

Review

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Review

Surface Intermediates in Important Catalytic Reactions: Formation, Identification and Reactivity Across Metals, Nanoparticles and Supported Catalysts

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Abstract

The performance and mechanism of heterogeneous catalytic reactions are fundamentally governed by the formation, stability, and reactivity of transient surface intermediates. These species—such as isocyanates, alkyl groups, carboxylates, formates, carbonates, alkoxy and acyl intermediates—often exist at low concentrations and with short lifetimes, making their identification challenging. This review summarizes current knowledge on the formation, spectroscopic identification, and thermal behavior of these intermediates on metal single crystals, metal nanoparticles, and oxide-supported catalysts. Emphasis is placed on key reactions including CO and NO oxidation–reduction, CO and CO₂ hydrogenation, Fischer–Tropsch–related pathways, and reforming of methane and light alcohols. Advanced surface-sensitive techniques (TDS, XPS, UPS, IR, HREELS) are highlighted for their role in elucidating intermediate structures and reaction pathways. The review also discusses how metal–support interactions, particle size, and surface morphology influence intermediate stability and catalytic selectivity. Overall, the work provides a comprehensive framework for understanding how transient surface complexes control technologically important catalytic transformations.

Keywords: CO oxidation; CO reduction; NO reduction; CO₂ hydrogenation; reforming reactions

1. Introduction

Heterogeneous catalysis offers many possibilities, enabling a wide range of technologically important reactions related to the production of fuels (including hydrogen), fine chemicals, and the mitigation of environmental pollution. Within this context, CO oxidation by O₂ and NO_x species, CO hydrogenation (including Fisher–Tropsch synthesis), CO₂ hydrogenation and methanation, as well as the reforming of methane and light alcohols (methanol and ethanol) for hydrogen production constitute the focus of the present review. Owing to the major advances in surface science, materials characterization techniques, and computational chemistry, the mechanistic understanding of these reactions has improved significantly in recent decades [1–9].

The activity, selectivity, and mechanisms of catalytic reactions are governed by several interrelated factors. It is extensively documented that the electronic structure and morphology of

active metal nanoparticles play a decisive role. Metals ranging from single atoms to nanoclusters and nanoparticles exhibit markedly different properties [3–8]. Sub-nanometer metal clusters (~1 nm) do not exhibit bulk-like electronic structures (e.g., a well-defined Fermi level), leading to distinct adsorption behavior and reactivity [7,9,10]. In addition, metal nanocrystals exposing high-index facets often show enhanced activity due to the high density of low-coordination sites such as steps, edges, and kinks. Size-dependent oxidation states can further influence reaction pathways and selectivity [11,12]. Moreover, strong metal-support interactions, as well as adsorbate-induced surface reconstruction, can significantly modify catalytic performance [13–18].

These structural and electronic characteristics of the catalytic surface strongly influence how reactant molecules interact with it. Rather than converting directly into final products, adsorbed species typically undergo a sequence of elementary steps, leading to the formation of transient surface intermediates. In most cases, these intermediates result from interactions between co-adsorbed species. The stability and reactivity of such surface intermediates species largely determine the overall activity and selectivity of catalytic processes [8–10,19–34]. Modern surface-sensitive techniques including temperature-programmed desorption (TPD/TDS), infrared spectroscopy, X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), and extended X-ray absorption fine structure (EXAFS) enable detailed investigation of these species. In parallel, their energetics can be quantified through both experimental and computational approaches. [35–38].

This review examines the chemical nature (stability and reactivity) of key catalytic intermediates (isocyanate, alkyl groups, carboxylate, formate, carbonyl, formyl, carbonates, alkoxy, aldehydes, acetyl, acetate) with particular emphasis on their identification and characterization as transient surface complexes in technologically important catalytic reactions.

2. Formation and Preparation of Possible Intermediates Existing in Reaction Conditions

Investigating the surface chemical nature of reaction intermediates remains a significant challenge in heterogeneous catalysis, particularly when attempting to distinguish their behavior on well-defined metal surfaces (e.g., single crystals), metal nanoparticles, supports, and metal-oxide interfaces. Such comparative approaches are essential for establishing reliable reaction mechanisms. Accordingly, considerable effort has been devoted to studying the formation, stability, and reactivity of surface intermediates under realistic (in situ and operando) reaction conditions, using both experimental and theoretical methods.

In many cases, primary insights into surface species are obtained from Thermal Desorption Spectroscopy (TDS). However, modern surface science techniques, especially vibrational spectroscopies (IR, DRIFTS, RAIRS, SFG, HREELS) enable the direct identification of adsorbed intermediates through their characteristic vibrational frequencies, which provides some of the most critical information for elucidating the nature of catalytic intermediates [39–64]. Furthermore, operando Fourier transform infrared (FTIR) spectroscopy can be combined with steady-state isotopic transient kinetic analysis (SSITKA) to obtain quantitative information on surface intermediates. This approach allows not only the identification of adsorbed species but also the determination of their surface lifetimes and relative abundances under reaction conditions [24,54,55]. Such combined methodologies have been successfully applied, for example, in CO₂ hydrogenation, where both the nature of intermediates and the selectivity of the catalyst could be evaluated simultaneously [24].

The results of photoelectron spectroscopy (XPS, UPS) together with EXAFS significantly contribute to the identification, formation and stability of surface complexes. Based on XPS and UPS measurements, the identification and surface reaction of alkyl intermediates (CH, CH₂, CH₃, C₂H₃ and C₂H₅) were determined from the decomposition of precursor molecules on metal and oxide surfaces. Such processes as formaldehyde formation from CH₂ oxidation, selective oxygen addition to adsorbed CH₂ and CH₃ and their coupling reactions, preparation of formate surface complex and activated, negatively charged CO₂ production on catalysts were easily followed by XPS and UPS [22,31,32,46–49,65–79]. Recent advances have further extended the capabilities of XPS, enabling not

only high-resolution measurements [80] but also operation under elevated pressures in so-called near-ambient pressure XPS (NAP-XPS) [81]. This latter development allows the investigation of surfaces in the presence of adsorbates under conditions much closer to realistic catalytic environments and provided valuable insights into reaction mechanisms during CO₂ hydrogenation and ethanol transformation [56,59,82,83].

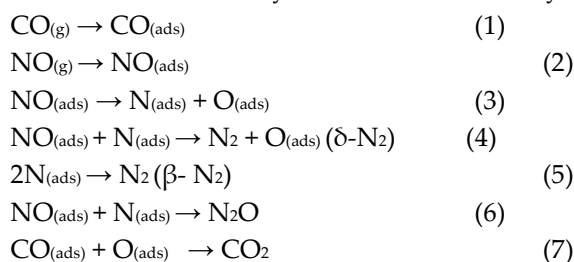
In many catalytic systems, key intermediates are formed on metal surfaces; however, their identification on metal single crystals and supported metal nanoparticles is not straightforward. One major difficulty arises from the inherently low surface concentration of these intermediates, which is often a consequence of their short lifetimes. Secondly, the oxide support can significantly influence the reactivity of intermediates formed on the metal, or the intermediates may migrate from the metal surface to the support [13–18]. To overcome these challenges, model precursor molecules are often employed as adsorbates, whose controlled dissociation yields the desired surface species. For example, HNCO dissociates to form NCO species [19,43], formic acid (HCOOH) decomposition produces surface formate species [32,75,76], and the dissociation of light alcohols leads to the formation of alkoxy intermediates [33,34,63,64]. Similarly, alkyl groups can be generated by the decomposition of alkyl halides [65–67]. In addition, photo-induced processes can significantly facilitate the formation of surface intermediates. Under low-temperature conditions, these methods can markedly increase the surface concentration of reactive species. This approach is particularly effective for the generation of alkyl fragments via the photo-induced dissociation of photoactive alkyl halides [66].

3. Catalytic Intermediates Formed on Metal Single Crystal Surfaces, Metal Nanoparticles and Oxide Supported Metal Nanoparticles

3.1. Intermediates in CO Oxidation, NO Reduction, NO + CO Reaction

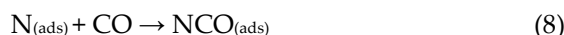
Carbon monoxide oxidation is a key process in environmental catalysis. Therefore, the CO + O₂ reaction has been extensively studied both theoretically and experimentally on model systems and supported catalysts [84,85]. Since the pioneering work of Langmuir [86], two fundamental pathways have been proposed: (i) a mechanism in which chemisorbed CO reacts with lattice oxygen (O_a), and (ii) a pathway in which adsorbed CO reacts with adsorbed oxygen species on the surface. The Eley-Rideal mechanism [87] may also operate, in which one reactant is adsorbed on the catalyst surface while the second reactant reacts directly from the gas phase. In this simple reaction, a key elementary step is the adsorption and activation of CO molecules on the catalyst surface.

The oxidation of CO by NO is another important reaction. The mechanism of the CO + NO reaction was also studied on metals, including single crystal surfaces [88–95]. This reaction can proceed via two main global pathways: one leading to the desired product N₂, and another resulting in the formation of the undesired by-product N₂O [88]. It is accepted that both reactants (CO, NO) must first adsorb on the catalytic surface, followed by a series of elementary reaction steps [88]:



It should be noted that the above set of reactions is not complete. There is possibility that the adsorbed nitrogen atom can react with CO to form isocyanate (NCO) species. However, experimental evidence for this intermediate is limited, with only a few reported observations. The formation of isocyanate species (characterized by infrared vibrational frequencies at ~2240 cm⁻¹) was tentatively identified by infrared reflection-absorption spectroscopy (RAIRS) on Pt(100) and Pd(111) [91,92]. While no clear experimental evidence for NCO formation has been reported on other metal surfaces

[93,94], its preferential formation on Pd(100) and Pd(111) surfaces has been supported by theoretical studies [95]. Theoretical calculations have also shown that the reaction of CO with NO to form adsorbed NCO and CNO species may occur on Cu₂O(111), with NCO formation being both thermodynamically and kinetically more favorable than CNO formation [96]. Furthermore, it has been clearly demonstrated that isocyanate surface complexes are genuine reaction intermediates on many oxide-supported metal catalysts [39–42,97–100]. In these systems, NCO species can be formed via the reaction of adsorbed atomic nitrogen (originating from NO dissociation) with either gas-phase or adsorbed CO molecules:



To study the formation and thermal stability of NCO experimentally, the surface dissociation of HNCO precursor was applied on several single-crystal metal surfaces, including Cu(111) [101(a)], Pt(110) [44,101(b)], Rh(111) [43,101(c),102], Pd(100) [19], Pd(111) [92] and Au(111) [103]. These studies consistently show that, depending on the metal, NCO species are stable only below room temperature. Upon heating, NCO decomposes into CO and adsorbed nitrogen, with decomposition typically initiating around 170 K, as evidenced by TDS and electron spectroscopies (AES, ELS). The presence of pre-adsorbed oxygen leads to a moderate stabilization of NCO species [19,44,98,101(a),102]. Isocyanate species could also be produced via oxidation of CN group on Cu(111) and Rh(111) surfaces [104–106]. Pre-adsorbed oxygen results in an increase in the relative amount of NCO, shifts the dominant vibrational band of NCO, and significantly stabilizes the NCO species on metals.

Moreover, vibration techniques (RAIRS and HREELS) offer a possibility to follow the temperature evolution of the isocyanate surface species in detail. For demonstration, the thermal behavior of NCO on Rh(111), Pd(100) and Au(111) surfaces is presented in Figure 1-3. At 95 K, the strong band at 2277 cm⁻¹ is detected due to the asymmetric stretch of molecularly adsorbed HNCO on Rh(111) (Figure 1) [43]. Upon heating to ~175 K, this species is removed (via desorption and dissociation), while a band at 2160 cm⁻¹ appears, indicating the formation of NCO. With further temperature increase, the intensity of this band decreases and disappears at 300–330 K, accompanied by the formation of linearly adsorbed CO at 2070 cm⁻¹.

