

## Application of Molybdenum Catalysts in Biorefinery

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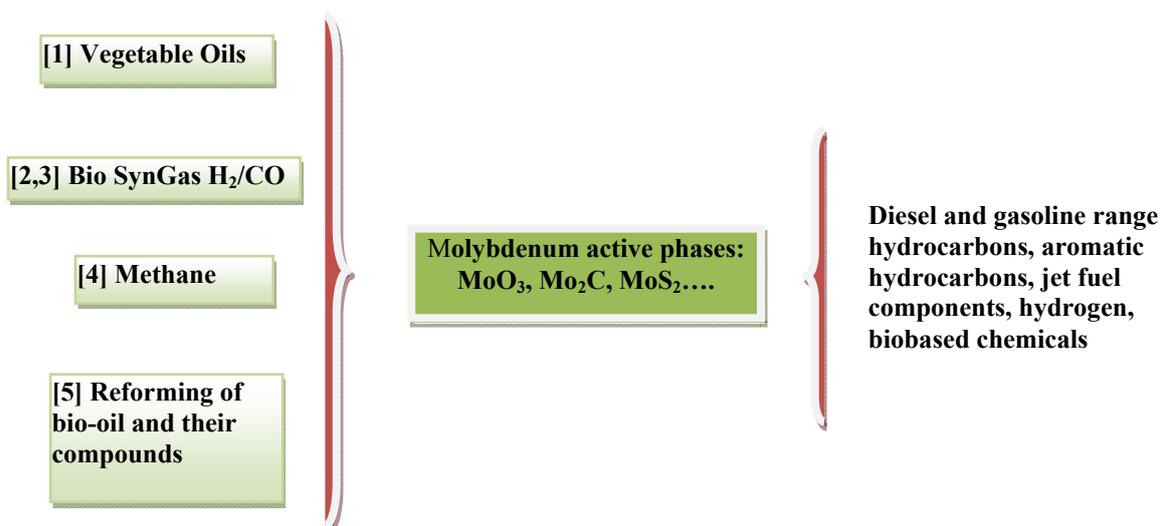
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Catalysis is one of the core technologies in modern chemistry, energy industry and recently with promising application in biorefinery for sustainable fuels and energy production. Reducing the cost of catalyst systems is one of the ways in which technology can be brought closer to full commercialisation. The replacement of noble metals by cheaper non-precious alternatives would bring valuable savings. One of the catalyst candidate for sustainable fuels and energy production is molybdenum based active phases like  $\text{Mo}_2\text{C}$ ,  $\text{MoS}_2$  and  $\text{MoO}_3$ . This article is dealing with the preparation techniques, regeneration of molybdenum based catalysts as well with giving examples of application these catalysts for conversion methane, synthetic gas, vegetable oils and other biorefinery resources originated from biomass.

**Keywords:** molybdenum based catalysts; sustainability; biofuels; renewables; biorefinery; biochemicals

### 1. Introduction

The limited resources of fossil fuels coupled with climate problems have prompted our society to look for sustainable resources as alternatives to meet the increasing energy demand. Biomass is widely available, friendly renewable resource from which various useful chemicals and fuels can be produced. Biorefinery is a system, similar to a petroleum refinery, producing fuels and useful chemicals from biomass. Both system are based on thermochemical processes using heterogeneous catalysts. Development suitable catalysts for conversion different type of biomass is intensively studied by researchers all the World. One of the most important issue is reducing the cost of catalyst systems allowing technology can be brought closer to full commercialisation. The replacement of noble metals by cheaper non-noble alternatives would bring valuable savings. One of the catalyst candidate for sustainable energy production is active phase based on molybdenum and supported by different carriers like zeolites, alumina, silica, carbon and others. The paper focus on different aspects of application molybdenum catalyst from point of view preparation, regeneration and activity for selected biomass conversion or renewable feedstock. Fig.1 presents some application of Mo catalyst in biorefinery processes like: decarboxylation of different type of vegetable oils towards hydrocarbons [1], application in Fischer-Tropsch synthesis [2,3], in methane dehydroaromatization [4] steam reforming of pyrolysis biooil components towards biohydrogen [5] and possibly new applications like highly active and durable nanostructured molybdenum carbide electrocatalysts for hydrogen production, which may become a promising alternative to platinum [6].



