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Supported MoO₃ catalysts in petroleum refining

A. Galadima^{1*} and B. M. Ibrahim²

¹Department of Pure and Applied Chemistry, Usmanu Danfodiyo University, P.M.B. 2346, Sokoto, Nigeria.

²Department of Pure and Industrial Chemistry, Bayero University, P.M.B. 3011, Kano, Nigeria

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ABSTRACT: The exploitation of supported metals and metallic oxides catalysts is increasingly becoming an issue of special interest in the petroleum industry. This is consistent with necessary need for mitigating separation, recycling and reusability problems coupled with increased production costs associated with free metals, unsupported or homogeneous catalyst systems. The current review focuses on the potentials of supported MoO₃ catalysts in refining technology, considering associated advantages such as thermal stability, lower costs than for example Pt or Pd supported zeolites, resistance to sulphur and nitrogen poisons and improved activity under modified conditions. Available supports, preparation and characterisation methods and areas of prominent applications have been discussed. Supported MoO₃ catalysts could be good future replacement materials in refining processes such as catalytic cracking, alkylation, hydrodesulphurisation, hydroisomerisation, hydrodenitrogenation and catalytic reforming.

Key Words: Molybdenum oxide, supported catalysts, exploitation, petroleum refining.

Introduction

The petroleum industry is a major important sector of the modern global economy that accounts for the sustenance of other industries. In addition to source of energy fuels the sector provides key industrial raw materials for the production of many chemical products such as organic solvents, pharmaceuticals, polymers, fertilisers, insecticides e.t.c. Series of complex processes involved ranged from oil and gas exploration to extraction and refining of which the refining process consists of several other sub-processes that are attracting catalysis chemists' attention, considering the numerous number of catalysts involved. Although the petroleum refineries differ in scale and refining capacity (Rigutto *et al.*, 2007), the sub-processes involved are generally the same and include fluid catalytic cracking (FCC), hydrotreating, dewaxing, reforming, alkylation and isomerisation. Initially, homogeneous catalysts such as mineral acids or metal complexes are employed because they offer advantages such as equal availability of the catalyst to the reactants leading to lower catalyst loading, longer catalyst life time, exothermal removal and easy kinetic monitoring potentials. However, these materials are currently abandoned due to high cost of catalyst separation and environmental disposal problems (Panchenkov and Kolesnikov, 1980).

*Corresponding Author: ahmadgldm@yahoo.com

Proper mitigation of these problems coupled with recent green environmental campaign account for a shift to more benign heterogeneous catalysts. Unlike the homogeneous materials, a wide range of heterogeneous catalysts could recycle and reused allowing lower cost and good environmental management in addition to promising activity and selectivity. Both supported and unsupported solid materials including Freidel crafts, zirconias, zeolites, heteropoly acids, silica e.t.c have been exploited in this respect (Sie, 1980; Sie, 1994; Corredores, 2000; Galadima *et al.*, 2009). Studies indicated that MoO₃ being cheaper than for example zeolites, easily characterizable and readily supportive over many catalyst carriers, allowing good selectivity is increasingly becoming an attractive material in the petroleum refining industry (Amberg, 1974; Lamic *et al.*, 2006), especially due to catalyst stability and high resistance to sulphur and nitrogen poisons in reaction stream. For example, the successful applications of MoO₃-C, MoO₃/ZrO₂, MoO₃/TiO₂, MoO₃/SiO₂ and MoO₃/ Al₂O₃ in different refining processes have been reported (Amberg, 1974; Delgallo, 1997; Zdrzil, 2001). This paper tailors the key issues from the type of supports/carriers involved to uses of supported molybdenum oxide catalysts in petroleum refining. It is aimed at identifying important processes where supported MoO₃ compounds could be employed to replace the currently used catalysts.

