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RESEARCH NOTE

Comparison of the C_3H_8 Oxidation by NO or by O_2 on Copper-Based Catalysts

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The selective reduction of NO by C_3H_8 is performed on copper-based catalysts, fresh and hydrothermally Cu-MFI with various Si/Al ratios and copper contents, Cu on conventional nonzeolitic supports with various Cu loadings. In the literature it is already known that the C_3H_8 oxidation by NO occurs mainly on isolated copper ions. However, the sites responsible for the C_3H_8 oxidation by O_2 are less studied. This note shows that nonisolated copper ions are active for the C_3H_8 oxidation by O_2. With or without NO in the feed, bulk oxides are more active for the C_3H_8-O_2 reaction than for the C_3H_8-NO (or NO_2) reaction. Furthermore, NO inhibits the hydrocarbon combustion by O_2.

Key Words: **$DeNO_x$; selective nitric oxide reduction; Cu-MFI catalysts; Cu on nonzeolitic supports; SCR mechanism.**

1. INTRODUCTION

It is generally accepted (1–7) that, on copper-based catalysts, isolated copper ions are effective for the selective reduction of NO by hydrocarbons. We have previously correlated the NO reduction rate, i.e. the oxidation of C_3H_8 by NO, to the amount of isolated copper ions accessible to gases and identified by FTIR spectroscopy of adsorbed CO (1–3). In lean-burn applications oxygen is present in a much higher amount than NO and the desired NO/C_3H_8 reaction must compete effectively for the catalytic sites with the undesired reaction O_2/C_3H_8 (8–10).

However, in the literature, the sites responsible for the oxidation of C_3H_8 by O_2 are generally not reported. This note focusses on the relation between C_3H_8 oxidation, in the presence and in the absence of NO, and the number of isolated or nonisolated copper ions in copper-based catalysts (zeolitic and nonzeolitic systems). The emphasis is on the question "Does the activity in the C_3H_8-O_2 reaction follow the same trends as the activity in the C_3H_8–NO reaction?

The rates of the C_3H_8–NO and C_3H_8–O_2 reactions will be compared:

$$C_3H_8 + 10\,NO \rightarrow 5\,N_2 + 3\,CO_2 + 4\,H_2O \qquad [1]$$

$$C_3H_8 + 5\,O_2 \rightarrow 3\,CO_2 + 4\,H_2O. \qquad [2]$$

However, if NO initially undergoes oxidation to NO_2, as many authors believe to be the case (11–14), and it if is this NO_2 which reacts with C_3H_8, then the stoichiometry of the reaction changes from 1 : 10 to 1 : 5 according to the reaction:

$$C_3H_8 + 5\,NO_2 \rightarrow 2.5\,N_2 + 3\,CO_2 + 4\,H_2O. \qquad [3]$$

Furthermore, under oxygen-deficient conditions the partial oxidation of C_3H_8 into CO has to be considered.

$$C_3H_8 + 3.5\,O_2 \rightarrow 3\,CO + 4\,H_2O. \qquad [4]$$

2. METHODS

The introduction of copper into the MFI zeolites with low Si/Al ratios (equal to 19 or 22) was performed using exchange or precipitation or impregnation procedures with copper nitrate. For high Si/Al ratios (equal to 78, 130, 151, 319), copper ions were introduced by impregnation. After drying, the solids were calcined under an oxygen flow at 773 K (heating rate 1 K min^{-1}), as already described (1). All the prepared Cu-MFI solids showed the XRD patterns of the parent zeolite and copper oxides were not detected. The solids are called Cu-MFI-(Si/Al)-EXC (or IMP or PRE) wt% Cu, with the value of the Si/Al ratio, the preparation procedure and the copper content. Some samples were hydrothermally aged under a (10 vol% H_2O–air) mixture at a total flow rate of 10 liter h^{-1} for 24 h at 923 K (15).

Cu catalysts on nonzeolitic supports (alumina and silica from Degussa, Ketjen silica-alumina) were prepared by impregnation with copper nitrate and calcined as above. The

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Cu content ranged from 0.3 to 6.4 wt% (2). The CuO phase was detected by XRD only in a solid containing 6.4 wt% Cu.

Catalytic tests were carried out in a fixed-bed flow reactor, using 100 mg of catalyst diluted with 400 mg of inactive α Al_2O_3 and a reactant mixture containing $[NO] \approx [C_3H_8] \approx 2000$ vpm, $[O_2] = 10$ vol%, and He as a balance, at a total flow of 10 $dm^3\ h^{-1}$, in the 298–773 K temperature range. The temperature was increased with a 4 K min^{-1} ramp and then decreased. At 623 K the influence of the oxygen content, between 0 and 10 vol%, was also studied, the initial C_3H_8 and NO concentrations were not modified and the total flow rate was held constant by varying the inert gas (He) flow.

