Lecture at CLEERS workshop, Ann Arbor, 04/30-05/01, 2002

NO_x Reduction with hydrocarbons or ammonia over zeolite based catalysts prepared by chemical vapor decomposition

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Abstract

De-NO_x catalysts for the emission from lean-burn engines must reduce NO_x to N_2 in the presence of a large excess of O_2 and H_2O. In view of the high space velocity such catalysts must be very active. They must also be highly selective, since the reductant should react specifically with the nitrogen oxides rather than with oxygen which is present at much higher concentration. As the emissions contain much H_2O, the performance of the catalysts should not be impeded by H_2O.

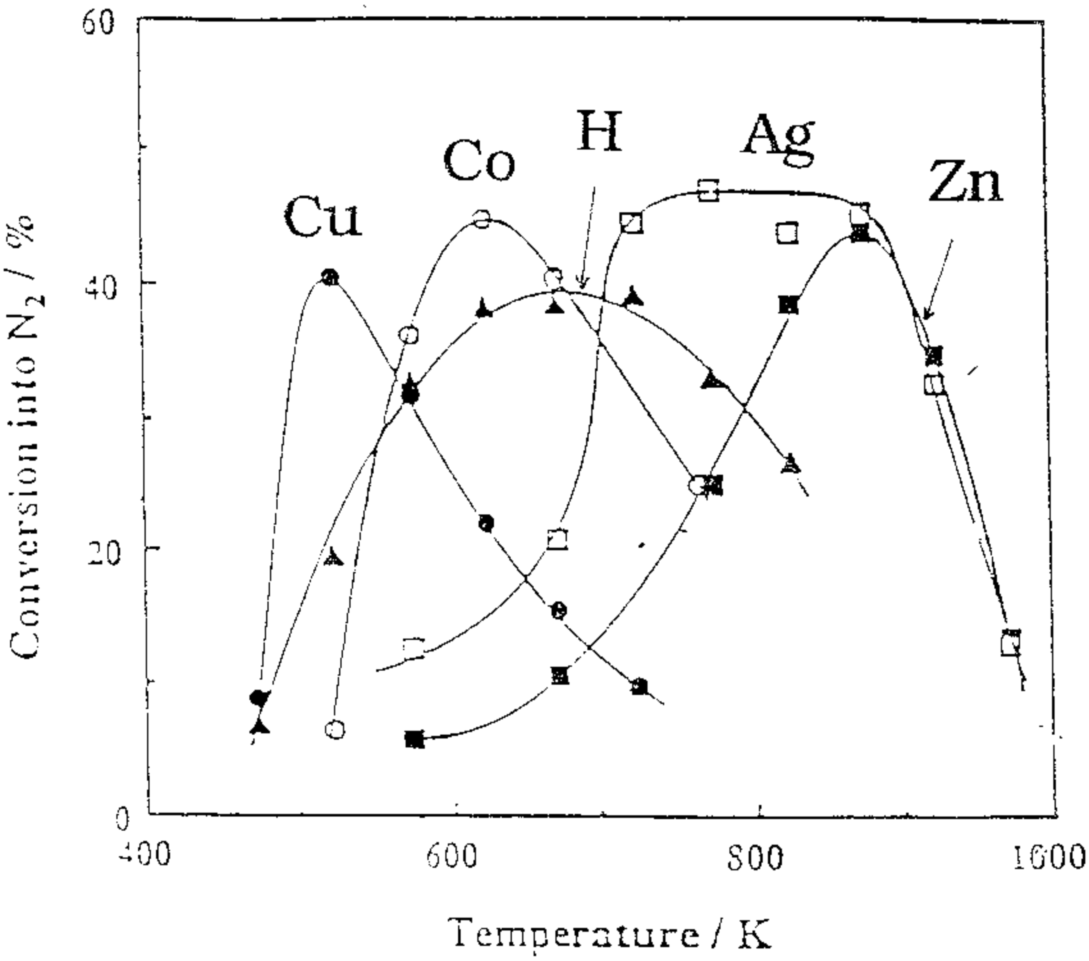
Catalysts which meet these criteria are Fe/MFI, Co/MFI and Pd/MFI, where MFI is the zeolite which is often called ZSM-5 by its commercial trade name. The lecture focuses on Fe/MFI. When prepared by traditional ion exchange from aqueous solution, the performance of Fe/MFI is very poor. Excellent catalysts are prepared, however, by a technique based on the interaction of $FeCl_3$ *vapor* with the H-form of the zeolite. This technique leads to a much higher Fe loading than wet ion exchange, without favoring the formation of oxide clusters, which are known to catalyze the undesired combustion of the reductant with oxygen. Modern characterization techniques show that dinuclear $[HO\text{-}Fe\text{-}O\text{-}Fe\text{-}OH]^{2-}$ ions are crucial sites. Studies of the reaction mechanism show that NO reduction with hydrocarbons includes three major steps:

(1) NO is oxidized to adsorbed nitro groups and nitrate ions,
(2) Reaction of these adsorbates with reductant molecules leads to amine-like structures,
(3) Adsorbed amines react with gas phase NO_x molecules forming N_2.

With ammonia as the reductant, the reaction mechanism is basically the analogue of step 3. The NOx reduction rate is much higher with ammonia than with hydrocarbons, because steps (1) and (2) are short-cut. Ammonia intercepts the oxidation product of NO already in the state of N_2O_3, so that the consumption ratio of NH_3/NO becomes 1/1.

Co/MFI, and Pd/MFI, unlike Fe/MFI or Cu/MFI, show a remarkable De-NO_x performance with methane as the reductant, presumably because methane is activated by Pd^o or Co^o

