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# Comment on "Direct Decomposition of $NO_x$ over $TiO_2$ Supported Transition Metal Oxides at Low Temperatures"

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In a recent paper entitled "Direct decomposition of $NO_x$ over $TiO_2$ supported transition metal oxides at low temperatures",[1] Damma *et al*. report highly promising results on the catalytic direct decomposition of NO to $N_2$ and $O_2$ at temperatures as low as 100 °C, with excellent tolerance to $O_2$, $H_2$ and $SO_2$, making the tested catalysts unique in the field of gas exhaust treatment for pollution control. Progress in this field is scarce,[2] and the development of efficient formulations for this reaction would be of the utmost interest to meet the ever more stringent emission regulations. However, as we attempted to reproduce the catalytic data of the above-cited paper,[1] we ended up with $NO_2$ as the product of NO conversion rather than $N_2$ and $O_2$, which is consistent with previous reports highlighting materials similar to those prepared by Damma *et al*. as NO oxidation catalysts.[3,4]

In our attempts to reproduce the catalytic data, we tested two samples of the Mn(20wt%)/$TiO_2$ Hombikat catalyst prepared according to the method reported by Damma *et al*., as this material exhibited the highest catalytic activity in the above-mentioned paper.[1] The first sample (here referred to as "sample 1") was prepared at LRS laboratory (France) using Hombikat $TiO_2$ (UV 100, Sachtleben Chemie GmbH). The second sample was kindly and diligently provided by one of the authors of the above-cited paper,[1] namely Prof. Smirniotis (University of Cincinnati, USA), following our request after we had informed him about the apparent discrepancy between our catalytic results obtained with sample 1 and those reported in his recent paper.[1] Prof. Smirniotis indicated that this second sample was not the one used to obtain the data reported in the original paper,[1] which was no longer available, but a newly-prepared batch (here referred to as "sample 2"). We wish to underline the constructive manner in which Prof. Smirniotis interacted with us as he prepared a fresh sample and sent it to us at his earliest convenience.

As shown in Figure A, both of the repeat Mn/$TiO_2$ samples 1 and 2 exhibit powder X-ray diffraction (PXRD) patterns similar to that of the original sample reported by Damma *et al*.,[1] displaying both peaks of anatase $TiO_2$ (JCPDS 21-1272) and of a Mn oxide phase. We actually identified the latter phase as $MnO_2$ (JCPDS 72-1984) and not $Mn_2O_3$, as indicated in the original paper by Damma *et al*.[1] The relative intensity of peaks was somewhat different, possibly due to a preferential orientation of crystallites over the measuring plates. The catalytic performance of the repeat samples in the decomposition of $NO_x$ at 200 °C as a function of the $O_2$ concentration in the feed, under conditions close to those reported in Figure 3 of the above-cited paper,[1] is given in Figure B(a) (data measured with a MKS MultiGas 2030 analyzer). The conversion of NO increases with increasing concentration of $O_2$ over both repeat samples. Although the NO conversions over the repeat samples were found to be lower than those measured over the original sample (Figure B(b)),[1] these data are consistent with the positive impact of $O_2$ reported in the above-cited paper.[1] However, NO was found to be fully converted into $NO_2$ rather than $N_2$, as illustrated in Figure C (data measured with a Pfeiffer Vacuum OmniStar mass spectrometer under 3 vol.% $O_2$) in which the $N_2$

trace remains essentially constant after contacting sample 1 with the reacting feed. The absence of $N_2$ was also ascertained by analyzing the gas flow with a µ-chromatograph (Agilent CP490).

Several hypotheses can be proposed to account for the observed discrepancy between the present catalytic data and those reported by Damma *et al*. in the above-mentioned paper[1]. Firstly, it might be that neither we nor Prof. Smirniotis succeeded in exactly reproducing the original synthesis of the Mn(20wt%)/$TiO_2$ Hombikat catalyst, which would mean that some key steps dictating the final physico-chemical properties of the latter material remain unclear. Secondly, the setup used by Damma *et al*. to perform the catalytic experiments reported in the above-cited paper[1] might have been contaminated at that time with a reducing agent ($NH_3$, for instance) having induced selective catalytic reduction (SCR) of NO to $N_2$, unbeknownst to the authors. As a matter of fact, Prof. Smirniotis previously reported on $NH_3$-SCR of NO at low temperatures over Mn-, Cr- and Cu-oxides supported on $TiO_2$ Hombikat.[5]

Whatever the origin of the discrepancy between our results and those reported by Damma *et al*.,[1] the promising catalytic performance of Mn(20wt%)/$TiO_2$ Hombikat in the direct decomposition of $NO_x$, as reported in the above-cited paper,[1] could not be reproduced by us at this point. Because of the major impact that the original paper by Damma *et al*.[1] may have on pollution control technologies, it appears crucial that the original authors reassess the validity of their data or other teams attempt to reproduce the work.