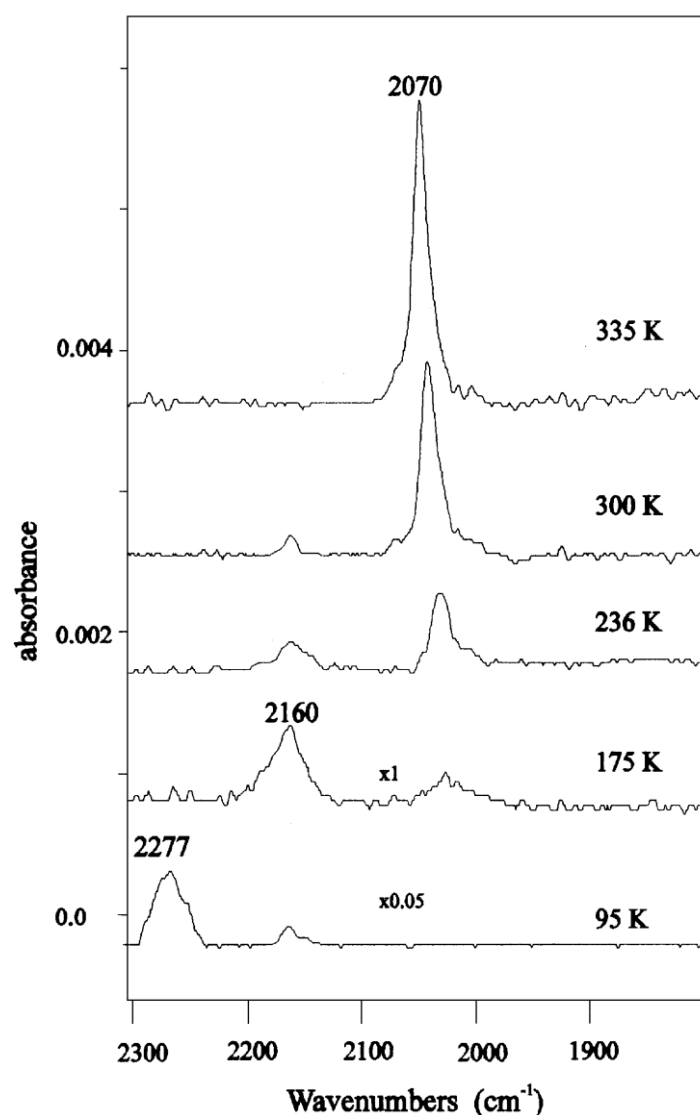


Figure 1. RAIR spectrum of adsorbed HNCO on Rh(111) and heated to higher temperature. (Reproduced from Ref. 43.).

A similar behavior was observed on Pd(100) (Figure 2) [19]. At low HNCO exposure (6.0 L), the dominant absorption band at 2274 cm^{-1} is assigned to molecularly adsorbed HNCO. The inset of Figure 2 shows the N–H stretching region with bands at 3374 and 3240 cm^{-1} . Coverage dependent NCO band for $\nu_a(\text{NCO})$ (2215–2147 cm^{-1}) detected between 160–280 K temperature range. From ~180 K, another peak evolved at 1910–1928 cm^{-1} , attributed to bridge-bonded CO formed via NCO decomposition.

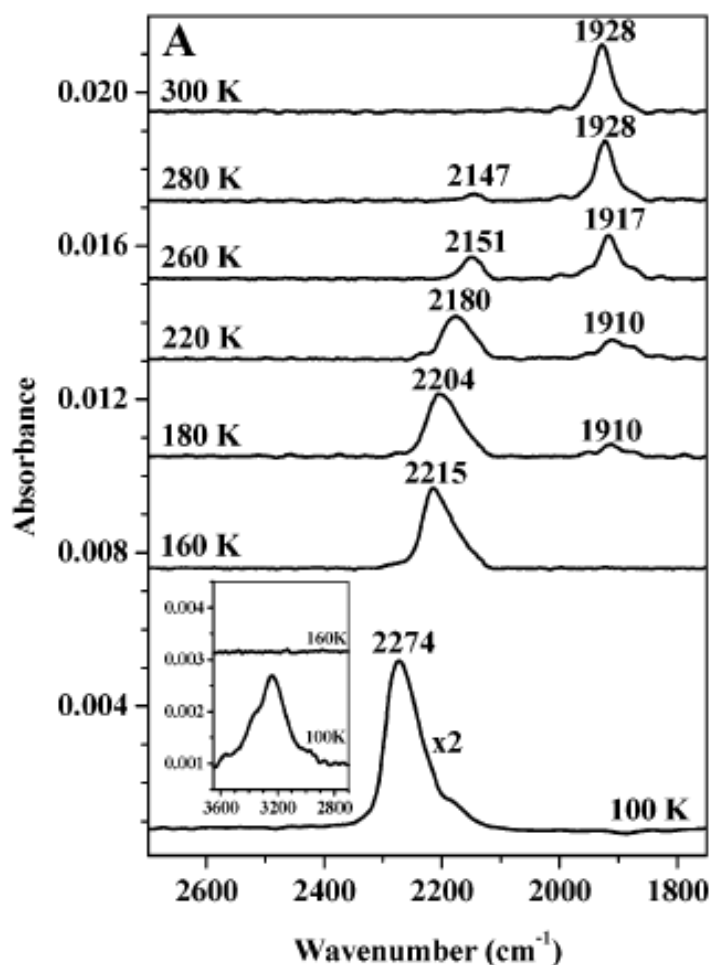
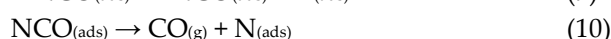
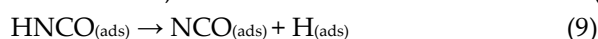


Figure 2. RAIR spectra of adsorbed HNCO on Pd(100) surface and effect of heating. (Reproduced from Ref.19.).

Representative HREELS spectra of Au(111) recorded at ~100 K under different HNCO exposures are shown in Figure 3A. The adsorption of HNCO gives rise to several vibrational losses at 515, 900, 990, 1390, 2270, 2780, and 3230 cm^{-1} [103]. The most prominent feature is the loss at the 2270 cm^{-1} , attributed to the asymmetric stretching of molecularly adsorbed HNCO ($\nu_a(\text{NCO})$). Additional losses at 2780 and 3230 cm^{-1} are assigned to N-H stretching modes while adsorption features of NCO group agree with the literature data obtained previously [107]. After heating the adsorbed layer, the attenuation of vibration loss at 2270 cm^{-1} was experienced, and a new spectral feature at 2185 cm^{-1} around 150 K, assigned to the asymmetric stretching mode of NCO, was observed (Figure 3B). This band together with the symmetric stretching mode of NCO ($\nu_s(\text{NCO})$) at ~1390 cm^{-1} remain detectable up to ~430 K, indicating a higher thermal stability of NCO on Au(111) compared to that on single crystal surfaces of Pt-group metals, like Pd, Rh. At the same time, no vibrational features corresponding to adsorbed CO were detected, as CO does not adsorb on clean Au(111) surfaces under these conditions.



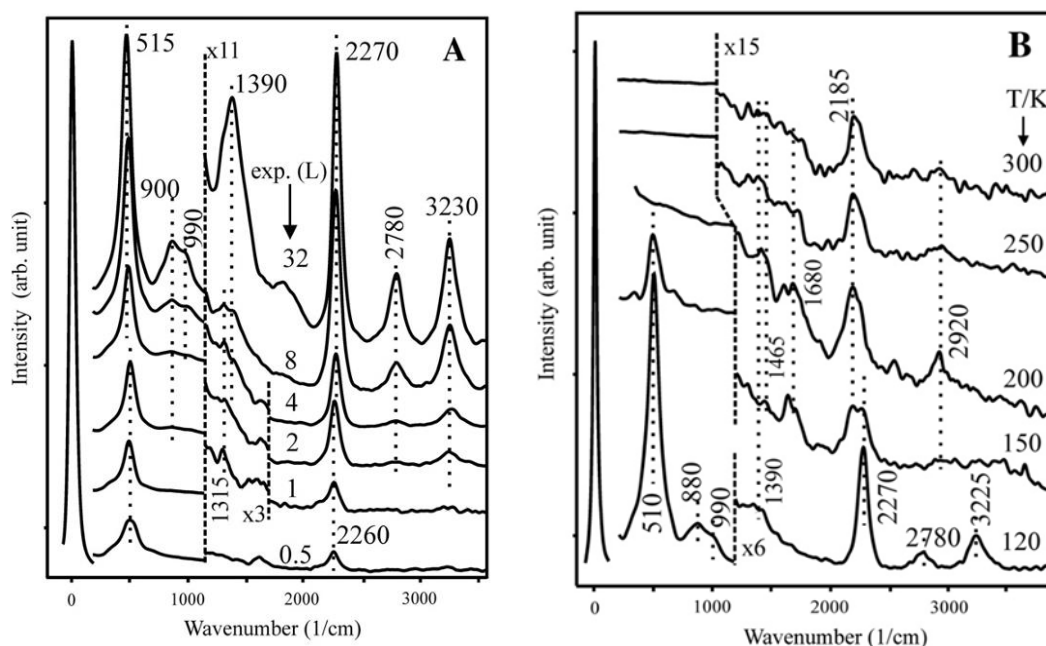


Figure 3. Effects of HNCO exposure on the HREEL spectra of untreated Au(111) at ~100 K (A), and subsequent annealing (B) (exposure of HNCO was 8.0 L). (Reproduced from Ref. 103.).

In contrast to clean, unsupported metal surfaces, the isocyanate exhibits substantially higher stability on oxide-supported metal catalysts, persisting under typical NO + CO reaction conditions [39–42,97–100,108–110]. Isocyanate intermediates were first identified by means of infrared spectroscopy by Unland on supported noble metals [39]. He proposed that NCO intermediate could be responsible for the formation of NH₃ in the presence of water at 400 °C during the NO + CO reaction.

Subsequent studies have systematically investigated the formation, stability, and reactivity of NCO species over various metal supported catalysts. Figure 4A illustrates the formation and thermal stability of NCO species on Pt/Al₂O₃ formed during NO + CO reaction [40]. Infrared bands corresponding to adsorbed NO appear in the 1500–1650 cm⁻¹ range, and linearly adsorbed CO was found at 2080 cm⁻¹. In a good agreement with findings of Unland [39], a characteristic $\nu_a(\text{NCO})$ mode of NCO at 2267 cm⁻¹ could be clearly identified.

The temperature dependence of NCO formation is shown in Figure 4B. This band appeared already at ~150 °C reaches a maximum around 400 °C, and then decreases, becoming barely detectable near ~500 °C. This behavior suggests that partially reduced metal sites (e.g., Pt) play a crucial role in activating NO molecules, promoting their dissociation, and facilitating the reaction between CO and adsorbed nitrogen atoms (step 8).

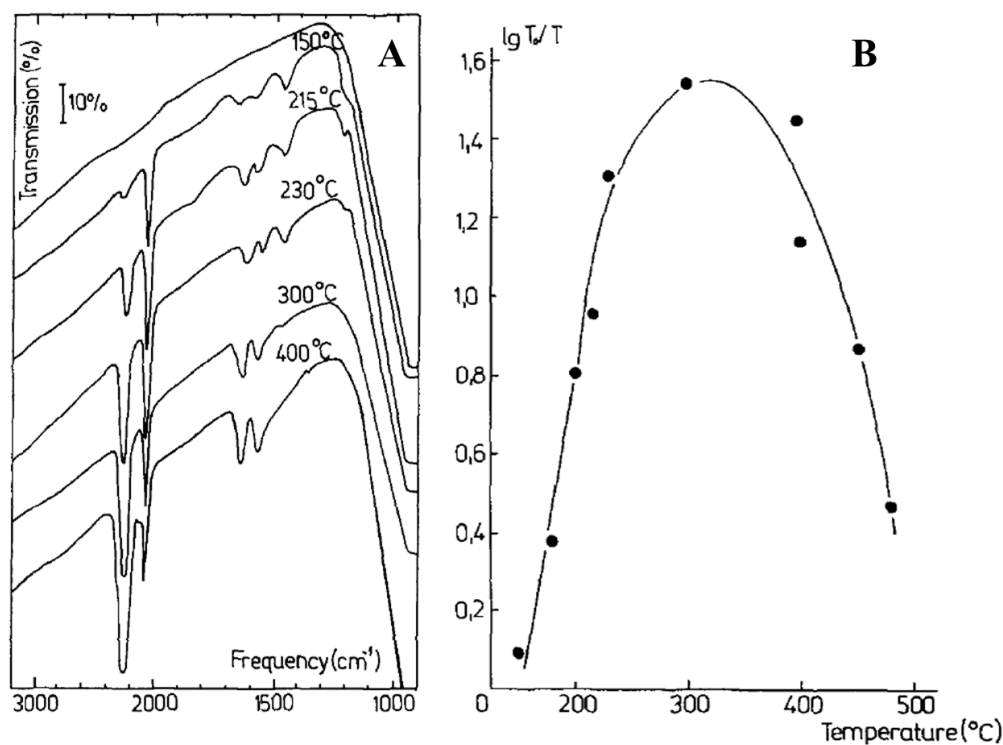


Figure 4. Infrared spectra observed at room temperature after dosing 5 % Pt/Al₂O₃ sample with a 10% CO, 5 % NO and 85 % N₂ mixture at different temperatures for 1 min (A). Dependence of the intensities of the band at 2267 cm⁻¹ (observed at room temperature) (B). (Reproduced from Ref. 40.).

