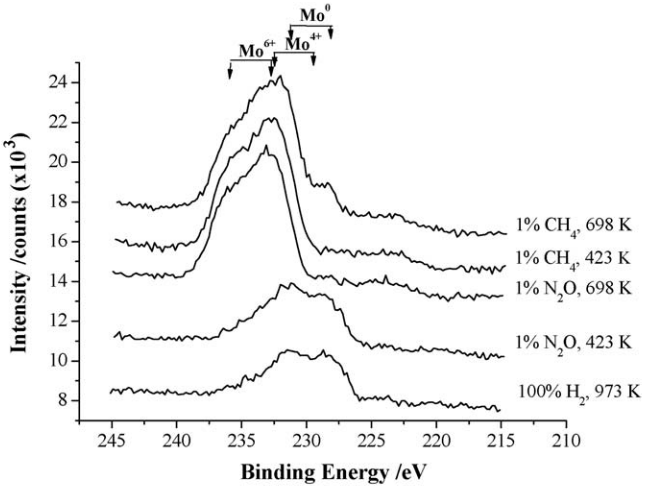

Fig. 1. Mo 3d XPS spectra of Mo/Ga/H-ZSM-5 catalyst. (XSAM-800 by KRATOS, Mg Kαcharacteristic X-ray line, 40 eV pass energy and FAT mode, Si 2p at 103.3 eV BE was used as internal reference for charge compensation). Pretreatments from bottom to top in the sequence of in situ treatments.

3.2. Reaction of CH_4 with oxygen species formed by decomposition of N_2O

The MoGa catalysts were treated in 1%N_2O/He at 698K for 1.5 h as described in Section 2.2. TPSR with CH4 is given in Fig. 3. It is clear that the oxidation of CH_4 with trapped surface oxygen starts already at room temperature. This suggests that the oxygen formed from N_2O is extremely active similarly to that suggested in the literature [2,3]. It is important to emphasize that oxidising the methane by these active sites at 300–400 K is not a catalytic turn over, since the low temperature reduction of the active sites is not followed by reoxidation at the same temperature. 1% N_2O/He mixture can reoxidise these reduced centres only at about 698 K.

3.3. Reaction of N_2O with surface CH_x species formed by CH_4 chemisorption

As described in Section 2.2, first the catalysts were treated with CH_4 pulses to produce chemisorbed CH_x which reacted with N_2O in TPSR mode. The results are given in Fig. 4 and Table 3. At low temperature CO_2 is formed in the surface reaction and desorption of N_2O dominates. At higher temperatures decomposition of N_2O starts producing N_2 and O_2. The MoGa catalyst is active in TPSR at much lower temperature and the N_2O decomposition starts also at lower temperature than on the sample not containing molibdenum.

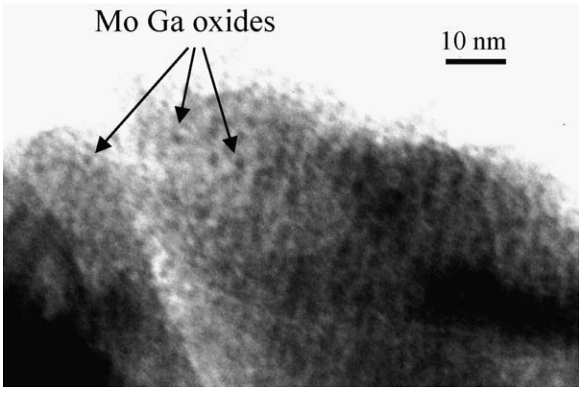

Fig. 2. TEM micrograph of Mo/Ga/H-ZSM-5 catalyst calcined (in 5% O_2/Ar at 773 K for 5 h).

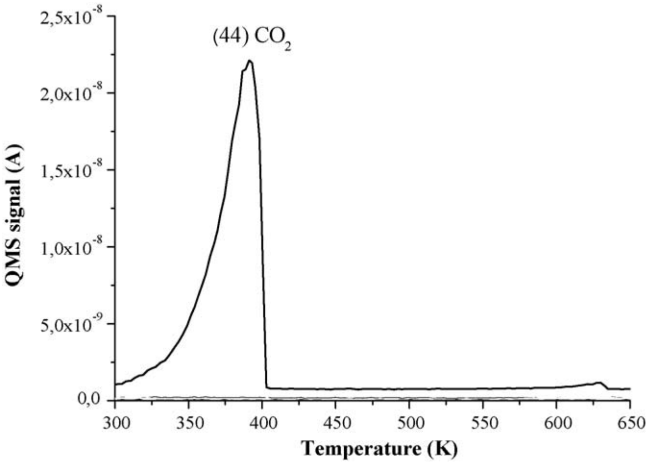

Fig. 3. TPS reaction between chemisorbed oxygen and gas phase methane on Mo/Ga/H-ZSM-5: MS profile of product. (Catalyst 30 mg; N_2O decomposition: $C_{N_2O/He} = 1\%$; flow rate = 25 cm^3 min^{-1}; temperature = 698 K; 1.5 h. Gas phase CH_4: $C_{CH_4/He} = 1\%$; flow rate = 25 cm^3 min^{-1}; temperature ramp rate = 20 K min^{-1}).