Supports/ Carrier Materials

The common carrier materials for supporting MoO₃ are presented in Table 1. The choice of a particular support depends on the nature of application and reaction conditions. In general, support materials are employed to promote the dispersion and stabilisation of MoO₃ fine particles and allow access to a large number of catalytically active atoms that could not be available to the reactants over MoO₃ species alone. Refinery reactions involving high pH values cannot be carried out using SiO₂ or Al₂O₃ support because these materials show stability decay at high pH. However, promising stability could be achieved over activated carbon in both basic and acidic media (Auer *et al.*, 1998). In reactions like hydrodesulphurisation (HDS) or hydrogenation (HYD) carrier materials such as TiO₂, ZrO₂, SiO₂ and Al₂O₃ could be employed yielding reliable properties. For example, Okamoto and Kubota (2003) performed HDS and HYD of thiophene and butadiene over these supports at 623K and 473K respectively. The reaction turn over frequency (TOF) increased in the order SiO₂< TiO₂< ZrO₂< Al₂O₃ for thiophene HDS and the reverse for butadiene hydrogenation. This implies a development of new edges specific active sites achieved over Al₂O₃ and SiO₂, accounting for their better performance in the respective reactions. In contrast, MoO₃/ZrO₂ shows higher turnover rates, that increases with increase in MoO₃ surface density than MoO₃/ Al₂O₃ system in the oxidative dehydrogenation of propane and this was attributed to the nature of MoO₃ and support interactions forming ZrMo₂O₈ and Al₂(MoO₄)₃ respectively (Chen *et al.*, 2001). Although a basic carrier, MgO, can allow the formation of high surface area (>200m²g⁻¹) MoO₃/MgO catalyst system comprising of various molybdena loadings that might be interesting for different refining processes including HDS and hydrodenitrogenation while significantly mitigating instability problems (Zdrzil, 2001). With regards to the zeolite supports, materials such as beta and mordenites are employed in dewaxing, reforming and alkylation processes. During hydroisomerisation of gasoline fractions, these sulphur and nitrogen resistance materials provide sufficient Bronsted acidity for carbenium ion formation and isomerisation (Galadima *et al.*, 2009), thereby offering a remarkable opportunity for bifunctional reaction. Generally, MoO₃ loadings over a given support material may range from 1-30% or more depending on the nature of the reaction.

Table 1: Common carriers for supporting molybdenum oxide catalysts

Support/ Carrier	Chemical formula
Alumina	Al ₂ O ₃
Silica	SiO ₂
Zirconia	ZrO ₂
Titania	TiO ₂
Ceria	CeO ₂
Magnesium oxide	MgO
Activated carbon	C
Tungsten oxide	WO ₃
Silica carbide	SiC
Zeolites	Eg MOR, ZMS-25 etc

Methods for Supported Catalysts Preparation

The most recommended procedures for industrial catalysts preparation are reported in the “manual of methods and procedures for catalysts characterisation” by International Union of Pure and Applied Chemistry (IUPAC) (Haber *et al.*, 1995). These include impregnations, ion exchange, gas phase deposition, solid-solid reactions, wash coat, precipitation and co-precipitation. Therefore, choice of most suitable method must depend on the type of catalyst to be prepared, availability of starting materials and intended application coupled with previous history of the heterogeneous catalysts. Industrially, supported MoO₃ catalysts are prepared by impregnation method (mostly incipient impregnation). The technique called “conventional or solution impregnation” (Figure 1) involved dissolution of known volume of MoO₃ in aqueous ammonia to form ammonium heptamolybdate tetrahydrate, which would be treated with appropriate quantity of support material. The resulting mixture is heated to dryness, usually by means of rotary evaporator at 60-80°C temperatures. Completely dried catalyst is obtained under oven conditions (usually 120-160°C) for 24 hours. Resulting catalyst is then calcined in pure air at normally 400-600°C for 3 to 6 hours depending on catalyst application. In some instances ammonium heptamolybdate is employed as the starting material. However, in the recent years Zdrzil (2001) and Ma *et al.* (2005) reported the preparation of MoO₃/C, MoO₃/SiO₂, MoO₃/ZrO₂ and MoO₃/MgO catalyst systems by a new method called “slurry impregnation” (Figure 2). The principle requires that slurry of MoO₃ in water is mixed with desired support material. According to them the solubility of molybdena is sufficient enough to allow gradual transportation of active species to the surface in pores of support at room temperature.