Recent qualitative measurements indicate that the number of adsorbed NCO species can exceed the number of surface Pt atoms [39,41], suggesting that a fraction of NCO species is located on the alumina support [41,98]. This hypothesis is further supported by the observation that NCO can also produce on non-metallic chromia/alumina catalysts [109]. It has also been demonstrated that the nature of the support strongly affects the vibrational frequency of NCO. For Pt catalysts of comparable particle size and under identical NO + CO reaction conditions, the $\nu_a(\text{NCO})$ band is observed at 2210 cm⁻¹ on Pt/TiO₂, 2241 cm⁻¹ on Pt/MgO, 2272 cm⁻¹ on Pt/Al₂O₃ and 2318 cm⁻¹ on Pt/SiO₂ [100]. The observed IR frequencies are collected in Table 1. While the thermal stability of NCO on supported Pt varies with the support, no NCO bands are observed in the absence of Pt, indicating that metal sites are essential for its formation. The stability of NCO increases in the following order:

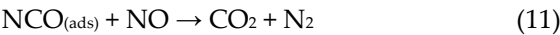
Pt/TiO₂ < Pt/Al₂O₃ < Pt/MgO < Pt/SiO₂

Table 1. The positions of the bands are due to surface isocyanate and carbon monoxide (Data are reproduced from Ref. 100).

Catalyst	Reaction temperature (°C)	Frequency (cm ⁻¹)		
		-NCO	[NCO]	-CO
Pt/Al ₂ O ₃	250	2272		-
	400	2080		
		2272	2138	2080

Pt/SiO ₂	250	2318	-
	400	2075	
		2318	-
		2075	
Pt/MgO	250	2241	-
	400	2067	
		2241	2213 2067
Pt/TiO ₂	250	2210	-
	400	2036	
		2210	
		2066	

Taken together, evidence from single-crystal metals, metal nanoparticles, and supported metal catalysts suggests the following mechanism: NCO forms initially on the metal surface, but it is highly unstable there. Therefore, it subsequently migrates to the metal/support interface or onto the support itself. In this way, NCO acts as an effective intermediate in the NO + CO reaction, capable of reacting with adsorbed or gas-phase NO:



Moreover, NCO species have been implicated in the formation of trace CN-containing products [101,110], and it has been proposed that NCO intermediates can contribute to NH₃ formation in the presence of water under conditions relevant to automobile exhaust [39–41,97]. Recent studies have experimentally confirmed that NH₃ can indeed form from NCO intermediates [99].



3.2. Identification and Reactivity of Alkyl Groups, Fisher-Tropsch Synthesis, CO Hydrogenation

Alkyl groups (CH, CH₂, CH₃, C₂H₃, C₂H₅ etc.) are key intermediates in Fischer-Tropsch synthesis and in the catalytic conversion of hydrocarbons into oxygenated products such as alcohols [20,47,65,66,73(ab),111-116], therefore, understanding their chemistry is crucial. In Fischer-Tropsch chemistry, two principal mechanistic pathways are generally considered. In the first pathway, the C–O bond of adsorbed CO (or CO-derived species such as C–OH) is cleaved, leading to the formation of CH_x species that participate in chain growth. In the second pathway, CO insertion into a growing hydrocarbon chain occurs, resulting in the formation of oxygenated intermediates of the type R–CH_x–OH [116]. A detailed understanding of these mechanisms requires the identification and characterization of the transient surface intermediates involved, particularly CH_x and C_xH_y species.

3.2.1. Identification and Dehydrogenation-Hydrogenation of Alkyl Groups

To address this, XPS, UPS, and various vibrational techniques (DRIFTS, RAIRS, and HREELS) have been employed to identify transient surface species and to provide valuable information on their stability and reactivity. In most cases, alkyl fragments were generated via thermal or photo-induced decomposition of alkyl halides. Previous studies reported the identification and stability of CH₃, CH₂, and CH species on Co and Ni polycrystalline surfaces using XPS and UPS following the thermal dissociation of CH₃Cl and CH₂Cl₂ [65]. The early cleavage of the C–Cl bond enabled the

investigation of the dehydrogenation of CH_x surface species without interference from other functional groups. Table 2 shows the photoemission (PE) energies for C 1s in XPS and the corresponding CH_x features in UPS obtained on Co and Ni surfaces. The binding energies are referenced to the Fermi level of the metal. The temperature ranges over which each species is observed, and the dominant are also indicated. The facile cleavage of the C–Cl bond enables the study of the stepwise dehydrogenation of CH_x surface species in the absence of significant interface from the support (eq. 2-4). Complementary TDS measurements indicate that a fraction of the adsorbed hydrogen recombines to form H₂, while another fraction reacts with CH₃ and CH₂ species to produce methane in the gas phase (eq. 5,6).

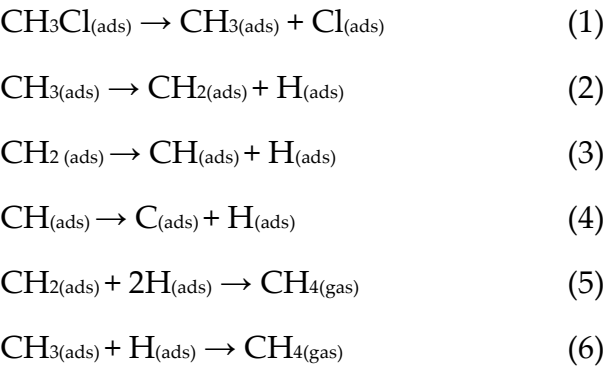


Table 2. Characteristic PE line energies for adsorbed on polycrystalline Co and Ni.

	Co			Ni		
species	XPS E _B ^F (eV)	UPS E _B ^F (eV)	Temperature regime (K)	XPS E _B ^F (eV)	UPS E _B ^F (eV)	Temperature regime (K)
CH ₃	285.8	6.8-6.9	170-250 150-300	285.6-285.8	6.5	170-210 150-380
CH ₂	284.9	-5.5	180-230 180-360	285.0-285.2	5.5-5.8	220-260 180-420
CH	283.8	5.0-5.1	200-360 190-450	283.8-284.0	5.2	270-470 200-650
C	293.3	4.7	360-570	283.5	4.3	480-850 300-850

The vibrational frequencies and assignments of alkyl intermediates have been reported for a wide range of metal surfaces, including Ag, Cu, Ni, Fe, Pt, Rh, and Ru, and are summarized in Table

3. In most studies, alkyl species were generated via thermal or photon-induced decomposition of alkyl halides, typically adsorbed at low temperatures (90–100 K). Notably, the vibrational frequencies of alkyl species exhibit only a weak dependence on the nature of the metal surface, indicating that their bonding characteristics are largely preserved across different metals.

Table 3. Vibrational characteristic for alkyl species on clean metals (Ag, Cu, Fe, Pt, Rh, Ru) surfaces.

Species	Assignment	Frequencies cm ⁻¹	Reference RAIRS HREELS	
CH ₃	v _a (CH ₃)	2918-2950	45 122-125	47(a), 66, 67 113(a), 117, 118
	v _s (CH ₃)	2775-2880		
	δ _a (CH ₃)	1350-1440		
	δ _s (CH ₃)	1141-1185		
	p(CH ₃)	760-820		
	v(M-C)	495-520		
CH ₂	v _a (CH ₂)	2940-3120	47(b) 121	46(a), 46(b), 48, 66 119
	v _s (CH ₂)	2880-2970		
	δ (CH ₂)	1295-1450		
	v (CH ₂)	1111		
	ω(CH ₂)	1020-1140		
	τ(CH ₂)	900-930		
	v(M-C)	460-590		
CH	v(CH)	2940-3010	124	46b, 48, 66
	δ (CH)	720-775		
C ₂ H ₅	v(CH ₃)	2905-2930	47(b),126	31, 47(a), 66, 67, 119
	δ(CH ₃)	1376-1430		
	ω(CH ₂)	1150-1205		
	p(CH ₃)	810-941		

The CH₃ species can be characterized on most metals by the asymmetric and symmetric stretching modes (v_a(CH₃)), v_s(CH₃)) typically observed at 2918-2950 cm⁻¹ and 2775-2821 cm⁻¹, as well as asymmetric and symmetric deformation modes (δ_a(CH₃)), (δ_s(CH₃)) which usually appear at 1350-1435 cm⁻¹ and at 1141-1185 cm⁻¹ (Table 3). Figure 5 shows the RAIR spectrum of CH₃ on a clean Rh(111) and on potassium-, iodine- and zinc-modified Rh(111) surfaces. In these experiments, the methyl radicals were generated by direct decomposition of azomethane (CH₃N₂CH₃) in front of the sample [45]. Three significant vibrations (v_a(CH₃), δ_a(CH₃), (δ_s(CH₃)) were observed on the clean sample (Figure 5A). The symmetric band of CH₃ cannot be detected by RAIRS due to dipole selection rules.

The thermal stability of CH₃ is illustrated in Figure 5B, which shows the temperature-dependent evolution of methyl species at 2918-2926 cm⁻¹ on clean and modified Rh(111) surfaces. This band disappears completely at 300-320 K, indicating the removal or transformation of CH₃ species.

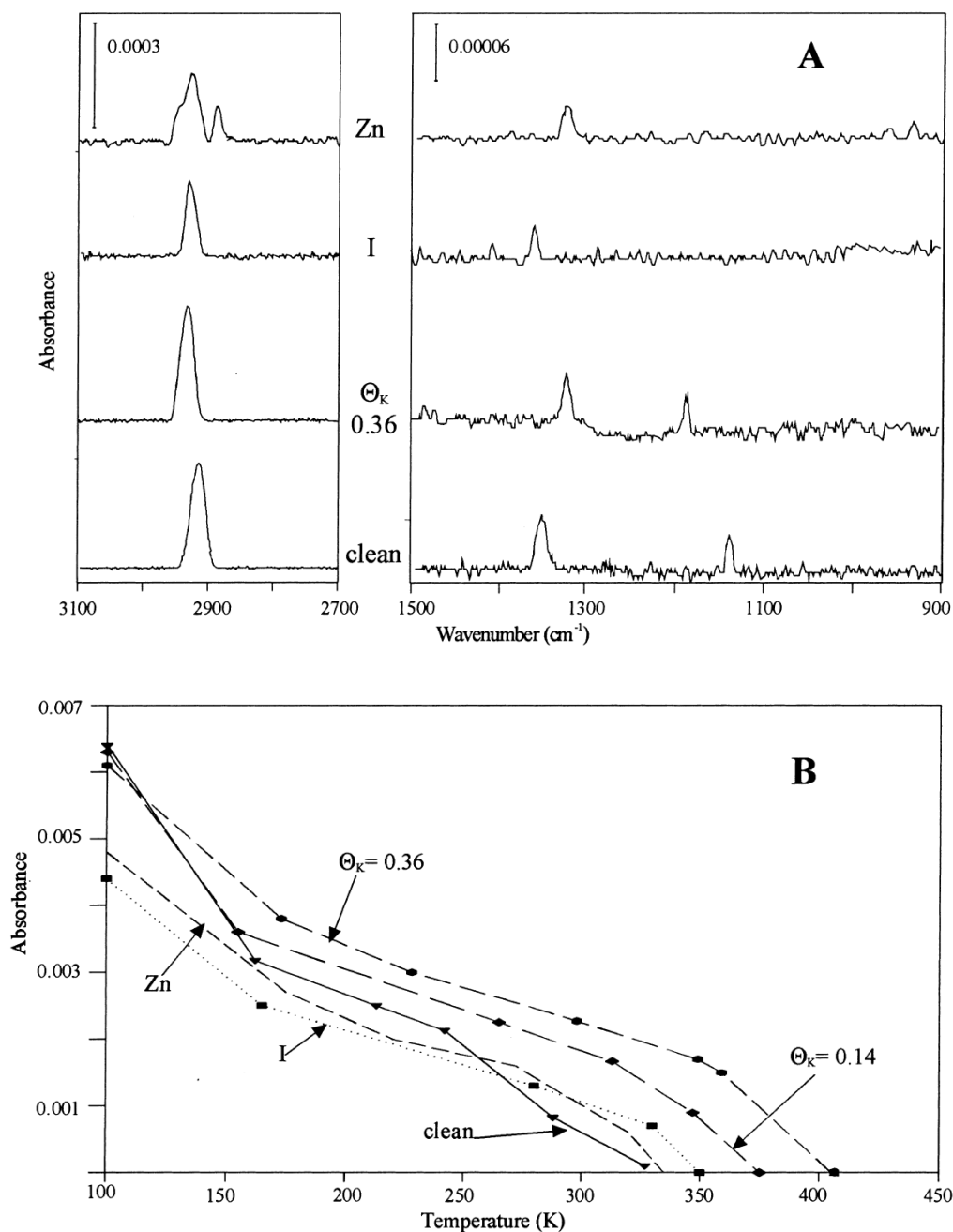


Figure 5. (A) RAIR spectra of the adsorbed CH₃ at saturation on clean and doped Rh(111) at 100 K. (B) Absorbance of the peak of CH₃ at 2918–2926 cm⁻¹ after heating the adsorbed layer on clean and doped-Rh(111). The coverage of I and Zn was ca. 0.3. Reproduced from Ref. [45].