CO_2, N_2O, O_2, N_2, CO, and C_3H_8 were analyzed by gas chromatography using a dual CTR1 column from Alltech (Porapak and molecular sieve) with a thermal conductivity detector and a Porapak column with a flame ionisation detector. The mixture was analyzed every 10 min. Furthermore NO, N_2O, NO_2, and CO_2 were analyzed continuously on line by means of IR and UV Rosemount analyzers. Helium was used as the carrier gas as well as the diluent gas. The formation of N_2O was negligible. CO was detected only with oxygen-deficient mixtures (0.5 vol% O_2). The activities were evaluated in terms of NO conversion into N_2 and of C_3H_8 conversion into $CO + CO_2$. The carbon and nitrogen balances were checked (1–3).

The rate of reaction [1] was calculated from the amount of N_2 formed, and, according to the 1 : 10 stoichiometry, the corresponding amount of consumed C_3H_8 was determined. The rate of reaction [2] was calculated from the global disappearance of propane from which the contribution of reaction [1] was subtracted. The rate of reaction [2] after subtracting the C_3H_8 conversion due to the possible reaction with NO_2 (reaction [3], i.e., 1 : 5 stoichiometry) (11–14) was also considered. Considering the accuracy for the initial commercial bottles (NO-He and C_3H_8-He) and for the N_2 analysis with a TCD detector we consider that, from one experiment to another one, the rates can be known to within 15%.

The FTIR spectroscopy of irreversibly adsorbed CO at room temperature on *in situ* calcined and evacuated solids has already been described (1–3). The optical density of the νCO bands were normalized taking into account the copper amount.

RESULTS AND CONCLUDING REMARKS

As previously described (1, 2), for all the Cu-MFI solids and for nonzeolitic supported copper solids with low copper loadings (0.3 and 1.7 wt% Cu) (Table 1), the presence of oxygen promotes the NO reduction into N_2. With high copper loadings (3.2 and 6.4 wt%) on nonzeolitic supports the NO reduction decreases as soon as O_2 is introduced (Table 1).

TABLE 1

Conversions of NO into N_2 (Reaction [1]) and Overall C_3H_8 Conversion as a Function of the Oxygen Content (vol%) and of the Copper Amount (wt%) with the Cu/Al_2O_3 Solids at 773 K and with the Cu-MFI (Si/Al = 19 or 22) Solids at 623 K

	NO into N_2 conversion (%)					Overall C_3H_8 conversion (%)			
	O_2 (vol%)					O_2 (vol%)			
Cu (wt%)	0	0.5	1	2	8	0.5	1	2	8
Cu/Al_2O_3 at 773 K									
0.3	2	10	13	13	7	6	9	10	17
1.7	11	19	23	21	19	40	44	48	56
3.2	36	21	16	12	0	55	58	65	73
6.4	40	25	20	14	0	70	77	83	90
Cu-MFI at 623 K									
1.2	-	62	70	75	65	20	32	46	61
2.6	-	75	75	60	43	79	82	79	79
3.8	2	99	99	77	56	68	92	95	98

Note. Cu-MFI solids: Cu-MFI(22)-IMP-1.2; Cu-MFI(19)-IMP-2.6; Cu-MFI(19)-PRE-3.8.

Furthermore, low Si/Al ratios, in the case of Cu-MFI solids, and low copper loadings, in the case of nonzeolitic supports, favour the formation of isolated copper species which are detected by the νCO band (2152–2160 cm^{-1}) of CO adsorbed on isolated Cu^+ ions arising from the reduction of isolated Cu^{2+} ions. High Si/Al ratios and high copper loadings favour the formation of bulk oxides. This formation is evidenced by the νCO band at 2135–2130 cm^{-1} due to CO adsorbed on the nonisolated Cu^+ ions arising from the partial reduction of bulk CuO (3). In MFI zeolites the isolated ions partially migrate to inaccessible sites upon hydrothermal treatments at moderate temperature (923 K), the optical density of the 2152–60 cm^{-1} band decreasing. An agglomeration into copper oxides is detected only when the aging treatment reaches 1173 K (15).

The selective reduction of NO has been previously related to the presence of these isolated copper species (3, 16). It might be supposed that the solids characterized by the presence of bulk oxides are more active for the C_3H_8–O_2 reaction than for the C_3H_8–NO reaction.

