

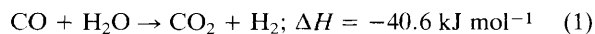
Photocatalysis of Metal Clusters in Cages: Effective Photoactivation of the Water Gas Shift Reaction catalysed on NaY Zeolite-entrapped Pt₁₂ and Pt₉ Carbonyl Clusters

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Pt carbonyl clusters [Pt₃(CO)₆]_n²⁻ (*n* = 3,4) in NaY zeolite pores are catalytically active for the water gas shift reaction (CO + H₂O) at low temperatures, and exhibited effective photocatalysis for this reaction with a marked enhancement (*ca.* 38 times higher at 293 K) under illumination from a Xe lamp compared with the dark reaction.

Intrazeolite synthesis of organometallic compounds such as metal carbonyl clusters has been of great interest recently,¹ because of the promise of such systems for rational preparation of tailor-made catalysts of discrete metal-alloy clusters^{2a,3} and potential quantum dots of semiconductor clusters^{2b} entrapped inside zeolite pores as the ultimate 'nano-vessels'. Some metal carbonyl clusters, Rh₆(CO)₁₆,^{4,5} Ir₆(CO)₁₆,⁶ Os₃(CO)₁₁²⁻,⁷ and Pd₁₃(CO)_x,⁸ and bimetallic clusters, [Fe₂Rh₄(CO)₁₅]²⁻,⁹ and Rh_{6-x}Ir_x (*x* = 2,3,4)³ have been prepared inside NaY by the 'ship-in-bottle' technique. Recently, we reported a novel synthesis of trigonal prismatic platinum cluster dianions of general formula [Pt₃(CO)₃(μ₂-CO)₃]_n²⁻ (*n* = 3,4,5) in Y and X zeolites which were characterized by EXAFS, FTIR and UV-VIS spectroscopy.¹⁰ We report here that the intrazeolite clusters [Pt₃(CO)₆]_n²⁻ (*n* = 3,4) are catalytically active for the water gas shift (WGS) reaction (1) under mild conditions, and exhibited a marked enhancement of this reaction on illumination with a Xe lamp.



The dark-green [Pt₁₂(CO)₂₄]²⁻/NaY (290, 445 and 640 nm in diffuse reflectance UV-VIS) was synthesized from Pt²⁺/NaY {4 wt% Pt loading, after calcination at 573 K of ion-exchanged [Pt(NH₃)₄]²⁺/NaY (Linde LZY-53, SiO₂/Al₂O₃ = 5.6, surface area 910 m² g⁻¹) in flowing CO with a trace of H₂O from 298 to 373 K by the method previously reported.¹⁰ The resulting intrazeolite Pt carbonyl cluster anions gives FTIR bands at 2080vs and 1841s cm⁻¹ as shown in Fig. 1(a) characteristic of linear and bridging CO, respectively, which resemble absorptions of [NEt₄]₂[Pt₃(CO)₆]₄ in tetrahydrofuran (THF) solution.¹¹ The orange-brown [Pt₉(CO)₁₈]²⁻/NaY (IR, 2056vs and 1798s cm⁻¹; UV-VIS, 300m, 435s and 710m) was prepared by the reductive carbonylation of [Pt(NH₃)₄]²⁺/NaY with CO at 298–378 K.

It is interesting that the bridging CO bands of the intrazeolite Pt₉ and Pt₁₂ carbonyl dianions shift on exposure to H₂O vapour (0.5–10 Torr) at 300 K to higher frequencies (10–38 cm⁻¹) depending upon the H₂O pressure [as shown in Fig. 1(b)–(f)], compared with the dehydrated samples. These CO frequency shifts are proposed to be interpreted in terms of the interaction between the bridging CO of Pt₉ and Pt₁₂ cluster anions with the solvated H₂O in NaY pores, as for [Rh₆(CO)₁₆]/NaY⁵ and [Pd₁₃(CO)_x]/NaY.⁸ Similar evidence for the activation of H₂O with anionic platinum carbonyl clusters such as Pt₁₂(CO)₂₄²⁻ in DMF (*N,N*-dimethylformamide) solution was reported previously,¹² suggesting the involvement of the cluster anions as active intermediates for the hydrogen transfer in the conversion of 1,4-benzoquinone to benzene-1,4-diol with water.

The WGS (CO + H₂O → CO₂ + H₂) and reversed WGS (CO₂ + H₂ → CO + H₂O) reactions were performed at 300–423 K using a closed circulating Pyrex glass reactor charged with the powdered samples: 0.5 g of [Pt₁₂(CO)₂₄]²⁻/NaY, [Pt₉(CO)₁₈]²⁻/NaY and Al₂O₃-supported Pt catalyst (Pt/Al₂O₃) (4 wt% loading). The products (CO, CO₂, H₂O and H₂) were analysed by GC using Poropak Q (2 m; 363 K) and MS-5A (1 m; 363 K) columns, with a thermal conductivity detector, coupled with a quadrupole mass spectrometer (QP-100, ANELVA Co.). As shown in Table 1, Pt₉ and Pt₁₂ clusters in NaY showed substantially higher activities in the

