Low-temperature hydrogen production using electrically activated catalysts

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Electrical current was flowed through indium oxide/tin oxide nanoparticles to create highly active catalysts for selective oxidation of methanol to H_2 and CO_2 with low concentrations of CO.

A new type of catalyst and catalyst activation procedure is presented for selective oxidation of methanol to H_2 and CO_2 at low temperatures. This catalyst is of interest as a way to use liquid methanol as a source of H_2 for fuel cells.[1–3] The catalyst was activated by passing electrical current through it while gas phase reactions took place.[4] The catalyst consists of a mixture of 90% In_2O_3 and 10% SnO_2 and will be referred to as indium tin oxide (ITO).

To prepare the catalyst, a mixed chloride was precipitated from an aqueous solution by adding NH_3(aq). The precipitate was filtered off, washed, and then calcined at 723 K. A mixture of 75% ITO (BET surface area 15.7 $m^2\ g^{-1}$) and 25% Al_2O_3 (surface area 61.7 $m^2\ g^{-1}$) nanoparticles was formed by milling the two powders together. The nanoparticles were deposited from a suspension onto porous (0.2–0.3 mm pores) honeycomb Al_2O_3 structures (3.8 × 1.3 × 0.6 cm). The two ends of the honeycomb were coated with a conductive paste, before the catalyst was deposited, so that electrical connections could be made. The honeycomb was placed in a circuit with a constant-current dc power supply. The deposited catalyst was reduced in 5–20% H_2 at 575 K; this lowered the resistance and changed the catalyst color to light blue. A chromel–alumel thermocouple (0.2 mm diameter) was inserted into a honeycomb pore near the center to record the temperature during reaction. The product and feed streams were analyzed by gas chromatography. The mass balances were checked by calculating the H/C and O/C atomic ratios for the products. Typical average deviation from the feed ratios were 5% for the H/C ratio and 9% for the O/C ratio.

Results presented here were obtained on several honeycomb structures. Methanol oxidation was carried out in three ways.

(1) The catalyst temperature was raised by thermally heating it with a small ceramic heating element directly attached to the honeycomb. No current passed through the catalyst.
(2) Electric current was passed through the catalyst, and ohmic heating raised the catalyst temperature.
(3) After the catalyst was used for reaction with the electrical current, the current was decreased to zero. The catalyst temperature was then increased using the attached ceramic heating element.

Fig. 1 shows the methanol conversion and selectivity for H_2 formation as a function of temperature during oxidation over an ITO catalyst honeycomb for the first two types of experiments. The selectivity for H_2 was defined as the molar ratio: $H_2/(H_2 + H_2O + CH_2O)$. These experiments used a 20% O_2/80% He gas feed and a MeOH/O_2 feed ratio of 1.3. When the reduced catalyst was heated by the ceramic heater alone, the reaction products were only detected above 473 K, and the same rates and selectivities were obtained when raising or lowering the temperature. The main products were H_2, CO_2, and H_2O. As the temperature increased, the rate of H_2 formation and the selectivity to H_2 both increased.

As shown in Fig. 1, the catalyst was much more active at a given temperature when an electrical current was passed through it.[4] At 373 K, methanol conversion was >5%, and by 473 K, methanol conversion was 80%. The H_2 selectivity increased with temperature as the conversion increased, so that the rate of H_2 formation increased dramatically above 425 K. The H_2 production rate was higher at all temperatures with electrical current through the catalyst than for the thermally heated catalyst. At 525 K, the rate of H_2 production was 50 times higher than seen with thermal heating. As with thermal heating, H_2, CO_2 and H_2O were the main products. Only slightly more than 1% of the products were CO at 532 K, and a much smaller percentage were CH_2O. The percentage of H_2 in the reactor effluent at 500 K was 17.5% on a wet basis; the current was 0.15 A and the voltage was 95 V dc.

