

# Enthalpic Stabilization of NO Oxidation Transition States by Microporous Silicates

N. Artioli<sup>1</sup>, R. F. Lobo<sup>2</sup>, E. Iglesia<sup>\*,3</sup>

<sup>1</sup> Laboratory of Catalysis and Catalytic Processes, Energy Department, Politecnico di Milano - p.za Leonardo da Vinci, 32 - 20133 Milan, Italy

<sup>2</sup> Center for Catalytic Science and Technology, Department of Chemical and Biomolecular Engineering, University of Delaware, Newark, DE 19716 USA

<sup>3</sup> Department of Chemical and Biomolecular Engineering, 201 Gilman Hall, University of California, Berkeley CA 94720-1462 USA

(\*) corresponding author: EIglesia@aol.com

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## 1 Introduction

Zeolite catalysts play essential roles in the chemical and petrochemical industries. They exhibit high surface areas, interconnected channels of molecular dimensions, and the ability to select reactants and transition states based on their size. In particular, acid and metal-exchanged zeolites catalyze NO oxidation even at ambient temperatures, in sharp contrast with the higher temperatures required on supported metal catalysts. Here, we examine the kinetic effects of reactant concentrations and the activation barriers for NO oxidation on amorphous mesoporous silica and on microporous pure silica forms of zeolites MFI, beta (BEA), and chabazite (CHA). These data show the remarkable reactivity of microporous structures of pure silicate frameworks, even in the absence of specific sites for chemical binding of reactants or transition states. These data, taken together with the measured negative activation barriers, lead us to conclude that reactivity is induced by mere physical confinement through van der Waals forces, which provide significant enthalpic stabilization for the relevant trimolecular transition states.

## 2 Experimental/methodology

MFI (Silicalite-1 SIL-1) was prepared using the fluoride method and Silicalite-1 (SIL-1D) with intracrystalline silanols was synthesized using OH<sup>-</sup> instead of F<sup>-</sup> as the mineralizing agent [1,2,3]. Pure-silica BEA was synthesized using 4,4'-trimethylene bis-N-methyl-N-benzylpiperidinium hydroxide (TMP(OH)<sub>2</sub>) as the structure director (SD), tetraethylorthosilicate (TEOS) as the silica source. Pure-silica chabazite (CHA) was prepared in fluoride media and using reported procedures [4]. Amorphous mesoporous SiO<sub>2</sub> (32-63 μm aggregates) was used to probe the reactivity of silicate surfaces in the absence of microporous confinement.

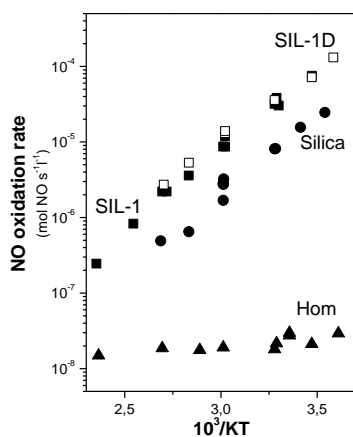
NO oxidation rates were measured on powders (125-177 μm) held onto a porous quartz frit within a U-shaped quartz tube (10 mm O.D.). Reactant mixtures (15% O<sub>2</sub>/He, 2% NO/He) and He were metered to give the desired O<sub>2</sub> (1–10 kPa) and NO (0.025–0.5 kPa) pressures. Inlet and outlet concentrations of NO and NO<sub>2</sub> streams were measured with an infrared analyzer (MKS Multi Gas Analyzer 2030, 2 cm<sup>3</sup> cell; 2 cm pathlength). Rates were measured at NO and O<sub>2</sub> conversions below 20% and plug-flow hydrodynamic formalisms were used to correct for small changes in reactant concentrations along the bed and to report rates at inlet conditions.