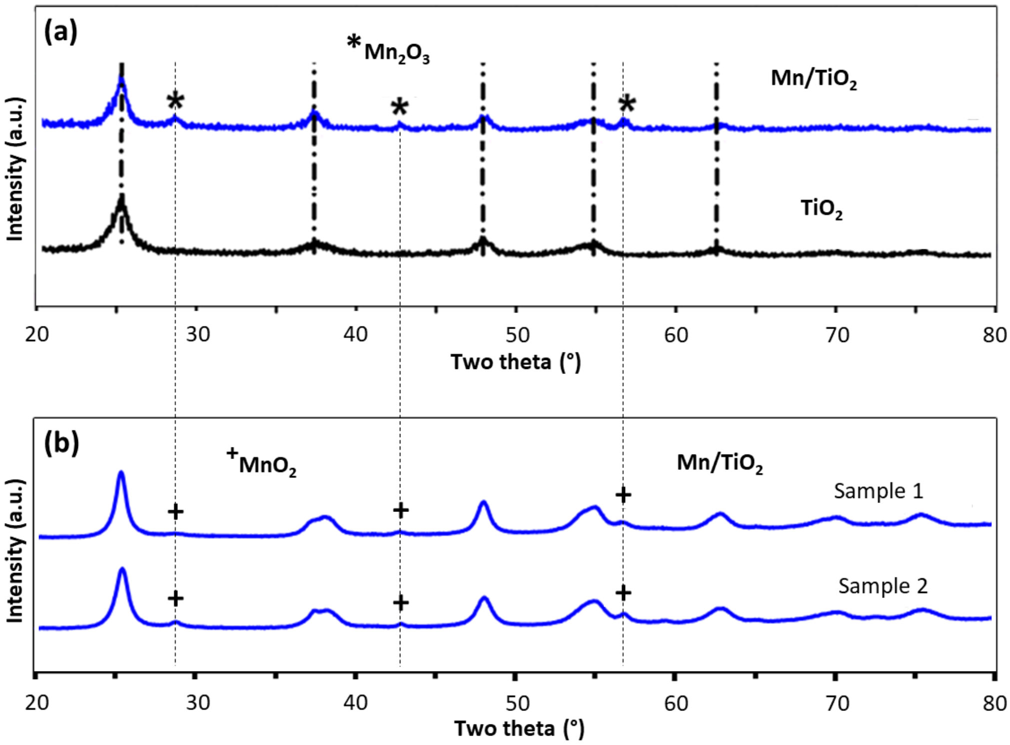

**Figure A.** (a) PXRD patterns of $TiO_2$ Hombikat and Mn(20wt%)/$TiO_2$ Hombikat adapted from Figure 1 of Damma *et al*.'s paper,[1] (b) PXRD patterns of the two newly-prepared Mn(20wt%)/$TiO_2$ Hombikat samples (sample 1 prepared at LRS, sample 2 prepared at the University of Cincinnati) tested at LRS in the catalytic direct decomposition of $NO_x$. In (a), peaks marked with a star (*) had been assigned by Damma *et al*. to $Mn_2O_3$.[1] In (b), those peaks are marked with a (+), because we actually assigned them to $MnO_2$ (JCPDS 72-1984). All non-marked peaks correspond to anatase $TiO_2$ (JCPDS 21-1272).

