Catalysis Letters 6 (1990) 409–416

NEW TYPE OF TiN SUPPORT FOR HYDROPROCESSING CATALYST

Naoto KIMBARA [1], Akio NISHIJIMA [1,2], Toshio SATO [2],
Yuji YOSHIMURA [2], Hiromichi SHIMADA [2], Nobuyuki MATSUBAYASHI [2]
and Akinori YUKIMURA [3]

[1] *Sumitomo Metal Mining Co., LTD., Ichikawa-shi, Chiba 272, Japan*
[2] *National Chemical Laboratory for Industry, Tsukuba-shi Ibaraki 305, Japan*
[3] *Science University of Tokyo, Noda-shi, Chiba 278, Japan*

Received 16 February 1990; accepted 12 September 1990

Hydroprocessing catalysts, TiN support

TiN supported molybdenum sulfide catalysts showed much higher activity for cleavage of C–C bonds than oxide supported molybdenum sulfide catalysts, indicating the possibility of a new generation of supports for hydroprocessing catalysts.

1. Introduction

Molybdenum sulfide catalysts containing nickel or cobalt promoters have long been used for hydrotreating in the petroleum industry. Oxide supports such as alumina or silica/alumina have been employed in the traditional catalysts. However, improvements in the selectivity of the molybdenum sulfide catalyst for the hydrotreating is required to minimize consumption of hydrogen and to produce clean fuels. The development of new supports that improve the catalytic selectivity appears to be one of the most promising approach for this objective. During the course of study on superior catalysts supports, the authors found that hydrocracking activity of molybdenum sulfide catalysts is highly dependent on the type of supports [1]. The order of effectiveness of the supports is $TiO_2 > SiO_2 > ZrO_2 > Al_2O_3 > MgO$. As the next step in the investigation of the catalyst support, many kinds of double oxides such as $TiO_2 \cdot Al_2O_3$ or $ZrO_2 \cdot TiO_2$ were prepared and tested. Among these candidates some of the double oxides supports gave higher hydrocracking activities than the single oxide supports [2]. However, much higher hydrocracking activity is required for a new generation of hydrotreating catalyst.

In the present work, nitride and carbide supports were prepared and tested with the objective of finding new supports for hydroprocessing catalysts which give higher hydrocracking activities than oxide supports. Titanium was selected as the cation species of nitride because of the stability of nitride and the highest hydrocracking activity among the single oxide supports investigated.

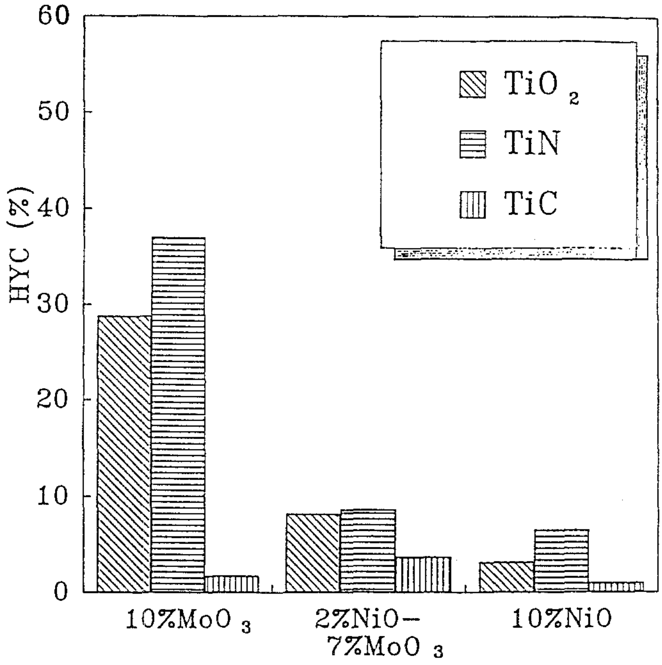
2. Experimental

TiN and TiC were synthesized by a thermal plasma arc jet method [3]. Oxide supports were also prepared and used for reference.

