

Alkali Metal–Naphthalene Adducts as Reagents for Neutralizing Oxide Surfaces, and the Effect of Alkali Metal Treated Surfaces in Rh-catalysed Synthesis Gas (CO + H₂) Conversion

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M⁺C₁₀H₈⁻ adducts (M = Li, Na, K) are effective reagents for eliminating acidity from the surfaces of SiO₂, ZrO₂, or zeolite Y; the treated surfaces [SiO₂ + Li⁺, Na⁺, K⁺ from M⁺C₁₀H₈⁻, SiO₂ + Na⁺ from NaNO₃, or ZrO₂ + Na⁺ from Na⁺C₁₀H₈⁻] function as novel supports for heterogeneous Rh [from Rh₄(CO)₁₂] catalysts in the conversion of CO + H₂ into MeOH with >90% selectivity at 40–95 bar and 250–300 °C, which contrasts with the formation of CH₄ over Rh on the untreated oxides.

The interaction of organometallic chemistry and heterogeneous catalysis is currently receiving much attention,¹ with a

particularly challenging area of application being that of selective syn gas (CO + H₂) conversion.² We report that

alkali metal-naphthalene adducts are effective reagents for eliminating the acidity present on the surfaces of oxides frequently used as catalyst supports. Such acidity often has an adverse effect on catalyst performance. Further, alkali metal doping of supports is found to give a significant change in selectivity from CH₄ to MeOH in syn gas conversion, when using Rh₄(CO)₁₂ as a catalyst precursor, on the untreated and treated oxides, respectively.

M⁺C₁₀H₈^{•-} adducts were prepared in tetrahydrofuran (THF) and added under dinitrogen to dried samples of SiO₂ (Grace-Davison, 300 m² g⁻¹), ZrO₂ (Alfa-Ventron, 8 m² g⁻¹), or zeolite Y (Union Carbide). The M⁺C₁₀H₈^{•-} complexes were added (i) in amounts stoichiometrically equivalent to 5 OH groups per nm² of surface (SiO₂ + Na⁺, K⁺), (ii) until no further discharge of the C₁₀H₈^{•-} colour took place (ZrO₂ + Na⁺, zeolite Y + Na⁺), or (iii) in excess (SiO₂ + Li⁺). The treated oxides were filtered, washed (THF), dried, and stored under air. These procedures led to SiO₂ containing 1.5 wt % Li⁺, 4 wt % Na⁺, and 7 wt % K⁺, ZrO₂ containing 0.2 wt % Na⁺, and zeolite Y containing 9.2 wt % Na⁺. The carbon contents of these samples were, respectively, 7.7, 5.4, 3.3, 0.2, and 5.3 wt %, indicating some incorporation of naphthalene, THF, or products derived from them.

Suppression of acidity was demonstrated by monitoring the gas-phase isomerization of 2-methylbut-1-ene, a molecule which can readily isomerize to the thermodynamically more stable 2-methylbut-2-ene *via* formation of a tertiary carbenium ion. 2-Methylbut-2-ene (3.27 mmol h⁻¹) in H₂ (11.6 mmol h⁻¹) was passed at 1 bar total pressure over samples (typically 0.5 g) of the oxides in a microflow reactor, using a programmed temperature increase (2 °C min⁻¹) and on-line g.l.c. detection of the products. Whereas the untreated oxides gave equilibrium amounts of 2-methylbut-2-ene at or below 300 °C (calculated for 300 °C: 74% 2-methylbut-2-ene, 26% 2-methylbut-1-ene) less than 10% isomerization was observed up to 350 °C over SiO₂ treated with Li⁺, Na⁺, or K⁺, or ZrO₂ treated with Na⁺. Less isomerization also occurred over zeolite Y treated with Na⁺C₁₀H₈^{•-} than over the commercially available Na⁺-exchanged form (*ca.* 10 wt % Na⁺) of the same zeolite. An analytical application of M⁺C₁₀H₈^{•-} complexes for determining hydroxyl content on oxides has been reported.³

The treated oxides were also tested as supports for Rh₄(CO)₁₂ in heterogeneously catalysed syn gas (CO + H₂) conversion. Rh₄(CO)₁₂ was impregnated on to the oxide samples from a hexane solution, and the resulting catalysts were tested in a microflow reactor at 40–95 bar (CO + H₂), 225–300 °C, and gas hourly space velocities (g.h.s.v.) of *ca.* 1000 (ml CO + H₂)

(ml catalyst)⁻¹ h⁻¹. Under these conditions Rh on doped supports (SiO₂ + Li⁺, Na⁺, K⁺ from M⁺C₁₀H₈^{•-}, SiO₂ + Na⁺ from NaNO₃, ZrO₂ + Na⁺ from Na⁺C₁₀H₈^{•-} gave 90–100% MeOH, in contrast to predominantly CH₄ obtained over Rh on the undoped supports. Activity is illustrated by 5% CO conversion over Rh–K⁺–SiO₂ (2.7 wt % Rh, 7 wt % K⁺) tested at 95 bar, 300 °C, CO:H₂ 1:1, and g.h.s.v. of 1000 (ml CO + H₂) (ml catalyst)⁻¹ h⁻¹. The significant change in selectivity[†] from CH₄ to MeOH may be related to the observation of high methanol selectivity from CO + H₂ over Rh₄(CO)₁₂ supported on basic oxides such as MgO, and tested at 1 bar and 220 °C.⁴ Possible explanations include (i) a substantially different interaction of the zero-valent cluster with a deprotonated and/or basic surface, compared to the reaction⁶ with an untreated SiO₂ surface, or (ii) an involvement of basic sites in the mechanism. For example, we note that a Cannizzaro reaction converting formaldehyde into methanol and the formate anion could play a role; spectroscopically detected formate has been linked to methanol production over a Pd–Na⁺–SiO₂ catalyst,⁷ and Rh catalysis of the Cannizzaro reaction (in water at 20 °C) has been reported.⁸

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[†] A blank experiment with Li⁺–SiO₂ showed that this oxide had no activity for syngas (CO + H₂) conversion; contamination of the Rh catalyst by Fe carbonyls, which can promote methanol formation,⁵ was avoided by installing a ZnO trap before the reactor.