

Metal-support interactions in supported platinum catalysts: zeolites and amorphous supports

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IR spectroscopy of adsorbed CO indicates that the electron density of supported platinum in Pt/LTL and Pt/SiO₂ catalysts increases with increasing level of alkali on the support. In addition, the neopentane hydrogenolysis TOF decreases with increasing support alkalinity. The Al-near edge structures of the LTL supports show an increased electron density on the aluminium with increasing alkalinity. Therefore, a metal-support interaction between the platinum and the support oxygen atoms is proposed to account for the changes in catalytic activity and electronic density of the metal particles.

1. INTRODUCTION

Metal-support interactions affect the activity of zeolite supported noble metal catalysts in benzene hydrogenation [1,2], propane [3,4] and neopentane [3-5] hydrogenolysis. Several studies have demonstrated that the specific activity of supported Pt or Pd decreases as the support acidity decreases from acidic to alkaline. Although the influence of the metal-support interaction is known for zeolite catalysts, similar behaviour on amorphous supports is less well studied. Generally, the specific activity of noble metals on silica-alumina is higher than that on either alumina or silica [16,17]. It is uncertain, however, whether this is due to a metal-support interaction similar to that in zeolites or to some other property.

In addition to its effect on the catalytic behaviour, the metal-support interaction has been shown to alter the electronic properties of the supported metal. Based on the catalytic results for competitive hydrogenation of benzene/toluene, Larsen and Haller suggested a decreased electron density of the platinum as the LTL zeolite acidity increased by cation exchange [2]. In addition, de Mallmann and Barthomeuf proposed that the shift to lower frequency in the infrared spectra of adsorbed CO was due to a higher electron density of platinum on alkaline Y zeolite [1,7]. Finally, by XPS, zeolite supported Pt and Pd have been shown to be electron deficient [4,8], compared to bulk Pd or Pt, on acidic supports and electron rich on alkaline supports [4,9].

Although the influence of the zeolite acidity/alkalinity on the catalytic properties and the electronic structure of the supported metal particles has been established, the nature of this

interaction is still uncertain. Several explanations for the metal-support interaction have been proposed including the formation of a metal-proton-adduct [5,10], charge transfer between the metal atoms and the zeolite oxygen atoms [1,2,7,9], polarisation of the metal particles by nearby cations [11,12], and a direct promotion of potassium on the metal particles [13-15]. The formation of positively charged Pd-H⁺ adducts for Pd in zeolite Y was proposed to account for electron deficient metal particles observed in acidic zeolites [5,10]. However, such adducts cannot account for an increase in electron density for metal particles on alkaline zeolites. Alternatively, it was suggested that the Sanderson electronegativity of the support oxygen atoms increases with increasing zeolite alkalinity [1,2]. Assuming that the metal particles are in close contact with the support oxygen atoms, charge transfer can account for a higher electron density for the metal particles on alkaline zeolites. A third model is based on the polarisation of a small metal cluster by a nearby cation [11,12]. Calculations indicated that metal atoms near cations attract electrons, thus resulting in electron deficient metal atoms at the opposite side of the cluster. Furthermore, a model involving a direct promoter effect was suggested. Potassium adsorption on single crystals [14] as well as catalysts [15] indicated the enhancement of local density of states on the platinum particles. If potassium is in direct contact with the metal this could explain the more 'electron rich' particles on alkaline zeolites.

In this study, the influence of the metal-support interaction on the catalytic and electronic properties is demonstrated for Pt supported on silica and zeolite LTL with varying acidity/alkalinity. The Turnover Frequency for neopentane hydrogenolysis and the ratio of linear to bridged bound CO in the infrared spectra decreased with increasing amounts of alkali. For zeolite LTL, Al XAFS spectroscopy demonstrated that the charge on the lattice Al is affected by the support acidity/alkalinity suggesting that the metal properties are modified by the charge of the support oxygen ions.

2. EXPERIMENTAL

2.1. Catalyst preparation

The acidity of the LTL zeolite support was varied by either impregnating a commercial K-LTL zeolite with KNO₃ or exchanging it with NH₄NO₃ to give K/Al ratios ranging from 0.63 to 1.25. Each LTL zeolite was calcined at 225°C and analysed for potassium and aluminium. Platinum was added by incipient wetness impregnation of [Pt(NH₃)₄](NO₃)₂ followed by drying at 120°C. The catalysts are designated Pt/LTL (*.**) with *.** representing the K/Al molar ratio.

