

Acoustic Wave Enhancement of Catalytic Reaction Rates over Platinum Surfaces

By Sven Kelling and David A. King

Department of Chemistry, University of Cambridge, England

Sonochemistry has been deployed in liquid and liquid-solid systems in recent years to generate rapid reaction rates and diverse chemical products (1). The underlying mechanism is based on acoustically-induced cavitation in the liquid phase, and is therefore not applicable in the gas phase – at least at low pressures.

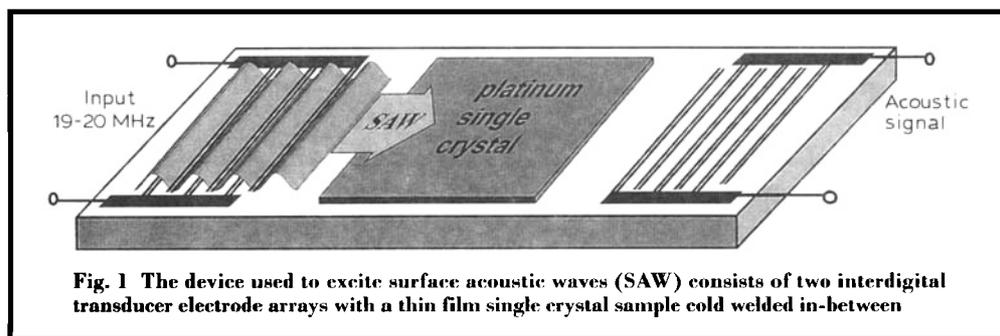
However, about five years ago Inoue and Matsukawa first reported remarkable increases in the rates of catalytic reactions at the gas-solid interface by exciting acoustic waves across the catalyst surface (2). These early studies, recently reviewed (3), were performed in a gas circulating apparatus operating at around 30 Torr with polycrystalline films as catalysts. Several important questions were raised by this work:

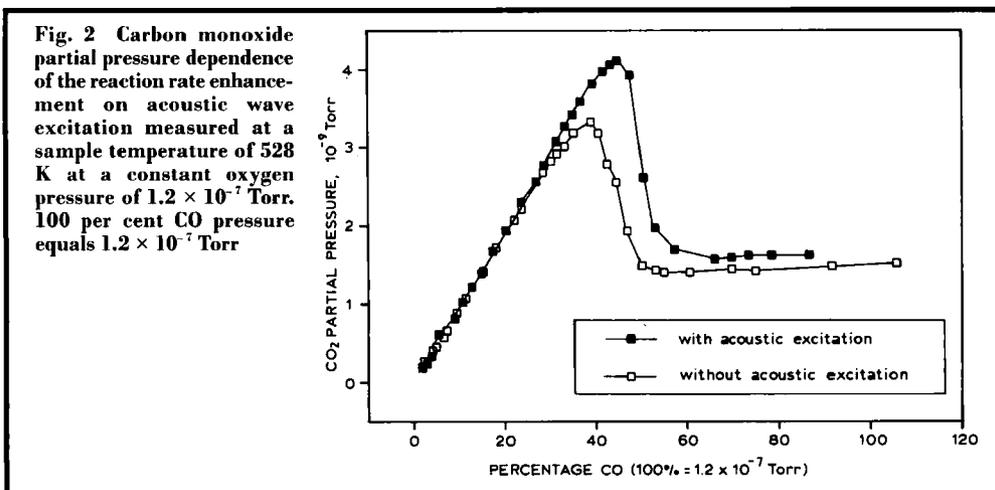
- Since significant acoustic power was dissipated at the metal surface, was the effect simply attributable to an increase in the surface temperature of the catalyst?
- At the pressures used in these experiments, reactant transport through the gas phase can become rate determining: is the effect attributable to acoustic-wave-induced mixing in the gas phase above the catalyst?
- Finally, if the effect could be attributable to a non-thermal surface process, what is the physical nature of this process?

This last question is intriguing, since the quantum of energy associated with acoustic waves in the range used ($\sim 10^7$ Hz) is about 10^7 times smaller than the barrier associated with a surface reaction.

