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Al₁₃Fe₄ selectively catalyzes the hydrogenation of butadiene at room temperature

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The hydrogenation of butadiene has been investigated for the first time on $AI_{13}Fe_4$. The model (010) surface of this non-noble metal combination appears to be both active and selective under mild reaction conditions. The performances of $AI_{13}Fe_4$ for C=C bond hydrogenation are compared with those of the reference noble metal, palladium.

Recent work by Armbrüster et al. has shown the unexpected ability of Al₁₃Co₄ and Al₁₃Fe₄ alloys to catalyze the semi-hydrogenation of acetylene, a reaction industrially applied in polyethylene production.^{1,2} This finding is of great importance due to the low cost of the metallic constituents as compared to conventionally used Pd and Pd-Ag. The same research group had previously evidenced that ordered compounds of the Ga-Pd system were efficient acetylene hydrogenation catalysts.^{3–6} The results have been conceptualized in terms of "site isolation", meaning that Pd atoms embedded in a Ga matrix form active, selective, and stable reaction sites.⁴ Such discoveries have also been driven by the recent advances in computational screening of catalysts, which has led to the identification of new non-noble bimetallic alloys, such as Ni-Zn, as potential alternatives to platinum-group metals for acetylene hydrogenation.7,8

 $Al_{13}Fe_4$ is considered, like other $Al_{13}M_4$ complex intermetallic compounds (M = Fe, Co, Ni...), to be a periodic approximant to decagonal quasicrystals.^{9,10} Recently, Ledieu *et al.* have revealed the complex surface structure of the (010) surface of $Al_{13}Fe_4$ using scanning tunnelling microscopy and density functional theory calculations.¹¹ The authors have proposed isolated Fe atoms protruding above pentagonal Al motifs as the catalytically active sites for acetylene conversion. On a similar single-crystal surface, *in situ* X-ray photoelectron spectroscopy (XPS) has revealed that the surface phase is essentially unaltered under acetylene hydrogenation conditions.² In this Communication, we report on the catalytic properties of $Al_{13}Fe_4(010)$ in butadiene hydrogenation. The Pd-catalyzed hydrogenation of 1,3-butadiene to butene is an industrially important reaction for butene purification in polymer synthesis and an interesting model-reaction for sequential C=C bond hydrogenation.¹²⁻¹⁶

The Al₁₃Fe₄(010) sample was purchased from Mateck GmbH (Germany). An ultrapure crystal was grown following the Czochralski method¹⁷ and cut perpendicular to its [010] direction into a small disk (10 mm × 1 mm). The final roughness and disorientation of the as-furnished Al₁₃Fe₄(010) surface were smaller than 0.03 µm and 0.1°, respectively. The surface was further cleaned by repeated cycles of Ar⁺ sputtering and annealing at 600–800 °C under ultrahigh vacuum. The cleaned surface was contaminant-free, as attested using Auger electron spectroscopy (Fig. 1, middle spectrum), and exhibited a sharp low energy electron diffraction (LEED) pattern (Fig. 1, inset). The LEED pattern corresponds to a (1 × 1) structure with an oblique unit mesh, in agreement with the previous findings.¹¹ The increase of



Fig. 1 Auger electron spectra for $Al_{13}Fe_4(010)$ after sputtering (bottom spectrum), annealing (middle), and reaction (top). Inset: LEED pattern of the clean annealed surface.

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the Al/Fe low-energy Auger peak ratio from 1.9 to 2.8 upon annealing of the sputtered surface can be explained either by preferential sputtering of Al during bombardment, or surface enrichment in Al during annealing as for $AlFe_3$ surfaces.¹⁸ However, surface segregation has been ruled out by Ledieu *et al.*¹¹