In the presence of 0.5 vol% O_2, the total C_3H_8 conversions for both the 3.2% and 6.4% Cu/Al_2O_3 and the 3.8 and 2.6% Cu-MFI catalysts cannot arise simply from reactions [1], [2], and [3] (C_3H_8–NO, C_3H_8–O_2, C_3H_8–NO_2 with the formation of CO_2). In the presence of 0.5 vol% O_2, the maximum C_3H_8 conversion due to reaction [2] would be of 50%. The difference corresponds to a partial oxidation into CO (reaction [4], for instance).

For the Cu-MFI solids and for a given oxygen content ($\geq$1 vol%), the total C_3H_8 conversion and the conversion

TABLE 2

Calculated C_3H_8 Conversions for Reaction [2] (C_3H_8/O_2) (in %) after Subtracting from the Overall C_3H_8 Conversion: The Conversion Due to Reaction [1] with NO (Column A); the Conversion Due to the Reaction [3] with NO_2 (Column B)

	A (overall minus conversion due to [1])				B (overall minus conversion due to [3])			
	O_2 (vol%)				O_2 (vol%)			
Cu (wt%)	0.5	1	2	8	0.5	1	2	8
Cu/Al_2O_3 at 773 K								
0.3	5.0	7.7	8.7	16.3	4.0	6.4	7.4	15.6
1.7	38.1	41.7	46.9	54.1	36.2	39.4	43.8	52.2
3.2	52.9	56.4	63.8	73.0	50.8	54.8	62.6	73.0
6.4	67.5	75.0	81.6	90.0	65.0	73.0	80.2	90.0
Cu-MFI at 623 K								
1.2	13.8	25.0	38.5	54.5	7.6	18.0	31.0	48.0
2.6	71.5	74.5	73.0	74.7	64.0	67.0	67.0	70.4
3.8	58.1	82.1	87.3	92.4	48.2	72.2	79.6	86.8

Note. Cu-MFI solids: Cu-MFI(22)-IMP-1.2; Cu-MFI(19)-IMP-2.6; Cu-MFI(19)-PRE-3.8.

of the C_3H_8/O_2 reaction increase continuously with the temperature (17). At the same time, as already reported (1), the reduction of NO into N_2 increases with the temperature, reaches a maximum (623–673 K range for the solids prepared by precipitation and impregnation) and then decreases. The formation of CO_2 begins at the same temperature as the NO reduction.

Generally, the C_3H_8 conversions (overall conversion and calculated conversion due to the reaction with O_2) (Tables 1 and 2) increase with the copper amount. However, with the oxygen-deficient mixture (0.5 vol% O_2), when CO is formed, the 2.6% Cu-MFI catalyst has a higher C_3H_8 conversion than the 3.8 Cu-MFI one. As the oxygen concentration increases the C_3H_8 conversion increases also, except for the overall conversion over the 2.6% Cu-MFI catalyst (Table 1). However, in all cases the calculated C_3H_8 conversion obtained after subtracting the conversion due to the reaction with NO_2 increases with the O_2 content (Table 2).

For low copper amounts on nonzeolitic supports, when oxygen promotes the NO reduction, the overall C_3H_8 conversion remains moderate (Table 1). For high copper loadings, when oxygen inhibits the NO reduction, it might be supposed that NO cannot be reduced because of the consumption of the reductant by oxygen. Such an explanation can also account, in the case of the Cu-MFI solids, for the maxima observed with the oxygen content and the temperature. As a matter of fact, with the Cu-MFI(19)-PRE-3.8 solid, at 623 K and with 2000 vpm NO and 10 vol% O_2, it has been observed that the NO reduction increases with the propane partial pressure, from 35 to 51, 59, and 69% for 1000, 2000, 3000, and 4000 vpm C_3H_8, respectively.

In any case the C_3H_8 conversion largely exceeds the conversion which can be expected from the reaction with NO or NO_2; the C_3H_8–O_2 reaction rate is higher than the C_3H_8–NO (or NO_2) reaction rate.