As the dissolved species are adsorbed onto the support more solid molybdena in slurry is dissolved. All the MoO₃ could be deposited and the catalyst appropriately dried. Unlike the conventional method the new slurry technique does not require calcinations. A number of advantages are offered by the later method. It is an equilibrium adsorption process suitable for environmental management because waste solutions and nitrogenous gases are not produced (Ma *et al.*, 2005). Similarly, highly dispersed amorphous supported catalysts that could be used in different refining and transesterification are produced.

MoO₃-C- modified catalysts on the other hand are prepared by low temperature oxidative treatment of either low specific area MoO₃ or high specific area Mo₂C. For example DelGallo *et al.*(1997) reported successful synthesis of high surface area material at 350°C by the reaction of MoO₃ (1m²g⁻¹) and hydrogen-hydrocarbon mixture. The catalyst shows extra-stability and yield 95% activity in n-butane hydroisomerisation. Similarly, York *et al.* (1997) synthesized a molybdenum oxycarbide catalyst with 145m²g⁻¹ surface area from MoO₃ (4m²g⁻¹) under the same conditions. The catalyst supported over SiC showed comparable selectivity to Pd/B-zeolite in the hydroisomerisation of C₇ to C₂₀ alkanes, yielding no crack hydrocarbons or coke deposition.

Characterisation Techniques

Many spectroscopic and temperature programmed methods are used for studying the structure and activity of supported molybdena and other catalyst systems industrially. It is beyond the scope of this article to elaborate all the available techniques reported in Table 2. However, the most commonly used methods would be briefly described. XRD method is employed to evaluate the structural properties of the powdered form of the catalyst. Measurements are carried out with steps of 0.05° of 2θ and 5s/step to obtain a reliable result. An XRD studies by Del Gallo (1997) showed diffraction lines for MoO₂ and molybdenum oxycarbide phase. SEM technique produces topographical images from back-scatter primary or low-energy secondary electrons in the sample under study (haber *et al.*, 1995). This method is very useful in studying the distribution and sizes of the mesopores. Solid state NMR could provide detail information regarding the Si and Al atoms in the supported catalysts as well as various atomic movements undergone. It is particularly important when the desired species does not exhibit long range atomic order, militating against the used of XRD method (Mackenzie, 2004). For instance Mastikhin *et al.* (1998) reported a superposition of two spectra with second order quadrupole splitting, accounting for structural inequivalence of Mo in MoO₃. FT-IR provides information concerning the nature of the dispersed MoO₃ surface species. An FT-IR of MoO₃/TiO₂ showed an associated molybdenyl species stabilised on the TiO₂ surface (Nova *et al.*, 1998).