3.4. Reaction of $N_2O + CH_4$ mixture and decomposition of N_2O

A stoichiometric mixture of N_2O and CH_4 in He was used as given in Section 2.2 and N_2, CO_2 and H_2O were the only products. No C_{2+} or oxygenates were detected. In the N_2O decomposition experiments only N_2 and O_2 were detected. Data given in Fig. 5 and Table 4 show a dramatic decrease in T_{50} for the MoGa catalyst in the $N_2O + CH_4$ reaction but only a slight decrease in the decomposition of N_2O. This means that the catalytically active sites for the two reactions are different and it is not the decomposition of N_2O which initiates the combustion of CH_4.

4. Discussion

The XPS identified Mo^0, Mo^{4+} and Mo^{6+} as well as Ga^0 and Ga^{3+} species. On molybdenum containing sample after N_2O treatment strong oxidation centers were formed which react with methane below 373 K. The active oxygen existing at low temperature is known in the literature. The oxygen formed at higher temperature produces stable ZO centers in the zeolite at 623 K [23]. These centers are decomposed at higher temperature and involved in the steady-state reactions.

Table 3
Initial temperatures[a] of N_2O decomposition in $(CH_4)_{ads}$[b] + $(N_2O)_{gas}$ TPS reactions ($C_{N_2O/He} = 1\%$, $C_{CH_4/He} = 1\%$, 20 K min^{-1} temperature ramp rate).

Catalyst	Temperature of pretreatment catalysts by CH_4 (K)	N_2O decomposition initial temperature at (K)
Ga/H-ZSM-5	423	820
	698	825
	973	825
Mo/Ga/H-ZSM-5	423	755
	698	760
	973	770

[a] Initial temperature measured by 0.1% conversion of N_2O.
[b] $(CH_4)_{ads}$—adsorbed products of methane chemisorption.

Table 4
Temperature of 50% conversion (T_{50}) for the catalysts.

Sample	T_{50} (K)		
	Direct N_2O decomposition	N_2O reduction with CH_4	
		N_2O conversion	CH_4 conversion
Ga/H-ZSM-5	819	755	755
Mo/Ga/H-ZSM-5	787	646	646

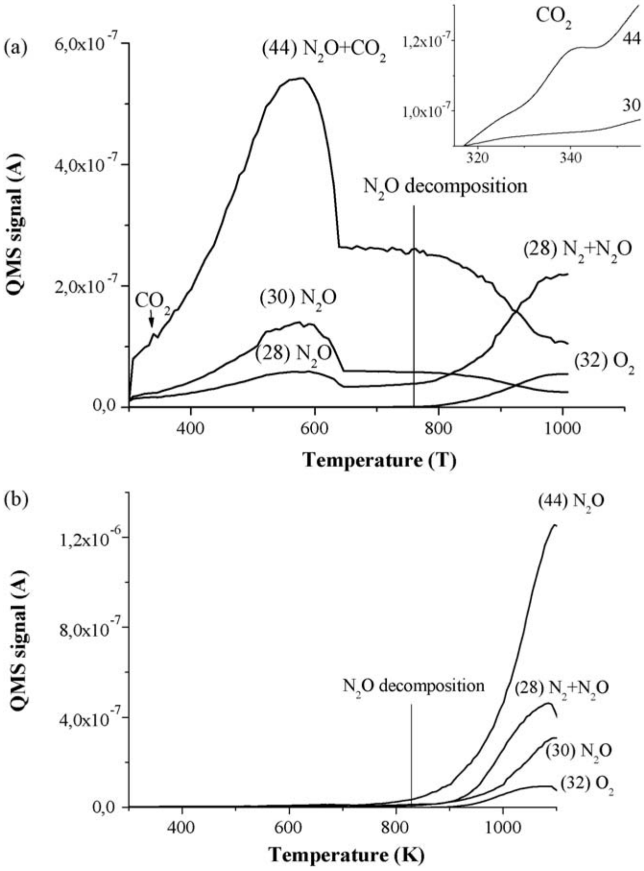

Fig. 4. TPS reaction between chemisorbed methane and gas phase N_2O: MS profiles of products (a-Mo/Ga/H-ZSM-5, 30 mg,; b-Ga/H-ZSM-5, 30 mg; CH_4 chemisorption: $C_{CH_4} = 100\%$; CH_4 pulse = 100 μl; number of pulses = 15; flow rate = 25 cm^3 min^{-1}, 973 K; gas phase N_2O: $C_{N_2O/He} = 1\%$; flow rate = 25 cm^3 min^{-1}; temperature ramp rate = 20 K min^{-1}). Insert is a magnified section for AMU = 44 and 30.

