High catalytic performance of Al–Pd–(Ru, Fe) icosahedral approximants for acetylene semi-hydrogenation†

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Three cubic crystalline icosahedral approximants (C phase: Al72.0Pd16.4Fe11.6, P20 phase: Al72.0Pd16.4Ru11.6, P20 phase: Al72.0Pd22.3Ru7.7) exhibit high ethylene selectivity of over 90% for hydrogenating acetylene at 150 °C. Moreover, the powdered P20 also demonstrates a high catalytic performance under an industry-like ethylene feed containing 0.5% acetylene as an impurity. Overall, icosahedral approximants in the Al–Pd–(Ru, Fe) systems are promising as a novel class of alloy catalysts.

1 Introduction

Intermetallic compounds (IMCs) exhibit a wide range of attractive functions and characteristics that are not attainable in ordinary elemental metals, such as a shape memory effect,2 superconductivity,3 and hydrogen absorption.4 They also possess excellent properties for hydrogenation catalysis, such as those demonstrated in Heusler alloys,5–7 Zintl phases,8 and hydrogen absorbing alloys.9–11 Quasicrystals12–18 are complex IMCs with aperiodic structures that often exhibit five-fold symmetry. Crystalline approximants, on the other hand, are periodic crystals having a similar chemical composition and atomic19,20 and electronic structures21 closely related to quasicrystals. The study of approximants is therefore crucial for understanding the structure and physical properties of quasicrystals. Despite earlier studies on quasicrystals as catalyst precursors,13–15 there has been a recent awakening of interest in the ability of quasicrystals and approximants themselves to catalyze useful reactions at their terminated surfaces.

Recently, Kovnir and Armbuster et al. demonstrated that GaPd, an IMC with a B20-type structure, is highly stable and selective for the semi-hydrogenation of acetylene to ethylene.22–24 These authors proposed that the isolation of the catalytic element, Pd, in the Ga matrix as well as an alteration of the electronic structure due to alloying are the keys to the high catalytic performance. This assessment was soon extended to Al13Fe4 (ref. 18) and Al13Co4 (ref. 19) complex IMCs as noble-metal-free semi-hydrogenation catalysts. The fundamental processes in these catalytic reactions has been discussed based on the active site geometry on the surface,28 as well as on the adsorption energies for the reactant molecules29–31

These studies revealed that the covalently bonded pentagonal TMAl5 (TM = transition metal) complex on the surface provides active sites for both chemisorption of hydrocarbon species and dissociative adsorption of hydrogen,32 and thus the specific surface structure plays a key role in the semi-hydrogenation of acetylene. The complex ensemble effect of TMAl5 pentagons was also shown to be the origin of the activity for butadiene semi-hydrogenation.33 On the other hand, density functional theory (DFT) calculations demonstrated that the (210) surface of an AlPd (or GaPd) IMC with a B20-type crystal structure exposes active sites for the semi-hydrogenation of acetylene with extraordinarily high activity.21,22 These active sites are associated with a triangular atomic configuration consisting of two Al (or Ga) atoms and one Pd atoms called a PdAl3 triplet.

In fact, similar triplets may play a key role in the case of Al13TM4 because the TMAl5 complex can be decomposed into five triangles each with two Al atoms and one TM atom, which is similar to the PdAl3 triplet arrangement. Similar atomic configurations to PdAl3 are frequently encountered in icosahedral quasicrystals and related approximants in Al–Pd–(Ru, Fe) systems. In other words, PdAl3 triplets are involved in the atomic arrangements within the constituent clusters of these compounds.

Moreover, theory has shown that the selectivity for ethylene increases with increasing number of Ga atoms in the 1st coordination shell of each Pd atom,24 and this trend probably also holds for Al–Pd. GaPd (or AlPd) which can be taken as the simplest analogue to the local atomic structure of icosahedral quasi-crystals, and has at most four Ga (or Al) atoms adjacent to each Pd atom exposed on the surface. An Al–Pd–(Ru, Fe) approximant, on the other hand, can have up to five Al atoms surrounding the Pd atom, thus it is expected to show more prominent catalytic performance. To date, however, the
catalytic performance of the Al–Pd–(Ru, Fe) approximants have rarely been investigated. We hereby present the first catalytic tests of three selected approximants in the Al–Pd–(Ru, Fe) systems for semi-hydrogenation of acetylene to experimentally demonstrate the high catalytic performance of these compounds. A possible origin of their catalytic properties is discussed in terms of their local atomic configurations.