The silica supports were prepared by ion exchange of SiO₂ (15g in 500mL H₂O at 60°C) with increasing amounts of KOH followed by calcination at 400°C. Also an acidic silica was prepared by ion-exchange of SiO₂ with excess of Al(NO₃)₃ followed by calcination at 400°C. Platinum was added by incipient wetness impregnation of [Pt(NH₃)₄](NO₃)₂ followed by calcination at 225°C. The catalysts are designated Pt/SiO₂-X (*.**) with X representing Al or K and *.** the wt.% of X. The elemental analysis of the catalysts together with the platinum dispersion as determined by H₂ chemisorption are given in Table 1.

Additional information about particle sizes was obtained from XAFS data-analysis, which revealed a decrease in Pt particle diameter from 18 Å for Pt/SiO₂-Al(0.10) to about 8 Å for Pt/SiO₂-K(1.14). No potassium could be detected in the neighbourhood of platinum. The H/PT ratio larger than 1 as determined with H₂-chemisorption is in agreement with the very small Pt particle sizes [33].

Table 1
Elemental analysis and platinum dispersion

Catalyst	Wt.% K	Wt.% Al	Wt.% Pt	H/Pt
Pt/LTL(0.63)	8.3	9.5	1.0	0.53
Pt/LTL(0.96)	11.8	8.5	1.0	0.89
Pt/LTL(1.25)	15.9	8.8	1.0	0.88
Pt/SiO ₂ -Al(0.10)	-	0.10	1.54	0.60
Pt/SiO ₂	-	-	1.40	0.58
Pt/SiO ₂ -K(0.39)	0.39	-	1.64	1.05
Pt/SiO ₂ -K(0.77)	0.77	-	1.56	1.30
Pt/SiO ₂ -K(1.14)	1.14	-	1.48	1.35

2.2. Neopentane hydrogenolysis

Neopentane hydrogenolysis was carried out in a fixed bed reactor using 1 vol.% neopentane in H₂ at 350°C and 390°C, for Pt/LTL and Pt/SiO₂ respectively. The catalysts were prerduced at the reaction temperature and conversion was adjusted to between 0.5 and 2.0% by varying space velocity. Selectivities are reported at 0.5% neopentane conversion. The Turnover Frequency (TOF) is calculated based on the H₂ chemisorption.

2.3. Infrared spectroscopy

The transmission infrared spectra were recorded on a Perkin-Elmer 1720-X Fourier Transform spectrometer at a spectral resolution of 4 cm⁻¹. The catalysts were pressed in thin self-supporting wafers and placed in an in-situ transmission infrared cell. The catalyst was reduced in H₂ at 300°C and subsequently cooled down to room temperature. Then the sample was purged with He for ten minutes followed by flowing 20% CO in He gas for ten minutes, whereafter the CO absorbance spectrum was collected. The spectra of the Pt/LTL catalysts were recorded under wet conditions to prevent ion-dipole interactions between K⁺ and adsorbed CO [18]. The spectra were corrected for the absorption of the support and gasphase CO.

2.4. X-ray absorption spectroscopy

The X-Ray absorption spectra of the Al K-edge of the LTL zeolites supports were recorded at the SRS (Daresbury, UK) station 3.4. The zeolite supports (without Pt) were mixed with carbon and mounted with epoxy to a sample holder. The sample holders were attached in a high vacuum chamber and spectra were recorded with pressure below 10⁻⁸ Torr. No signal from the epoxy or the sample holder could be detected. Standard procedures were used to analyse the spectra. Background subtraction was done using cubic spline routines and the spectra were normalised by the height of background at 50 eV after the edge [19,20].

3. RESULTS

3.1. Neopentane hydrogenolysis

Analysis of the reaction products, by the Delplot method [21], for neopentane conversions between 0.5% to 2.0 % indicated that the primary reaction products were methane, isobutane (hydrogenolysis) and isopentane (isomerisation). The selectivities for neopentane hydrogenolysis and isomerisation are given in Table 2. The isomerisation selectivity on Pt/LTL increases with increasing support alkalinity, while on Pt/SiO₂ the isomerisation selectivity decreases with increasing support alkalinity. In addition, the initial isomerisation selectivity on Pt/SiO₂ is higher than on Pt/LTL despite the higher reaction temperature.

