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論文題目	Development of Early Transition Metal Hydride Catalysts for Ammonia Synthesis （アンモニア合成触媒用の前期遷移金属ヒドリド化合物の開拓）		

（論文内容の要旨）

Ammonia is not only vital for the production of fertilizers and industrial chemicals, but also a potential hydrogen storage material and future fuel alternative. Ammonia is the main agricultural feedstock of synthetic fertilizers and also a potential hydrogen storage molecule. The synthetic ammonia industry is based on the Haber-Bosch process, which involves the exothermic reaction between a mixture of nitrogen gas and hydrogen gas over iron-based catalysts promoted with K_2O and Al_2O_3 at 400−500 °C under high pressure (100−200 atm). High temperature could improve the reaction kinetics and high pressure could benefit a shift of the reaction equilibrium to the product ammonia. It is a high-energy consumption process and consumes 1%~2% of manmade energy per year. The demand of harsh reaction conditions is due to the considerable activation barrier of breaking the N≡N triple bond (bond energy 945 kJ/mol). Therefore, it is of great significance for the development of ammonia synthesis process with low energy consumption and high thermodynamic efficiency.

The development of new and efficient ammonia synthesis catalysts is extremely challenging, especially for ammonia synthesis under mild reaction conditions. Early or late transition metals are incapable to catalyze this reaction efficiently, because they have either larger or smaller nitrogen adsorption energy, leading to poor turnover rates. However, recently some early transition metal hydride compounds have been found to effectively counteract this effect, imparting catalytic activity on a wider range of elements. With these hydride catalysts, hydride (and nitride) bulk diffusion mechanisms have been proposed; if so, more open structures should enhance their activity. There is still much to discover about the scientific principles and technological applications of early transition metal hydrides for ammonia synthesis. The typical problems include: the bulk structure and hydride composition need to be further optimized; the activity is still low and the reaction conditions are at high pressure/high temperature; there is an enhancement of activity by introducing hydrides into the early transition metals, however there is no real data to explain such hydride-promoting mechanism, thus it is necessary to go deeper and know why hydrides work; how to expand the scope of catalytically active metals as well as hydride catalysts.

In Chapter 1, the author expanded the study to hydrides of other early transition metals, i.e., V and Nb. These metals benefit from body-centered cubic (bcc) related structures which enhance hydride diffusion, in addition to having relatively lower M-N bond strengths. The activity of vanadium hydride, most likely with an active composition of $VH_{0.44}N_{0.16}$, is superior to the previously reported TiH_2 and $BaTiO_{2.5}H_{0.5}$, and comparable to Cs-Ru/MgO at 400 °C under 5 MPa. These results show that there is more potential for developing new single-phase hydride catalysts of previously overlooked elements without sacrificing activity.

Topochemical reactions have led to great progress in the discovery of new metastable compounds with novel chemical and physical properties, making it an effective method of synthesizing new hydride materials. With these reactions, the overall crystal structure of the host material is generally maintained. In Chaper 2, the author reported a topochemical synthesis of a new hexagonal nitride hydride, h-Ca_3CrN_3H, by heating an orthorhombic nitride, o-Ca_3CrN_3, under hydrogen at 673 K, accompanied by a rotational structural transformation. The hydrogen intercalation modifies the Ca-N rock-salt-like atomic packing in o-Ca_3CrN_3 to a face-sharing octahedral chain in h-Ca_3CrN_3H, mimicking a 'hinged tessellation' movement. Impressively, the h-Ca_3CrN_3H exhibited stable ammonia synthesis activity when used as a catalyst, even though the early transition metal Cr is not an active element for ammonia synthesis.