2 Experimental

2.1 Samples

The samples used in this work were cubic crystalline approximants [C phase: Al72.0Pd16.4Fe11.6, P40 phase: Al72.0Pd16.4Ru11.6, P20 phase: Al70.0Pd22.3Ru7.7] related to icosahedral quasicrystals. The pure Al, Pd, and Ru and/or Fe metals were melted under an argon atmosphere by using an arc furnace. Each ingot was typically of about 5 g. Parts of the ingot were annealed under an Ar atmosphere for up to 120 h (see Table S1 of ESI,‡ for annealing condition of all sample and see Section 1 of ESI,‡ for more details on sample preparation). The target approximant phases were confirmed by using powder X-ray diffraction (PXRD) patterns. Moreover, former evidence of the approximant phases was provided by selected area electron diffraction (SAED) patterns.

2.2 Catalytic test

The samples for catalytic test were prepared in a glove box under an Ar atmosphere to prevent surface oxidation. The samples were crushed in an agate mortar and sieved to size in the range of 25–75 μm. About 150 mg of fine-grained samples was packed in a quartz glass plug-flow reactor (inner diameter 7 mm) and plugged both ends by a ball bulb. The C2H2 hydrogenation tests were performed under a gas feed of 2% C2H2/80% H2 in He, 0.1 MPa, with a flow rate of 30 mL min⁻¹. The hydrogenation under industrial like condition was performed with reaction gases 0.5% C2H2/49% C2H4/12.5% H2 in He, 0.1 MPa, with a flow rate of 32 mL min⁻¹ (see Section 3 of ESI,† for calculations of C2H4 selectivity and conversion).

3 Results and discussion

The PXRD patterns of C–AlPdFe, P20–AlPdRu, and P40–AlPdRu indexed as approximants were shown in Fig. 1(a). Fig. 1(b) and (c) show SAED patterns for the P20–AlPdRu sample along three-fold and pseudo five-fold axes, respectively. In Fig. 1(b), the periodic array of spots can be indexed to a cubic crystal with a lattice constant of about 20 Å, as reported by Pavlyuchkov et al.28

The reaction rates (molC2H2 s⁻¹ m⁻²) for C2H2 and the C2H4 selectivity (%) are shown in Fig. 2(a) and (b), respectively. All three approximants showed a high ethylene selectivity of above 90% at 100 °C to 150 °C, and the P20–AlPdRu specimen exhibited a maximum value of 98% at 150 °C. All approximants showed roughly the same selectivity, with all three having higher activity than Al13Fe4, which was reported to have high performance for semi-hydrogenation of C2H2, as shown in Fig. 2.

Assuming Langmuir–Hinshelwood (LH) mechanism on a catalytic cycle of the acetylene semi-hydrogenation reaction, reaction steps can be given as follows:

![Fig. 1](image1.png)  
**Fig. 1** (a) PXRD patterns for Al–Pd–(Ru, Fe) icosahedral approximants. (b and c) SAED patterns for P20–AlPdRu phase. (b) [111], (c) pseudo five-fold zone axis.

![Fig. 2](image2.png)  
**Fig. 2** (a) Reaction rate per surface area of catalyst and (b) selectivity for C2H4 over different Al–Pd–(Ru, Fe) icosahedral approximants and Al13Fe4 (reaction gas: 2.0% C2H2/80% H2 in He; total pressure: 0.1 MPa; flow rate: 30 mL min⁻¹).
Step 1:

\[ \text{H}_2 \rightarrow [\text{H}_2(a)] \rightarrow 2\text{H(a)} \]

Step 2:

\[ \text{C}_2\text{H}_2 \rightarrow \text{C}_2\text{H}_3(a) \]

Step 3:

\[ \text{C}_2\text{H}_3(a) + 2\text{H(a)} \rightarrow [\text{C}_2\text{H}_3(a) + \text{H(a)}] \rightarrow \text{C}_2\text{H}_4(a) \]

Step 4:

\[ \text{C}_2\text{H}_4(a) \rightarrow \text{C}_2\text{H}_4 \]

Step (1) and step (2) are the dissociative adsorption of H₂ and adsorption of C₂H₂ on the catalyst surface, respectively. Step (3) is the hydrogenation of C₂H₃(a) to form C₂H₄(a) (x = 3 or 4). Step (4) is the desorption of C₂H₄(a) into gas phase as C₂H₄. Note here that an adsorbed state is represented by the symbol, (a).