Table 2
Selectivity of neopentane catalysis*

Catalyst	Reaction Temperature	Hydrogenolysis Selectivity	Isomerisation Selectivity
Pt/LTL(0.63)	350°C	0.82	0.18
Pt/LTL(0.96)		0.77	0.23
Pt/LTL(1.25)		0.68	0.32
Pt/SiO ₂ -Al(0.10)	390°C	0.39	0.61
Pt/SiO ₂		0.58	0.42
Pt/SiO ₂ -K(0.39)		0.69	0.31
Pt/SiO ₂ -K(0.77)		0.76	0.24
Pt/SiO ₂ -K(1.14)		0.79	0.21

* Atmospheric pressure and 1 vol% neopentane in H₂. Selectivities determined at 0.5% neopentane conversion.

The neopentane hydrogenolysis Turnover Frequencies are given in Table 3. Although the initial activity for Pt/SiO₂ is lower than that for the zeolite catalysts, for both series the TOF continuously decreases with increasing alkali level of the support. An increase of about 1%K on Pt/SiO₂ results in a decrease in TOF by 10².

Table 3
Neopentane hydrogenolysis Turnover Frequencies*

Catalyst	TOF (mol./sec.surface Pt atom)	Catalyst	TOF (mol./sec.surface Pt atom)
Pt/LTL(0.63)	1.8 * 10 ⁻¹	Pt/SiO ₂ -Al(0.10)	3.1 * 10 ⁻²
Pt/LTL(0.96)	3.7 * 10 ⁻²	Pt/SiO ₂	5.5 * 10 ⁻³
Pt/LTL(1.25)	4.9 * 10 ⁻⁵	Pt/SiO ₂ -K(0.39)	4.5 * 10 ⁻⁴
		Pt/SiO ₂ -K(0.77)	2.2 * 10 ⁻⁴
		Pt/SiO ₂ -K(1.14)	8.0 * 10 ⁻⁵

* Determined at 350°C and 390°C, for Pt/LTL and Pt/SiO₂ respectively.

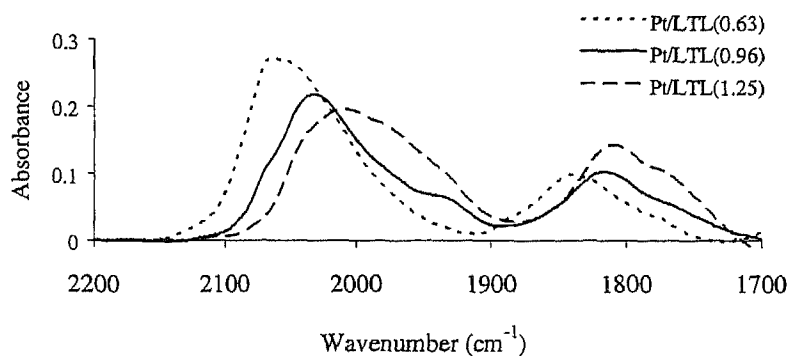


Figure 1. Transmission FT-IR spectra of CO adsorbed on Pt/LTL catalysts.

3.2. Infrared spectroscopy

The transmission infrared spectra of Pt/LTL and Pt/SiO₂ are shown in Figure 1 and 2, respectively. Two regions of adsorbed CO can be assigned: at higher wavenumbers an absorption band due to linearly coordinated CO and at lower wavenumbers an absorption due to CO in bridged coordination to the metal atoms. For both Pt/LTL and Pt/SiO₂ the linear- as well as the bridged-coordinated CO absorption band shift to lower wavenumbers as the support alkalinity increases. The shifts are more pronounced for the Pt/LTL series than for the Pt/SiO₂ series. The line shapes for Pt/SiO₂-Al(0.10) and Pt/SiO₂ are sharper than those of the Pt/SiO₂-K catalysts. This can be explained by the differences in metal particle size between the catalysts. The surface of a metal particle consists of atoms with different coordination numbers (C_n) due to their location in edges, corners or faces [22].