Consistent results have been obtained by HREELS, where CH₃ species were generated via thermal or photo-induced dissociation of alkyl iodides or methane. Overall, the thermal stability of CH₃ on Rh surfaces is comparable to that observed on other clean metal surfaces [47,66,67,113,117,118,120,122–124]. Figure 5B further demonstrates that potassium significantly enhances the stability of CH₃, whereas Zn and I induce only minor stabilization effects. In contrast, co-adsorbed CO does not affect either the vibrational frequencies or the thermal stability of CH₃ species [122]. The influence of oxygen is more complex and will be discussed separately.

In Fischer–Tropsch synthesis, hydrogenation-dehydrogenation reactions of alkyl species play a critical role. As observed by Co and Ni, TDS studies confirm that both these pathways occur on noble

metals, leading to the formation of CH_2 , CH , C , and CH_4 [113]. Notably, coupling reactions of CH_3 species were not observed under these conditions.

The identification, stability, and reactivity of CH_2 species have also been extensively investigated on metal surfaces using a combination of spectroscopic techniques (XPS, UPS, RAIRS, HREELS) and mass spectrometry [46,47,117–119]. Figure 6 illustrates the general features of CH_2 surface chemistry on Pt(111), providing a representative example applicable to other metal surfaces. In this case, chloriodomethane (ClCH_2I) was used as a precursor due to its favorable dissociation characteristics [46]. At 100 K, monolayer of ClCH_2I exhibits losses at 500, 725, 1140, 1365, 2955, and 3020 cm^{-1} . In harmony with TPD and XPS results, the

C-halogen bond cleavage occurs in the temperature range 170–200 K. Subsequently, CH_2 species identified by their symmetric, asymmetric and deformation modes at 1440, 2880 and 2940 cm^{-1} appear above ~230 K [46]. These bands disappear around 320 K; the higher-frequency band already contains contributions from CH species. Isotope exchange experiments indicated the formation of methane in hydrogenation reactions of surface CH_2 . In addition, minor halogen-assisted CCH formation has been detected around ~540 K, attributed to the reaction between adsorbed C and CH species, with a characteristic band at 3035 cm^{-1} [48].

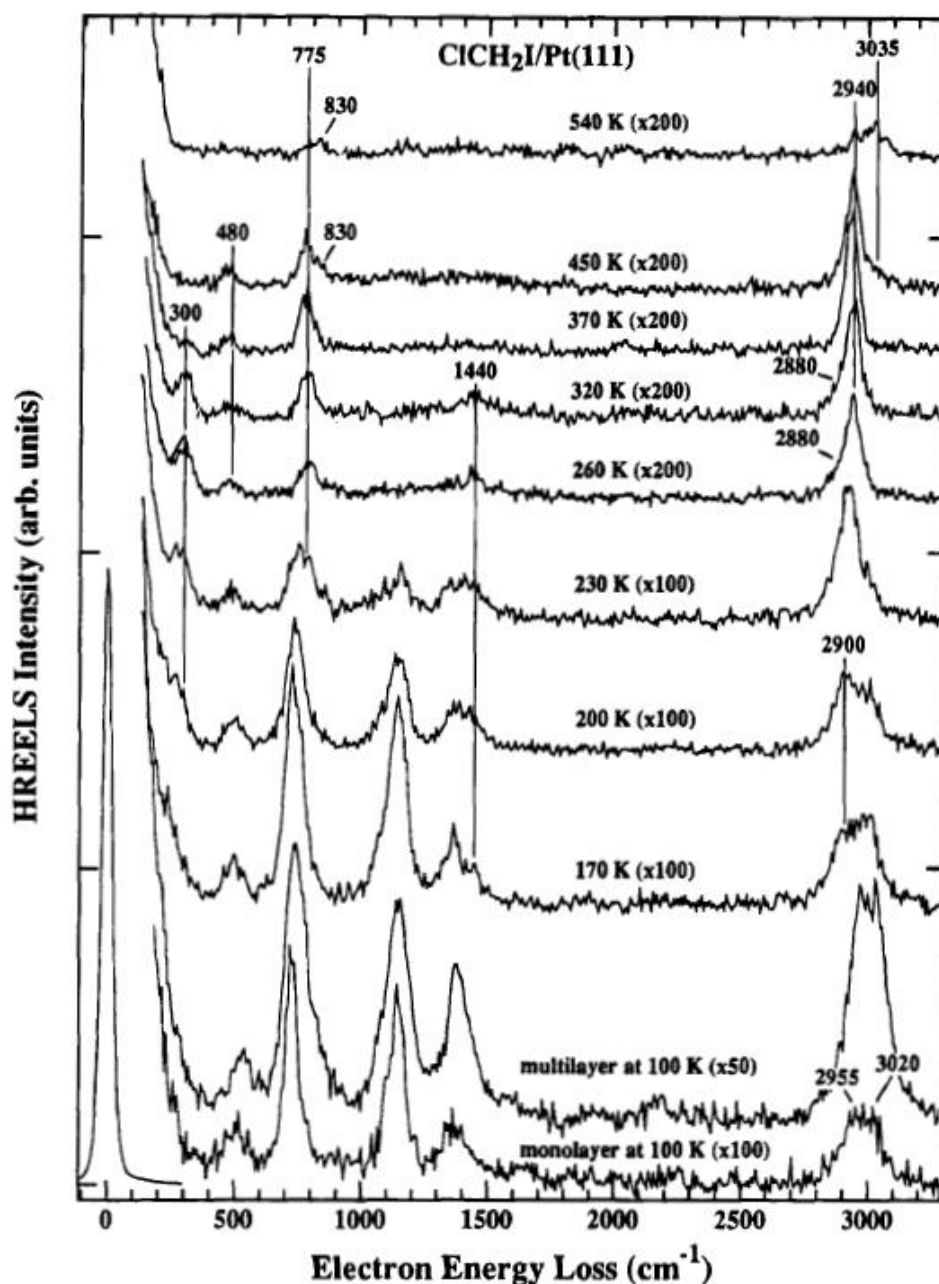


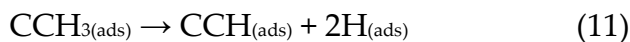
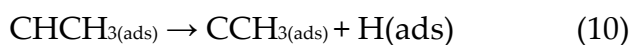
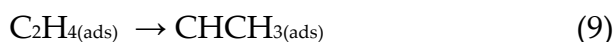
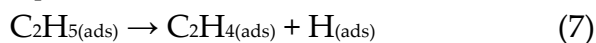
Figure 6. HREEL spectra for monolayer and multilayer of ClCH_2I at 100 K on Pt(111) and for multilayers warmed up briefly to various temperatures as indicated. All spectra were taken at 100 K. Reproduced from Ref. [46].

In contrast to Pt and Rh surfaces, the CH_2 species on Ru(001) and Pd(100) not only undergo hydrogenation to form CH_4 but also readily dimerize to produce C_2H_4 in the temperature range 160–230 K, as demonstrated by XPS, UPS, and TDS measurements [73,74]. A fraction of the formed ethylene, adsorbed in a π -bonded configuration, desorbs, while the remaining fraction, adsorbed in a di- σ configuration, is further transformed into vinyl and ethynyl species between 220 and 300 K; these species decompose only above 450 K. On Cu surfaces, CH_2 species similarly react to form C_2H_4 at 160–230 K, which desorbs with a peak temperature (T_p) of 240 K. In contrast to Pt-group metals, no self-hydrogenation of CH_2 to CH_4 is observed on Cu(100) [71]. On Ag(111), $\text{CH}_{2(a)}$ couple with neighboring $\text{CH}_{2(a)}$ to form ethylene, which desorbs in a reaction-limited process at 230–260 K, as evidenced by TPD and RAIRS experiments [121].

The formation and reactivity of adsorbed C_2H_5 species on Rh(111) was studied by means of RAIRS and TDS. In these experiments, hydrocarbon fragments were also produced via thermal and

photo-induced dissociation of corresponding iodo compounds. The conclusions drawn for Rh(111) are generally applicable to other Pt metals, too (Table 3). Figure 7A shows spectra for the clean surface, while Figure 7B illustrates the effect of potassium modification. At 100 K, the observed vibrational features correspond gas-phase and adsorbed $\text{C}_2\text{H}_5\text{I}$, consistent with data reported for Pt(111) [126]. During annealing, C–I bond cleavage occurs at ~140 K on clean Rh(111), and by 200 K, the spectra exhibit bands characteristic exclusively of adsorbed C_2H_5 species (see assignments in Table 3). Further heating to ~240 K leads to the disappearance of C_2H_5 features and the emergence of new bands at 2975, 2879, 1380, and 1125 cm^{-1} , which are characteristic of ethylidyne species, likely formed via intermediate vinyl species [66]. Simultaneously, dehydrogenation produces C_2H_4 , which desorbs at $T_p = 185$ K, while a fraction of the species undergoes hydrogenation to form C_2H_6 at similar temperatures. At higher temperatures (>330 K), a band at ~3030 cm^{-1} indicates the formation of stable CCH species.

The presence of potassium significantly alters the reaction pathway. It promotes the direct formation of adsorbed C_2H_4 (bands at 2947, 2912, 1195, and 1117 cm^{-1}) at ~190 K, which subsequently desorbs at higher temperatures. In addition, potassium induces coupling reactions of ethyl species, leading to the formation of butene and butane (see eq. 12). Similar reaction pathways have been reported for other clean Pt-group metals [47b,49,66,68,69,126]. In general, C_2H_5 species transform to yield C_2H_4 and C_2H_6 at 160–240 K. A fraction of resulting C_2H_4 is further converted into vinyl species, which remain stable up to ~450 K (eq. 7–11).



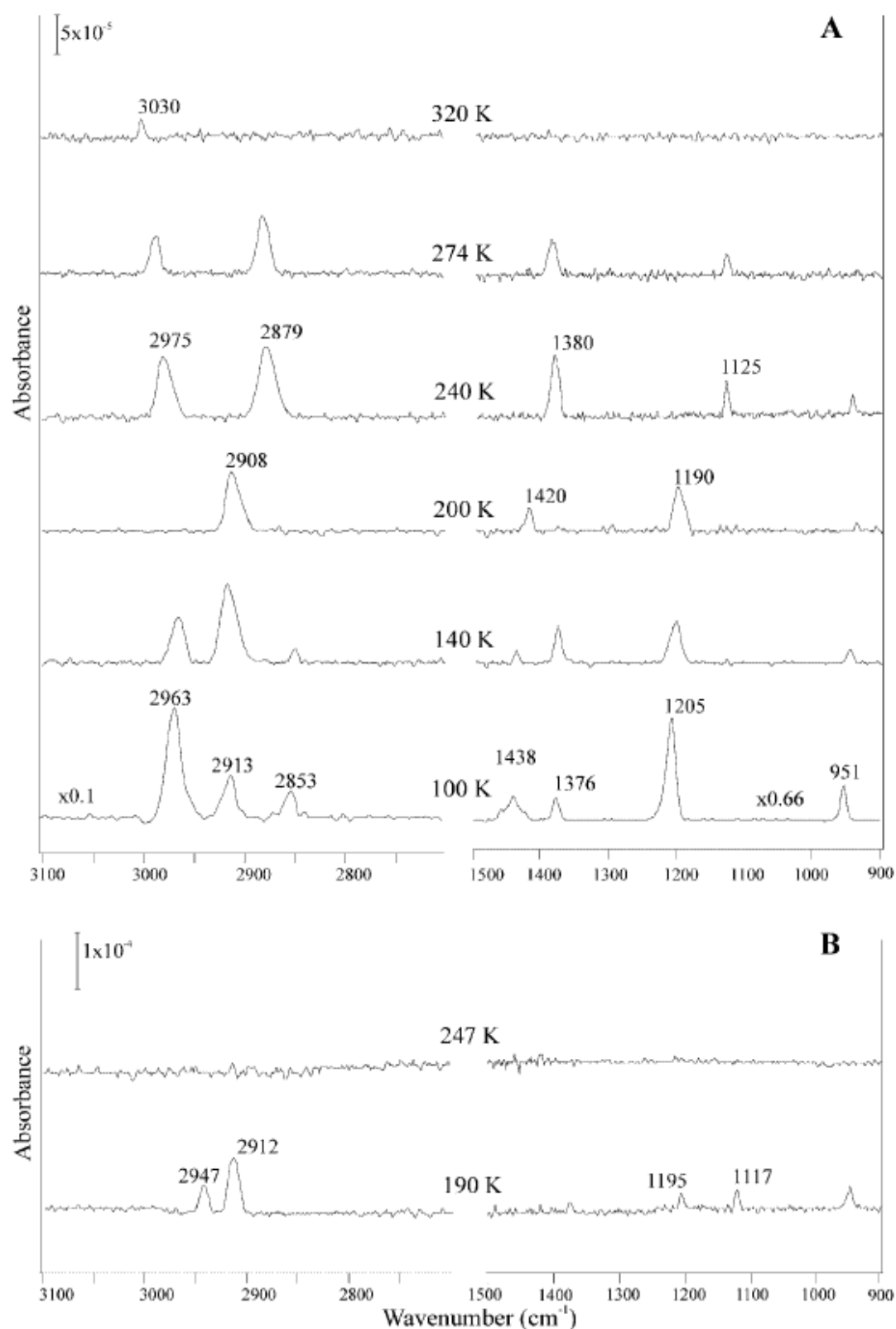


Figure 7. Effects of temperature on the RAIR spectra of adsorbed C_2H_5I on Rh(111). **(A)** Clean Rh(111); **(B)** K-dosed Rh(111), $\theta_K = 0.36$. In the latter case, potassium was deposited on the adsorbed C_2H_5I heated to 190 K. (Reproduced from Ref. 47b.).