Krajči and Hafner identified catalytically active sites for C₂H₂ semi-hydrogenation in a PdAl₂ triplet exposed on the pseudo five-fold surface ([/210] of B20-type AlPd. According to their atomistic scenarios via LH mechanism, step (1) occurs on Pd sites that are slightly protruding towards the gas phase. Step (2) and step (3) proceed on PdAl₂ triplet sites that again involve a protruding Pd site. At step (2), C atoms in C₂H₃(a) are di-s bonded to two Al atoms in the Al–Al bridge position. At step (3), when an H atom is incorporated to from a CH₂ group, that end of the molecule is shifted towards and weakly bonded to the Pd atom whereas the bonding of the other end to the Al atom remain rather strong. After another H atom is incorporated, the C atoms are no longer bonded to the Al atoms, so that the molecule C₂H₄(a) is only weakly π-bonded on top of the Pd atom. The desorption energy of C₂H₄(a) is reportedly lower than that of H₂, so that ethylene desorbs at the final step. As shown in Fig. 3(c) and (d), the present icosahedral approximants in the Al composition to the P₂O₁⁻AlPdRu phase but are structurally much simpler, did not compete with the P₂O₁⁻AlPdRu phase in the catalytic activity and selectivity (see Section 4 of the ESI). According to Krajči et al., dissociation of hydrogen is possible only at transition metal atoms on the surface, but the Pd atoms need to be isolated because agglomerated transition metal atoms act as strong adsorbent for hydrogen and hydrocarbons, thereby reducing their mobility. Therefore, the high catalytic performance of the present approximants can be attributed to their complex crystal structures.

The specimens sieved under air did not show the high C₂H₄ selectivity (see Section 6 of the ESI). This is attributed to surface oxidation. Decomposition of the surface structure to Al₂O₃ and Pd by oxidation seems to trigger Pd aggregation, thus lowering the C₂H₄ selectivity. This is additional evidence that the surface structure is a key to the high catalytic performance.

The selective hydrogenation of C₂H₂ in the C₂H₄-rich gas is an important reaction for synthesizing polyethylene in the petrochemical industry, and so we also examined the present samples under a more industry-like C₂H₂-rich gas feed. In Fig. 4, the catalytic performance of the present P₂O₁⁻AlPdRu powder is compared with those of a commercial Lindlar catalyst and the Al₁₃Fe₇ powder under an industry-like C₂H₂-rich gas containing a 0.5% C₂H₂ impurity component (0.5% C₂H₂/49% C₂H₄/12.5% H₂ in He, 0.1 MPa, 32 mL min⁻¹). The P₂O₁⁻AlPdRu phase sample...
again maintained a high conversion rate of over 80% along with a high ethylene selectivity of more than 83% (for detailed information on how to calculate the conversion and selection rates, see Section 3 of the ESI†). $P_{20}^{20}$–AlPdRu showed higher selectivity than the commercial Lindlar catalyst and Al$_{13}$Fe$_4$.

A decrease in the conversion rate from the initial value of 92% was observed up to 6% after 6 h. This can be attributed to the deposition of carbon or higher hydrocarbons, referred to as green oil, on the surface of the catalyst as indicated by a carbon-loss rate of about 10% throughout the reaction experiment. Still, it is important to note that the $P_{20}^{20}$–AlPdRu catalyst showed higher selectivity under industry-like conditions without specific optimization of the surface state such as coating with inert elements or suppressing hydrogenation by CO gas.

4 Conclusion

The quasicrystals and approximants are novel materials with many potential applications that are actively being explored, such as for low friction coefficients, high hardness, brittleness, and low thermal and electrical conductivity. However, their crystal structures are often so complex that they are difficult to precisely determine. The structure of $P_{20}^{20}$–AlPdRu, for instance, has yet to be clarified, and those of C–AlPdFe$^{27}$ and P$_{40}^{40}$AlPdRu$^{26}$ are still being argued. Nevertheless, recent crystallographic studies have revealed that their structures include common building blocks involving PdAl$_2$ triplets, which are the key to the semi-hydrogenation reaction. This study showed for the first time that high order Al–Pd–(Ru, Fe) approximants related to icosahedral Al–Pd–Mn quasicrystal are promising as alloy catalysts for the semi-hydrogenation of acetylene, and we expect to see further developments in this respect in the years to come.

Conflicts of interest

There are no conflicts to declare.

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