**Fig.1** Application of molybdenum catalyst for production biofuels, hydrogen and chemicals

Methane is widely available resource, also produced as a biomethane using an anaerobic digestion process. Usually natural gas coexists with crude oil but there are possible for exploration new resources like shale gas, clathrate methane trapped in ice, coal bed methane and biogas including land fill gas. There is large interest in developing new catalytic routes for converting this low-cost resource to chemicals normally made from more expensive naphtha. Conventional production of monoaromatics (benzene, toluene, and the xylenes (BTX) by reforming naphtha in a refinery or by

extracting them from ethylene steam cracker pyrolysis gas will be limited in future. These compounds are the building blocks of all the industrial chemistry. Fischer–Tropsch synthesis is well-known for the valorization of methane in the case of important gas fields, the methane dehydroaromatization (DHA) reaction remains an interesting solution to convert methane by new route.

Molybdenum catalysts were intensively studied in DHA process for last decade. Direct conversion of methane to aromatics (benzene, naphthalene, toluene, light olefins and xylene) and hydrogen was first reported by Wang [7]. DHA is promising process from point of view conversion of biomethane for production renewable fuels, chemicals and hydrogen. The reformer with 6% Mo/ZSM5 was applied in biogas demonstration plant on Hokkaido in Japan [8]. 200 Nm<sup>3</sup>/day of biogas was reformed, and 134 Nm<sup>3</sup>/day of hydrogen and 8.6 L/day of benzene were produced. Moreover, to control coking and to regenerate the catalyst for the dehydroaromatization reaction, hydrogen was circulated through the catalyst for 1 h every 24 h, as a result, the formation rates of hydrogen and benzene were kept for a long time. Methane not converted was circulated through catalyst bed after separation in membrane filter. We have to remember that reaction is thermodynamically limited up to 12% of conversion of methane. The concept of future production renewable fuels and chemicals from methane compared with current petrochemical route is shown in Fig.2.

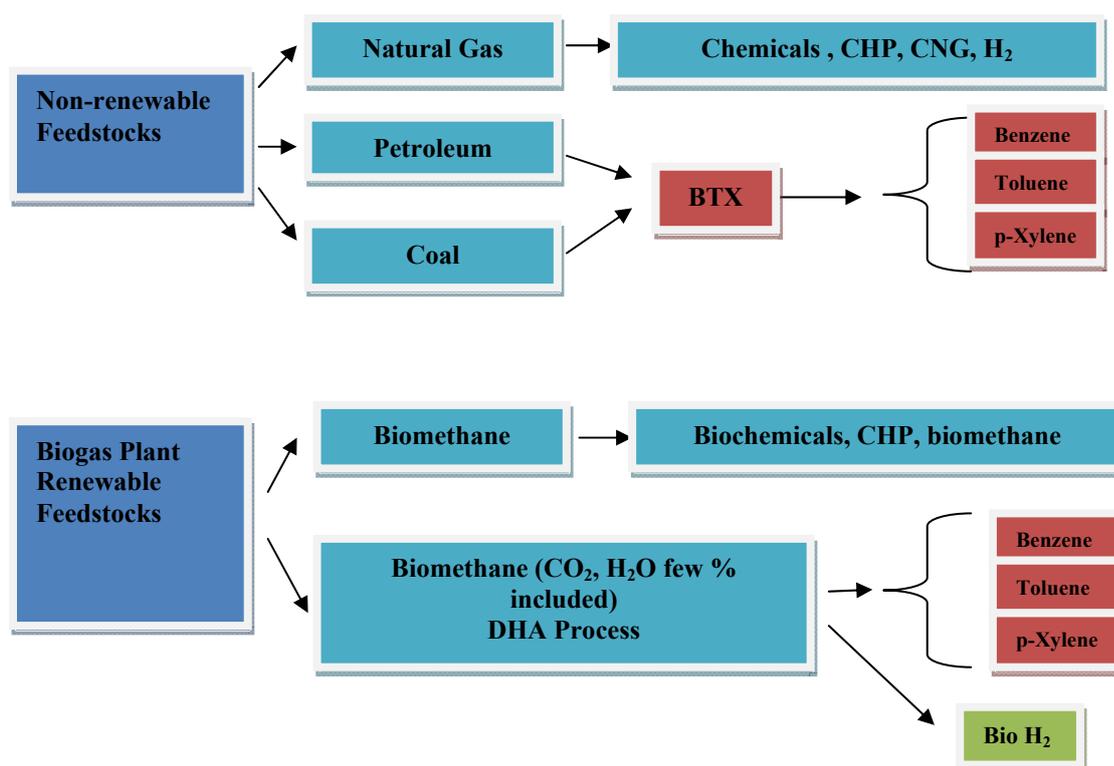


Fig.2 The concept of renewable and non-renewable conversion of methane into fuels and chemicals