Both C_3H_8–NO (or NO_2) reaction rates and calculated C_3H_8–O_2 reaction rates (after subtracting either the reaction with NO or the reaction with NO_2), expressed per gram of copper (moles converted s^{-1} g^{-1}Cu), decrease with the increase in copper amount and with the decrease in the number of isolated copper ions (the number of isolated Cu ions is proportional to the optical density of the 2152–60 cm^{-1} band assigned to CO adsorbed onto isolated Cu^+ ions) (Tables 3 and 4). Such behaviour is in accordance with the classical decrease of the dispersion when the active phase content increases. However, the dependency on Cu content and/or dispersion is different between the two reactions. The ratio of the rate (expressed per gram of copper) of reaction [2] (C_3H_8-O_2) to rate of reaction [1] (C_3H_8-NO) or [3] (C_3H_8-NO_2) increases with the copper amount

TABLE 3

C_3H_8 Oxidation by NO (or NO_2) and Calculated C_3H_8 Oxidation by O_2 Expressed in Moles of Converted C_3H_8 per Gram Copper (in 10^{-6} mol C_3H_8 s^{-1} g^{-1} Cu) in the Presence and in the Absence of NO with Low Copper Amounts on Nonzeolitic Supports

	Mixture C_3H_8-NO-O_2		Mixture C_3H_8-O_2	
Solids	C_3H_8-NO (or NO_2) reaction [1] (or [3])	Calculated C_3H_8-O_2 reaction [2]	C_3H_8-O_2	O.D./g Cu
Cu-Al 0.3 wt% Cu	9 (18)	65 (56)	81	1024
Cu-Al 1.7 wt% Cu	3 (6)	46 (43)	54	351
Cu-Si-Al 1.7 wt% Cu	1.8 (3.6)	31 (29.2)	36	215
Cu-Si 1.7 wt% Cu	1.1 (2.2)	20 (18.9)	23	136

Note. Reaction temperature 773 K. Oxygen amount 1 vol%. The numbers in brackets correspond to the calculations considering the reaction of C_3H_8 with NO_2. The optical densities normalized per gram copper (after 10 min in vacuo at 298 K) are also given. Supports: Al (alumina), Si (silica), Si-Al (silica-alumina).

TABLE 4

NO (or NO_2) Reduction into N_2 and Calculated C_3H_8 Oxidation by O_2 Expressed in Moles of Converted NO (or NO_2) (Reaction [1] or [3]) and in Moles of Converted C_3H_8 (Reaction [2], Subtracting Reaction [1] or Reaction [3]) per Gram Cu (in 10^{-6} mol s^{-1} g^{-1}Cu) and Normalized per Isolated Cu Ions (in 10^{-6} mol s^{-1} O. D.$^{-1}$) as a Function of the Optical Density (O.D.) of the 2152 cm^{-1} band (O.D. Normalized per Gram Cu and after 1 h under CO at 298 K) for Various Cu-MFI Solids (Fresh or Aged at 923 K, Various Si/Al Ratios, Preparation Procedure and Copper Amounts)

	Moles of converted NO_x reaction [1] or [3] C_3H_8–NO_x		Moles of converted C_3H_8 calculated rate of reaction [2] (C_3H_8–O_2)			
			Subtracting reaction [1]		Subtracting reaction [3]	
O.D./g Cu	Rate/g Cu	Rate/isolated Cu	Rate/g Cu	Rate/isolated Cu	Rate/g Cu	Rate/isolated Cu
3972	107	0.027	103	0.026	92.3	0.023
3580	83	0.023	94	0.026	85.7	0.024
3220	66	0.020	80	0.025	73.4	0.023
2335	61	0.026	65	0.028	58.9	0.025
1765	36	0.020	56	0.032	52.4	0.030
1700	39	0.023	55	0.032	51.1	0.030
1500	25	0.017	52	0.035	49.5	0.033
1150	26	0.023	45	0.039	42.4	0.037
800	15	0.019	37	0.046	35.5	0.044
665	7	0.011	34	0.051	33.3	0.050
0[a]	7	—	15		14.3	

Note. Reaction temperature 623 K. 10 vol% O_2 in the reactants.

[a] Cu-MFI solid with a strong Si/Al ratio (Si/Al = 316, 3.5 wt% Cu) containing only bulk oxides (νCO band at 2135–30 cm^{-1}).

and the number of isolated copper ions decreases. Let us remark that the data in Table 3 seem to be inconsistent with the data in Table 2, but these data originated from different experiments.