In Chapter 3, the author further examined the catalytic performance of this new Ca_3CrN_3H compound and when it is used as a catalyst support for Ru. Ca_3CrN_3H exhibits good ammonia synthesis activity and the absence of hydrogen poisoning is presumably associated with the facile hydride diffusion within face-shared 1-D octahedral channel of Ca_3CrN_3H, as well as the superior hydrogen exchangeability of lattice hydride with reactant H_2 gas. DFT calculations reveal that nitrogen reduction could be effectively achieved through an associative mechanism. The surface Ca_3 hollow sites formed at the Ca_3CrN_3H (001) surface play a critical role in N_2 adsorption and activation to the successive hydrogenation. The topochemical synthesis of h-Ca_3CrN_3H and the following catalytic application encourage the expansion and exploration of a large group of A_3MN_3H hexagonal antiperovskite nitride-hydride materials as promising ammonia synthesis catalysts.

AB_2-type intermetallic compounds, such as $ZrCr_2$, etc., are of great interest for hydrogen storage. In Chapter 4, the author found a dissociative hydrogen chemisorption together with nitrogen storage proceed on Laves phase compounds to form intermetallic nitride hydrides, which exhibit the potential as ammonia synthesis catalysts. However, these catalysts have low surface area and insufficient activity so far. For the application of hydrogen storage alloys for ammonia synthesis, further investigations could be focused on the further activity promotion with electropositive elements, such as barium which has previously been demonstrated to be excellent promoter for Ru or Fe-based catalysts.

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（論文審査の結果の要旨）

本論文は、前期遷移金属を含むヒドリド化合物からなるアンモニア合成触媒の開発を目的とし、結晶構造と触媒特性の相関、ならびに触媒反応機構を検討した結果についてまとめたものである。複数の系においてヒドリドを導入することで高い活性が発現することを見出し、貴金属に頼ることなく、これまで見過ごされていた前期遷移金属元素にまで不均一系触媒のレパートリーを拡げた。論文は 4 章で構成され、得られた成果の概要は以下の通りである。
V、Nb、Cr、Zr などの前期遷移金属元素は、強い M-N 結合を持つため、アンモニア合成のハーバーボッシュプロセスに不活性であることが知られていた。第 1 章では、水素化物化合物 $VH_{0.39}$ と $NbH_{0.6}$ が、アンモニア合成触媒として高い活性を示すことを見出した。特に、優れた活性を示す水素化バナジウムについて、バルク格子を介した水素化物（および窒化物）の拡散と、拡散を促進する構造の特徴について議論した。これらの結果は、Ti で見出されていた優れた触媒特性は Ti に固有なものではなく、前期遷移金属元素全般に当てはまることを示している。第 2 章では、さらに、Cr 含有化合物へと研究対象を拡張した。直方晶の窒化物 o-Ca_3CrN_3 に着目し、この化合物をアンモニア合成条件下で処理したところ、予期せぬことに、水素化されながら構造ユニットが回転して六方晶構造に変換するというユニークなトポケミカル反応が起こることを発見した。第 3 章では、h-Ca_3CrN_3H の触媒性能を検討したところ、優れたアンモニア合成活性を示した。本触媒系において水素被毒が起こらないことは、同物質の面共有のカルシウムからなる 1 次元八面体チャネル内でヒドリドが容易に拡散することに関連していると推定した。さらに DFT 計算により、本触媒における反応は稀な会合性の機構で進行することを明らかにした。第 4 章では、Zr を含有するラーベス相を検討し、窒化物水素化物を形成することを発見し、アンモニア合成触媒として期待できることを明らかにしたした。

以上のように本論文は、前期遷移金属を有するヒドリド含有化合物の合成、構造制御、並びにアンモニア合成触媒機能の開拓に関して新規性と独創性のある結果を報告するものであり、博士（工学）の学位論文として価値あるものと認める。よって、学術上、実際上寄与するところが少なくない。よって、本論文は博士(工学)の学位論文として価値のあるものと認める。
また、令和 5 年 2 月 21 日、論文内容とそれに関連した事項について試問を行って、申請者が博士後期課程学位取得基準を満たしていることを確認し、合格と認めた。

要旨公開可能日：　2023 年　6 月　23 日以降