## 2. Method used for synthesis molybdenum based catalysts and regeneration

The uniform dispersing of active phase as a monolayer on the surface of the support is a crucial in any catalytic reaction. Molybdenum based catalysts can be synthesized by impregnation methods either wetness or with excess of ammonium heptamolybdate solution. Previous work showed that using MoO<sub>3</sub> for preparation of active Mo/H-ZSM5 by CVD method in static mode is relatively simple, solvent free, and is in accordance with green chemistry methods [9]. In that work from MoO<sub>3</sub> and ZSM-5 was prepared series of catalysts in the range of 1-10% initial concentration of Mo. Screening these catalysts in dehydroaromatization of methane shown maximum and relatively high and stable formation rate of benzene for 3% Mo catalyst while over this amount, reaction abruptly decline in activity. Another method and solvent free is mechanochemical preparation by using mortar and pestle or ball-milling equipment for allowing to control preparation catalyst powder. The catalyst impregnation method required drying at about 100 °C for several hours, followed by calcinations at 500-700 °C for up to 24 hours. On the other hand CVD and mechanochemical techniques by using for example MoO<sub>3</sub> allows to get catalyst in oxidized state. Molybdenum catalysts prepared by three mentioned methods were compared in the methane dehydroaromatization reaction, see table 1. Preparation catalysts is described elsewhere [4,9]. Molybdenum carbide (Mo<sub>2</sub>C) is believed to be active phase to perform the dehydrogenation and coupling of methane to ethylene. The formed C<sub>2</sub>H<sub>4</sub> further reacts and get oligomerized to aromatics on the Brønsted acid sites of the zeolite. It still unclear the role of acid sites. They probably provide anchoring points for the

molybdenum inside the channels of the ZSM-5, which after induction period and reduction into Mo<sub>2</sub>C is able to perform the ethylene oligomerization. Brønsted acid sites possibly are responsible for the dimerization of benzene to naphthalene, polymer aromatics and in consequence to coke formation. Table 1 compare the catalysts prepared by different methods, it can be observed similar activity of catalysts except 10% Mo prepared by CVD, probably due to blocking of channels by the excess of molybdenum. 3% Mo CVD catalysts seems to be most active towards benzene formation and at the same time resistant for coke formation. The mechanochemical and CVD methods are eco-friendly and cost-effective. They are solvent free methods comparing with impregnation one.

**Table 1** Comparison of catalytic performance on Mo/H-ZSM5 in methane dehydro-aromatization reaction on catalysts prepared by: impregnation, mechanochemical mixing and chemical vapour deposition (CVD). The catalytic reaction was conducted at 1023 K, 0.3 MPa, and SV= 2500 ml h<sup>-1</sup> g<sup>-1</sup> with 1% H<sub>2</sub>O and 2% CO<sub>2</sub> in methane feed.

Catalyst/ wt %	Time/h	Conv. <sup>b</sup> /%	Selectivity <sup>c</sup> / %					Formation rate <sup>c</sup> / nmole s <sup>-1</sup> g cat <sup>-1</sup>		
			C <sub>2</sub>	Bz	Tol	Naph	Coke	Bz	Naph	H <sub>2</sub>
<b>Impregnation (I)</b>										
10% Mo	7	7.3	4	63	4	14	15	980	220	2054
<b>Mechanochemical Mixing (MM)</b>										
3% Mo	7	8.9	4	42	2	10	42	890	200	2108
10% Mo	7	5.3	10	65	5	9	11	730	100	1879
<b>CVD</b>										
3% Mo	6	6.3	5	74	5	8	8	923	95	2026
10% Mo	3	5.0	12	6	1	0	81	50	4	1341