WGS reaction to form an equimolar mixture of CO₂ and H₂ at lower temperatures (323–403 K) compared with the conventional Pt/Al₂O₃ catalyst. [Pt₉(CO)₁₈]²⁻/NaY gave higher rates for WGS and reversed WGS reactions than [Pt₁₂(CO)₂₄]²⁻/NaY. The apparent activation energies for the WGS reaction on the intrazeolite Pt₉ and Pt₁₂ carbonyl clusters are relatively low (*E_a* = 70–76 kJ mol⁻¹) for the WGS reaction, compared with those on Pt/Al₂O₃ (122 kJ mol⁻¹), Cu-Zn-Al₂O₃ (110 kJ mol⁻¹)¹³ and MgO (135 kJ mol⁻¹).¹⁴ Upon exposure of [Pt₁₂(CO)₂₄]²⁻/NaY to CO (100 Torr) and H₂O (10 Torr), *in situ* FTIR studies demonstrated that the intrazeolite Pt₁₂ carbonyl clusters retained their cluster framework in the WGS reaction at 323–423 K without any particular bands assignable to a formate intermediate at 1600–1300 cm⁻¹. The WGS

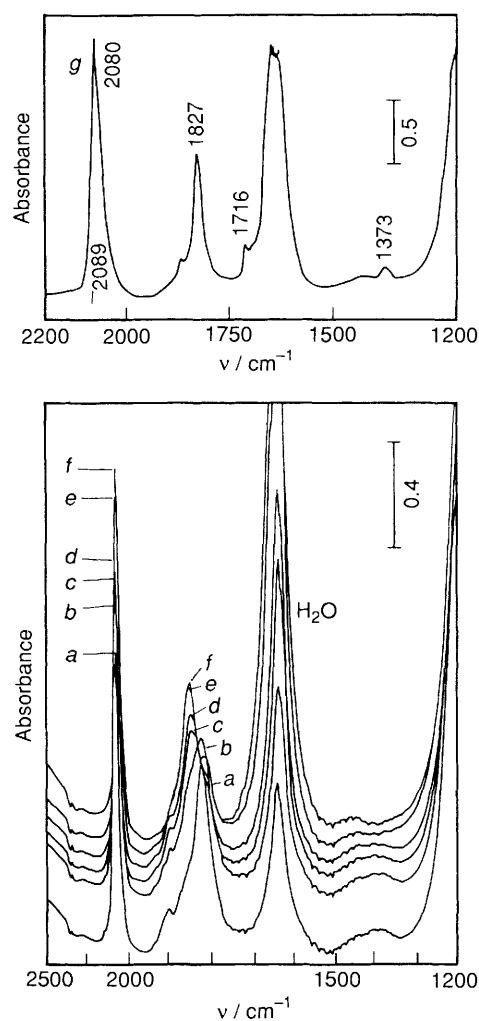


Fig. 1 IR spectra of [Pt₁₂(CO)₂₄]²⁻/NaY: (a) after evacuation at 323 K (10⁻⁴ Torr), and on exposure to 0.5(b), 1(c), 2(d), 5(e) and 10(f) Torr of H₂O at 300 K; (g) after illumination with a Xe lamp for 0.5 h in 2 Torr of H₂O at 300 K

Table 1 Catalytic performance of $[\text{Pt}_9(\text{CO})_{18}]^{2-}/\text{NaY}$, $[\text{Pt}_{12}(\text{CO})_{24}]^{2-}/\text{NaY}$ and $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$ (4.0 wt% Pt; 0.5 g) in WGS and reversed WGS reactions in the dark at 323–388 K

Catalysts	WGS		Reversed WGS	
	r_f^a	E_f^c	r_b^b	E_b^c
$[\text{Pt}_9(\text{CO})_{18}]^{2-}/\text{NaY}$	125	70	380	103
$[\text{Pt}_{12}(\text{CO})_{24}]^{2-}/\text{NaY}$	30	76	140	106
$\text{Pt}/\gamma\text{-Al}_2\text{O}_3$	0.3	122	—	—

^a r_f , rate of formation ($\text{mmol Pt}_{\text{atom}}^{-1} \text{min}^{-1}$) $\times 10^{-2}$ at 373 K of CO_2 and H_2 in the WGS reaction; $P_{\text{CO}} = 100$ Torr, $P_{\text{H}_2\text{O}} = 10$ Torr. ^b r_b , rate of formation ($\text{mmol Pt}_{\text{atom}}^{-1} \text{min}^{-1}$) $\times 10^{-2}$ at 373 K of CO and H_2O in reversed WGS reaction; $P_{\text{CO}_2} = P_{\text{H}_2} = 100$ Torr. ^c E_f and E_b : activation energies (in kJ mol^{-1}) for WGS and reversed WGS reactions, respectively.

reaction on the intrazeolite Pt carbonyl clusters may proceed *via* oxidation–reduction between H_2O and CO or *via* an undetectable formate intermediate as proposed on conventional oxide catalysts such as $\text{Cu-ZnO-Al}_2\text{O}_3$,¹³ MgO and ZnO .¹⁴