## 3 Results and discussion

NO oxidation rates were measured in empty reactors and in the presence of SIL-1 and SIL-1D samples (Figure 1). These pure silica zeolites showed much higher NO oxidation rates than homogeneous routes prevalent in empty reactors (by factors of 10-10<sup>4</sup>) in spite of the absence of acid or metal sites. Also amorphous SiO<sub>2</sub> (Figure 1), even though it lacks micropores, shows evident catalytic properties, indicating that mere physical adsorption on mesoporous surfaces can increase NO oxidation rates over homogeneous values. However the even higher rates observed on SIL provide compelling evidence for the stabilization of the relevant transition states by confinement within voids of nanometer size. Such catalytic enhancements become stronger with decreasing temperature as a result of negative apparent activation energy that become more so in the presence of microporous solids. The same trends were observed on BEA and CHA pure silica zeolites and the detailed data are described in Table 1.

In the temperature range investigated (283-423K), rates on all catalysts are proportional to O<sub>2</sub> pressure and second order in NO, as also found for homogeneous NO oxidation routes. These findings are consistent with elementary steps in which quasi-equilibrated exothermic formation of NO dimers is followed its kinetically-relevant decomposition by reaction with oxygen, in analogy with the homogeneous gas phase reaction [5].

We conclude from these data and the remarkable effects of physical confinement that these catalytic effects reflect the enthalpic stabilization of the relevant transition state via van der Waals forces. Physical confinement renders both enthalpies and entropies of transition states more negative relative to NO and O<sub>2</sub> gaseous reactants (Table 1), because confinement decreases the degrees of freedom of such transition states. At the near ambient temperatures of catalytic NO oxidation reactions, enthalpy effects become pre-eminent in minimizing the Gibbs free energy of activation<sup>6</sup> and lead to catalytic enhancements in the absence of specific binding sites.



**Figure 1** Forward NO oxidation rate (100 Pa NO, 5 kPa O<sub>2</sub>) on SIL-1 (■), SIL-1D (□), silica (●) and without catalytic solids (▲)

	$\Delta H_{\text{meas}}$ [kJ mol <sup>-1</sup> ]	$\Delta S_{\text{meas}}$ [J mol <sup>-1</sup> K <sup>-1</sup> ]
homogeneous reaction	-3.9	-229.0
Silica	-31.0	-270.5
BEA	-35.8	-262.4
SIL-1D	-39.5	-263.1
SIL-1	-37.5	-257.1
CHA	-41.2	-276.0

**Table 1** Measured activation energies and entropies for NO oxidation in the homogeneous gas phase and on silica, SIL-1, SIL-1D, BEA and CHA zeolites measured in the range 278-373 K

## 4 Conclusions

This work shows that purely siliceous microporous zeolites are effective catalysts for NO oxidation at near-ambient temperatures. This reaction proceeds via elementary steps reminiscent of those in homogeneous reactions, but with selective stabilization of the relevant termolecular transition states via physical confinement. Such confinement decreases the free energy of activation and lead to negative apparent activation energies, as a result of enthalpic effects that compensate for the ubiquitous loss of transition state entropies upon confinement. These data and their mechanistic interpretation provide compelling evidence for the preeminent influence of enthalpy over entropy in transition state stabilization at low temperatures, as well as one of the clearest practical manifestations of what has been described as physical catalysis.

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## References

- [<sup>1</sup>]P. Cautlet, J.L. Paillaud, A. Simon-Masseron, M. P.Soulard, *J. Comptes Rendus Chimie* (2005) 8, 245.
- [<sup>2</sup>]S Bordiga, I. Roggero, P. Ugliengo, A. Zecchina, G. Artioli, R. Buzzoni, G.L Marra., F.Rivetti, G.Spano', C. Lamberti *Journ. Chem. Soc. Dalton Trans.* (2000), 3921.
- [<sup>3</sup>]R. F H. L Koller, S. L Burkett., M. E Davis., *Journ. of Phys Chem* (1995), 99, 12588
- [<sup>4</sup>]E. A Eilertsen, B. Arstad, S. Svete, K.P. Lillerud, *Micropore. Mesopor. Mater.* (2012), 153, 94.
- [<sup>5</sup>]H.Beckers, X. Q. Zeng, H.Willner, *Chemistry-a European Journal* (2010), 16, 1506.
- [<sup>6</sup>]R.Gounder, E. Inglesia, *Acc of Chem Res* (2012), 45, 229.