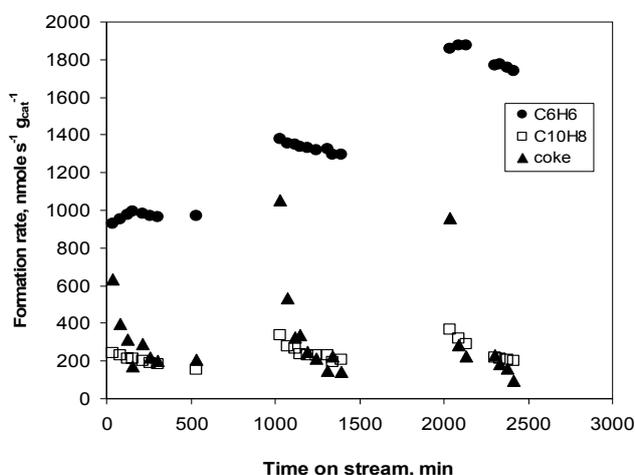
<sup>b</sup> Methane conversion.

<sup>c</sup> C<sub>2</sub> = ethane+ethylene, Bz = benzene, Tol = toluene, Naph = naphthalene.

As it was mentioned at beginning, depends on the reaction different state of molybdenum active form is required. For example molybdenum carbide (Mo<sub>2</sub>C) is an active phase not only in dehydroaromatization of methane reaction [4,9], but also in catalytic upgrading of bio-oil [10], as an alternative for platinum catalyst for hydrogen production [6], and for reforming of ethanol to hydrogen [11]. Transformation of molybdenum oxide form into carbide one can be realized by carburization in hydrocarbons. Effect of carburizing agent on the structure of molybdenum carbides was investigated by T Xiao et al. [12]. Researchers prepared molybdenum carbides by the temperature programmed reaction method using mixtures of hydrogen and methane, hydrogen and ethane, and hydrogen and butane. The results show that the choice of hydrocarbon used to synthesize molybdenum carbide significantly affects the structure and texture of the resultant materials. They found, that increasing the chain length of the carburizing agent reduces the particle size and the temperature for complete phase transformation from molybdenum oxide to carbide is lowered. Carburizing with a mixture of hydrogen and methane gives rise to hexagonal closed packed (hcp) carbide, while when using butane as the carbon source, molybdenum oxide is mainly reduced to face centred cubic (fcc) carbide. However, using ethane as the carbon source, the resultant carbide has a mixed phase composition with the hcp phase predominant. The molybdenum carbide prepared with ethane as the carbon source has the roughest surface and highest hydrogen adsorption capacity, while that prepared with butane had a very condensed surface. There was a substantial difference in the molybdenum co-ordination environments present among the carbides prepared with different carburizing agents. In some reaction like dehydroaromatization of methane formation of active phase of Mo<sub>2</sub>C is a part of an induction period. Another treatment can be applied, when molybdenum oxide is supported by carbon e.g. carbon nanotube (CNT). After impregnation of carbon with ammonium heptamolybdate solution, the dried suspension was treated in air at 673 K for 3h. Afterwards the sample was heated in the catalytic reactor in hydrogen flow up to 973 K and this way MoO<sub>3</sub> can be transferred into Mo<sub>2</sub>C [11]. Another important Mo based catalysts predominant in MoS<sub>2</sub> phase are bimetallic catalysts Co–MoS<sub>2</sub> and Ni–MoS<sub>2</sub>, known as an effective catalysts for the hydrodeoxygenation (HDO) and hydrodesulphurization (HDS) reactions and are widely applied in the refinery for traditional hydrotreating process [13]. In these catalysts, Co or Ni play role of promoters, donating electrons to the molybdenum atoms. This weakens the bond between molybdenum and sulphur and thereby generates a sulphur vacancy site. These sites are the active sites in both HDS and HDO reactions [14]. MoS<sub>2</sub> was studied for synthesis of alcohols from synthetic gas. Prior to the reaction, the catalyst is activated into sulfide form by heating in gas mixture containing few mole percentage of H<sub>2</sub>S in H<sub>2</sub>. Many catalytic systems containing Mo are using zeolites as a support. In zeolites we can distinguish internal and external surface. In case of molybdenum dispersion as an active phase many factors can influence on location of metals. These are

temperature, calcinations time, preparation technique applied, and especially initial concentration of molybdenum. Some of molybdenum in zeolite matrix is associated with Brønsted acid sites. It was generally accepted that the molybdenum is anchored on the Brønsted acid sites of the zeolite as  $(\text{Mo}_2\text{O}_5)^{2+}$  species. However this aspect is still unclear and as was suggested by French scientist, the Si/Al ratio of the zeolite, and consequently the density of available Brønsted acid sites, plays a dramatic role on the anchoring mode of the molybdenum and on its catalytic activity [15].