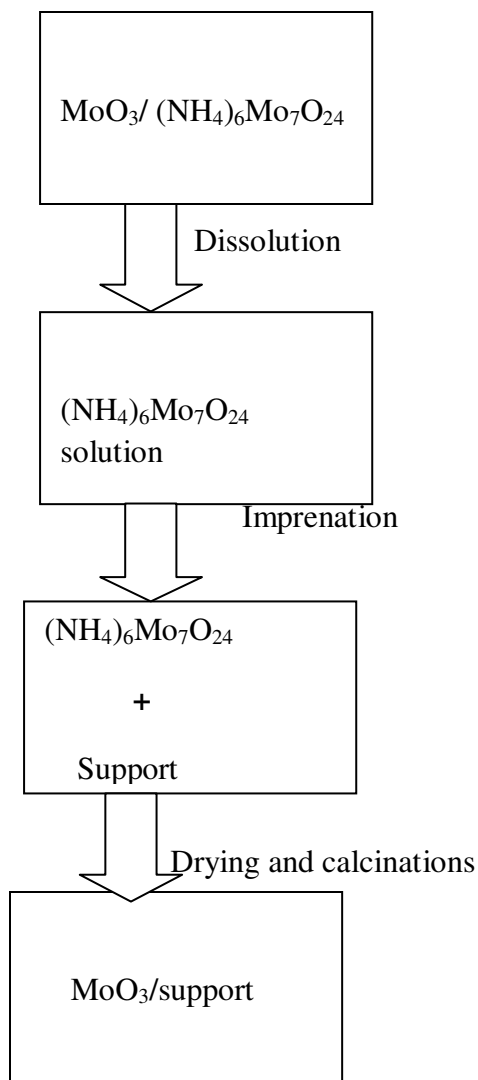


Figure 1: Conventional/solution method

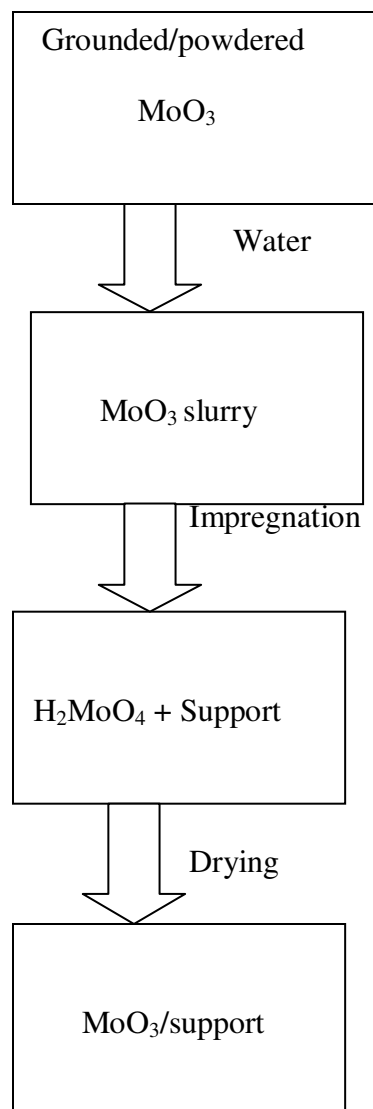
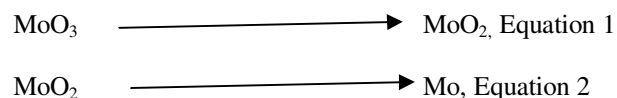


Figure 2: Slurry method

The species promoted the activity of the system as De-NO_x SCR catalyst. UV-Visible spectroscopy coupled with some other methods could provide information on the nature of MoO₃ species formed in connection to support homogeneity. Generation of new acid sites on the catalyst surface of for example aluminium and silicate supports could be exploited (Henker and Wendlandt, 1991).

TPR method provides quantitative and qualitative picture of the reproducibility of the catalyst surface, as well as its high sensitivity to chemical changes resulting from promoters or metal-support interactions. The reducibility of supported MoO₃ was found to proceeds in two steps (equations 1 and 2).



This occurs at different temperatures depending on the support (Chary *et al.*, 2004). TPD otherwise called thermal desorption spectroscopy (TDS) is important for evaluating the kinetic and thermodynamic parameters of decomposition reactions or deposition processes. Specific information relating to effects of lateral interactions among adatoms, surface heterogeneity, initial surface coverage and energy of desorption could be determined (Rivera and Hitzel, 1991). Pulse chemisorptions technique, which can be linear, bridge or twin type (Nakai and Nakamaru, 2003) is required to determine the dispersion of MoO₃ over the support. An increase in dispersion causes increase in the number of active sites that are effective to reaction and also promote selectivity due to interaction with the support.

Table 2: Available techniques for characterising supported MoO₃ catalysts.