The same steps were observed on Ni surfaces; however, the dehydrogenation proceeded much faster [128]. Cu surfaces exhibited comparable behavior in C_2H_5 transformation, although with a stronger dependence on surface orientation (facet selectivity) [72].

3.2.2. Interaction of Alkyl Groups with Adsorbed Oxygen on Metals

CH₃ + oxygen reaction

The interaction of alkyl groups with adsorbed oxygen, leading to the formation of alkoxide species (e.g., CH₃O, CH₂O, C₂H₅O), provides important insight into the formation of oxygenated products such as aldehydes and alcohols during Fischer–Tropsch synthesis [127,128]. Among these, the interaction between methyl species and adsorbed oxygen has been studied in detail, as it represents the simplest model system for understanding alkoxide formation. This interaction has been investigated primarily by RAIRS, in which methyl groups were generated in situ via the decomposition of azomethane, thereby avoiding the influence of halogen-containing precursors [45].

As discussed previously, the characteristic vibrational bands of adsorbed CH₃ are observed at 2918 cm⁻¹ (ν_a(CH₃)), 1353 cm⁻¹ (δ_a(CH₃)) and 1141 cm⁻¹ (δ_s(CH₃)). These features are also present when CH₃ is adsorbed on oxygen-covered Rh(111) surfaces (Figure 8A). In addition, new bands appear at 2960, 1440 and 1040 cm⁻¹, which are assigned to methoxide (CH₃O) species, corresponding to ν_a(CH₃), δ_s(CH₃) and ν(C-O) vibrational modes, respectively [47(a),127,128,131,132]. The formation of CH₃O species has also been confirmed by HREELS measurements [47]. Methoxide is a key intermediate in the synthesis of alcohols and in reactions such as CH₄ + CO₂ conversion [28,33,62,64]. As shown in Figure 8A and 8B, CH₃O species can form both when CH₃ is adsorbed on an oxygen-precovered Rh(111) surface and when oxygen is introduced onto a CH₃-saturated surface. Upon heating the co-adsorbed layer, decomposition begins at ~158 K, leading to the formation of adsorbed CO. The methoxide intermediate remains stable up to 188–220 K (Figure 8). Subsequently, adsorbed CO and hydrogen (produced via dehydrogenation of CH_x species) react with oxygen to form CO₂ and H₂O.

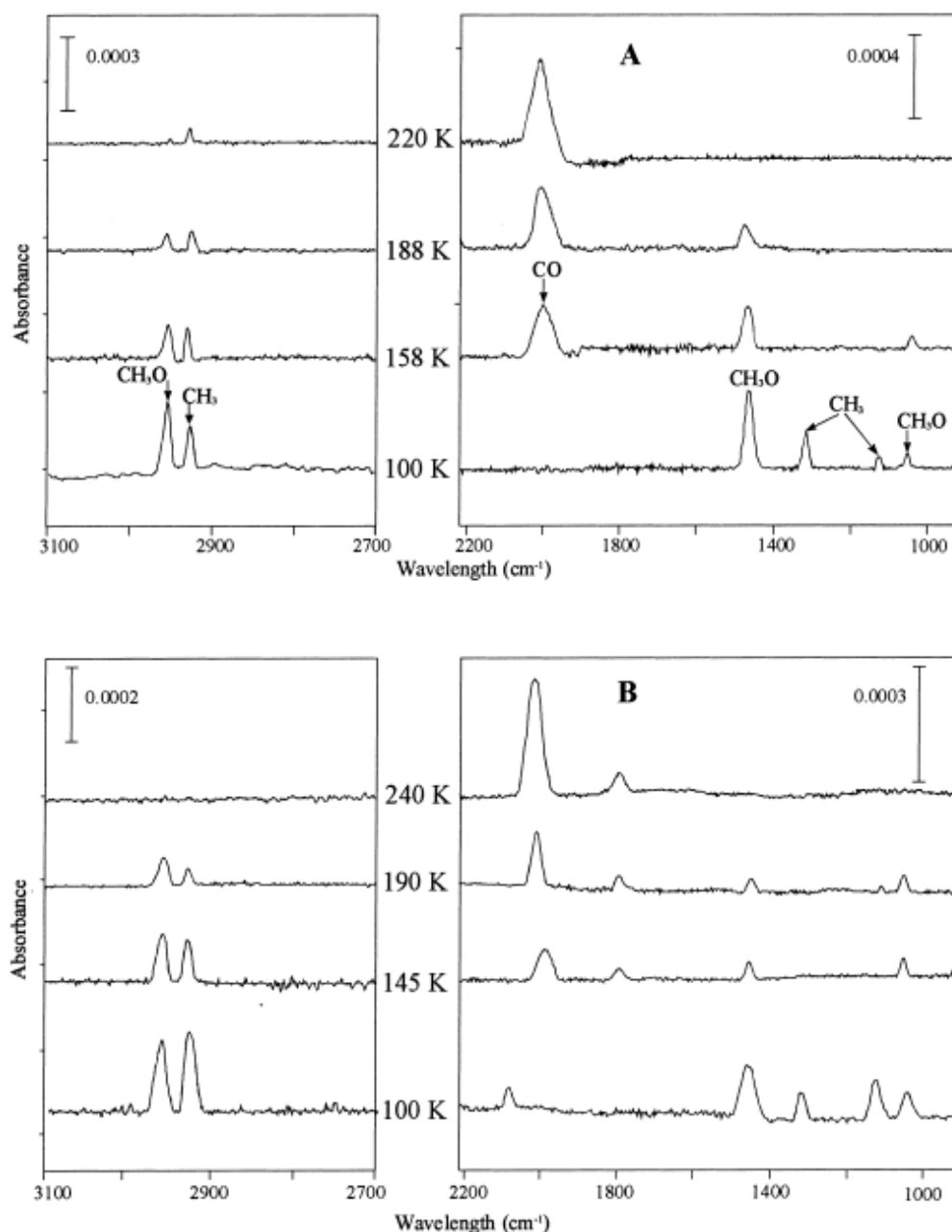
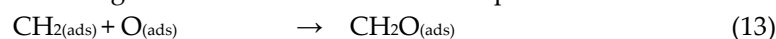
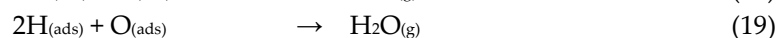
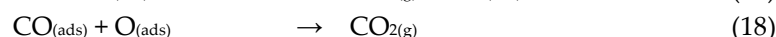
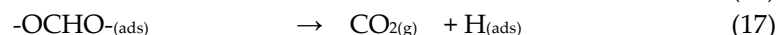
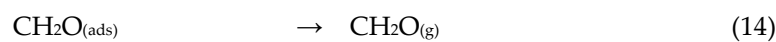


Figure 8. RAIR spectra of Rh(111) (A) following the adsorption of CH₃ on O-covered surface (θ_O = 0.5), and (B) following the adsorption of oxygen on the CH₃-saturated surface. Both compounds were adsorbed at 100 K. (Reproduced from Ref. 45.).

CH₂ + oxygen reaction

A general feature observed across metal surfaces is that pre-adsorbed oxygen slightly suppresses the dissociation of the C-halogen bond in CH₂I₂, while simultaneously strengthening the interaction of the resulting CH₂ species with the surface. In addition, increasing oxygen coverage leads to a decrease in the formation of CH₄ and H₂ – typical products in the absence of oxygen. A key outcome of the interaction between CH₂ and adsorbed oxygen is the formation of formaldehyde (CH₂O), the surface concentration of which depends strongly on the nature of the metal. On Pt-group metals and several other surfaces, CH₂ reacts with adsorbed oxygen above ~170 K to form CH₂O; however, this species desorbs rapidly after formation in a rate-limiting step, making its direct spectroscopic detection difficult [46(a),46(b),49,71-74,77,121]. Consequently, temperature-programmed desorption (TPD) provides more detailed insight into its formation and subsequent transformation:





Ru is an excellent catalyst for the synthesis of higher hydrocarbons; therefore, it was interesting to examine its effect on the coupling of CH_2 with O [73]. XPS measurements indicate that C–I bond cleavage in CH_2I_2 occurs around 200 K, leading to the formation of CH_2 species that react readily with adsorbed oxygen; a significant fraction of the resulting CH_2O desorbs immediately in a rate-limiting step (eqs. 13-14) [73]. Similar behavior has been reported for Pt(111), Rh(111), and Pd(100) [46(a),46(b),74].

However, the subsequent transformation of formaldehyde on Ru(001) is more complex than on other metals. TDS measurements at an oxygen coverage of $\theta_{\text{O}} = 0.25$ reveal a rich reaction network (Figure 9). Compared to the clean surface, molecular desorption of CH_2I_2 occurs at higher temperatures, while CH_4 formation at 220–230 K indicates that partial self-hydrogenation of CH_2 still takes place. Smaller amounts of H_2 are also detected ($T_{\text{p}} \approx 270$ and 490 K). The most significant feature is the formation of CH_2O ($T_{\text{p}} = 298$ K), confirming its role as a primary intermediate. At higher temperatures (>500 K), CO, CO_2 , and H_2O appear as final decomposition and oxidation products.

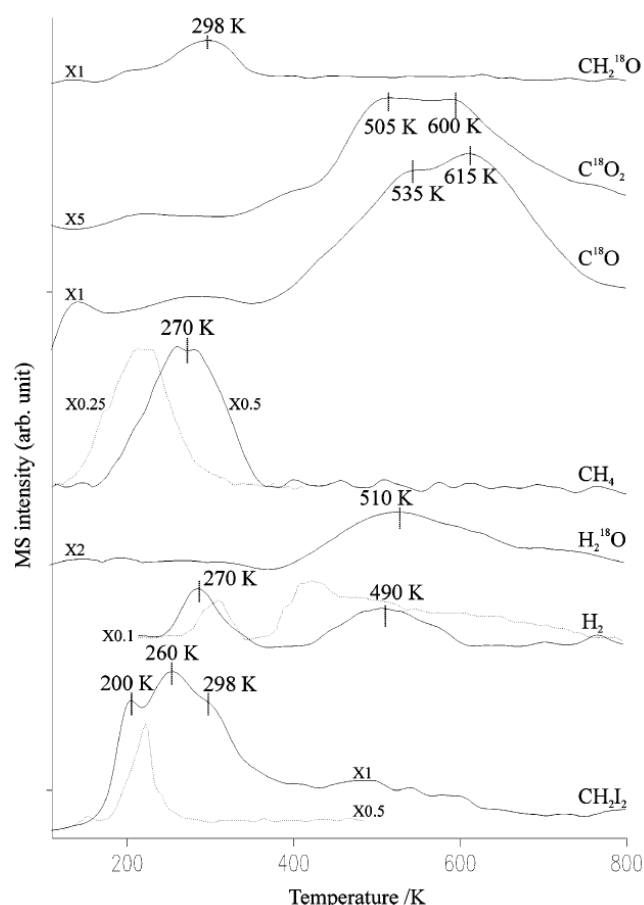


Figure 9. Thermal desorption spectra for various products at $\text{O} = 0.25$. CH_2I_2 exposure was 6 L. Dotted curves represent TPD products from a clean surface. (Reproduced from Ref. 73).

UPS further reveals the nature and evolution of surface intermediates (Figure 10.). At 110 K, the spectra showed the molecular orbitals of adsorbed CH_2I_2 on Ru(001), which were detected also on Pd(100) and Cu(100) previously [74,71(ab)]. Upon heating to 219 K, new photoemissions were

experienced at 5.7, 8, 8, and 11.0 eV due to adsorbed CH₂O [70]. This spectroscopic observation indicates that CH₂O can remain adsorbed on Ru(001) surface, similar to its behavior on Cu(110).