If the rates are normalized per isolated copper ion (by dividing the rate expressed per gram of Cu by the O.D. of the 2152–2160 cm^{-1} band), the rates of reaction [1] are approximately constant: around 0.085×10^{-6} mol NO reduced into

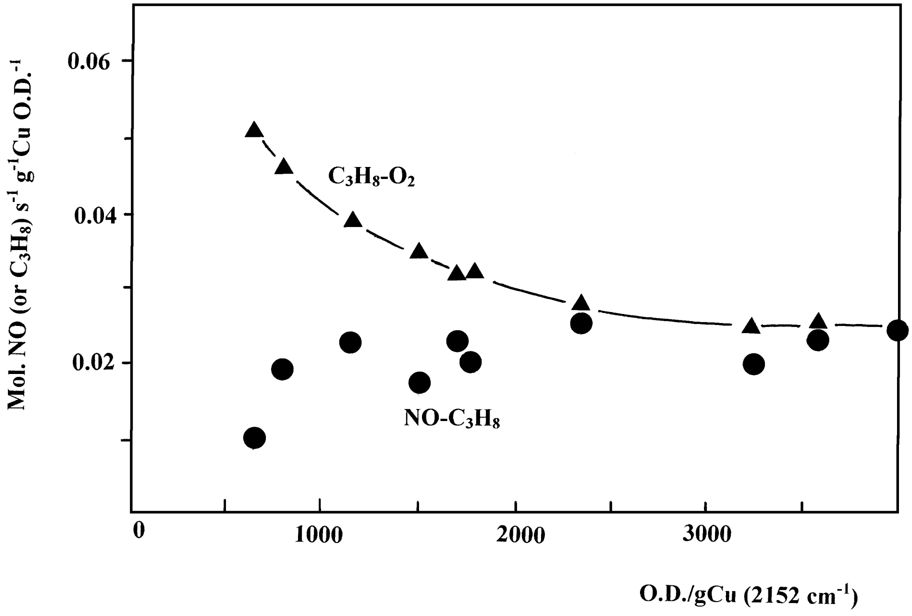

FIG. 1. Rates of the C_3H_8–NO and C_3H_8–O_2 reactions as a function of the amount of isolated Cu ions, this number being proportional to the optical density O.D. (normalized per gram Cu) of the 2152 cm^{-1} band. The rates of reaction are expressed in moles of converted NO (reaction [1]) and in moles of converted C_3H_8 (reaction [2], subtracting reaction [1]) per gram Cu (mol s^{-1} g^{-1} Cu) and normalized per isolated Cu ions (mol s^{-1} g^{-1} Cu O.D.$^{-1}$). The reactions were performed at 623 K in the presence of 10 vol% O_2 over various Cu-MFI catalysts (various Si/Al ratios, preparation procedures, copper amounts).

N_2 s^{-1} (isolated Cu^{-1}), i.e., 0.0085×10^{-6} mol C_3H_8 converted (case of reaction [1]) for the nonzeolitic supports at 773 K and with 1 vol% O_2, between 0.020 and 0.025×10^{-6} mol NO reduced to N_2 s^{-1} (isolated Cu^{-1}) for the Cu-MFI solids at 623 K and with 10 vol% O_2. On the contrary, the C_3H_8 oxidation rate by O_2 decreases when the number of isolated copper ions increases (Fig. 1, Table 4). This variation occurs considering the reaction of C_3H_8 either with NO or with NO_2. In other words, dispersed cations are less active for the total combustion of C_3H_8 by O_2 than for the C_3H_8–NO reaction, as has been already noted for Co, Ag, and Au supported on alumina (18).

In the case of the nonzeolitic supports, the activities in C_3H_8 oxidation have been compared, at 773 K, in the presence of NO (1 vol% O_2, 2000 vpm C_3H_8, 2000 vpm NO in He) and in the absence of NO (1 vol% O_2, 2000 vpm C_3H_8 in He). In both cases, the C_3H_8–O_2 reaction rate normalized to the number of isolated ions decreases when the number of isolated Cu ions increases (Table 3). Furthermore, NO inhibits the hydrocarbon combustion (Table 3), as previously mentioned (18, 19). It could be attributed either to a competitive adsorption between NO and O_2 or to a reaction of NO (or NO_2) with a partially oxidized hydrocarbon, as sometimes postulated (11–14). In that case the volcano NO reduction dependence on temperature and on oxygen content could be explained by an optimum concentration of such a partially oxidized species and not only by the consumption of the reductant. Such a hypothesis would be corroborated by the fact that, whatever the solid, some secondary products, benzene, propene, and propanone, are detected in small quantities (around 20 ppm from mass spectrometry analysis).

The main conclusion concerns the fact that nonisolated copper ions (copper oxides) are more active for the C_3H_8–O_2 reaction than for the C_3H_8–NO (or NO_2) reaction which occurs on isolated ions. **However, let us note that, with** a Cu-MFI solid containing only bulk oxides the NO reduction is not equal to zero (Table 4).

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