Characterisation Technique	Abbreviation
X-ray diffraction	XRD
Scanning electron microscopy	SEM
Solid state nuclear magnetic resonance	SS-NMR
Fourier transformed infrared spectroscopy	FT-IR
Ultra violet-visible spectroscopy	UV-Vis
Photoelectron spectroscopy	PES
Diffusion reflectance spectroscopy	DRS
Photo acoustic spectroscopy	PAS
Electron spin resonance	ESR
Scanning auger microscopy	SAM
Temperature programmed reduction	TPR
Temperature programmed oxidation	TPO
Temperature programmed desorption	TPD
Pulse chemisorptions technique	PCT
BET surface area measurement	BET

Potential Uses of the Catalysts in Petroleum Refining

Petroleum refining is complex technology considering the large number of processes involved, which can either be catalytic or non-catalytic in nature. Catalytic processes such as catalytic cracking, alkylation, hydrodesulphurisation, hydroisomerisation, hydrodenitrogenation and catalytic reforming are very sensitive because the choice of catalysts materials and the reaction conditions determine the success of a particular process. Although different catalysts ranging from Freidel crafts chlorides to metal supported zeolites could be employed, yielding desired activities, supported MoO₃ systems could potentially surpass many catalysts due to associated advantages. A 12.5wt% MoO₃/Al₂O₃ has been reported to show up to 95% activity at temperatures ranging from 400-1200K in the hydrodenitrogenation of pyridine and carbazole. This could be attributed to high catalyst surface area (245m²g⁻¹), good thermal stability and resistance to nitrogen poisons in the reaction stream (Nagai *et al.*, 1998). Recently, Pereira *et al.* (2006) reported supported MoO₃ catalysts to display high catalytic performance (>95%) in terms of conversion and selectivity during thiophene hydrodesulphurisation. This had been attributed to improved surface area (270m²g⁻¹) due to good MoO₃ dispersion and resistance of the catalyst systems to sulphur poisons and coke deposits with time.

Hydroisomerisation of n-alkanes is another environmental friendly process that converts the linear alkanes to corresponding branched alkanes, thereby increasing octane number of gasoline. The most appropriate catalysts are not yet resolved. Chlorides, heteropoly acids and some zeolites had been tested and are currently abandoned due to corrosion, poor thermal stability and production of cracked hydrocarbons respectively. However, Del Gallo *et al* (1997) isomerised n-butane over MoO₃-C modified catalyst, yielding 95% isobutene between 350-365°C for 48 hours without catalyst deactivation. Similarly, Meunier *et al* (2006) hydroisomerised n-alkanes (>C₄) over promoted MoO₃, achieving shorter induction period and higher selectivity than a supported platinum zeolite. Alkanes reforming over MoO₃/Al₂O₃ have been reported (Keller *et al.*, 2000). The superior catalytic activities obtained were attributed to acidic and metallic isomerisation and dehydrogenation properties of the catalyst as well as ability to allow metallocyclo-butane intermediates formation.

Conclusion

Molybdenum oxide can be supported over a wide range of metal oxides and zeolites to form important catalyst systems with good potentials in petroleum refining. The catalysts are usually prepared by conventional solution impregnation or the newly reported slurry method. The latter have advantages of shorter preparation time, requiring no calcinations and producing clean catalyst free from nitrogenous gases. Successful characterisation can be achieved using common spectroscopic techniques.

These materials offer good thermal stability than for example chlorides and heteropoly acids. Resistance to catalyst poisons such as sulphur and nitrogen coupled with improved activity can account for the replacement of other catalysts in refining processes like hydrodesulphurisation and hydrodenitrogenation. On the other hand, because Mo is cheaper than Pd and Pt, supported MoO₃ catalysts could be employed to replace Pt or Pd supported zeolites in hydroisomerisation of n-alkanes for increasing octane number of gasoline. Other areas of potential applications include catalytic cracking and reforming processes.

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