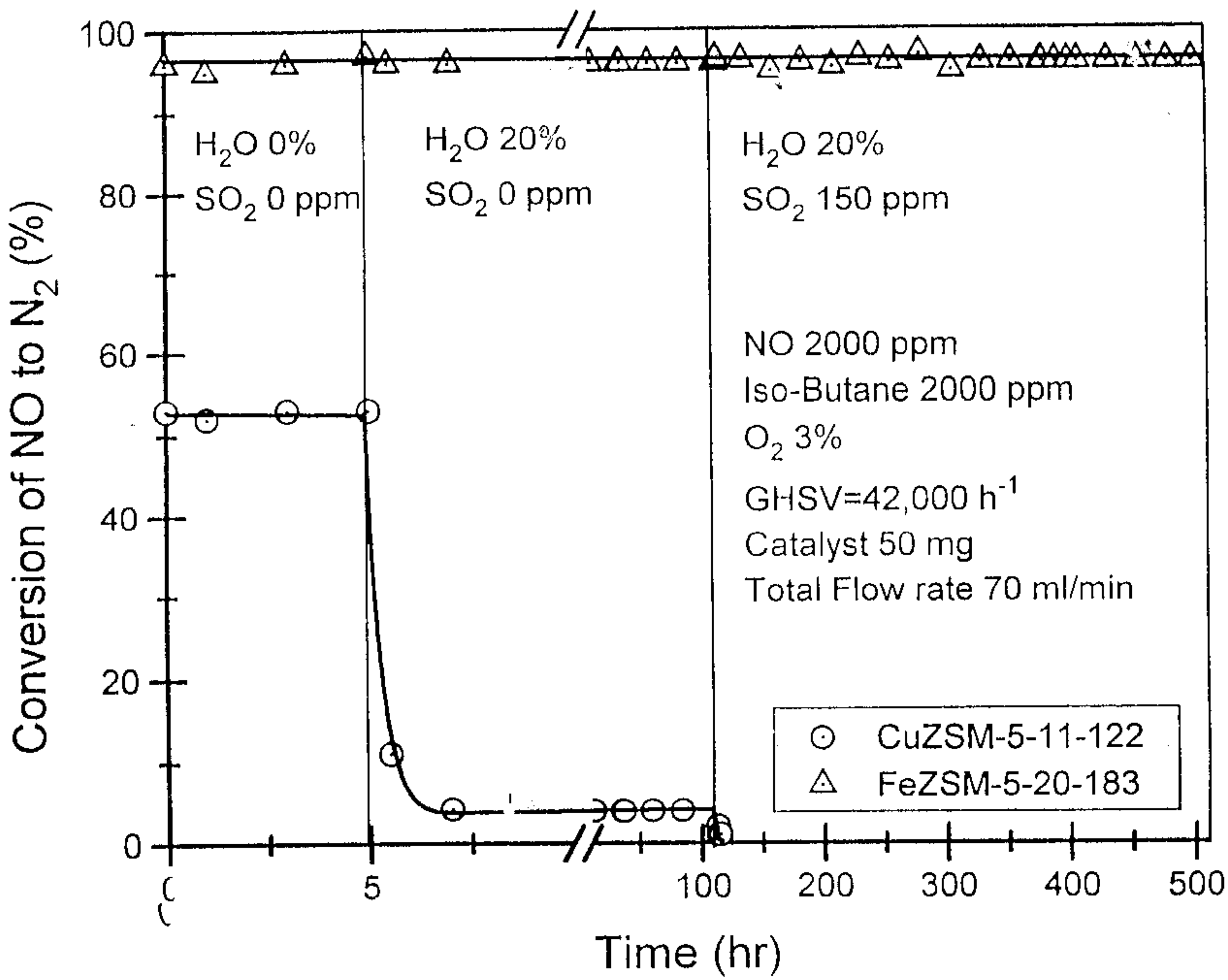
SCR of NO over ZSM-5 Catalysts



Experimental

NO = 1000 ppm, C_2H_4 = 250 ppm, O_2 = 2 %

Weight = 0.5 g, Flow Rate = 150 cc/min



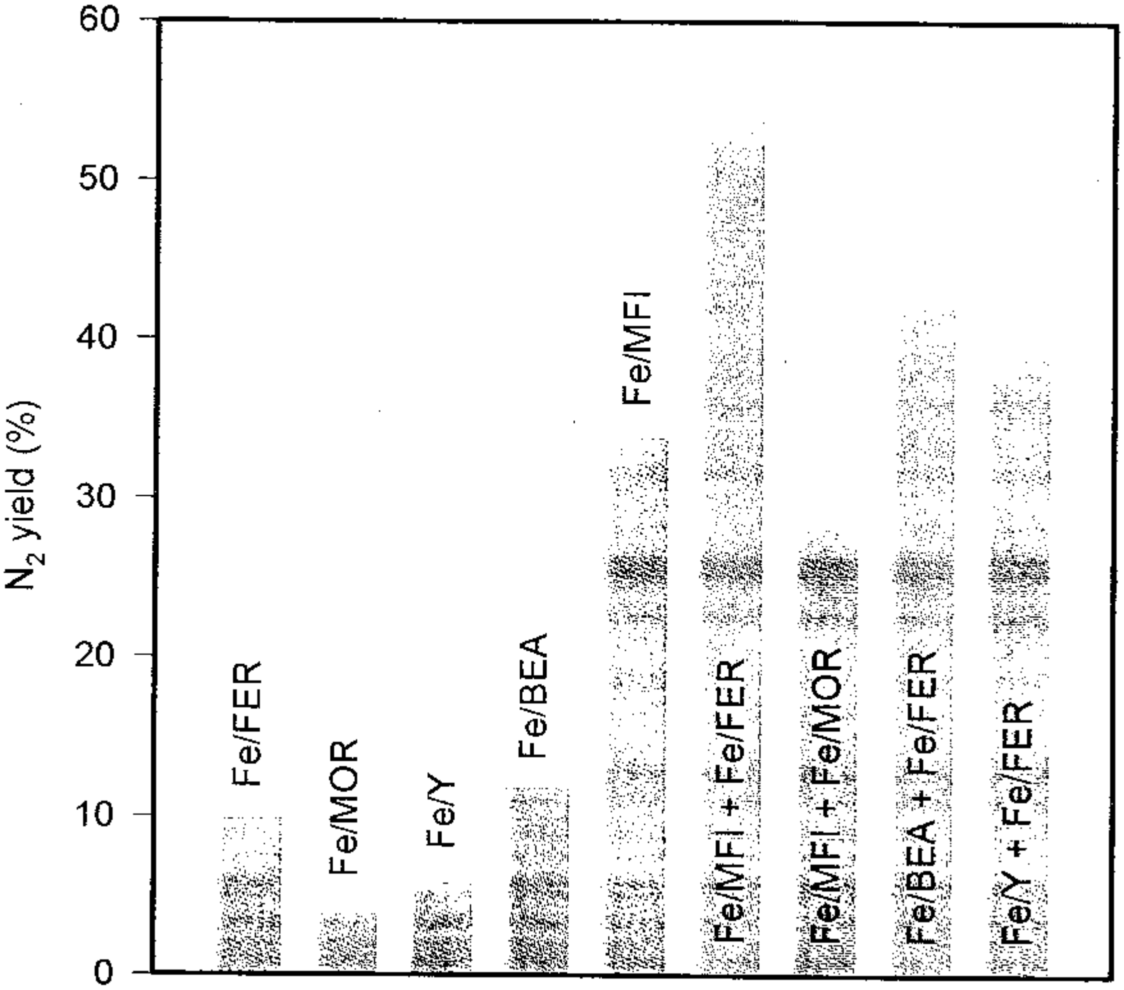
H2O 0%
SO2 0 ppm
H2O 20%
SO2 0 ppm
H2O 20%
SO2 150 ppm
NO 2000 ppm
Iso-Butane 2000 ppm
O2 3%
GHSV=42,000 h-1
Catalyst 50 mg
Total Flow rate 70 ml/min
CuZSM-5-11-122
FeZSM-5-20-183
Conversion of NO to N2 (%)
Time (hr)
0
20
40
60
80
100
5
100
200
300
400
500

Preparation of Fe/MFI with Fe/Al =1 by "sublimation method"

$$\mathbf{FeCl_3\ vapor + H^+/_{MFI} \rightarrow [FeCl_2]^+/_{MFI} + HCl \uparrow}$$

$$\mathbf{[FeCl_2]^+/_{MFI} + 2H_2O \rightarrow [Fe(OH)_2]^+/_{MFI} + 2HCl}$$

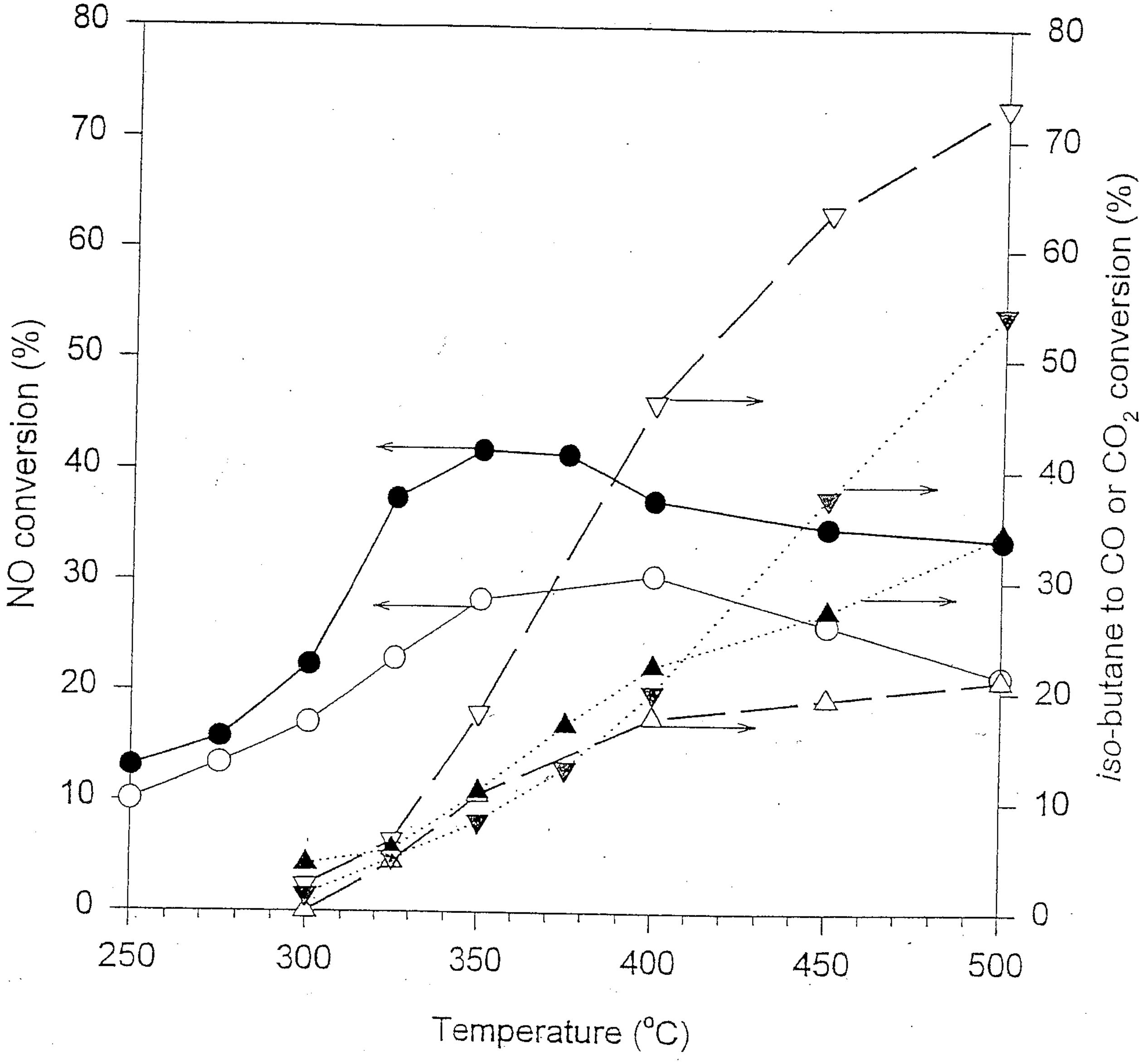
$$\mathbf{2[Fe(OH)_2]^+/_{MFI} \rightarrow [HO\text{-}Fe\text{-}O\text{-}Fe\text{-}OH]^{2+}/_{MFI} + H_2O \uparrow}$$