A turnover frequency (TOF, the number of molecules reacting per surface site per second) was estimated using the BET surface area of the ITO powder. At 450 K, where the conversion was *ca.* 50%, the TOF was 0.15 s^{-1}. Since the reaction was run for 30–60 min or longer at each temperature, this TOF shows that each site reacted with a large number of methanol molecules without deactivation.
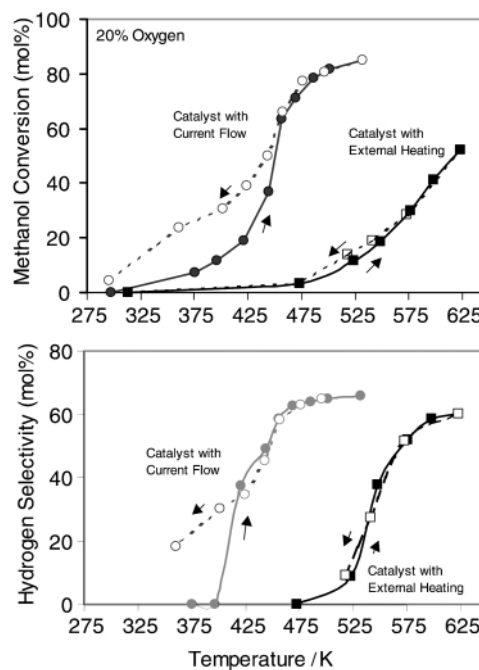

Fig. 1 (a) Percent methanol conversion and (b) selectivity [$H_2/(H_2 + H_2O + CH_2O)$] for H_2 formation *vs.* temperature for oxidation of methanol on an indium oxide/tin oxide catalyst. The results for thermal heating were obtained as the catalyst temperature was increased (—, ■) and decreased (-----, □). The results when an electrical current flowed through the catalyst were obtained as the current (and temperature) was increased (—, ●) and decreased (-----, ○).

After the catalyst temperature had reached 525 K, the current was decreased in increments, and steady state measurements were made at several temperatures. Interestingly, the catalyst was more active at a given temperature during these measurements than when the current increased. That is, after the catalyst was exposed to the reaction mixture at 525 K with electrical current, it was more active at lower temperatures.

When 60% O_2/40% He was used as the gas feed instead of 20% O_2/80% He, the selectivity to H_2 was lower. After the catalyst had been exposed to the reaction mixture at 625 K with the electrical current, it was active for methanol oxidation even at 360 K with the current turned off. The percentage of H_2 in the reactor effluent was 12% on a wet basis with zero power. The reaction was reproducible and stable for at least 48 h, suggesting that this is not a transient artifact. When the electrically activated catalyst was heated thermally, it was much more active than when the original catalyst was heated thermally. Moreover, as shown in Fig. 2, the methanol conversion at low temperatures was higher for the activated catalyst (heated thermally) than for the catalyst with current flow. The selectivity to H_2 formation (Fig. 2) was higher at all temperatures after the catalyst had been activated by electrical current.

The products from electrically activated ITO catalysts were predominantly H_2, H_2O and CO_2. On 1% Pd/ZnO, Cubeiro and Fierro[5] reported selective oxidation of methanol to H_2 and CO_2 at 503–543 K, though more than 20% of their product was CO. On $Cu_{40}Zn_{55}Al_5$ catalysts, Alejo et al.[6] reported selective H_2 formation and low CO formation for MeOH oxidation near 500 K, but the O_2/MeOH feed ratio was only 0.06, so conversions were 20% or lower.

Previous studies have used electrical current to activate heterogeneous catalysts, but the present process is quite different. In the previous studies, a voltage applied across a solid electrolyte caused reversible increases in catalytic activity and dramatic changes in selectivity of metals supported on the electrolyte. These results have been explained using the non-Faradaic electrochemical modification of catalytic activity (NEMCA) effect.[7] For oxidation reactions, the rate increased by up to a factor of about 100 when an electrical current was applied. For most systems, NEMCA was attributed to electrochemically controlled back spillover of oxygen from a solid electrolyte such as yttrium-stabilized zirconia, and the rate enhancement depended dramatically whether the voltage was positive or negative. When the current was turned off, the NEMCA effect disappeared. The mechanism on the ITO catalyst appears to be quite different from the NEMCA effect for several reasons: (1) reversing the electrical leads to the catalyst did not change the reaction kinetics or selectivity, (2) when the current was shut off, the ITO catalyst was still active, and (3) reaction takes place on the ITO semiconductor oxide deposited on a porous insulating substrate and not on a metal deposited onto a solid ion conducting electrolyte.