Regeneration of catalysts is very important from point view of technological application. Methane dehydroaromatization reaction condition with high temperature approximately 700 °C especially favor the formation of carbonaceous deposits. The previous results showed that at low temperature peak at ca. 490 °C can be attributed to carbon deposits associated with molybdenum, while the high temperature peak at ca. 580 °C is linked to carbon deposits on the Brønsted acid sites of the zeolite [16]. Honda *et al.* concluded that the carbonaceous deposits were predominantly formed on the Brønsted acid sites of the zeolite [17]. The same author [18] shown that the periodic switching of the gas flow through the catalyst between  $\text{CH}_4$  and  $\text{H}_2$  remarkably promoted the catalyst stability and then aromatics formation. In the experiment we performed the spent catalyst 10% Mo/HZSM-5 (0.3 g) after few hours in methane stream (reaction condition in table 1) was regenerated in hydrogen. The temperature was ramped from room temperature up to 750 °C at 8.3 °C/min, in flow of hydrogen amounted 30  $\text{cm}^3/\text{min}$ . There was carried out reaction with fresh catalyst at 725°C, then performed regeneration-reaction two times, Fig.3. After first and second regeneration temperature of reaction was increased up to 750 °C and 780 °C, respectively.



**Fig. 3** The spent catalyst 10% Mo/HZSM-5 (0.3 g) after few hours in methane stream (reaction condition in table 1) was regenerated in hydrogen. The temperature was ramped from room temperature to 750 °C at 8.3 °C/min and flow of hydrogen amounted 30  $\text{cm}^3/\text{min}$ . There was carried out reaction with fresh catalyst at 725°C, then performed regeneration-reaction two times. After first and second regeneration temperature of reaction was increased up to 750 °C and 780 °C, respectively.

There was observed significantly increasing rate formation of benzene but naphthalene and coke formation remain practically on the same level. Even increased reaction temperature the kinetic sequence related with the dimerization of benzene to naphthalene and coke formation was practically unchanged. Sequence switching between  $\text{CH}_4$  and  $\text{H}_2$  is very promising way of regeneration and extension life of catalyst. In further part of this work will be presented processes, where above mentioned molybdenum active phases are applied for renewable feedstock conversion.

### 3. Application of Molybdenum catalysts for renewable feedstock conversion

We assume that application of molybdenum catalysts can be extended on conversion other resources like synthetic gas obtained from biomass or different type of vegetable oil and production of hydrogen by reforming of biooil or even by photocatalysis. Some examples will be given below. In the last few years there are increasing amount of research papers devoted conversion of renewables. Liu *et al.* [2] tested Mo/HZSM-5 catalysts in Fischer–Tropsch synthesis (FTS). The catalysts were evaluated with typical of a synthesis gas derived from biomass gasification ( $\text{H}_2/\text{CO}=1$ ). Liquid hydrocarbons formed on the Mo/HZSM-5 were composed mainly of alkyl-substituted aromatics and lower branched and cyclized alkanes. Aliphatic hydrocarbons were detected only in trace amounts. Lower hydrocarbons produced included mainly methane, ethane, propane and iso-butane. Higher alcohols and carboxylic acids ( $\text{C}_1\text{--}\text{C}_6$ ) were detected in the water phase liquids from FTS. It was supposed that the formation of hydrocarbons on Mo/zeolite is through bifunctional-zeolite acidity and molybdenum metal catalysis via mixed alcohols as the intermediates. Another report in the same FTS process is devoted alumina-supported molybdenum carbide catalyst prepared by temperature-programmed carburization [19]. Reaction has been evaluated for FT synthesis between 473K and 515K with feed gas containing  $\text{H}_2/\text{CO} = 1:5\text{--}5:1$ . Mo-based catalysts had high hydrocarbon selectivity unless they are promoted with alkali

