# Selective Catalytic Reduction of $NO_x$ in Lean Burn Engine Exhaust by Highly Active Pt Supported on V-impregnated MCM-41

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On the Pt/V/MCM-41 catalyst with 1 wt% Pt and 4 wt% V, the maximum conversion of NO reduction into $N_2 + N_2O$ by $C_3H_6$ was about 73%, which was 10% higher than on 1 wt% Pt/silica, and this maximum conversion was maintained over a temperature range of 70 °C between 270 and 340 °C.

Nitrogen oxides ($NO_X$) present in lean-burn and diesel engine exhaust containing excess $O_2$ have yet to be effectively converted to innoxious $N_2$. For the selective reduction of this lean $NO_X$ by hydrocarbon, supported Pt is considered to be a promising catalyst because it is active at low temperature and is both (hydro)thermally stable and resistant to $SO_2$.[1,2] It is, however, only active over a narrow temperature range and a large part of the $NO_X$ reacted on it goes to $N_2O$, a gas which contributes to the greenhouse effect and causes ozone layer destruction.[3] Pt therefore requires a new support material or a promoter to overcome the shortcomings.

We investigated various metal-substituted MCM-41 molecular sieves (V-, Ti-, Fe-, Al-, Ga-, La-, Co-, Mo-, Ce- and Zr-MCM-41) and vanadium oxide-impregnated MCM-41 to assess their potential as new support materials for Pt in the reduction of NO with $C_3H_6$. These metals have all been reported to be able to be incorporated into the silicate framework of MCM-41.[4–6] For comparative purpose, alumina (Strem Chem., 185 $m^2 \cdot g^{-1}$) and silica (Davison 952, 310 $m^2 \cdot g^{-1}$) were also tested as a Pt support.

Figure 1 shows the activity test results for the catalysts in which 1 wt% Pt was impregnated on these metal oxides using platinum acetylacetonate dissolved in toluene. 0.1 g of the catalyst was loaded in a quartz tubular reactor, and tested under the 140 $cm^3 \cdot min^{-1}$ (42000 GHSV) of total gas flow consisting of 2000 ppm NO, 2700 ppm $C_3H_6$, 3% $O_2$ in He. Metal-substituted MCM-41 (Si/metal = 50 on the basis of metal precursors) and pure MCM-41 were synthesized by a similar method to that of Grubert et al.[4] Vanadium oxide-impregnated MCM-41 (V/MCM-41) was prepared by impregnating MCM-41 in a toluene solution of vanadium acetylacetonate, followed by calcining at 550 °C after drying.

Of the investigated catalysts, Pt supported on V/MCM-41 (Pt/V/MCM-41) having 1 wt% Pt and 4 wt% V showed the best activity for the reduction of NO by $C_3H_6$. The peak conversion of NO into $N_2 + N_2O$ ($C_N$) was about 73%, a 10% higher value than that on Pt supported on silica, which has been known to be the best Pt support for the reduction of NO by $C_3H_6$.[7] Moreover, the peak $C_N$ of Pt/V/MCM-41 was maintained over a temperature range of 70 °C from 270 to 340 °C, dissimilarly to a general trend on Pt-based catalysts wherein the peak $C_N$ decreases sharply after attainment. In the case of Pt/silica and alumina we can see this trend in Figure 1(a).

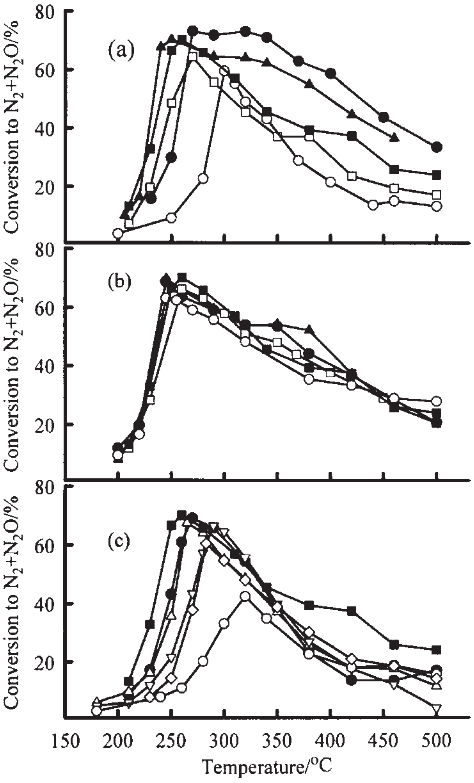

**Figure 1.** Conversion of NO into $N_2 + N_2O$ on Pt supported on (a) V/MCM-41 (●), V-MCM-41 (▲), silica (□), alumina (○); (b) Ce-MCM-41 (●), Mo-MCM-41 (▲), Ti-MCM-41 (□), Zr-MCM-41 (○); (C) Al-MCM-41 (●), Fe-MCM-41 (△), Ga-MCM-41 (▽), La-MCM-41 (○), Co-MCM-41 (◇); (a) (b) (c) MCM-41 (■).