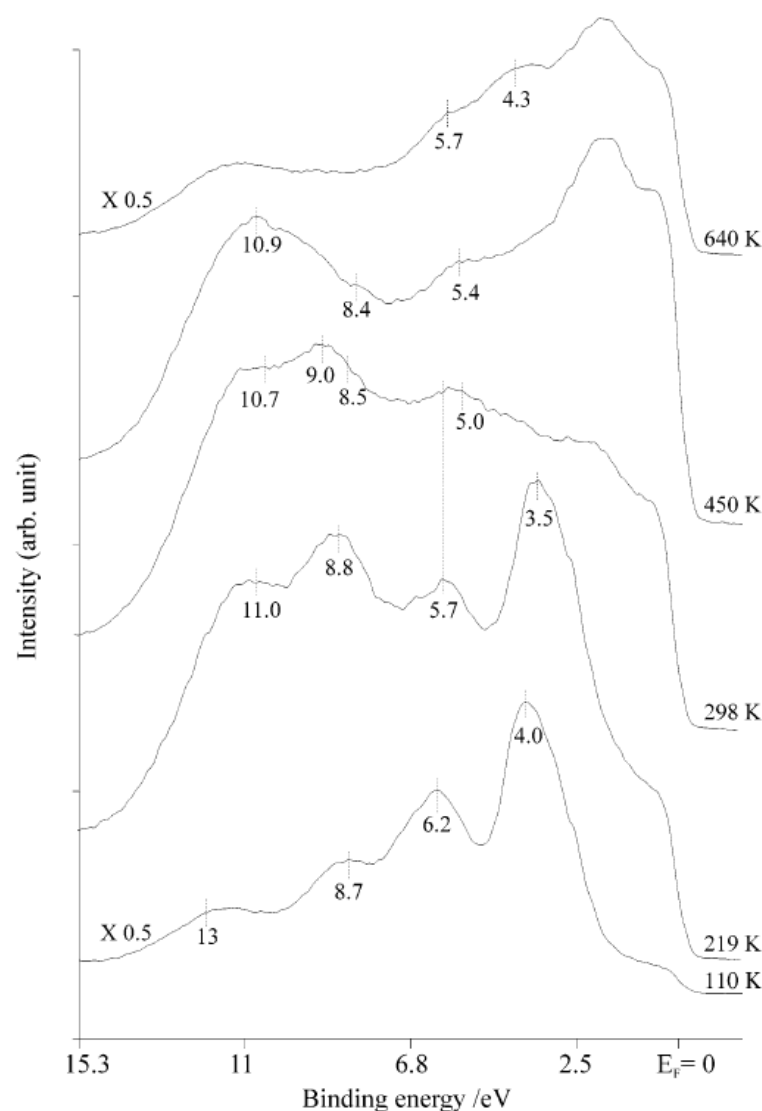
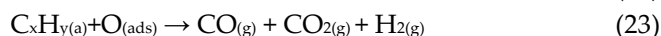
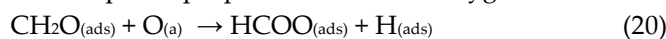


Figure 10. He UPS spectra of Ru(001) as a function of annealing temperature at $\Theta_{\text{O}} = 0.5$. CH₂I₂ exposure was 6 L. (Reproduced from Ref. 73.).

In contrast, formaldehyde species did not remain on Pt(111), Rh(111) and Pd(100) [46(ab),74]. At 298 K, additional spectral features (5.0, 8.5, 9.0 and 10.7 eV) appear, which can be attributed to adsorbed formate (HCOO) species [32,70,75,76]. Formate formation has also been suggested on Ag(111) based on RAIRS measurements [121]. At temperatures above ~450 K, peaks characteristic of adsorbed CO (8.4 and 10.9 eV) and water (6.2, 8.5, and 12.3 eV) are observed [76–78]. Based on these findings, the following additional steps are proposed to occur on oxygen covered Ru(001):



Independent studies of formaldehyde adsorption on Ru(001) confirm that its thermal stability, decomposition pathways, and formate formation are consistent with those observed during CH₂ + O reactions. Moreover, formate species have been directly identified by HREELS, and infrared studies demonstrate that adsorbed formaldehyde can be converted to formate on oxide-supported metal catalysts [133,134].

C₂H₅ + oxygen reaction

C₂H₅ surface groups and their interaction with oxygen play an important role in the formation of oxygenated hydrocarbons as well. The oxidation of C₂H₅ was studied on Rh(111) and Ru(001) surfaces [47,69,129]. In contrast to CH₃ species, transiently formed ethoxy (C₂H₅O) is hardly detectable experimentally by spectroscopic methods. This is most likely the case due to its limited thermal stability; for example, ethoxy species generated via ethanol decomposition on clean Rh(111) decompose completely below 250 K, yielding adsorbed hydrogen and CO [129]. Upon heating, the interaction of adsorbed C₂H₅ with oxygen leads to the formation of H₂O, CO₂, and small amounts of CH₃CHO and CO. The formation of acetaldehyde is generally attributed to β-hydrogen elimination of adsorbed ethoxy species, as established by Houtman and Barteau [62]. Spectroscopic measurements only reveal a loss in the CO stretching region (2040-2050 cm⁻¹) when the T ≥ 2070 K, suggesting that oxygen-containing C₂ intermediates are present only in low concentrations on Rh(111).

On Ru(001), significantly different oxidation products were experienced during C₂H₅ oxidation [69]. The presence of adsorbed oxygen suppressed the formation of ethane and ethylene which were dominant on clean Ru(001) and instead promotes the formation of oxygenated products. A notable feature of this system is the strong dependence of product distribution on oxygen coverage, as evidenced by TPD-MS measurements (Figure 11). At low oxygen coverage, diethyl ether is formed, likely via coupling of two ethyl species; the involvement of short-lived ethoxy intermediates in this process cannot be excluded. At higher oxygen coverages, acetaldehyde becomes the dominant product, consistent with hydrogen abstraction from transient ethoxy species.

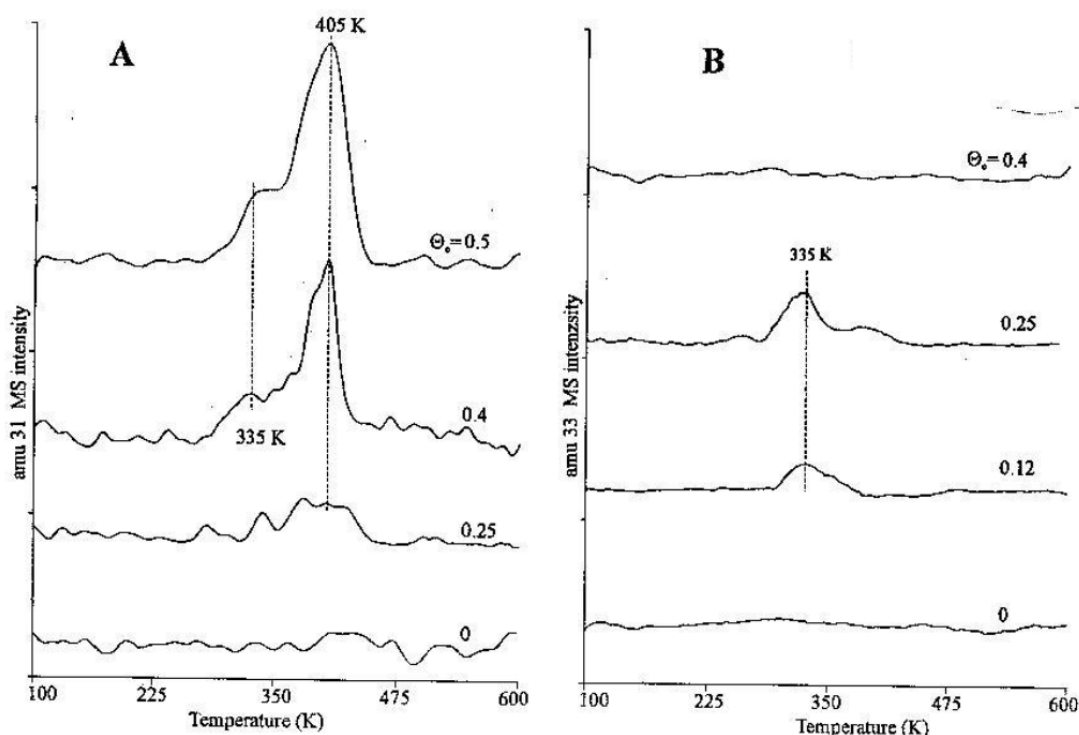
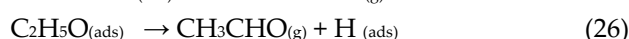
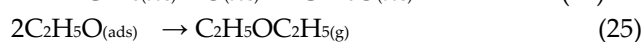
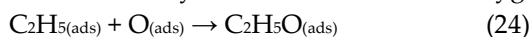
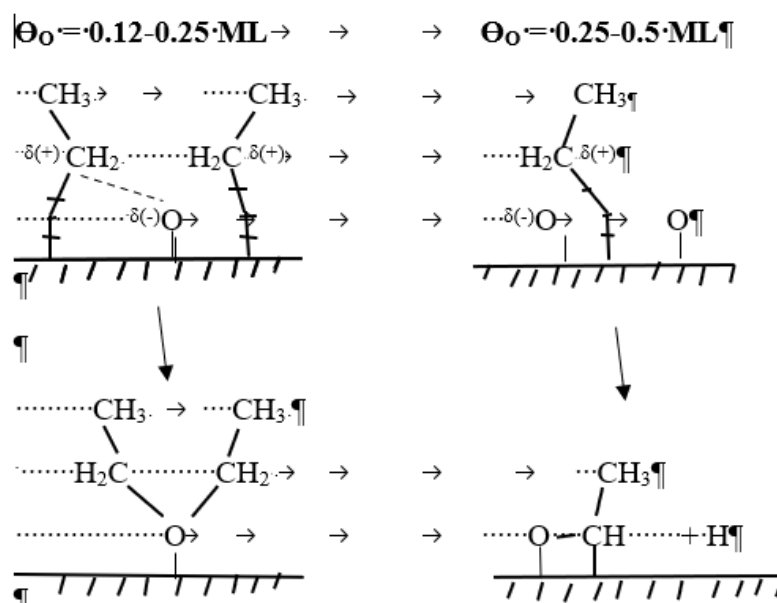


Figure 11. TPD spectra of (A) acetaldehyde and diethyl ether (B) as a function of oxygen coverage. The exposure of C₂H₅I was 3.6 L. (Reproduced from Ref. [69].).

This pathway is analogous to ethanol decomposition mechanisms reported for Pt-, Rh-, and Ir-based systems [33,34]. CO formation is also observed and may originate from the oxidation of CCH surface species, which are likely formed via ethylene transformation on oxygen-free sites (steps 9-11).



Thus, the overall reaction network on Ru(001) reflects a competition between hydrocarbon coupling and oxidation pathways, strongly modulated by oxygen coverage (Scheme 1).



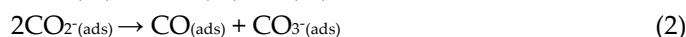
Scheme 1. Representation of formation of diethyl ether and acetaldehyde on oxygen-covered Ru(001).

It is worth mentioning, that the formation of C–O bonds is not limited to ethyl species; similar behavior has been reported for higher alkyl groups. For instance, propoxide formation has been identified by XPS and RAIRS following thermal activation of 2-propyl groups in the presence of chemisorbed oxygen on Ni(100) [135].

In contrast to metal surfaces, alkyl species are more readily stabilized on oxide supports, where they preferentially bind to surface oxygen atoms to form alkoxy species. The stability and reactivity of these intermediates are primarily governed by the nature of oxide and the characteristics of the metal-oxide interface. Both the bonding strength and coordination mode of alkoxy species play a decisive role in determining the pathways leading to oxygenated hydrocarbons on supported catalysts.

3.3. CO₂ Hydrogenation and Methanation on Metals and Supported Catalysts

The activation of the relatively inert CO₂ molecule represents the first and most critical step in CO₂ conversion reactions on both metal and oxide surfaces [22,23,78,79(abc)]. The formation, characterization and dissociation of electronically excited CO₂[−] have been widely investigated on metal surfaces [78,79(abc)]. Electron donation to CO₂ is typically facilitated by alkali-promoted metals or by co-adsorbed hydrogen species. At low surface coverage, activated CO₂ species can dissociate into adsorbed CO, which may subsequently desorb; XPS and UPS measurements indicate that this process can occur at temperatures as low as ~130 K. At higher coverages, CO₂[−] species may undergo disproportionation, yielding CO and carbonate species:



The catalytic conversion of CO₂ is of major importance for mitigating CO₂ emissions and producing value-added fuels and chemicals. Among the most relevant processes are CO₂ hydrogenation and reforming reactions with hydrocarbons (e.g., CH₄) [4,5,28,136–140]. Methane reforming reactions (CH₄ + CO₂ or CH₄ + CO) can also serve as a source of hydrogen and synthesis gas for energy applications [28]. The products of CO₂ conversion include fuels (e.g., CH₄) and chemicals such as CO and methanol, as illustrated in Figure 12.