The butadiene hydrogenation reaction was carried out in a dedicated static catalytic reactor (volume *ca*. 120 cm³) coupled to the surface preparation/analysis chamber.^{19,20} Similar experiments were performed on $Al_{13}Fe_4(010)$ and Pd(100), which serves here as a reference. The Al-Fe sample could be heated from the back by an infrared laser beam and its surface temperature was measured by an infrared pyrometer (surface emissivity set to 0.3). A mixture of ultrapure gases (5 Torr hydrogen, 0.5 Torr butadiene, and 0.5 Torr Ar for internal calibration)[†] was prepared in a separate chamber before injection into the reactor. During the reaction, the gases were continuously sampled through a leak valve and analyzed by mass spectrometry (MS).[‡] At the end of the reaction run, the products were evacuated, and the reaction-evacuation cycle was again performed two times to assess the catalyst stability. The hydrogen and hydrocarbon partial pressures were obtained from the MS signal by taking into account product-dependent sensitivity, ion fragmentation, and gaseous matter conservation.²¹

Fig. 2 shows the results of a catalytic test of the clean annealed $Al_{13}Fe_4(010)$ surface at room temperature (straight lines). Strikingly, butadiene is fully converted into butane within 50 min on this material. This is exactly the time needed for the same conversion on clean Pd(100) (see Fig. 2, dotted lines). Moreover, the hydrogenation of butadiene is highly selective to butene. The selectivity is 100% at initial time, and 89% when averaged over the whole semi-hydrogenation period (Table 1). Only after butadiene has been fully converted, the butane formation rate increases steeply. Interestingly, the butene hydrogenation rate (r_2) is greater than the butene formation rate (r_1), whereas it is the opposite on palladium ($r_1 > r_2$). This is consistent with an even greater selectivity of Pd(100), which is 100% whatever the extent of butadiene conversion (Fig. 2).



Fig. 2 Hydrocarbon partial pressures during butadiene hydrogenation on $AI_{13}Fe_4(010)$ (straight lines) and Pd(100) (dashed lines) at 24 °C.

Table 1 Effect of temperature on reaction rates for clean Al₁₃Fe₄(010)

Temperature (°C)	r_1^a (10 ⁻⁸ mol min ⁻¹)	r_2^a (10 ⁻⁸ mol min ⁻¹)	r_2/r_1	$S_1^{\ b}(\%)$
24	9.3	38	4.1	89
110	79	98	1.2	96
200	51	15	0.3	100

^{*a*} r_1 and r_2 are the butene and butane formation rates averaged on the first and second hydrogenation periods, respectively (initial rates were hardly measurable due to their high values). ^{*b*} S_1 is the selectivity to butene averaged on the first hydrogenation period (the initial selectivity is always 100%). $S_1 = r_1/r_1^{\text{tot}}$, where r_1^{tot} is the averaged butadiene consumption rate.

Conversely, some butane is produced during the first hydrogenation period on $Al_{13}Fe_4(010)$.

The reaction was also carried out at 110 °C and 200 °C. As reported in Table 1, both rates increase from RT to 110 °C, and decrease from 110 to 200 °C. This suggests that above 110 °C, the reaction rate is limited by hydrocarbon desorption. However, the extent of these variations is different between butadiene and butene hydrogenations. As a matter of fact, the butene formation rate becomes higher than the butane one at 200 °C ($r_1 \approx r_2$ at 110 °C).

Only in the case of palladium, a gradual increase of the butadiene conversion rate is observed (Fig. 2). This is due to the dissolution of hydrogen in the subsurface, as previously demonstrated.²¹ The more hydrogen dissolved, the faster the surface hydrogenation rate.§ Conversely, $Al_{13}Fe_4$ does not absorb hydrogen, which is a further advantage of this material.²

Unlike Pd, Al₁₃Fe₄ deactivates in the course of the reaction cycles (not shown). For example, at 200 °C, r_1 is decreased by more than 40% from the first to the second reaction run, then by less than 30% from the second to the third run. However, the selectivity to butenes is preserved. In addition, butene hydrogenation appears less sensitive to deactivation. As suggested using post-reaction Auger electron spectroscopy (Fig. 1, top spectrum), the deactivation is caused by chemisorbed oxygen (and not carbon), which is most probably due to adsorption of water impurities inherently present in UHV chambers and research-grade gases. On-run deactivation may explain the gradual decrease of the butene formation rate in Fig. 2, and the corresponding decrease of butene selectivity. Nevertheless, this behaviour disappears at higher temperatures. Together with previously mentioned observations, this excludes that the decrease of r_1 and r_2 averaged rates from 110 to 200 °C (Table 1) could be explained by thermally-enhanced deactivation rates. Note that a flash desorption above 600 °C allowed an at least partial regeneration of the surface. The deactivation issue was also mentioned by Armbrüster et al. during long-term acetylene hydrogenation on Al₁₃Fe₄ powder.² Besides, the authors detected oxygen (in the form of Al oxides) and carbon on their single-crystal surface using XPS.