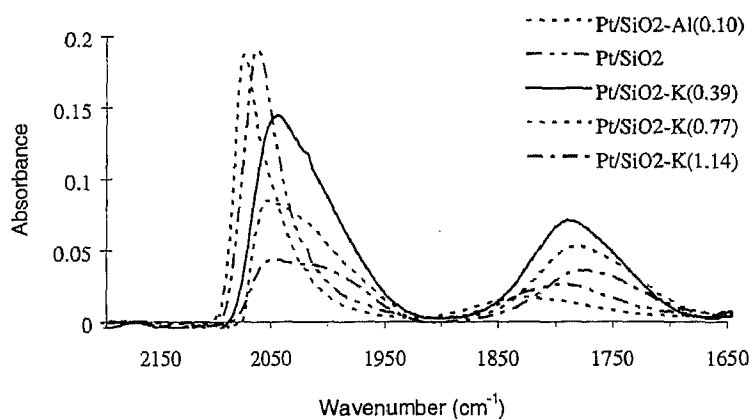


Figure 2. Transmission FT-IR spectra of CO adsorbed on Pt/SiO₂ catalysts.

Table 4
FT-IR data of adsorbed CO on Pt/LTL and Pt/SiO₂

Catalyst	Integrated intensity ratio linear/bridged bound CO	Catalyst	Integrated intensity ratio linear/bridged bound CO
Pt/LTL(0.63)	3.2	Pt/SiO ₂ -Al(0.10)	3.8
Pt/LTL(0.96)	2.3	Pt/SiO ₂	3.1
Pt/LTL(1.25)	1.7	Pt/SiO ₂ -K(0.39)	1.7
		Pt/SiO ₂ -K(0.77)	1.3
		Pt/SiO ₂ -K(1.14)	1.1

The CO adsorption on these different sites determines the observed CO line shape. The CO absorption band can be deconvoluted into the separate absorptions of CO on the different metal sites, with the wavenumber of CO increasing with increasing metal atom coordination number [23]. As larger platinum metal particles exhibit more coordinately saturated atoms, there will be relatively more adsorption of CO on Pt with high C_n than on Pt atoms with low C_n. This results in a sharper absorption band, with the maximum positioned at a higher wavenumber. The larger particles of Pt/SiO₂-Al(0.10) and Pt/SiO₂, as determined with H₂ chemisorption, are thus reflected in the CO absorption line shapes. For Pt/LTL the line shape does not change in this way, which is in agreement with the smaller deviation in particle size for these samples. The small shoulder visible at 1940 cm⁻¹ in the FTIR spectrum of Pt/LTL(0.96) can be assigned to an ion-dipole interaction between K⁺ and adsorbed CO [18] in spite of the wet conditions in which the spectrum was taken.

Table 4 shows the integrated intensity ratio linear/bridged bound CO as calculated from the spectra. The ratio linear/bridged CO decreases with increasing support alkalinity for Pt/LTL as well as Pt/SiO₂. In other words, CO prefers bridged coordination to the platinum atoms above linear coordination with increasing support alkalinity.

3.3. X-ray absorption spectroscopy - Al near-edge structure

Figure 3 shows the normalised Al near-edge structures of the zeolite LTL supports (without Pt). Generally, the shape and intensity of the Al near-edge structure is related to the transition of 1s electrons to the 3p valence band. The edge position and line shape are determined by the amounts of tetrahedral and octahedral coordinated aluminium as they have different edge energies, 1566.7 eV and 1568.3 eV respectively [24]. The XAFS spectra of the three LTL zeolite supports show the same edge energy and line shape. There is no additional absorption peak at 1570 eV that should indicate the presence of octahedral aluminium. Therefore, the LTL supports only consist of tetrahedral coordinated aluminium.

The whiteline *intensity* (or edge intensity) is directly correlated to the electron density on the aluminium atoms. A decrease in whiteline intensity indicates an increase in electron density on the aluminium. From Figure 3 it can be seen that the whiteline intensity continuously decreases, indicating an increased electron density on the aluminium with increasing support alkalinity.

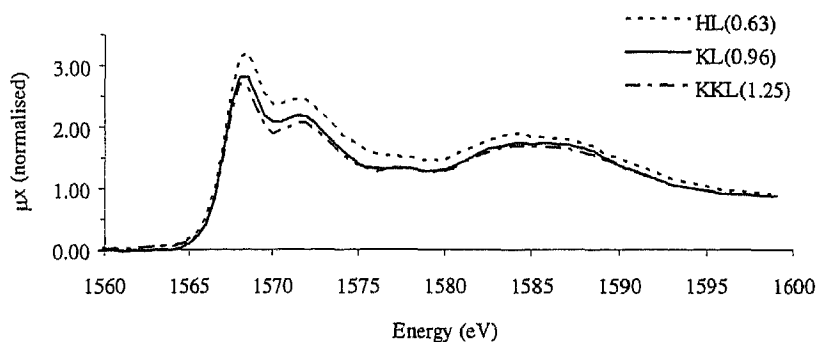


Figure 3. The Al X-ray absorption near-edge structure of the LTL supports.