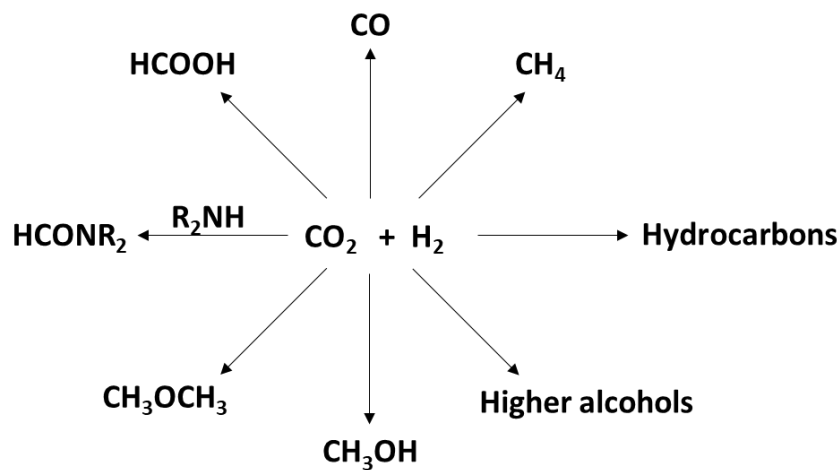
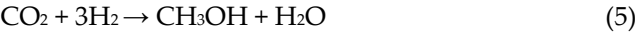


Figure 12. Products from CO₂ hydrogenation. (Reproduced from Ref. 138.).

This review focuses primarily on the identification and reactivity of intermediates formed during CO₂ hydrogenation leading to CO, CH₄, and light alcohols [3–5,114,131,132,139–144], as well as on hydrogen production via reforming of methane and alcohols (methanol and ethanol) [6,28,33,34,63,64,157–160]. One of the most promising reactions of CO₂ conversion is the CO formation via reverse water gas shift (RWGS) reaction. The other important reaction in CO₂ hydrogenation is methane formation (called Sabatier reaction) [21,51]. Also, an effective way for CO₂ utilization is methanol formation [21,37]. These processes often occur simultaneously, with RWGS competing with methanation and methanol formation, producing CO and H₂O as by-products.



Mechanistically, CO₂ hydrogenation can proceed via multiple pathways, including direct CO₂ dissociation (the RWGS route) and the formate-mediated pathway [21,51,146]. The identification and characterization of surface intermediates are therefore essential for elucidating reaction mechanisms. Table 4 summarizes the key intermediates detected primarily by DRIFTS, including species relevant to both CO₂ hydrogenation and reforming reactions.

Table 4. The assignments of IR bands of intermediates formed in CO₂ hydrogenation, and reforming of methane and light alcohol (methanol, ethanol).

Species	Vibrational mode	Wave numbers	References
linearly, bridge, twin CO	$\nu(\text{C-O})$	1900-2100	17, 19, 26, 40, 43, 53. 60
Carbonyl hibride H_nCO	$\nu(\text{C-O})$	1840-1880	28, 53, 56
Bicarbonate HCO_3^-	$\nu_a(\text{O-C-O})$	1555-1671	10, 24-26
	$\nu_s(\text{O-C-O})$	1396-1500	50, 52, 54-61
	$\delta(\text{O-H})$	1220-1260	
Carboxylate HCO_2^-	$\nu_a(\text{O-C-O})$	1631-1670	24, 26, 52
	$\nu_s(\text{O-C-O})$	1245-1298	54-56, 58-60

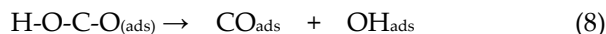
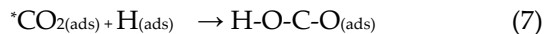
Formate HCOO ⁻	$\nu_a(\text{O-C-O})$	1575-1587	
	$\nu_s(\text{O-C-O})$	1433-1399	10, 25, 26
	$\gamma(\text{O-C-O})$	1338-1327	28, 52-61
	$\nu(\text{C-H})$	2848-2830	
Formaldehyde, formyl H ₂ CO	$\nu(\text{C-O})$	1716-1712	46, 56, 73, 133,
	$\nu(\text{C-H})$	2800-2820	134(a)
Acetaldehyde CH ₃ CHO	$\nu(\text{C=O})$	1695-1752	33, 34, 63, 64, 134(b) 158-160
Acetyl CH ₃ CO	$\nu(\text{C=O})$	1610-1680	33, 64, 159
Methoxy CH ₃ O	$\nu_a(\text{CH}_3)$	2910-2930	45, 47(a), 127-
	$\delta_a(\text{CH}_3)$	1350-1360	132,
	$\delta_s(\text{CH}_3)$	1100-1150	152, 153
Ethoxy C ₂ H ₅ O	$\nu_a(\text{CH}_3)$	2966-2979	
	$\nu_s(\text{CH}_2)$	2914-2934	33, 34,
	$\nu_s(\text{CH}_3)$	2871-2898	60, 62-64,
	$\delta_a(\text{CH}_3)$	1447-1455	158-160
	$\delta_s(\text{CH}_3)$	1382-1424	
	$\nu(\text{CO})_{\text{mono}}$	1069-1101	
Carbonate monodentate CO ₃ ²⁻	$\nu_a(\text{O-C-O})$	1446-1590	25, 26, 28,
	$\nu_s(\text{O-C-O})$	1370-1395	33, 34, 50, 52,
	$\nu(\text{C-O})$	1040-1090	56, 60,
Carbonate bidentate CO ₃ ²⁻	$\nu_a(\text{O-C-O})$	1535-1670	5, 25, 26, 33,
	$\nu_s(\text{O-C-O})$	1243-1355?	34, 50,
	$\nu(\text{C-O})$	1010-1015	52, 56, 60,

The formation, stability, and reactivity of these intermediates are strongly influenced not only by the active metal but also by the nature of the support, the strength of metal-support interactions, and the structure of the metal-oxide interface. Although many intermediates are formed on metal sites, their stabilization and accumulation often occur at the metal-support interface or on the support itself. On oxide surfaces, CO₂ activation is further assisted by surface hydroxyl groups or adsorbed hydrogen, leading to the formation of bicarbonate (HCO₃⁻), mono- and bidentate carbonate (CO₃²⁻), and carboxylate (HCO₂⁻) species [22(a),50]. These intermediates are readily identified by infrared spectroscopic techniques, as summarized in Table 4.

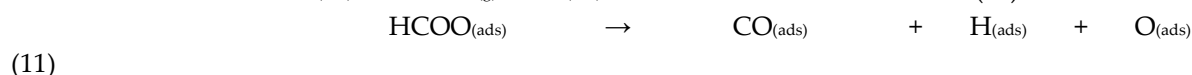
On clean metal surfaces, intermediates involved in CO₂ hydrogenation are often difficult to detect experimentally due to their low surface concentration and short lifetimes. Fisher and Bell [20] proposed that CO₂ hydrogenation on Rh proceeds via mechanisms analogous to CO hydrogenation, with C–O bond cleavage as the rate-limiting step. This cleavage may occur either via direct CO dissociation or through hydrogen-assisted pathways involving HCO intermediates. Methane formation is explained by the surface hydrogenation of H_xCO species.

On Pt(111), experimental investigation of CO₂ hydrogenation is particularly challenging, and studies on Pt nanoparticles – especially in the absence of oxide supports –remain limited. The observed low catalytic activity is often attributed to the scarcity of low-coordination sites and weak interaction with inert supports such as SiO₂ [51]. Supporting uniform Pt nanoparticles (~5 nm) on

defect-free hexagonal BN enabled more controlled studies of elementary steps and the distinct activity of Pt nanoparticles could be experimentally determined [147,148]. RWGS mechanism was established in the absence of oxide support in harmony with DFT calculations [21,51]. In Pt/h-BN system, CO production from CO₂ hydrogenation occurs via a HOCO intermediate, as evidenced by DRIFTS:



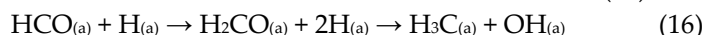
The formate pathway plays a central role in CO₂ hydrogenation on supported catalysts; however, formate species could not be detected on clean metal surfaces. To address this limitation, formic acid (HCOOH) is commonly used as a precursor, as it readily dissociates on metal surfaces to produce adsorbed formate species [32,75,76]. This approach also facilitates the identification of formate species on supported catalysts [26,60,136]. Formate is generally unstable on metal surfaces, decomposing below ~300 K to yield adsorbed CO and gaseous CO₂. Its stability can be moderately enhanced by electropositive promoters such as potassium or by co-adsorbed oxygen, while impurities such as boron can facilitate O-H bond cleavage [149]. On oxide surfaces, formic acid can also lead to the formation of formaldehyde at oxygen vacancy sites, which may subsequently decompose to adsorbed CO:



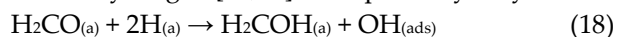
In CO₂ catalytic reduction the final product CO could form from direct dissociation of CO₂ (eq. 1.2). The formation of methane (or other alkanes) can be rationalized by carbon-hydrogen reactions in which the carbon originates from C–O bond cleavage in CO₂ or CO molecules. Methane formation may also proceed via RWGS-related pathways involving the formation and subsequent reactions of alkyl species, as discussed in the previous chapter.

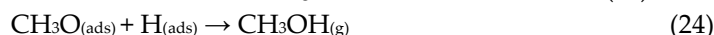
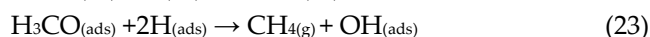
In the RWGS mechanism, one of the key intermediates is the carboxylate species (H–O–C–O, HCO₂[−]) [21,51], which can be identified by DRIFTS at 1653–1631 cm^{−1} for ν_a(O–C–O) and 1298–1245 cm^{−1} for ν_s(O–C–O) modes. This intermediate appears to be strongly dependent on surface morphology; it was detected on mesoporous Co₃O₄ but not on cubic Co₃O₄ [60]. This observation suggests a shift in the methanation mechanism from the RWGS pathway to direct C–O bond cleavage. Another important intermediate is hydrogen-perturbed CO (HCO), which has been detected by DRIFTS (see Table 4), for example on NiO, CuCo, and Co₃O₄ [56,60,88].

This species can be hydrogenated to formyl-type intermediates (CH₂CO), which may undergo further hydrogenation ultimately leading to CH₄:



Within this reaction sequence, formyl species play a key role, as supported by both thermodynamic considerations and experimental observations. On the one hand, formyl species can decompose to adsorbed CO at surface vacancies (eq. 13); on the other hand, they can be further hydrogenated to CH₄ or converted into methoxy (CH₃O), which can subsequently yield CH₄ in the presence of hydrogen [21,51]. This pathway may also involve methanol formation [141,142]:

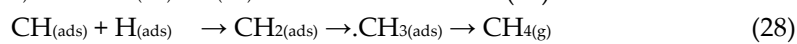
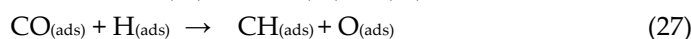
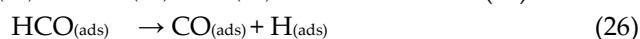
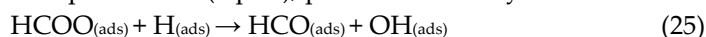




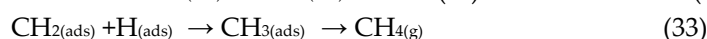
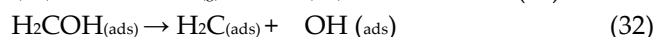
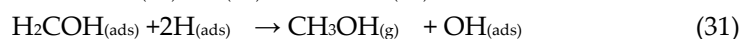
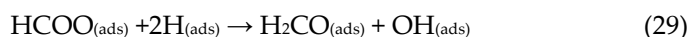
Literature data suggest that the RWGS pathway via carboxylate intermediates occurs predominantly on non-reducible oxide-supported catalysts.

A significant fraction of CO₂ hydrogenation, particularly methanation, proceeds via the formate pathway [21]. This route is especially relevant when formate or its precursor, bicarbonate, is formed on reducible oxide supports (e.g., ceria), where hydrogen spillover is possible [24–26,55,56,141,144,146]. However, this does not exclude the simultaneous participation of carboxylate species in the reaction mechanism. DRIFTS-MS studies on Ru/Al₂O₃ have shown that formate reacts with hydrogen more rapidly than carboxylate species, while the latter may remain on the surface and transiently block CO₂ adsorption sites [58]. Formate is therefore widely recognized as a key intermediate in CO₂ reduction with both hydrogen and methane and has been extensively studied (see Table 4).

It is generally accepted that direct CO₂ dissociation is negligible on most metal surfaces. Instead, spectroscopic studies, including transient DRIFTS-MS, indicate that CO₂ first reacts with surface hydroxyl groups on oxide supports to form bicarbonate species ($\nu_a(\text{O}-\text{C}-\text{O})$, $\nu_s(\text{O}-\text{C}-\text{O})$ and $\delta(\text{C}-\text{O}-\text{H})$). Bicarbonates subsequently react with adsorbed hydrogen on metal sites to form surface formate (HCOO), which exhibits characteristic $\nu_a(\text{O}-\text{C}-\text{O})$, $\nu_s(\text{O}-\text{C}-\text{O})$, and $\delta(\text{C}-\text{H})$ vibrations. Formate can then decompose to CO (eq. 10), part of which may further react with hydrogen to produce CH₄.