SCR of NO with *iso*-C_4H_{10} over Fe/zeolite catalysts

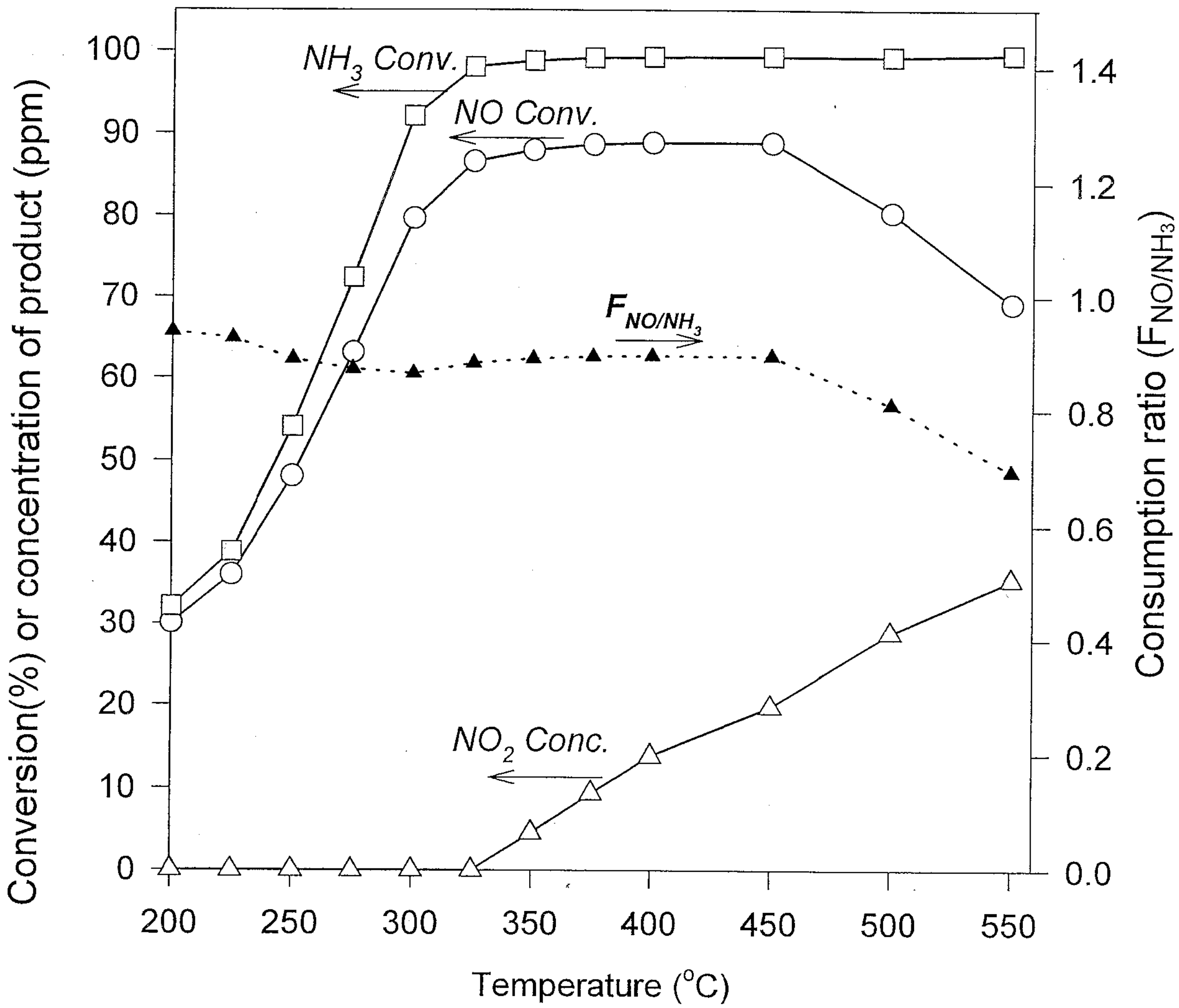
Catalyst 0.20g ([illegible]),
NO 0.2%, *iso*-C_4H_{10} 0.2%, O_2 3%, GHSV 42,000h^{-1}

Temp. 300°C, TOS 30 min



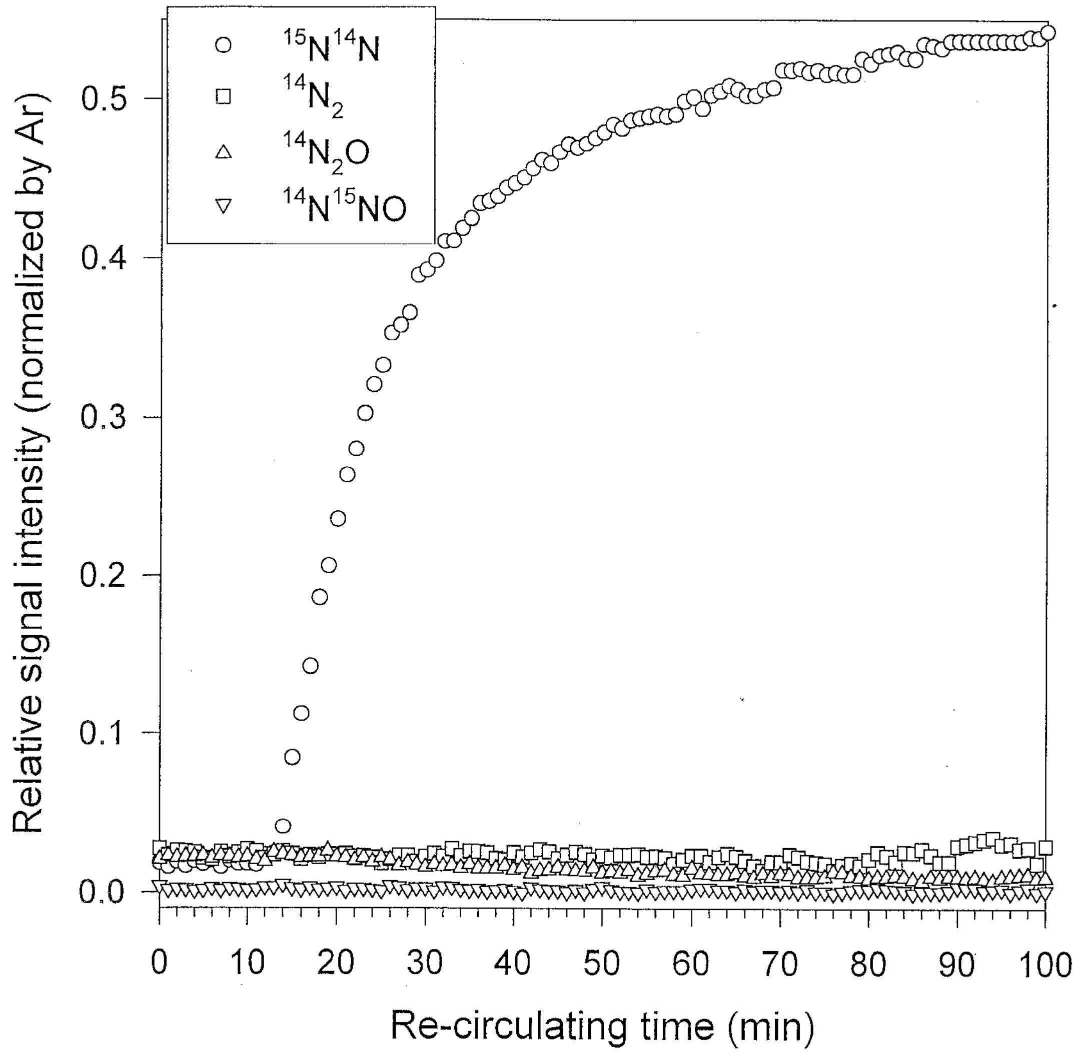
NO_x reduction with *iso*-C_4H_{10} over Fe/MFI catalyst prepared by sublimation
Feed: NO: 0.1%; *iso*-C_4H_{10} : 0.1%; O_2: 2.0%; GHSV = ~~3.6*105 h^-1^~~