4. DISCUSSION

4.1. Catalysis

The slightly increasing isomerisation selectivity with increasing support alkalinity for the Pt/LTL series is in accordance with other studies [6,25]. For Pt/SiO₂, on the contrary, the isomerisation selectivity is decreasing with increasing support alkalinity. It is known that the isomerisation selectivity decreases with decreasing particle diameter [26]. However, when the selectivities of the catalysts with the same metal particle size are compared (e.g. Pt/SiO₂-Al(0.10) with Pt/SiO₂, and Pt/SiO₂-K(0.39) to Pt/SiO₂-K(1.14)) there still is a decrease in isomerisation selectivity with increasing alkalinity that cannot be explained by a particle size effect. It is not clear whether this decrease is the result of the increasing support alkalinity or of another parameter. Furthermore, it is known that a higher reaction temperature gives a lower isomerisation selectivity [26]. However, the initial isomerisation selectivity for Pt/SiO₂ is higher than for Pt/LTL, despite the higher reaction temperature. The difference in isomerisation selectivity for the two catalyst series is probably due to different properties of the support material.

Figure 4 shows the logarithm of the TOF as a function of the amount of potassium in the support (wt.% Al is regarded as -wt.% K). Both Pt/LTL and Pt/SiO₂ show a continuous decrease in neopentane hydrogenolysis Turnover Frequency with increasing alkalinity of the support. This decrease in TOF is in the order of 10³-10⁵ throughout the whole series, for Pt/SiO₂ and Pt/LTL respectively. According to the high H/Pt ratios as determined with H₂ chemisorption, the platinum atoms are still accessible, even in the catalysts with high amounts of potassium. The decrease in TOF observed for Pt/LTL as a function of support alkalinity is in agreement with previous studies [6]. This study shows that the effect of increasing support alkalinity on the catalytic activity of the Pt/SiO₂ catalysts is similar to that of the Pt/LTL catalysts. The continuous decrease in TOF with increasing alkalinity, not only for acidic to neutral, but also proceeding to an alkaline support, indicates a metal-support interaction that is the same throughout the series.

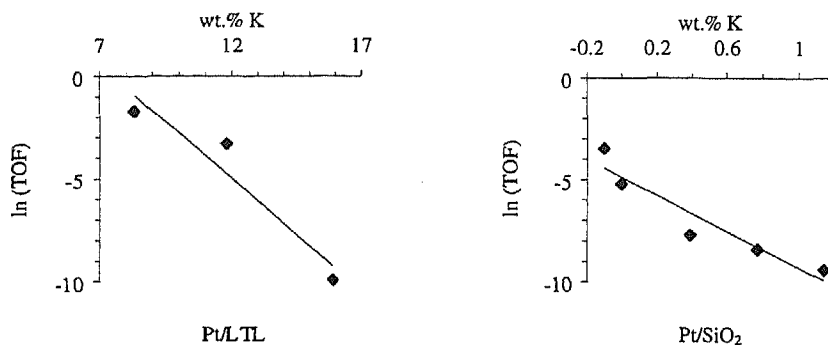


Figure 4. \ln (TOF neopentane hydrogenolysis) versus wt.% K in the support. (wt.% Al = -wt.% K) left: Pt/LTL right: Pt/SiO₂

4.2. Infrared spectroscopy

Shifts in the CO band position are generally interpreted as evidence of changes in the electronic properties of supported metals. Typically on noble metals CO is bound in linear and bridged coordination with the C-O stretching frequency in the spectral regions 2100-2000 cm⁻¹ and 1950-1800 cm⁻¹, respectively. The exact peak position depends on the metal particle size [23], surface coverage [27], and changes in the metal electronic structure [28]. As the particle sizes for the catalysts in this study are not the same within a series, the shifts in band position are not a reliable indication of a change in electronic properties of the metal particles.