An alternative route for formate scheme is described containing CH₄ and CH₃OH formation, too:



In certain structures and configurations, close to the interface, the carbonates could take part in hydrogenation process [23,25,28,52].

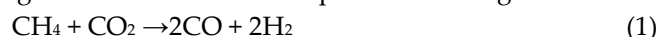
From technological point of view, the activity and mainly selectivity are fundamental challenges in CO₂ hydrogenation catalyst design. Selectivity is governed by multiple factors; however, catalyst structure and the bonding mode and reactivity of surface intermediates appear to be particularly decisive. For example, two Co₃O₄ structures exhibit markedly different behavior in CO₂ methanation. On the cubic structure, only carboxylate species were detected, and both CO and CH₄ were formed [60(a)]. In contrast, on mesoporous Co₃O₄, formate intermediates dominate, leading to nearly 100% CH₄ selectivity with negligible CO formation. When both cobalt oxides are modified with small amounts of Pt, the basicity increases and the selectivity remains largely unchanged, while the activity is significantly enhanced [60(b)].

Szanyi and co-workers demonstrated for Ni-based catalysts that, over a temperature range of 300–1100 K, selectivity shifts from high CH₄ formation to predominantly CO production. This behavior is associated with the formation of carbide-like surface species, which weaken CO adsorption and favor its desorption rather than further hydrogenation. Upon regeneration of the catalyst (removal of surface carbide), high CH₄ selectivity was restored [61]. A similarly pronounced effect on selectivity has been reported for In–Pd intermetallic compounds (InPd₂, InPd, and In₃Pd₂) [150]. Electronic interactions can change widely in In–Pd system as a result the bimetallic structures

formation enabling tunable product distributions. Compared to monometallic Pd, InPd enhances methanol selectivity by ~70%, whereas In₃Pd₂ exhibits nearly 100% selectivity toward CO in CO₂ hydrogenation.

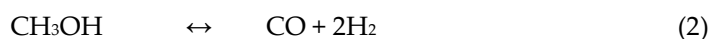
3.4. Importance of Intermediates in Hydrogen Evolution from Reforming of Methane, Methanol and Ethanol

The investigation of hydrogen sources as potential energy carriers is at the forefront of current research. The transiently formed intermediates discussed above play also significant role in reforming reaction. The reaction of carbon dioxide with methane (dry reforming) utilizes two abundant greenhouse gases to produce industrially important synthesis gas (CO + H₂ mixture). From this CO-H₂ mixture, both fuels and valuable chemicals such as methanol can be produced using established technologies. The overall reaction proceeds through a series of surface intermediates:

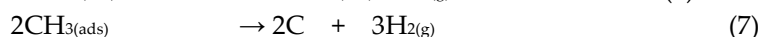
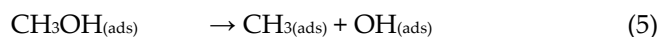
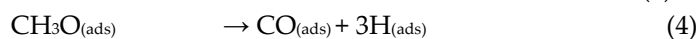
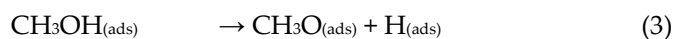


Besides the main route, methane direct decomposition, RWGS, methanation, Boudouard reaction (CO disproportionation to C and CO₂) and carbon gasification can proceed depending mainly on bonding mode of adsorbed CO formed. Methane activation primarily occurs on metal sites, whereas the nature of the intermediates formed is strongly influenced by the oxide support [28]. Consequently, species such as carboxylates, carbonates, formates, alkyls, and alkoxy intermediates may be present during methane reforming, depending on catalyst structure (Tables 3 and 4) [10,28,57,151,152]. Light alcohols, particularly methanol and ethanol, are also important feedstocks for hydrogen production via reforming reactions, with their behavior strongly dependent on the nature of the metal and the support [6,33,34,62–64,129,131,153,154]. One of the primary objectives in studying alcohol transformations is efficient hydrogen generation.

The decomposition and the steam reforming of methanol have been investigated on Pt-group metals supported on oxides, as well as on carbon-based supports such as Norit and multiwalled carbon. The main products are H₂ and CO with a very small amount of methane. The efficiency of the metals follows the order: Ru > Rh > Ir ≥ Pt > Pd, while hydrogen selectivity above 623 K ranges between 60-95% [152].



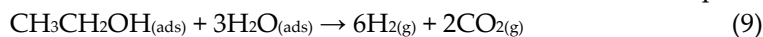
The dominant dissociation pathway of methanol involves the cleavage of O–H bond, i.e. the formation of methoxy species [155], which is easily identified with different spectroscopies including vibrational techniques (Table 4.). Methoxy subsequently decomposes to CO and hydrogen. DFT studies indicate that formaldehyde can also form as an intermediate during methanol conversion [155]. In addition, XPS, SIMS, and TPD studies on Co, Ni, and Pd(100) surfaces suggest that partial C–O bond cleavage may occur, producing methyl species to some extent [65,156]. Important reactions are:



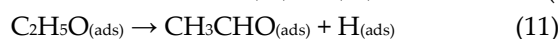
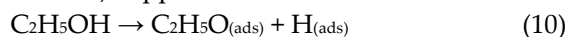
It was pointed out that the size-induced oxidation state of metals, including Pt, can influence the activity and selectivity of catalyst in methanol reaction. Under oxidizing conditions, formaldehyde is favored especially when the Pt particle size is ~1 nm [12].

Ethanol steam reforming has been widely studied over noble metal catalysts supported on oxides, particularly ceria-based systems, for sustainable hydrogen production [6,33,63,64,157]. Among these catalysts, Rh, Pt, and Ru exhibit the highest performance, with Rh showing superior activity due to its efficient C–C and C–H bond cleavage [6,33,62,157] and high resistance to carbon deposition [6]. The exceptional performance of Rh is further demonstrated in bimetallic systems, where the addition of a small amount of Rh (0.1%) to Co results in catalytic behavior like monometallic Rh supported on ceria [34]. In contrast, Pd/CeO₂ and Au/CeO₂ primarily produced

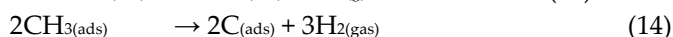
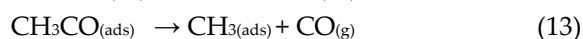
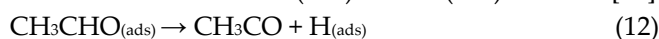
acetaldehyde due to preferential C-H bond scission [157]. On oxide-free supports, such as Au on hexagonal boron nitride (h-BN) nanomesh supported on Rh(111), ethanol is converted to acetaldehyde with nearly 100% selectivity [158]. The selectivity of ethanol steam reforming is strongly influenced by the nature of the support [34]. Acidic supports such as Al₂O₃ favor ethylene formation, while SiO₂ promotes acetaldehyde production. Ceria-based supports are most effective for hydrogen production. The ethanol conversion and H₂ formation can be expressed by the following equation:



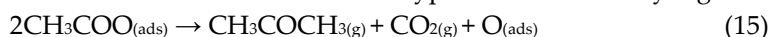
It is generally accepted that ethanol is activated on active sites of the catalysts, mainly on metallic components forming ethoxide. Its characteristic bands obtained by DRIFT can be seen in Table 4 together with their vibration modes in agreement with several literature data. On noble metals (and some other metals) supported on ceria the ethoxide can transform to acetaldehyde:



A certain part of acetaldehyde desorbs as final product in the ethanol steam reforming; other fractions of acetaldehyde dehydrogenate forming acetyl species where the C-O bond cleavage becomes more favorable. Although acetyl intermediates play an important role, their detection is challenging due to their short surface lifetime. Acetyl species were identified on Rh/CeO₂ at 1684 cm⁻¹ (C=O stretching mode) during ethanol transformation [159]. An easy C-C and C-H bond scissure has been confirmed earlier on Rh(111) and Pd(111) surfaces [62].



Methane formation (eq. 7) also occurs to a limited extent. Adsorbed acetaldehyde can undergo multiple reaction pathways: it can desorb, decompose to acyl, or react with hydroxyl groups or with lattice oxygen to form acetate. Acetate species are characterized by the $\nu_s(\text{OCO})$ and $\nu_a(\text{OCO})$ bands at 1452 and 1567 cm⁻¹ [33,34,64,159,160]. Stable acetate surface product was also detected by near-ambient pressure XPS [83]. The findings show that acetate is a terminal and non-reactive product under the examined conditions. The acetate species were identical regardless of the supported metal (Pt, Pd, Ir, Rh, Ru), indicating that the formation of acetate species takes place on the oxide support [33,160]. Depending on metal and support and the nature of interface, the acetate may couple through aldol condensation to form acetone as byproduct at relatively high temperatures (from 720 K) [33,34].



Overall, spectroscopic and catalytic studies demonstrate that Pt-group metals, particularly Rh, are among the most effective catalysts for hydrogen production via ethanol reforming. However, the reaction pathway and efficiency are strongly influenced by the oxide support. From the perspective of hydrogen production, ceria and ceria-modified supports appear to be the most favorable supports for noble metal catalysts [6,33,34,62–64,160].

4. Summary and Outlook

This review summarizes the identification and reactivity of intermediates formed in the CO + NO, in the CO and CO₂ hydrogenation and in the reforming of methane and light alcohols on metals, metal nanoparticles on oxide supports. The isocyanate surface complex is an existing intermediate in NO reduction with CO, and NCO is responsible for NH₃ formation in real condition in exhaust gases. Alkyl groups and their reactions are important in Fischer-Tropsch mechanism. CO₂ hydrogenation proceeds via formation and reaction of several intermediates which determine (together with the nature of active components of catalysts) the mechanism and the final products (CO, CH₄, CH₃OH).

Some intermediates can be investigated during the real catalytic conditions, but some intermediate surface complexes, due to their short lifetime, should be prepared from their parent's molecules (HNCO, HCOOH, alkyl halogenates, alcohols, aldehydes) via their surface dissociation (thermal or photo driven) at low temperature, where the intermediate species could be accumulated.

There is important information that not only the nature of metals, but the acidity, basicity and the reducibility of the supports basically influence the efficiency of the catalysts. In the future a certain investigation should be directed to the oxide less support application (carbide, carbon, graphene, BN, BCN, Mo₂S, etc.) or modified oxide-containing supports where the disadvantageous metal-oxide interaction in the given reaction is hindered and a new route could be opened. The efforts in RWGS reactions in growing carbon length to produce heavy hydrocarbons and oxygenated hydrocarbons initiate extensive research nowadays and in the immediate future [145,161]. Up to now, the M/CeO₂ (M=Pt, Rh, Ir, Ru) seems to be the best catalyst for hydrogen production from ethanol reforming. Decreasing the formation of the adsorbed side products (acetate), with suitable modification of support composition, could increase the selectivity to hydrogen production [64,160].

This review focuses mainly on thermal excitation. There is some evidence that photo-induced chemistry can open new reaction paths, for example in CO₂ hydrogenation on Au/TiO₂ catalysts [10]. Photothermic driven reactions have a bright future in technological applications. The results obtained by thermal-, photo- and electrochemical ways would increase the level of technology in this field in the near future.

Author Contributions: János Kiss: Conceptualization, Writing -review & editing, Writing -original draft. Imre Szent: Investigation, Writing-original draft, Formal analysis. Anastasiia Efremova: Investigation, Writing original draft, Formal analysis, Validation. Imre Kovács: Investigation, Writing original draft, Formal analysis. Aranka Deér: Visualization, Validation. András Sápi: Conceptualization, Project administration. Zoltán Kónya: Resources, Funding acquisition.

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Abbreviations.

TDS – Thermal Desorption Spectroscopy

TPD – Temperature-Programmed Desorption

AES – Auger Electron Spectroscopy

XPS – X-ray Photoelectron Spectroscopy

UPS – Ultraviolet Photoelectron Spectroscopy

IR – Infrared Spectroscopy

FTIR – Fourier Transform Infrared Spectroscopy

DRIFTS – Diffuse Reflectance Infrared Fourier Transform Spectroscopy

RAIRS – Reflection Absorption Infrared Spectroscopy

SFG – Sum Frequency Generation Spectroscopy

HREELS – High-Resolution Electron Energy Loss Spectroscopy

EXAFS – Extended X-ray Absorption Fine Structure

NAP-XPS – Near-Ambient Pressure X-ray Photoelectron Spectroscopy

SSITKA – Steady-State Isotopic Transient Kinetic Analysis

RWGS – Reverse Water Gas Shift (reaction)

DFT – Density Functional Theory

PE – Photoemission

EBF – Binding Energy relative to the Fermi level

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