$3.6 \times 10^5 h^{-1}$



NO_x reduction with NH_3 over Fe/MFI catalyst prepared by sublimation
Feed: NO: 0.1%; NH_3: 0.1%; O_2: 2.0%; GHSV = ~~3.6*105 h~~$^{-1}$

$3.6 \times 10^5 h^{-1}$



Reaction of [$^{15}N_2O_3 \Leftrightarrow {}^{15}NO + {}^{15}NO_2$] over Fe/MFI, covered with adsorbed $^{14}NH_3$ at 300 K

Reaction of N_2O_3 (gas) with adsorbed NH_3

$$^{15}N_2O_{3,\ gas} + 2\,^{14}NH_{3,\ ads} \Longrightarrow 2\,^{14}N^{15}N + 3H_2O$$

Result: $^{14}N^{15}N$: 100%
$^{14}N_2$: 0%

Considering oxidation states, this means:

$$N^{3-} + N^{3+} \Longrightarrow N_2$$

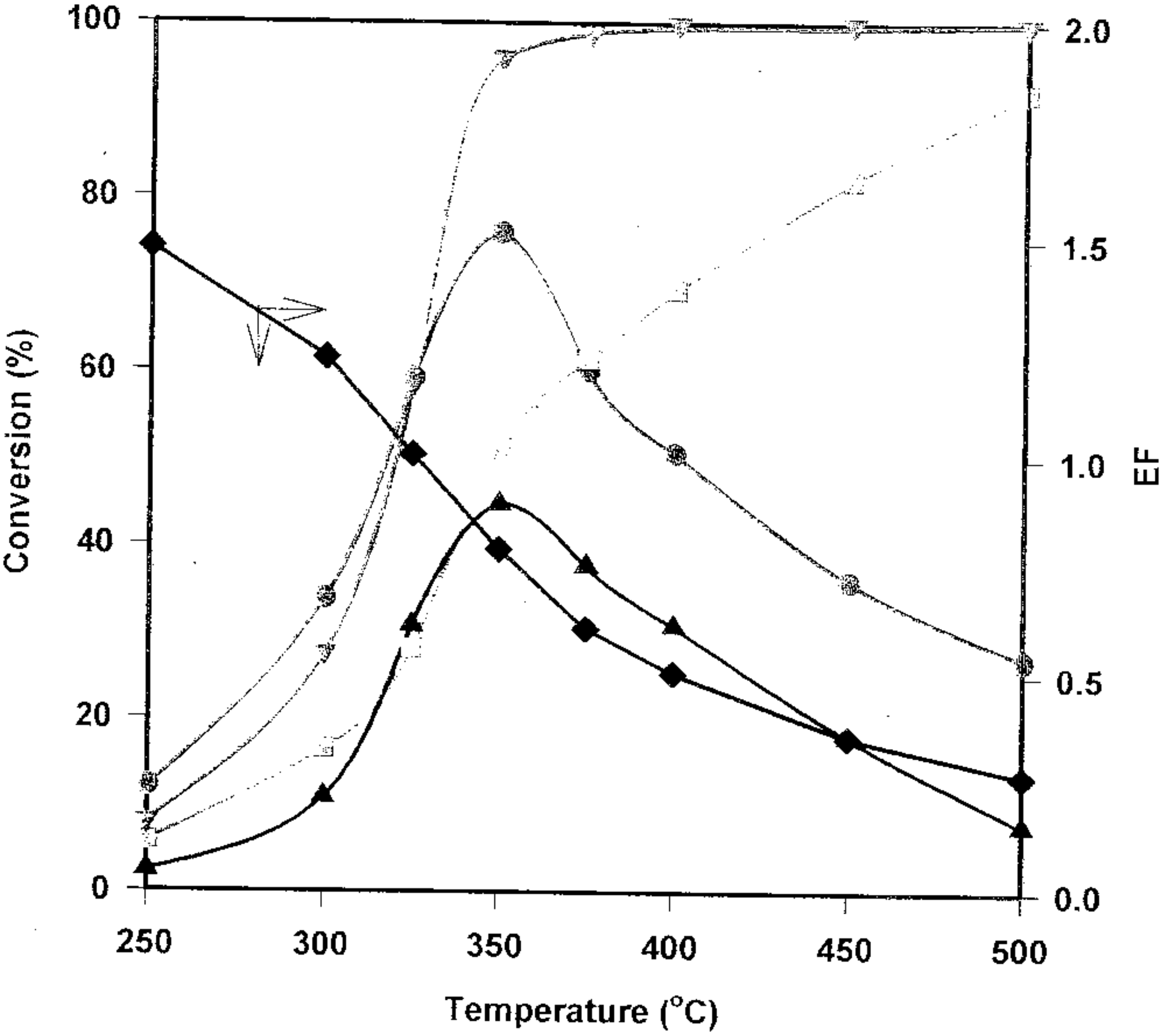
Reduction of NO_x to N_2 with ammonia over three catalysts under identical conditions

\ Catal. Temp. \	Cu/MFI	Fe/MFI (wet ion exch.)	Fe/MFI (sublim)
200°C	------	------	30%
250°C	5%	9%	48%
300°C	20%	27%	80%

Conditions:

Gas composition: 0.1% NO, 2.0% O_2, 0.1% NH_3 He to 1 bar

Space velocity: 360,000 h^{-1}

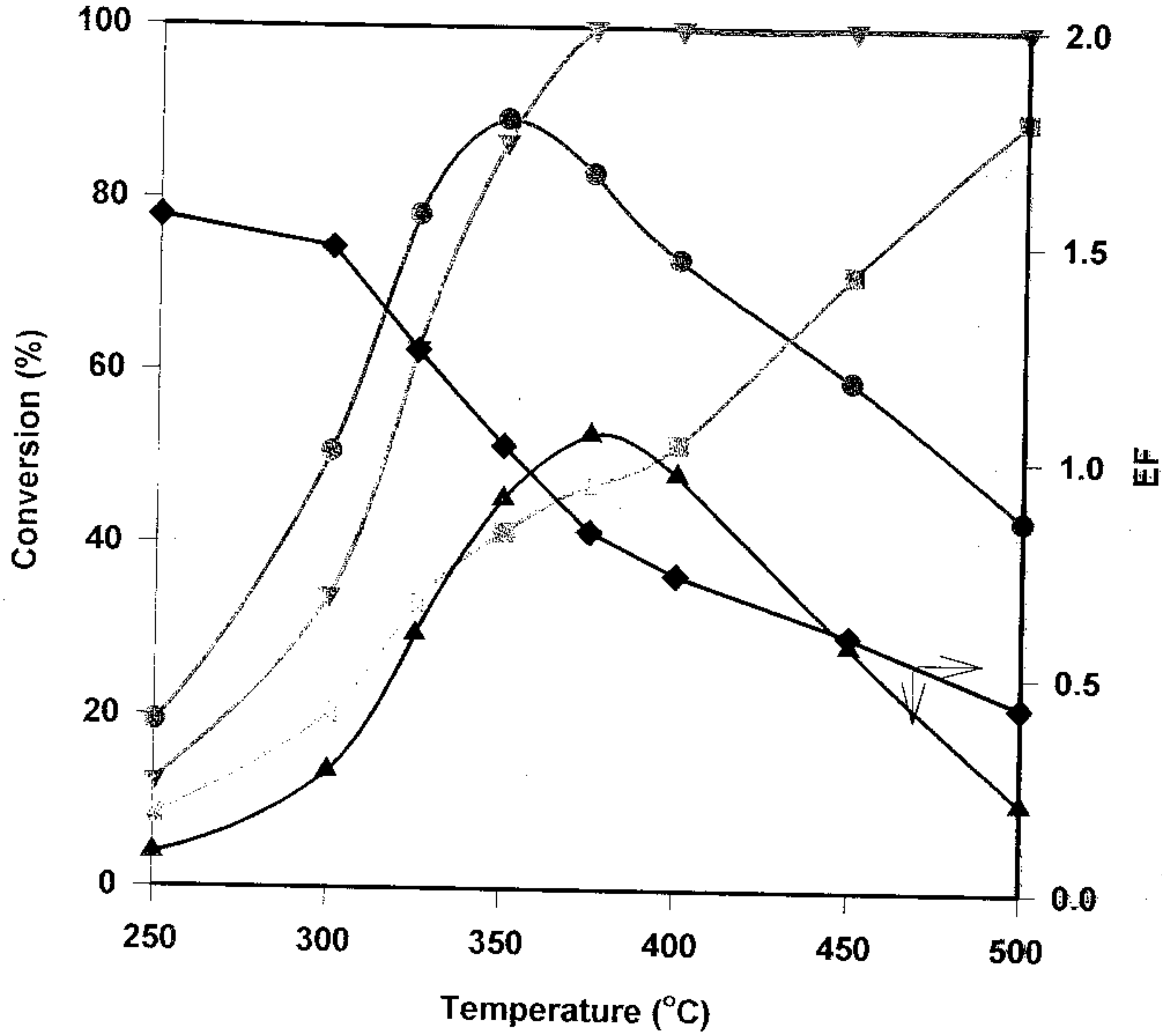


Effect of reaction temperature on the selective catalytic reduction of NO over Fe/ZSM-5(Subl.) in the absence of H_2O

NO 0.2%; i-C_4H_{10} 0.2%; O_2 3%; GHSV 42,000h^{-1}

● NO to N_2 □ i-C_4H_{10} to CO_2 ▲ i-C4H10 to CO

▼ i-C_4H_{10} ◆ effectiveness factor



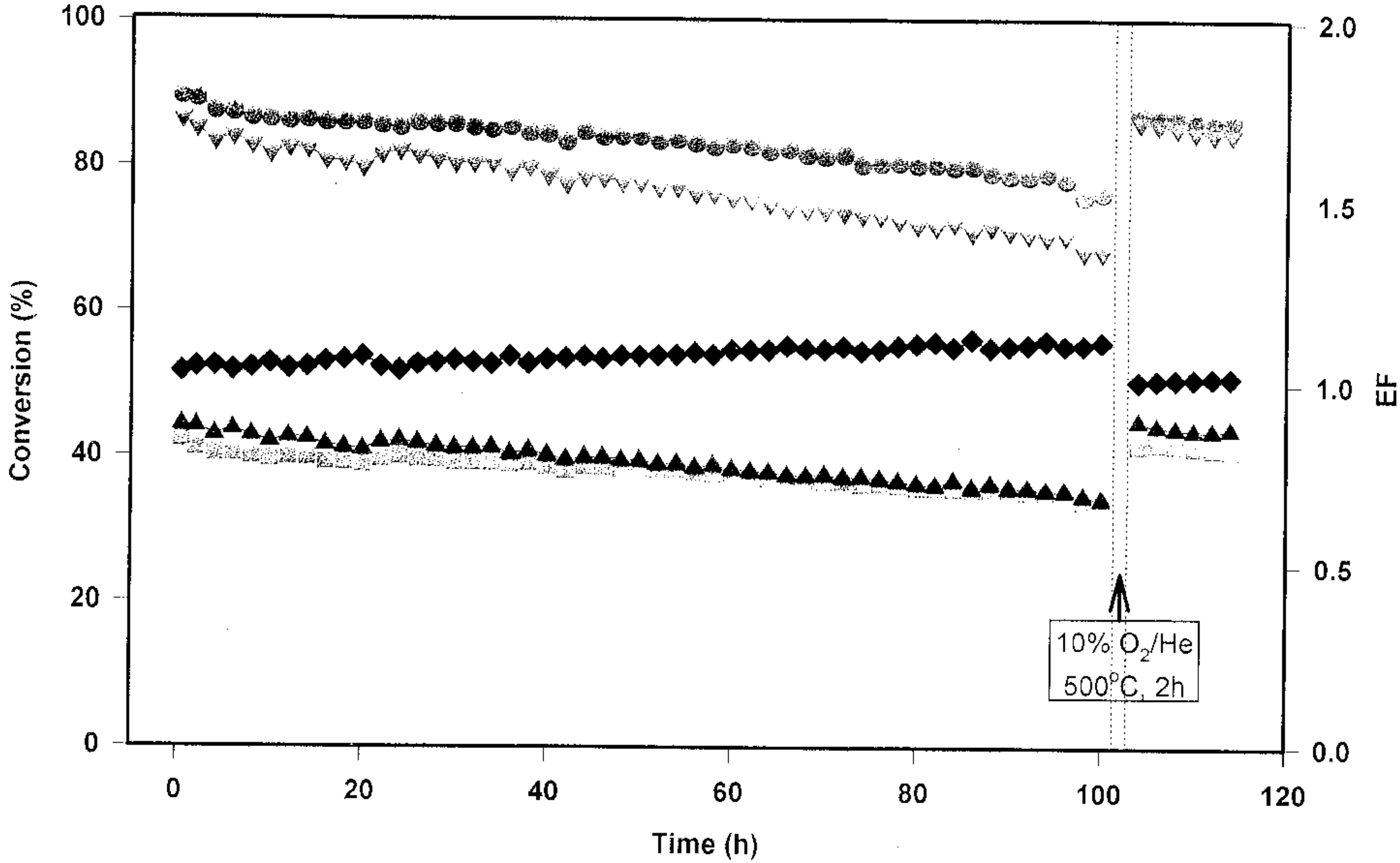
Effect of reaction temperature on the selective catalytic reduction of NO over La-promoted Fe/ZSM-5(subl.) in the presence of H_2O