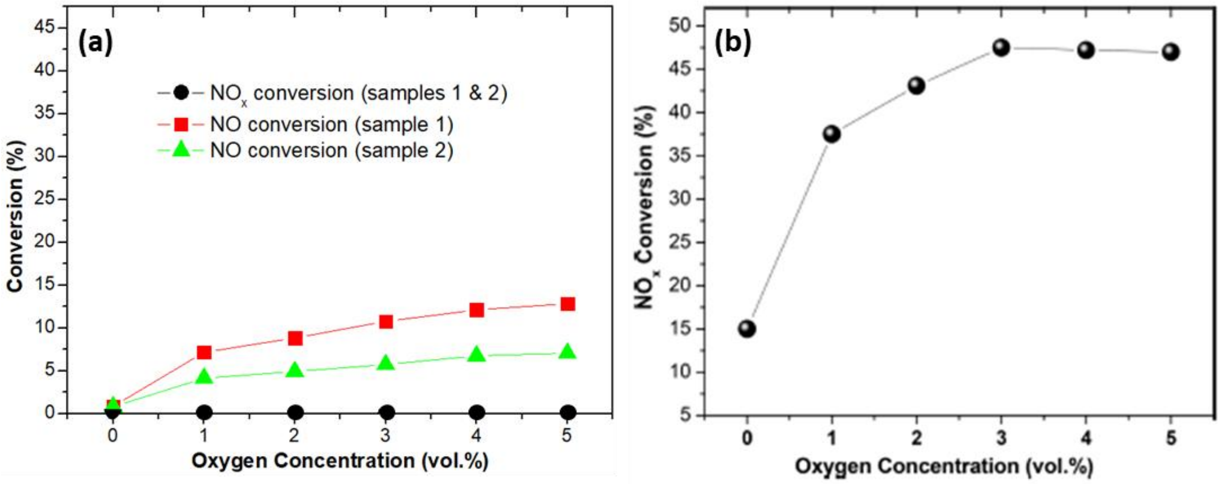

**Figure B.** (a) Catalytic performance of the two newly-prepared Mn(20wt%)/$TiO_2$ Hombikat samples tested at LRS (sample 1 prepared at LRS, sample 2 prepared at the University of Cincinnati) in the catalytic direct decomposition of $NO_x$ at 200 °C as a function of the concentration of $O_2$ (GHSV = 80000 $h^{-1}$, catalyst weight = 60 mg, total flow rate = 140 mL/min, NO concentration = 2000 ppm, Ar concentration = 8 vol.%, $O_2$ concentration = 0-5 vol.%, He is used as a carrier gas), (b) Figure 3 of Damma *et al*.'s paper.[1]

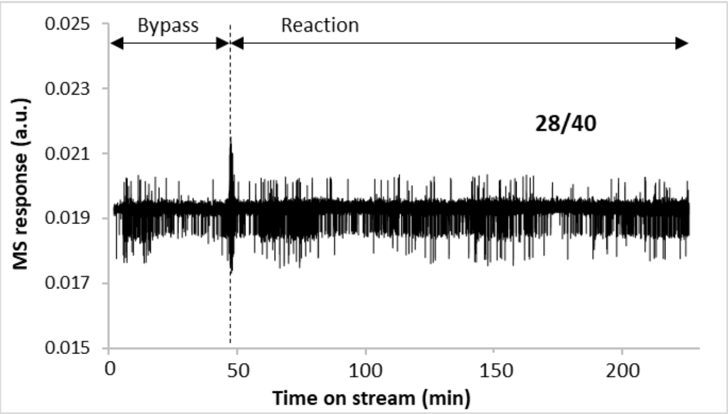

**Figure C.** Mass to charge (m/z) ratio 28 associated with $N_2$, normalized by m/z 40 associated with Ar (8 vol.% in the reaction feed), as a function of time on stream in the catalytic direct decomposition of $NO_x$ at 200 °C under 3 vol.% of $O_2$ over the Mn(20wt%)/$TiO_2$ Hombikat sample newly-prepared at LRS (sample 1 in Figures A and B). During the "Bypass" period, the reacting feed is analyzed by the mass spectrometer without being contacted to the sample.

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## Notes

The authors declare no competing financial interests.

## REFERENCES

1. Damma, D.; Boningari, T.; Ettireddy, P. R.; Reddy, B. M.; Smirniotis, P. G., Direct Decomposition of $NO_x$ over $TiO_2$ Supported Transition Metal Oxides at Low Temperatures. *Industrial & Engineering Chemistry Research* **2018,** *57* (49), 16615-16621.
2. Haneda, M.; Hamada, H., Recent progress in catalytic NO decomposition. *Comptes Rendus Chimie* **2016,** *19* (10), 1254-1265.
3. Park, E.; Chin, S.; Jeong, J.; Jurng, J., Low-temperature NO oxidation over Mn/$TiO_2$ nanocomposite synthesized by chemical vapor condensation: Effects of Mn precursor on the surface Mn species. *Microporous and Mesoporous Materials* **2012,** *163*, 96-101.
4. Tang, N.; Liu, Y.; Wang, H.; Wu, Z., Mechanism Study of NO Catalytic Oxidation over $MnO_x/TiO_2$ Catalysts. *The Journal of Physical Chemistry C* **2011,** *115* (16), 8214-8220.
5. Smirniotis, P. G.; Peña, D. A.; Uphade, B. S., Low-Temperature Selective Catalytic Reduction (SCR) of NO with $NH_3$ by Using Mn, Cr, and Cu Oxides Supported on Hombikat $TiO_2$. *Angewandte Chemie International Edition* **2001,** *40* (13), 2479-2482.