Our approach was to tackle each of these questions in turn, using well characterised platinum single crystals in an ultrahigh-vacuum-compatible excitation system, with a base pressure of 2×10^{-10} Torr. Acoustic waves were excited across a $500 \text{ nm} \times 10 \text{ mm} \times 10 \text{ mm}$ Pt{110} crystal, and detected by an interdigital transducer (IDT) (3). The platinum crystal was grown on a suitable cut, polished and irradiated NaCl substrate and floated away from it in water, before cold-welding it onto a poled Y-cut LiNbO₃ single crystal substrate with both input and output aluminium IDTs, as shown in Figure 1. The system operates by exciting Rayleigh waves in the frequency range 19 to 20 MHz. A tunable ultrahigh amplitude and frequency resolution vector-analyser spectrometer were used both for excitation and to detect the acoustic signal transmitted across the platinum crystal surface (4). The RF power generated across the crystal during the experiments described here is of the order of 1 watt.

A novel method had to be developed to

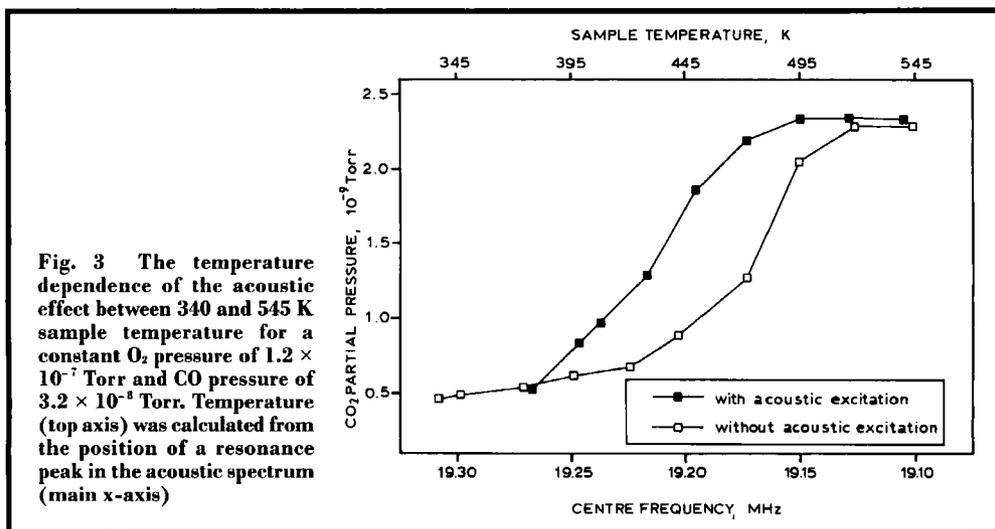




measure accurately the temperature of the metal crystal both before and after acoustic excitation. The method is based on the remarkable thermal sensitivity of the frequency at which resonance peaks occur in the acoustic spectrum. We found shifts in the region of 2 kHz per degree temperature change, which could be detected with high accuracy using our acoustic spectrometer (5). Experiments could be conducted under accurately isothermal conditions.

As a test reaction we chose CO oxidation with O₂, and the experiments demonstrated unequivocal evidence for a non-thermal enhancement

of the reaction rate at relatively low partial pressures of the reactants. The magnitude of the enhancement factor was between 1 and 4, depending on partial pressures (6). At these pressures gaseous flow is strictly molecular (there are negligible numbers of molecule-molecule collisions in the gas phase) and this result therefore also demonstrates that, at least under these conditions, this is a *surface* effect not attributable to acoustic-wave-induced mixing in the gas phase. Interestingly, it was also found that the effect was *not* dependent on the acoustic wave frequency; in particular it was not attributable



to acoustic wave resonances observed in the acoustic wave spectra, as had been suggested by Boronin and co-workers (7).