NO 0.2%; i-C_4H_{10} 0.2%; O_2 3%; H_2O 20%; GHSV 42,000h^{-1}

● NO to N_2 ▒ i-C_4H_{10} to CO_2 ▲ i-C4H10 to CO

▼ i-C4H10 ◆ effectiveness factor

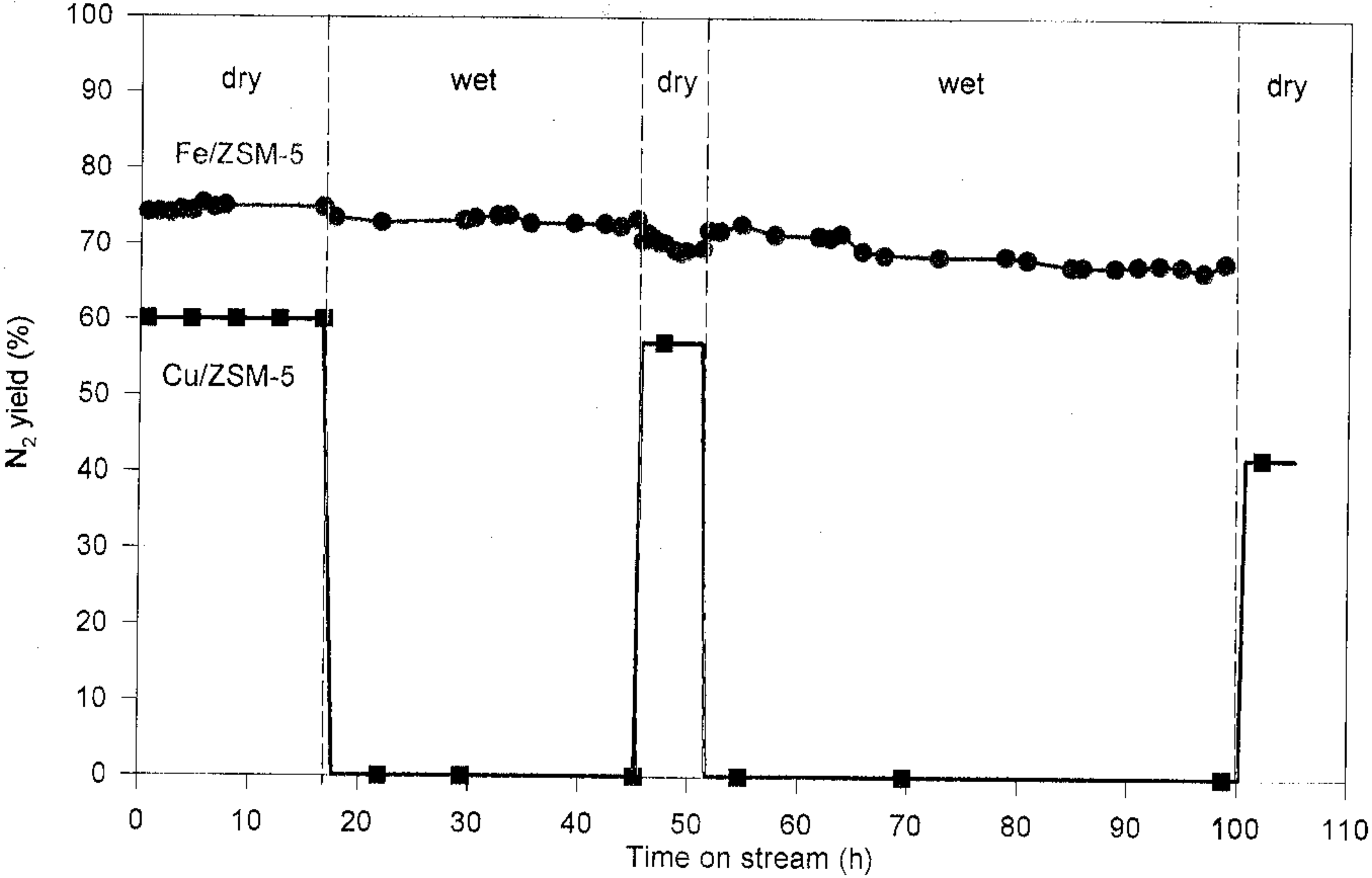
Powder catalyst, h/d=2*10^3



Stability test over La-promoted Fe/ZSM-5(subl.)

NO 0.2%; i-C_4H_{10} 0.2%; O_2 3%; H_2O 20%; GHSV 42,000h^{-1}; 350°C

NO to N_2 — i-C_4H_{10} to CO_2 — i-C_4H_{10} to CO — i-C_4H_{10} — effectiveness factor



Comparison of Cu/ZSM-5 and unpromoted Fe/ZSM-5 for NO_x reduction in dry and wet (10% H_2O) atmospheres

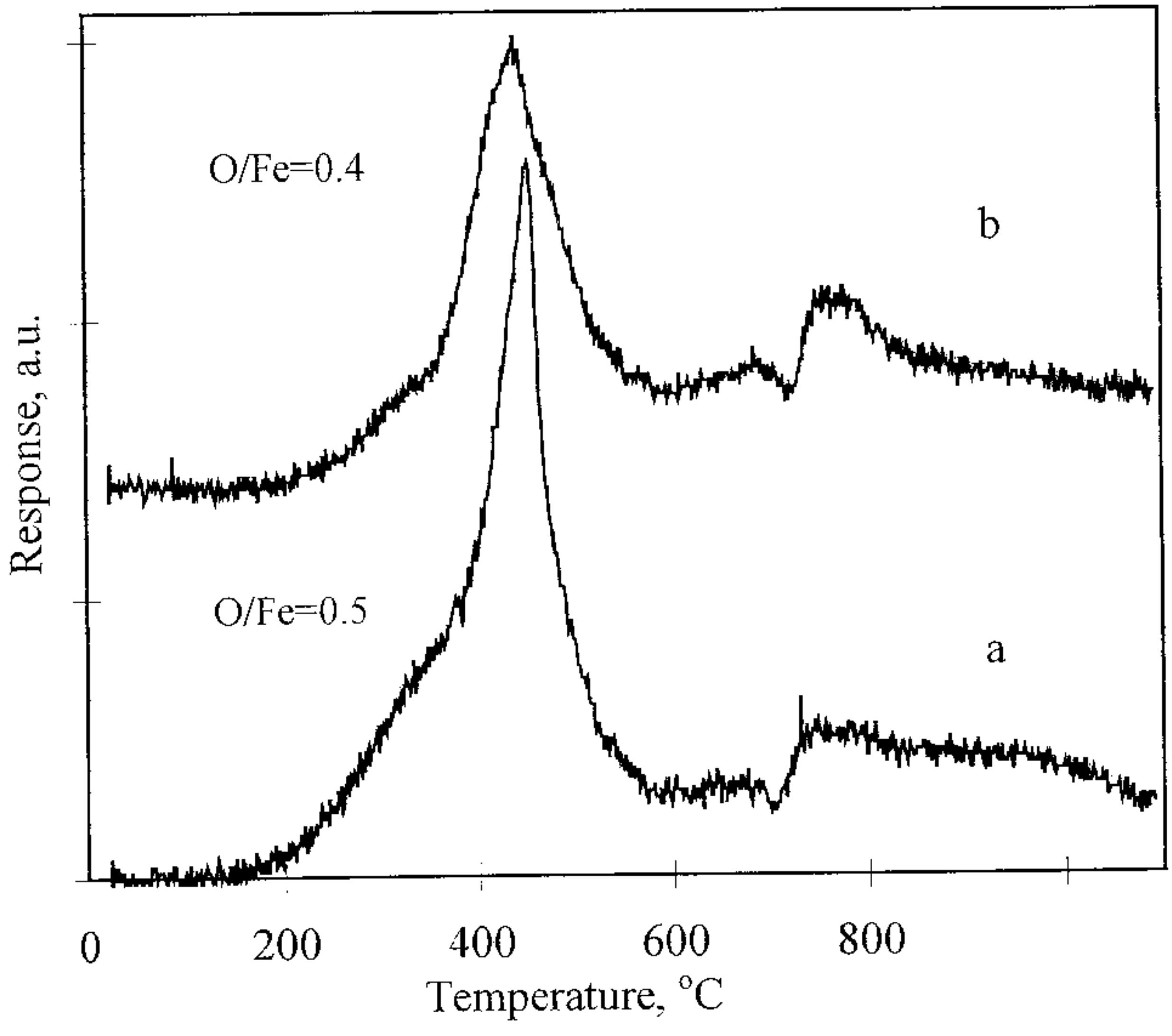
Binuclear, oxygen-bridged Fe site

$[HO\text{-}Fe^{3+}\text{-}O\text{-}Fe^{3+}\text{-}OH]^{2+}$

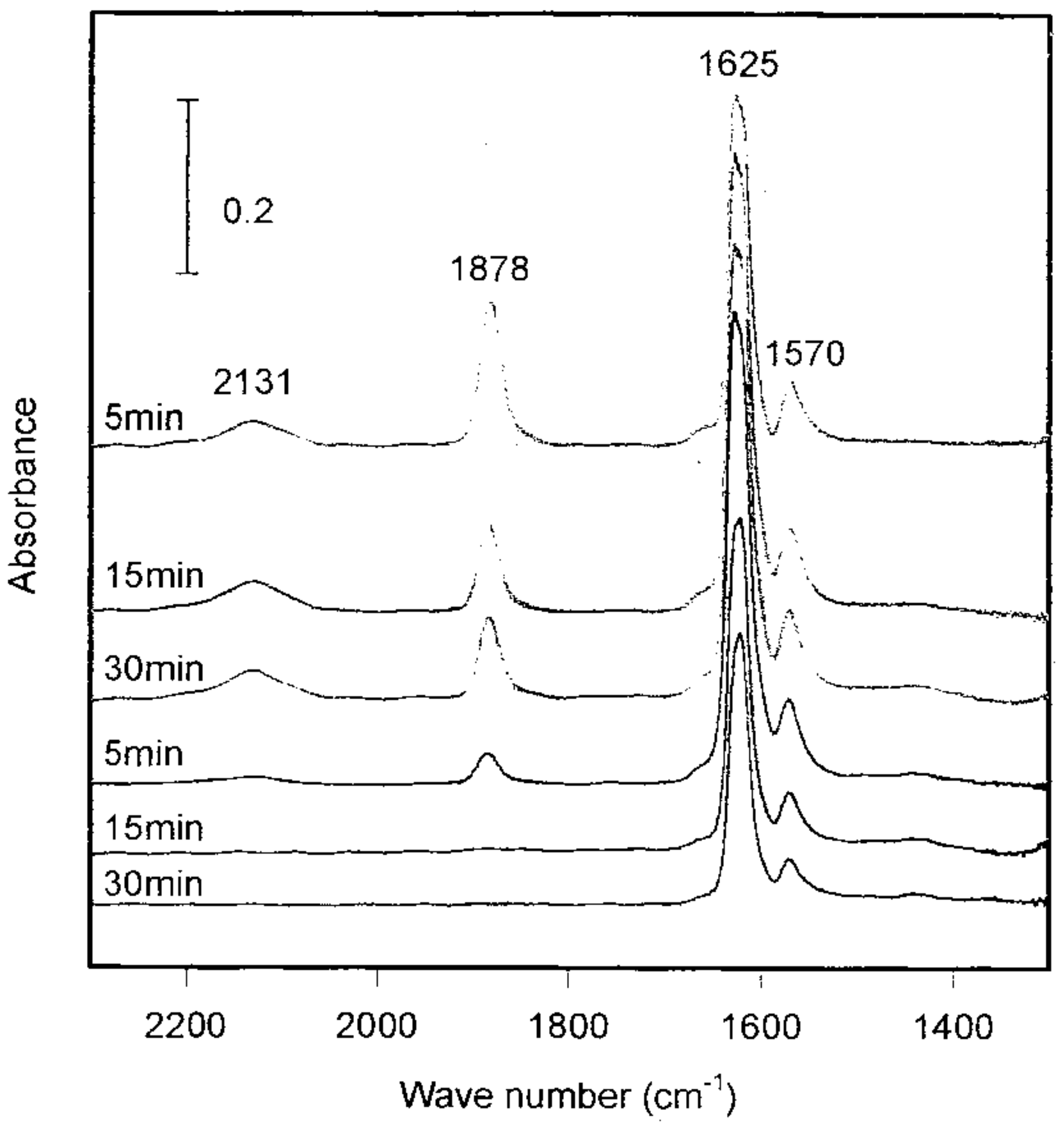
Follows from:

- loading: $Fe/Al_{lattice} = 1/1$
- TPR: $H_{cons}/Fe = 1/1$; $CO_{cons}/Fe = 1/2$
- ESR: antiferromagnetic coupling
- EXAFS (Res. Groups of Prins, Zürich and Koningsberger, Utrecht)

CO TPR of Fe/ZSM-5:
a) calcined
b) calcined and heated in flowing He to 600°C



Thermal Stability of NO_y

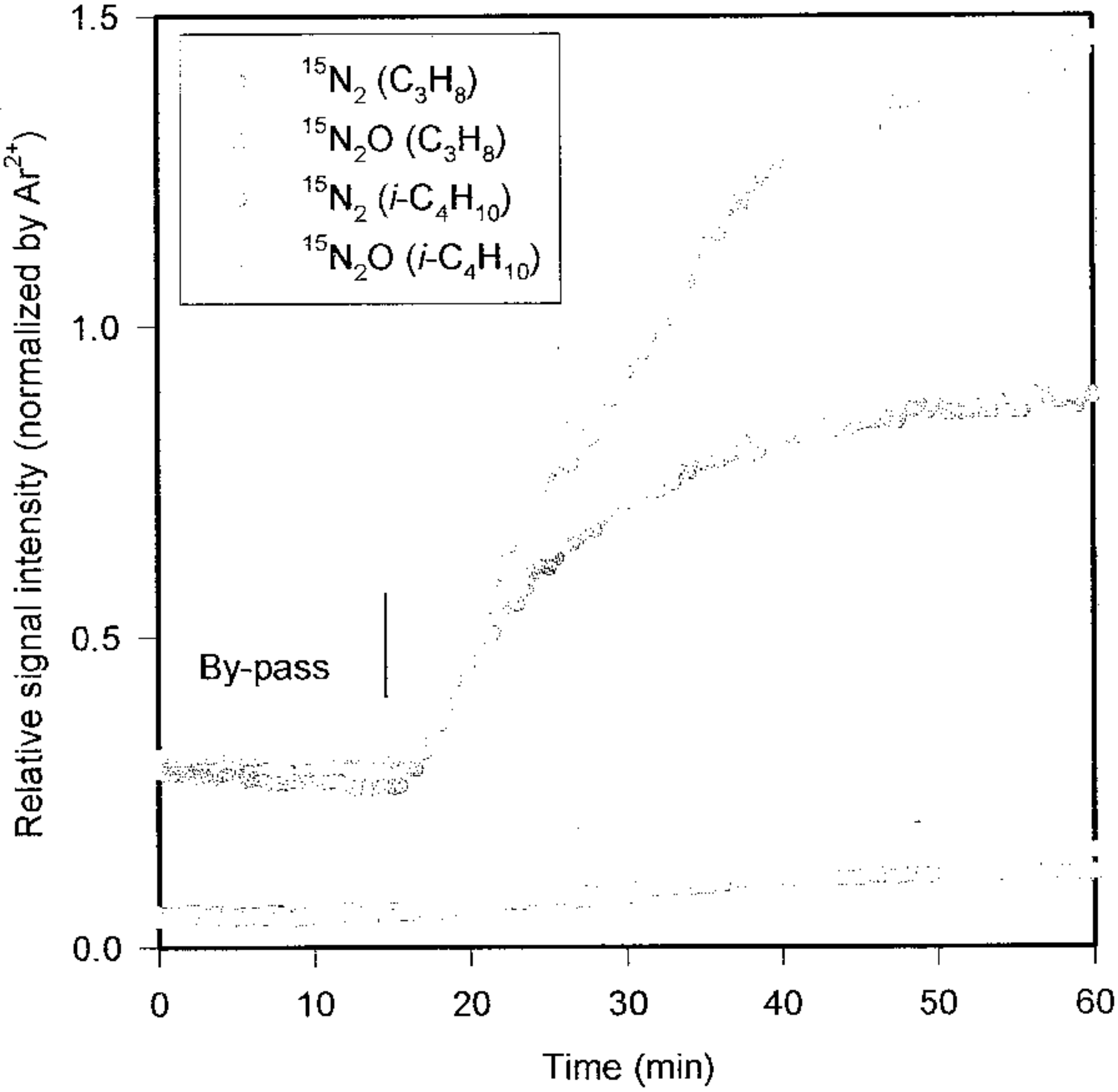


FTIR spectra of NO_y on Fe/ZSM-5 at 200°C

—— under a flow of 0.5% NO + 3% O_2 + He

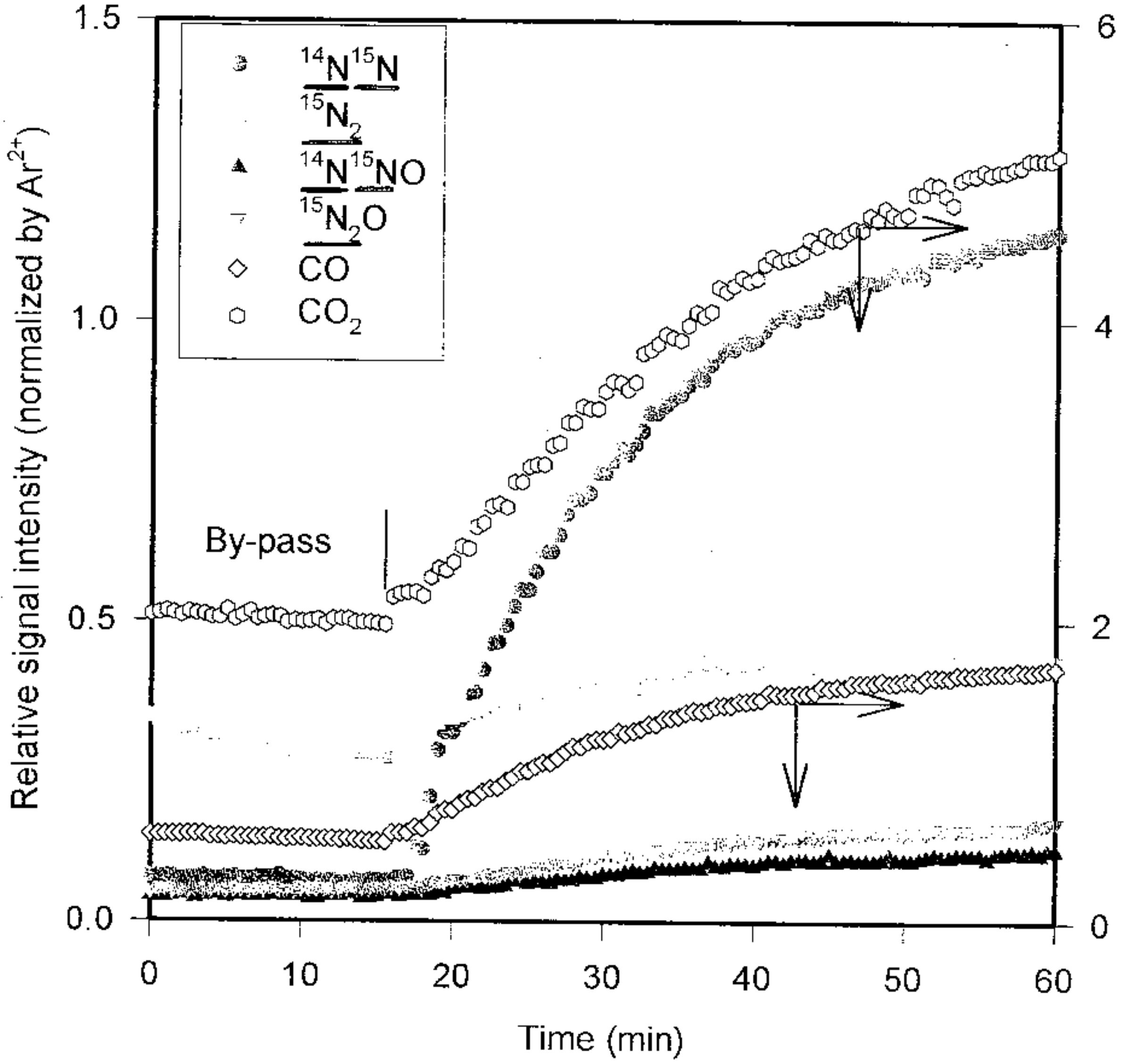
—— after exposure for 30min and purging with 3%O_2 + He