It should be noted that the propensity of $Al_{13}Fe_4$ to catalyze the hydrogenation of C=C bonds is not limited to butadiene and butene. The same experiment as that reported in Fig. 2 was carried out with ethylene instead of butadiene. Ethylene was fully converted into ethane in less than one minute on the clean $Al_{13}Fe_4(010)$ surface. For butadiene at RT under our pressure conditions, the turnover frequency (TOF) is of the order of 10 molecules converted per second per surface palladium atom. If we assume that protruding Fe atoms constitute the centres of the catalytically active sites in the case of $Al_{13}Fe_4(010)$,¹¹ the TOF per active site is of the order of 100 s^{-1} , which is extremely high. \parallel Importantly, the freshly sputtered surface (see the corresponding Auger spectrum in Fig. 1) was found *ca.* 10 times less active than the freshly annealed one (not shown), in spite of the increases in surface area and roughness due to Ar⁺ sputtering. This implies that the high activity of $Al_{13}Fe_4(010)$ is related to the specific structure of the well-crystallized and chemically well-ordered surface.

Although the physical origins of the high activity and selectivity of Al13Fe4 in butadiene hydrogenation still have to be determined, some insights can be gained from the theoretical work of Krajčí and Hafner in the case of acetylene hydrogenation over $Al_{13}Co_4(100)$.^{22,23} The authors have shown that the catalytically active sites consist of pentagonal CoAl₅ clusters with strong internal Co-Al bonding and low atom coordination at the cluster edges, the latter being induced by the complex surface topology. The resulting surface electronic structure provides optimal surface bonding and reaction energies to the adsorbates. The high selectivity to ethylene is explained by the lower desorption barrier for this molecule with respect to its hydrogenation barrier. Similar arguments can be formulated for selective butadiene hydrogenation on $Al_{13}Fe_4(010)$, as was previously done in the case of highly selective Au-Pd surfaces, in which gold favours butene desorption.¹⁹

In conclusion, the first work on alkene hydrogenation over the $Al_{13}Fe_4$ system has been reported. The hydrogenation of 1,3-butadiene was performed under mild conditions (20–200 °C, 800 Pa) on an *in situ* cleaned $Al_{13}Fe_4(010)$ surface, as well as on Pd(100) for comparison. The non-precious metallic compound is highly active, both for butadiene and butene hydrogenation, and highly selective to butene during butadiene hydrogenation, even at room temperature. Based on previous work on $Al_{13}M_4$ systems, these unexpected catalytic performances are ascribed to complex ensemble effects on FeAl₅ active sites. Future studies will aim at addressing the deactivation issue and understanding the reaction mechanism through further investigation of the kinetics.

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Notes and references

 \dagger 1 Torr = 133 Pa. This unit is the most widely employed in surface and vacuum sciences.

[‡] MS intensities for m/z = 2, 40, 54, 56, and 58 were recorded for hydrogen, argon, butadiene (C₄H₆), butene (C₄H₈), and butane (C₄H₁₀), respectively. Butene isomers are not distinguished here.

§ Consequently, the Pd surface is more active for butene formation in the subsequent reaction runs, and $r_1 \gg r_2$ (not shown).

¶ Nothing can be rigorously said from AES on a possible Al–Fe compositional change at the surface during the reaction, due to the large amount of oxygen significantly masking Al and Fe after the reaction.

 \parallel In the authors' model, the surface unit mesh contains 4 Fe atoms including 2 protruding ones, and 22 Al atoms. The surface atom density is 14.0 nm⁻², vs. 13.2 nm⁻² for Pd(100).

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