In tests under the presence of water or $SO_2$, it was ascertained that the activity of Pt/V/MCM-41 was not significantly reduced. Vanadium oxide is a main catalytic component used for the reduction of $NO_X$ from a stationary source by $NH_3$. V as well as Pt have been well known to be resistant to $SO_2$.[8] Pt/V/MCM-41 consisted of Pt and oxides of V and Si was not deactivated greatly under the 500 ppm of $SO_2$. Figure 2 shows the effect of water on $C_N$. At 250 °C, at which $C_3H_6$ was not yet depleted by the reaction, $C_N$ increased with increasing amounts of water, and then decreased gradually at water concentrations above 3.7%. Although $C_N$ decreased at high water concentration, even at 8%

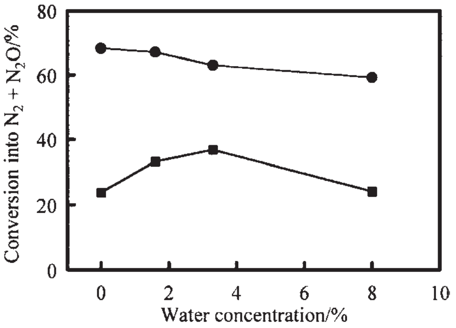

**Figure 2.** Effect of water on the conversion of NO into $N_2 + N_2O$ on Pt/V/MCM-41 at 250 (■) and 350 °C (●).

water the activity of the Pt/V/MCM-41 catalyst was higher than at 0% water. On the other hand, at 350 °C, at which $C_3H_6$ was completely depleted, the activity of Pt/V/MCM-41 decreased with the concentration of water, but only slightly; $C_3H_6$ was consumed 100% at temperature where the $C_N$ reach its maximum in all the catalytic reductions of NO investigated and $CO_2$ was the only gaseous product from $C_3H_6$.

Meanwhile, Pt supported on pure MCM-41 (Pt/MCM-41) showed slightly better activity than Pt/silica, as has been reported by Schießer et al.[9] When metal (V, Ti, Fe, Al, Ga, La, Co, Mo, Ce and Zr) was substituted into this MCM-41 framework and Pt was impregnated on it (Pt/metal-MCM-41), the catalytic activity decreased, rather than increased, by the incorporation of the metal except for V, although the Ce- and Mo-substituted catalysts had somewhat higher activity than the unsubstituted Pt/MCM-41 in the limited region between 320 and 420 °C. Of the investigated metals, only V enhanced the activity of Pt/MCM-41 in a large temperature range when incorporated into MCM-41.

Metal is generally incorporated into both the inside and surface of the pore wall of MCM-41 during the hydrothermal synthesis of MCM-41. The incorporation into the pore wall surface is attained through bonding with a surface hydroxyl group of MCM-41. The enhanced activity of Pt/V-MCM-41 was thought to be due to this pore wall surface-incorporated V species or others present on the pore wall surface of MCM-41 as in Pt/V/MCM-41, because Pt/V/MCM-41 had higher activity than Pt/V-MCM-41.

Presented in Figure 3 are the conversions of NO into $N_2$ ($C_{N2}$) on the Pt/V/MCM-41, Pt/MCM-41 and Pt/silica catalysts. The $C_{N2}$ curves for Pt/MCM-41 and Pt/silica showed two peaks, meaning that at least two different reaction routes and/or active sites of the catalysts were involved. We can see that in the $C_{N2}$ curve of Pt/V/MCM-41 the first peak (a low temperature peak) was shrunken; conversely, the height and the width at half–height of the second peak were markedly increased compared to those for Pt/MCM-41 and Pt/silica. By virtue of this enlarged $C_{N2}$ peak, the selectivity toward $N_2$ on Pt/V/MCM-41 became higher than on Pt/MCM-41 and Pt/silica at temperatures above 300 °C. $C_3H_6$ used as a reductant was consumed completely by the reaction at the corresponding first peak position for each catalyst. Hence, $C_3H_6$ was not present above 270 °C on Pt/V/MCM-41. It is noticeable that the $C_{N2}$ is higher in this condition than in the presence of unconverted $C_3H_6$. A peculiar reactional feature observed on Pt/V/MCM-41, absent on other catalysts, was that the NO concentration read by a $NO_X$ analyzer oscillated considerably during the reaction at isothermal condition above 300 °C. The oscillation of NO concentration was much severer with increasing temperature, and then damped after showing a maximum around 400 °C. This phenomenon might be caused by a structural change or reduction–oxidation cycle of the catalyst, or a periodic variation of the amount of activator or deactivator such as cokes.[10] We are conducting further study to elucidate the oscillation characteristic and the reaction mechanism for the reduction of NO on Pt/V/MCM-41.

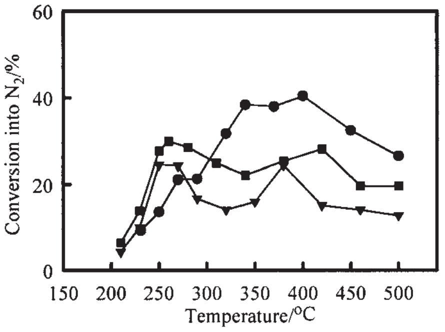

**Figure 3.** Conversion of NO into $N_2$ on Pt/V/MCM-41 (●), Pt/MCM-41 (■) and Pt/silica (▼).

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