NO_2 + Deposit ==> N_2

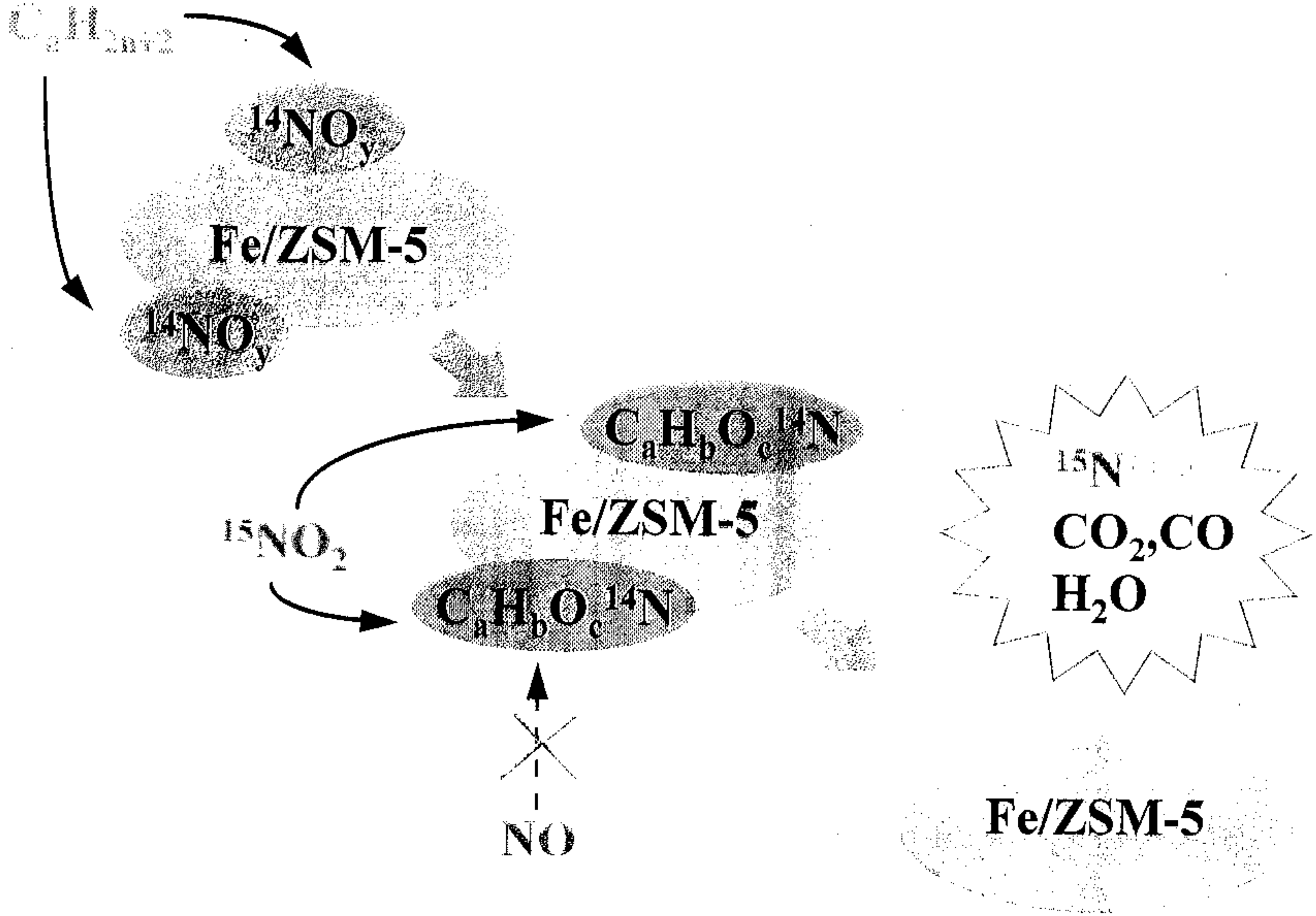


MS signal intensity upon circulating 10torr ^{15}NO + 80torr O_2 +10torr Ar over Fe/ZSM-5 covered with $C_xH_yO_z{}^{15}N$ deposit

$^{15}NO_2$ + ^{14}N-Deposit ==> $^{14}N^{15}N$



MS signal intensities upon circulating 10torr ^{15}NO + 80torr O_2 + 10torr Ar over Fe/ZSM-5 covered with $C_xH_yO_z{}^{14}N$ deposit


C_nH_{2n+2}
$^{14}NO_y$
Fe/ZSM-5
$^{14}NO_y$
$C_aH_bO_c{}^{14}N$
$^{15}NO_2$
Fe/ZSM-5
$C_aH_bO_c{}^{14}N$
NO
^{15}N
CO_2,CO
H_2O
Fe/ZSM-5

Formation of diazonium salt

from amine with NO_2:

$$\mathbf{R{-}NH_2 + 2NO_2}$$

$$\Rightarrow \quad \mathbf{[R{=}N{=}N]^+ [NO_3]^- + H_2O}$$

Decomposition of diazonium salt and hydride

transfer from *iso*-C_4:

$$\mathbf{[R{=}N{=}N]^+ [NO_3]^- + (CH_3)_3CH} \quad \Rightarrow$$

$$\mathbf{N_2 + (CH_3)_3C^+[NO_3]^- + RH}$$

Conclusions

1. **Active and Selective Fe/MFI Catalysts with Fe/Al = 1/1 can be prepared by *Sublimation.***

2. **With iso-C_4 as reductant and GHSV = 42, 000 h^{-1} these catalysts give high SCR yield at 350°C.**

3. **Water vapor in the feed *increases* SCR activity below 350°C.**

4. **Reaction mechanism includes oxidation steps ($NO \Rightarrow NO_2$) and reduction steps ($-NO_2 \Rightarrow -NH_2$).**

5. **Fe/MFI(SUB) Catalysts are even more active with NH_3 as the reductant.**

Articles published

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14 "Mono- and Multinuclear Oxo-Cations in Zeolite Cavities" Hai-Ying Chen, El M. El Malki, Xiang Wang and Wolfgang M.H. Sachtler, in "*Catalysis by Unique Metal Ion Structures in Solid Matrices; From Science to Application*" pp. 75-84; G. Centi B. Wichterlová, A.T. Bell Eds. (2001 NATO Science Series II Mathematics, Physics and Chemistry Vol 13, Kluwer Academic Publishers, Dordrecht, The Netherlands (**20010**

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23 "Characterization by EXAFS of Co/MFI Catalysts Prepared by Sublimation" V. Schwartz, R. Prins, X. Wang, W.M.H. Sachtler *J. phys Chem.* subm.

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