Results were compared with and without acoustic wave excitation over a wide range of crystal temperatures and CO partial pressures, at fixed O₂ partial pressure (6). From the results, samples of which are shown in Figures 2 and 3, the following observations were made. There was no acoustic excitation at low CO pressures (high O₂:CO ratios), but as the CO pressure was raised the rate of CO₂ production was found to be shifted towards a lower O₂:CO ratio with the acoustic wave excitation on. Similarly the temperature dependence of the reaction rate at constant O₂:CO ratio showed that a given reaction rate was reached at a lower temperature with the acoustic wave switched on. From Arrhenius plots, however, it was shown that the overall activation energy for the process was unaffected by acoustic wave excitation.

In further exploratory experiments we found, first, that acoustic wave excitation had no detectable influence on the clean surface Pt{110} (1 × 2) LEED pattern, although microscopic examination of samples after extensive excitation did reveal significant morphological changes. Secondly, using Reflection Absorption Infrared Spectroscopy we could detect no change in the CO absorption band from chemisorbed CO on the Pt{110} surface due to acoustic excitation; in particular, no site switching was induced.

More work, both theoretical and experimental, is required to understand the physical mechanism underlying the process. In order to examine the mesoscopic-scale distribution of adsorbate on the surface, and its possible alteration by acoustic waves, we are currently undertaking experiments with Rotermund in Berlin using a Photoelectron Emission Microscope: the coupling of low frequency, long wavelength vibrational modes into the reactive behaviour of adsorbates must presumably involve mesoscopic-scale substructures on the surface, and we hope to find direct evidence for this. In the meantime, Inoue and his group at Nagaoka in Japan have reported some very large catalytic

enhancement factors in catalytic processes at relatively high pressures (8) and, whatever the mechanism, the technological potential in the use of acoustic waves across catalyst beds deserves attention.

References

- 1 K. S. Suslick, *Science*, 1990, **247**, 1439
- 2 Y. Inoue and Y. Matsukawa, *Chem. Phys. Lett.*, 1992, **198**, 246
- 3 M. Gruyters, T. Mitrelias and D. A. King, *Appl. Phys. A*, 1995, **61**, 243
- 4 T. Mitrelias, V. P. Ostanin, M. Gruyters and D. A. King, *Appl. Surf. Sci.*, 1996, **101**, 105
- 5 S. Kelling, T. Mitrelias, Y. Matsumoto, V. P. Ostanin and D. A. King, *J.C.S. Faraday Discuss.*, in press
- 6 S. Kelling, T. Mitrelias, Y. Matsumoto, V. P. Ostanin and D. A. King, *J. Chem. Phys.*, 1997, **107**, 5609
- 7 V. N. Brezhnev, A. I. Boronin, V. P. Ostanin, V. S. Tupikov and A. N. Belyaev, *Chem. Phys. Lett.*, 1992, **191**, 379
- 8 Y. Inoue, Y. Watanabe and T. Noguchi, *J. Phys. Chem.*, 1995, **99**, 9898

Cold Platinum Cathode

Field emission displays which use cold cathodes to generate the electron beam are highly suitable for future flat panel displays as they provide complete colour capability, have a large viewing angle and are cost efficient. But until now, cold cathodes have produced an electron emission efficiency of less than one per cent.

Now, however, a team from Pioneer Electronic Corporation, Japan, has developed a cold cathode with a greatly increased electron emission efficiency using a Pt/SiO₂/Si/Al structure on a thermally oxidised silicon substrate (N. Negishi, T. Chuman, S. Iwasaki, T. Yoshikawa, H. Ito and K. Ogasawara, *Jpn. J. Appl. Phys., Part 2*, 1997, **36**, (7B), L939-L941).

The silica and silicon films, 400 nm and 5 μm thick, respectively, and platinum, 10 nm thick, were deposited onto a 300 nm thick film of aluminium, with the platinum and aluminum films used as the cathode electrodes. The electron emission was evaluated using a glass plate coated with a transparent electrode of indium-tin oxide and phosphors as anode and screen, respectively.

At room temperature and with an applied voltage of 110 V and accelerating voltage of 5 kV, an electron emission efficiency of 28 per cent was achieved together with brightness for green emission of 80 kcd m⁻², using ZnS:Cu,Al. The high emission efficiency may be closely linked to the occurrence of negative resistance.