X-Ray photoelectron spectroscopy analysis was carried out on samples before and after reduction and after electrical activation in the methanol/air mixture. A reduced sample that was reacted in the methanol/air mixture at elevated temperature was also analyzed. A Physical Electronics Quantum 2000-1 system was used with electron and ion guns for charge neutralization. The reduced sample and the electrically activated sample had surface compositions that were 85–90% In and 10–15% Sn, and the sample reacted without electrical activation was 95% In. The bulk composition of the catalyst was 90% In, so surface enrichment does not appear to be responsible for the enhanced activity of the electrically activated catalyst. Small binding energy shifts (0.6 eV) toward more reduced states were observed for the indium peak on two out of three locations on the electrically activated catalyst, but the peak shifts could not be unambiguously assigned. Thus, the electrically activated catalyst may be reduced more than the H_2 pretreated catalyst.

The enhanced rate on the electrically activated catalyst could perhaps be due to reaction on local regions of the catalyst that were hotter than the temperature measured by the thermocouple. While we did not observe any hot spots on the visible external surfaces of the catalyst, such hot spots may exist internally. Alternatively, at contact points of the catalytic particles, the grain boundaries may be hot because of the ohmic heating. Given the nanostructured form of the catalysts, these microscopic hot spots may be localized. As shown in Fig. 1, the temperature to obtain 50% conversion is 200 K lower for the catalyst with current flow. If only a fraction of the catalyst is at a higher temperature than the average, then the temperature difference would have to be more than 200 K to yield the same conversion as when the entire catalyst was 200 K hotter. Since the ITO catalyst is expected to be a good thermal conductor (e.g. SnO_2 has a thermal conductivity similar to graphite) such large temperature differences over the short distances between particle contact points seems unlikely. Moreover, localized heating cannot explain why the conversion and selectivity are lower on raising the current than on lowering the current. Nor would localized heating explain why the catalyst was active when the current was off after electrical activation.

More extensive studies are necessary to determine the reasons for the enhanced activity, low carbon monoxide concentration in product gas, and other unusual effects observed when current is passed through the catalyst. The method of using electrical current to activate heterogeneous catalysts may be broadly useful to many other chemical reactions. In preliminary studies we have observed electrically activated ITO to catalyze methane reforming and the remediation of toluene and acetone.

Fig. 2 (a) Percentage methanol conversion and (b) selectivity [H_2/(H_2 + H_2O + CH_2O)] for H_2 formation vs. temperature for oxidation of methanol in 60% O_2 on an indium oxide/tin oxide catalyst. The results were obtained when the current through the catalyst was increased (—, ●) and decreased (-----, ○). The point where the power was turned off is indicated. After the current was shut off, the catalyst temperature was raised thermally (—, ■) and then decreased again (-----, ○).

Notes and references

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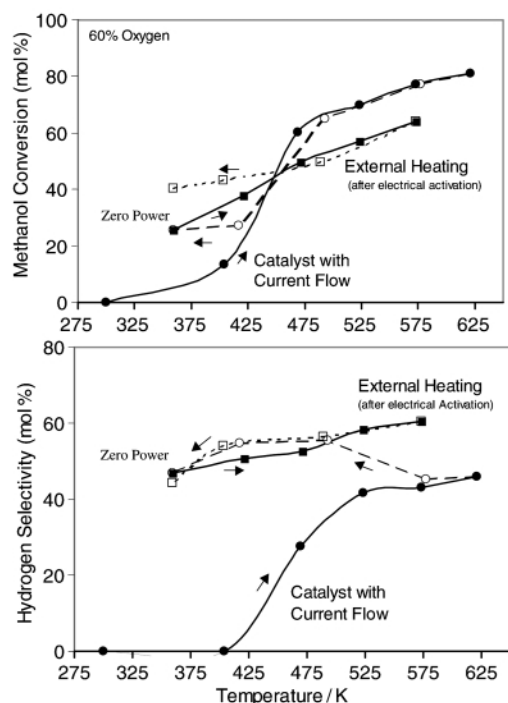7 C. G. Vayenas and S. Bebelis, *Catal. Today*, 1999, **51**, 581.