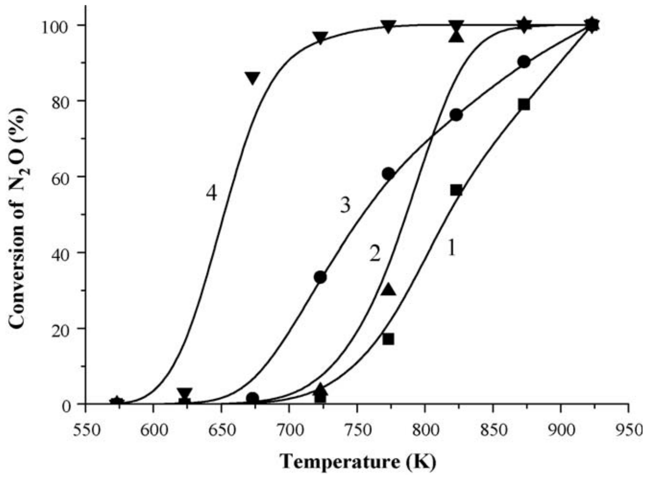

Fig. 5. Comparison of catalytic properties in steady-state conditions: in direct N_2O decomposition (1-Ga/H-ZSM-5; 2-Mo/Ga/H-ZSM-5) and in N_2O reduction with CH_4 (3-Ga/H-ZSM-5; 4-Mo/Ga/H-ZSM-5). (Direct N_2O decomposition: N_2O/He = 19.8%/80.2%; flow rate = 50 cm^3 min^{-1}; N_2O reduction with CH_4: N_2O/CH_4/He = 19.8%/4.9%/75.3%; flow rate = 50 cm^3 min^{-1}).

In the decomposition of N_2O first N_2O reacts with the active sites on Mo/Ga/H-ZSM-5 meanwhile N_2 molecules evolve, the oxygen remains chemisorbed forming ZO centers with some mobility. The mobility of the ZO centers ensures recombination to form molecular O_2. Beside the stable O_a (accommodated oxygen), O_n (nascent oxygen) also forms during the reaction between N_2O and ZO redox centers and it is desorbed as oxygen molecules, too.

The reaction of N_2O is fully changed when CH_4 is in the system. The active centers are not directly oxidised by N_2O [24], but they react with GaMo–OCH_3 species created by the interaction of methane with active oxygen on the surface. The reaction intermediates of methoxy Fe–OCH_3, and formate Fe–OOCH species over the Fe-BEA catalysts were also observed during the reaction in work [25]. The oxidation rates of these surface species with N_2O and O_2 were measured, and found that the methoxy species were oxidised with N_2O more rapidly than with O_2, while the formate species were oxidised with both N_2O and O_2 almost the same rate.

The possible complex oxygen-transfer mechanism in reaction between nitrous oxide and methane can be presented as follows.

- Initial steps:

$$Z + N_2O \rightarrow N_2 + ZO \quad (1)$$

(Z—Mo-Ga-zeolite complex site)

$$CH_4 + Z \rightarrow ZCH_4 \quad (2)$$

$$ZO + ZCH_4 \rightarrow ZOH + ZCH_3 \quad (3)$$

- Catalytic cycle:

$$CH_4 + ZOH \rightarrow ZCH_3 + H_2O \quad (4)$$

(ZOH—active centre of catalytic turnover)

$$ZCH_3 + N_2O \rightarrow ZOCH_3 + N_2 \quad (5)$$

$$ZOCH_3 + 3N_2O \rightarrow ZOH + CO_2 + H_2O + 3N_2 \quad (6)$$

[the step (6) is a complex oxygen transfer]

- The overall reaction (1)–(6) expressed as follows:

$$CH_4 + 4N_2O \rightarrow CO_2 + 2H_2O + 4N_2$$

In the initial steps formation of O_a oxygen on the complex catalyst sites (ZO) plays important role in the formation of ZOH species, which are the active centres of the catalytic turnover and their reformation completes the catalytic cycle. Note that in step (4) methane reacts with the strong redox ZOH centers and CH_x surface radicals are formed. These radicals are extremely effective reducing agents for N_2O. The regeneration of the ZOH centres from ZCH_3 occurs via a complex oxygen transfer, in that the ZOH reforms not directly by oxidation with N_2O, but in reaction between N_2O and $ZOCH_3$ produced by participation of N_2O and ZCH_3.

5. Conclusions

1. It was established that the oxidation/reduction of the Mo/Ga/H-ZSM-5 sample is more favoured in the interaction with N_2O/CH_4 as compared to that with O_2/H_2 and the mechanism of the redox reactions might also be different.
2. Strong oxidation centers are formed in the interaction of the catalyst with N_2O above 698 K. These have key role in the initial steps of the formation of catalytic sites. These centers oxidise methane to CO_2 below 373 K, but the reoxidation of these sites is not possible at this low temperature.
3. High activity of Mo/Ga/H-ZSM-5 in reductive transformation of N_2O in presence of CH_4 is determined by the co-existence of Ga/H-ZSM-5 with strong acid character, Mo with unsaturated d-orbital and CH_4.
4. The reduction of N_2O with CH_4 cannot be described by the simple Mars–van Krevelen mechanism, but a complex oxygen transfer process is involved, when N_2O does not directly reoxidise the reduced active centers but via a MoGa–OCH_3 species.

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