Since theoretical calculations indicate that the amount of bridged bound CO increases at the expense of linear bound CO when the electron density on the metal atoms increases [29], the integrated intensity ratio linear/bridged bound CO was calculated. This integrated intensity ratio significantly decreases with increasing support alkalinity for both the Pt/LTL and Pt/SiO₂ catalysts. Therefore, the decreased ratio linear/bridged bound CO for Pt/LTL and Pt/SiO₂ points to an increasing electron density on the metal atoms with increasing support alkalinity. This increase in electron density is in agreement with previous studies. XPS experiments showed an increased electron density on Pd/LTL [5] and Pd/SiO₂ [30] with increasing amount of alkali. Moreover, with ¹⁹⁵Pt-NMR an increase of local density of states for Pt/TiO₂ was observed upon addition of alkali metal salts [15].

Figure 5 shows the logarithm of the neopentane hydrogenolysis TOF as a function of the integrated intensity ratio linear/bridged bound CO. For the Pt/SiO₂ series there is a linear relationship between the integrated intensity ratio and the neopentane hydrogenolysis Turnover frequency. This strongly indicates that the electronic modification of the platinum particles influences the catalytic activity. Although for Pt/LTL there is no linear decrease in integrated intensity ratio, there still is a general decrease throughout the series. The non-linear relationship for the Pt/LTL catalysts can be caused by the additional influence of the zeolite pores on the adsorbed CO. Nevertheless, the continuous decrease in catalytic activity for both Pt/LTL and Pt/SiO₂ can be related to increase in electron density of the metal particles induced by the support acidity/alkalinity.

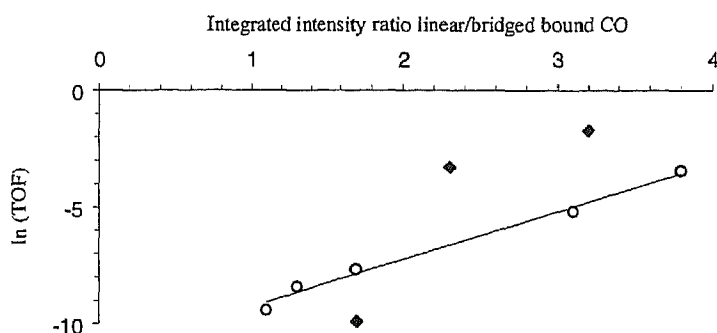


Figure 5. Relation between Ln(TOF neopentane hydrogenolysis) and integrated intensity ratio linear/bridged bound CO. Closed diamonds: Pt/LTL; open circles: Pt/SiO₂.

4.3. X-ray Absorption Spectroscopy - Al near-edge structure

The Al- near edge structure of the LTL supports shows that there is an increase of electron density on the aluminium with increasing alkalinity of the support. Even with excess alkali in the zeolite, the electron density on the aluminium is increased. The increase in electron density with increasing support alkalinity is in agreement with theoretical calculations for zeolite clusters. It was calculated for $H^+AlSiO_3(OH)_6^-$ that the charge on the aluminium is 0.09 electrons less than for the $Na^+AlSiO_3(OH)_6^-$ system [31]. From the X-ray absorption spectra reported here, it can be concluded that the electron density increases on the Al as the alkali level of the support increases, even beyond the ion-exchange capacity.

This increased electron density on the aluminium with increasing amount of alkali in the zeolite indicates that adding alkali has a direct influence on the support material by changing the distribution of charge density on the lattice atoms. Since the alkali is not bound to the aluminium, the change in electron density must be the result of a change in electron density through the bound oxygens. So, the support oxygens are also electronically influenced by the amount of potassium in the support. Previous EXAFS studies showed that platinum particles in zeolite LTL are in close contact with the support oxygen atoms [32]. Therefore, we propose that the observed changes in catalytic activity and electronic properties of the platinum for both Pt/LTL and Pt/SiO₂ result from the direct interaction of the metal particles with the support oxygen atoms.

5. CONCLUSION

The support acidity/alkalinity has a significant influence on the catalytic properties of noble metal catalysts by altering the electronic structure of the metal particles through the support. Not only zeolites but also modified amorphous supports can influence the electronic properties and catalytic activity of the supported metal. For both Pt/LTL and Pt/SiO₂ catalysts the

catalytic activity is decreased and the electronic density increased with increasing levels of alkali in the support. The Al-near edge structure of the LTL supports points to the influence of alkali through the bound oxygen atoms. It is, therefore, proposed that the metal properties are modified by a metal-support interaction between the metal atoms and the support oxygen atoms.

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