metals and/or Group VIII metals. Promoted MoS<sub>2</sub> and MoP showed alcohol selectivities of 80 % (CO<sub>2</sub>-free basis) at typical operating conditions (5–8 MPa, H<sub>2</sub>/CO = 2–1, 537–603 K), whereas on promoted Mo<sub>2</sub>C, alcohol selectivities are 60% [20]. Russian scientist [21] studied conversion of synthesis gas into alcohols on supported cobalt–molybdenum sulfide catalysts promoted with potassium Catalysts based on molybdenum sulfide of different compositions (promoted with Co and K) were synthesized with the use of various supports (aluminum oxide, aluminum oxide modified with silicon oxide, Sibunit, and titanium silicate) and tested in the reactions of alcohol synthesis. They concluded catalysts based on molybdenum sulfide are suitable for the production of alcohols from synthesis gas. Interesting application of Mo<sub>2</sub>C for fast pyrolysis of biomass showed Patel *et al.*[10]. They performed in situ catalytic upgrading of bio-oil using supported molybdenum carbide. Conclusion was that, Mo<sub>2</sub>C/Al<sub>2</sub>O<sub>3</sub> does not produce deoxygenated bio-oil, but can be used to increase the furan and phenol concentration in bio-oil. Furans are valuable starting products for transportation fuels such as methyltetrahydrofuran (MTHF). Phenols can be used for the production of phenolic resins and other petrochemical products. Recently vegetable oils were found as suitable substitutes for fossil fuels due to its high energy density, low oxygen content and renewable character. Spanish group of scientist reported catalytic conversion of rapeseed oil into raw chemicals and fuels over Mo-modified nanocrystalline ZSM-5 zeolite [1]. Nanocrystalline zeolite were applied due to chemical characteristics of vegetable oils, which are markedly different from those of petroleum oil. The relative narrow channels of zeolites lead to diffusion limitations and hinder the access to active catalytic sites for large reactants molecules such as triglycerides. There was observed total conversion of rapeseed oil on molybdenum catalysts at reaction temperature 550 °C and weight hour space velocity (WHSV) = 7.6 h<sup>-1</sup>. The Mo/HZSM-5 samples favored the formation of liquid hydrocarbons, with a high proportion of aromatics in the gasoline range. The incorporation of Mo into the nanocrystalline HZSM-5 zeolite causes important changes in its acid and textural properties. Mo oxide was homogeneously distributed over the zeolite support, being located mainly inside the micropores. The last example of application of molybdenum based catalysts are that one applied in photocatalysis. The photocatalytic production of hydrogen from water is a key process that may lead to the feasibility of hydrogen-powered energy production devices. The most efficient catalyst at the moment is platinum, but there is large effort for replace noble metals with low cost materials. Photocatalytic H<sub>2</sub> evolution over Mo<sub>2</sub>C/TiO<sub>2</sub> samples was investigated under UV light irradiation [22]. The results show that the Mo<sub>2</sub>C/TiO<sub>2</sub> photocatalysts exhibit a coexistence of both hexagonal Mo<sub>2</sub>C and anatase TiO<sub>2</sub> phases. The Mo<sub>2</sub>C/TiO<sub>2</sub> catalyst not only exhibits higher photocatalytic activity but also presents higher resistance to sulfur poisoning as compared to either pure anatase TiO<sub>2</sub> or reference Pd/TiO<sub>2</sub> catalyst. Reserchers from China [23] applied mechanocatalytic preparation MoS<sub>2</sub>/CdS photocatalysts for visible-light-driven water splitting into H<sub>2</sub> for the first time. They used ball-milling technique, thus allowing under control condition preparation physical mixture. The optimized 0.9 mol % MoS<sub>2</sub>/CdS photocatalyst exhibited a H<sub>2</sub> evolution rate of 1315 μmol h<sup>-1</sup>, much larger than the highest H<sub>2</sub> evolution rate reported in the literature. Given examples of molybdenum based systems are very promising in the new field of catalysis for renewable production.

#### 4. Conclusion

Molybdenum based catalysts has attracted much attention for its some outstanding properties especially catalytic performance, thermal stability, mechanical hardness and surface reactivity. Its catalytic properties are usually superior to noble metal catalysts in terms of selectivity, stability and resistance to poisoning, indicating that MoX (X=C, S, O, N) may be an inexpensive alternative to the noble metal-based catalysts.

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