Furthermore, as shown in Fig. 2(a), it is interesting to find that the WGS reaction on $[\text{Pt}_{12}(\text{CO})_{24}]^{2-}/\text{NaY}$ was dramatically [*ca.* 38 times higher at 293 K than in the dark, Fig. 2(c)] enhanced by illumination with a Xe lamp covering the wavelength region 250–1200 nm. A fine crystalline sample of $[\text{Pt}_{12}(\text{CO})_{24}]^{2-}/\text{NaY}$ (0.8 g) was uniformly spread in a quartz reactor (*ca.* 200 ml) which was kept in a temperature-controlled water-bath. The rates of CO_2 formation were decreased by substitution of water with D_2O ($k_{\text{H}_2\text{O}}/k_{\text{D}_2\text{O}} = 1.8$ at 393 K) [Fig. 2(b)], possibly owing to the isotopic effect for cleavage of the hydrogen–oxygen bond in water. Preliminary studies using selected light from the Xe lamp through cut-off filters suggested that the WGS reaction is effectively enhanced by irradiation with visible region light in the 300–700 nm wavelength region on $[\text{Pt}_{12}(\text{CO})_{24}]^{2-}/\text{NaY}$. The visible light is likely to diffuse and penetrate the zeolite crystallites (1 μm in size) entrapping the Pt carbonyl clusters. In addition, as shown in Fig. 1(g), the FTIR spectra showed a set of new bands (1714 and 1373 cm^{-1}) appearing upon exposure of a disk sample of $[\text{Pt}_{12}(\text{CO})_{24}]^{2-}/\text{NaY}$ to the Xe lamp illumination for 0.5–2 h in the presence of 1–5 Torr of H_2O at 300 K. The new bands may be assigned to unstable carboxylate $[\text{C}=\text{O}(\text{OH})]$ ($\nu_{\text{C}=\text{O}}$ 1716, $\nu_{\text{O}-\text{C}}$ 1370 cm^{-1})¹⁵ or monodentate formate species $[\text{O}(\text{C}=\text{O})]$ similar to those in $\text{C}(\text{HgOCOH})_4$ and $\text{Cd}(\text{HCOO})_2$ ($\nu_{\text{C}=\text{O}}$ 1677–1700, $\nu_{\text{O}-\text{C}}$ 1337–1360 cm^{-1}).¹⁶ These intermediate bands were not detected on the sample in dark reactions with H_2O or $\text{CO} + \text{H}_2\text{O}$ at 300–398 K and were drastically suppressed on introducing an excess of CO (40 Torr) or H_2O (10 Torr) to the sample after the Xe lamp irradiation. The intermediate is eventually converted to give a mixture of CO_2 and H_2 , followed by regeneration of the original $[\text{Pt}_{12}(\text{CO})_{24}]^{2-}$ in the CO atmosphere. Additionally, we found that a small amount of CO_2 with H_2 was detected on exposure of water to the fresh $[\text{Pt}_{12}(\text{CO})_{24}]^{2-}/\text{NaY}$ under illumination with the Xe lamp at 293 K; the CO_2 formation was rapidly terminated. From this evidence, it is proposed that the photoexcited intrazeolite Pt_{12} carbonyl cluster anions may enhance the oxidation of water, resulting in formation of an active intermediate ‘COOH’ by the nucleophilic attack of ‘OH’ on the cluster carbonyls. The catalytic redox cycle of the WGS reaction effectively proceeds to produce CO_2 and H_2 under the illumination, as in reactions (2) and (3).

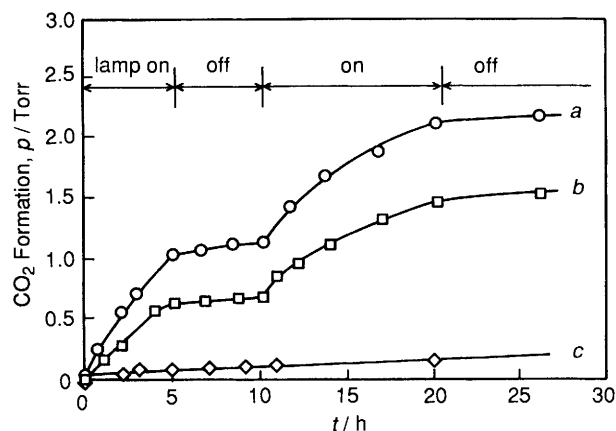
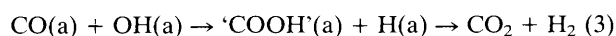


Fig. 2 Formation of CO_2 ($+\text{H}_2$) in the WGS reaction ($P_{\text{CO}} = 40$ Torr, $P_{\text{H}_2\text{O}}$ or $P_{\text{D}_2\text{O}} = 10$ Torr balanced with He, $P_{\text{He}} = 100$ Torr) at 293 K for (a) $\text{CO} + \text{H}_2\text{O}$ and (b) $\text{D}_2\text{O} + \text{CO}$ measured with and without illumination with the Xe lamp in sequence; (c) $\text{H}_2\text{O} + \text{CO}$ in the dark at 293 K

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