

Novel Palladium on Magnesium Oxide Catalysts for Alkane Aromatisation

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High activity and selectivity in methylcyclopentane aromatization is observed with chlorine-free Pd/MgO catalysts prepared from organometallic precursors.

Derouane and coworkers¹ have reported that enhanced aromatization yields in the *n*-hexane reforming reaction are observed with Pt supported on Al³⁺-stabilized MgO.

Here we report the remarkable activity and selectivity in methylcyclopentane aromatization of non-acidic Pd/MgO catalysts obtained from chlorine-free organometallic precursors. Methylcyclopentane has been chosen as a probe molecule since it can differentiate between monofunctional and bifunctional reaction pathways.² Secondly, its strong tendency to form hard coke residues makes it a more demanding probe than *n*-hexane for long-term stability studies.

Reagent-grade MgO (Carlo Erba RPE) was refluxed in doubly distilled water for 2 h, heated in flowing oxygen from 25 to 500 °C and then evacuated ($P = 10^{-3}$ mbar) at this temperature for 5 h. KL zeolite (Linde LTL type) was heated in flowing argon from 25 to 400 °C. For liquid phase impregnation, a weighed amount of the organometallic precursor was dissolved in a suitable solvent {H₂O for [Pd(NO₂)₂(NH₃)₂]; CH₂Cl₂ for [Pd(η³-C₃H₅)Cl]₂} and added to the MgO support under argon. The resulting slurry was then dried *in vacuo* ($P = 10^{-3}$ mbar) at room temp. Chemical vapour deposition (CVD) of [Pd(η³-C₃H₅)(η⁵-C₅H₅)] was used for both MgO and KL supports, following the methodology developed in our laboratory.³ Metal loading was 2 wt% in all samples. Reduction of the supported organometallics was done in the catalytic reactor, by flowing hydrogen at 500 °C for 1 h. Catalytic studies of methylcyclopentane (MCP) reforming were performed in a continuous-flow microreactor, at 500 °C and 1 atm, using a H₂/MCP ratio of 20. Reaction products were analysed by on-line GC.

Table 1 reports benzene yields and selectivities for a series of Pd/MgO catalysts as a function of the organometallic precursor. The high activity and selectivity of the two chlorine-free Pd/MgO catalysts for benzene formation, indicating a monofunctional (metal-only) reaction pathway, is evident both at the beginning of the catalytic run, and after 300 min on stream. In particular, the highest activity and selectivity are shown by the material prepared *via* CVD of the [Pd(η³-C₃H₅)(η⁵-C₅H₅)] precursor. The presence of chloride ions in the precursor, instead, results in a dramatic loss of activity and selectivity to benzene.

The reported⁴ high aromatization activity of Pt supported on Mg(Al)O was explained on the basis of a strong metal-support interaction (SMSI) yielding an electron-rich metal

surface. The same kind of metal-support interaction can be invoked in the chlorine-free Pd/MgO catalysts, involving electron transfer from the strongly basic O²⁻ surface ions to the metal surface. The first consequence of such interaction is the 'anchoring' of the metal to the support, preventing sintering of the supported Pd clusters to large particles. A highly dispersed metal surface is a primary requirement to achieve high selectivity to benzene in hydrocarbon reforming.⁵ Secondly, the desorption of aromatic products is favoured on an electron-rich surface, minimizing the risk of possible condensation by-reactions, leading to polycyclic aromatic hydrocarbons formation, and eventually to coke deposition. At the same time, undesirable C-C fission reactions by carbene mechanisms should be reduced.⁶ In this way, catalyst stability should be greatly enhanced, reducing the need for frequent catalyst regeneration, as in the traditional bifunctional catalysts. First results on simulated regeneration cycles (sequential O₂-H₂ treatments at 500 °C) show the absence of any significant decrease in their catalytic performance.

The Pd/MgO catalyst derived from the [Pd(η³-C₃H₅)Cl]₂ complex shows, instead, low activity and selectivity to benzene. In addition, significant amounts of cracking by-products are also formed from MCP. This unexpected behaviour, resembling that of a typical bifunctional reforming catalyst, is to be related to the formation of acidic MgCl sites, as the consequence of the surface chemistry of chlorine-containing organometallic complexes.⁷

The comparison of magnesium oxide with basic KL zeolite as support for Pd reforming catalysts is noteworthy, since enhanced aromatization yields are reported with Pt supported on basic KL zeolite.⁸ A Pd/KL catalyst has thus been prepared *via* CVD of the volatile [Pd(η³-C₃H₅)(η⁵-C₅H₅)] precursor, in order to avoid any unwanted formation of protonic acidity.³ However, its catalytic performance, particularly benzene yield, is significantly lower than the analogous catalyst supported on MgO (Table 1).

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Table 1 Benzene yield and selectivity in MCP reforming at 500 °C and 1 atm

Metal precursor	Support	Yield; selectivity ^a	
		TOS ^b = 30	TOS = 300
[Pd(NO ₂) ₂ (NH ₃) ₂] ^c	MgO	60.6; 74	53.3; 73
[Pd(η ³ -C ₃ H ₅)Cl] ₂ ^c	MgO	8.0; 50	4.2; 50
[Pd(η ³ -C ₃ H ₅)(η ⁵ -C ₅ H ₅)] ^d	MgO	68.6; 75	60.7; 76
[Pd(η ³ -C ₃ H ₅)(η ⁵ -C ₅ H ₅)] ^d	KL	21.5; 65	14.2; 70

^a Expressed as mol%. ^b TOS = time on stream/min. ^c *Via* solvent impregnation. ^d *Via* CVD.

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