The physical properties of these supports are summarized in table 1. 10 wt% MoO_3, 2 wt% NiO-7 wt% MoO_3 and 10 wt% NiO were loaded on these supports by an impregnation method [5]. The catalysts were subsequently dried under nitrogen atmosphere at 110 °C for 16 h then calcined at 300 °C for 2 h in a nitrogen atmosphere to prevent oxidation of the supports. The form of these catalysts was powder. The catalysts were presulfided with $5\%H_2S$-$95\%H_2$ gas for 2 hours before the reaction. The hydrocracking activity of C–C bond and the hydrogenation of the aromatic rings were examined by using model test reactions. The hydrocracking of diphenylmethane (DPM) and the hydrogenation of 1-methylnaphthalene (1-MN) were chosen as probe reactions for estimating hydrocracking and hydrogenation activities, respectively. All the activities of the catalysts were studied under high hydrogen pressure for better understanding of the hydrocracking and hydrogenation activities of the catalysts. A stainless steel microreactor (50 cm^3) charged with 0.5 g of the catalyst and 10 cm^3 of DPM or 1-MN were used for the hydrocracking or the hydrogenation reaction. The unit was pressurized with H_2 to an initial pressure of 6.9 MPa and then injected into an oven heated at 430 °C. The oven was shaken automatically during the reaction. The hydrocracking reaction was performed at 400 °C for 60 min, while the hydrogenation reaction of 1-MN was done at 350 °C for 60 min. The reactions were repeated at least twice and averaged values were calculated. Reaction products were analyzed by gas chromatography equipped with an OV-1 capillary column (50 m). X-ray photoelectron spectra were obtained using a Shimadzu ASIX-1000 spectrometer with Mg Kα X-ray. For XPS analysis samples were pressed into pellets, which were fixed on the holder. The binding energies, which were referenced to gold (Au $4f_{7/2} = 83.8$ eV) evaporated on the sample, were reproducible within $+0.1$ eV.

Table 1
Physical properties of supports

Support	$S \cdot A$ (m^2/g)	$P \cdot V$ (cm^3/g)
TiO_2	149	0.34
TiN	53	0.14
TiC	29	0.04



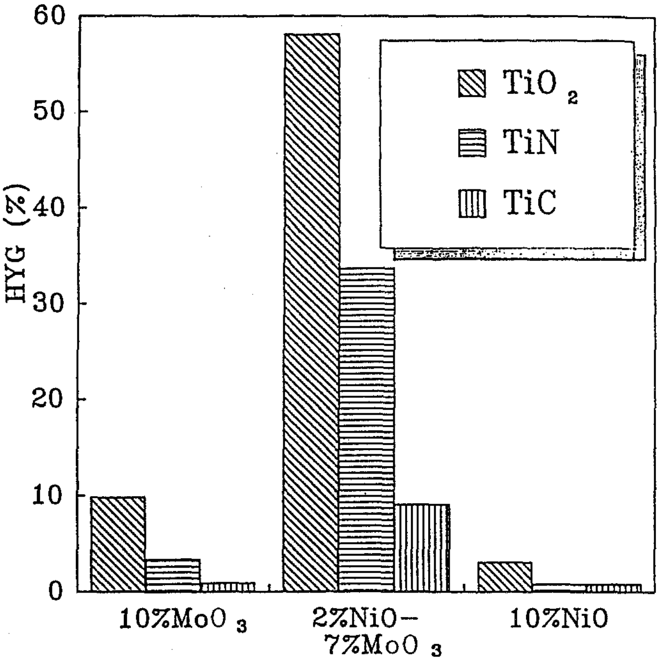
HYC (%) : Hydrocracking activity which means the yields of toluene and benzene from diphenylmethane.

Fig. 1. Hydrocracking on various supports.

3. Results

No hydrocracking or hydrogenation activities were observed on TiN, TiC and TiO_2 supports alone, indicating that the active species (Mo or Ni) are essential for activity to take place.

The hydrocracking and hydrogenation activities of the catalysts on various supports are summarized in figs. 1 and 2. A wide range of activities and selectivities were observed among the various catalysts. The TiN support gave the highest hydrocracking activity among the MoO_3 catalysts (fig. 1). Despite the MoO_3/TiN catalysts having a much smaller surface area than the MoO_3/TiO_2 support (table 1), much higher hydrocracking activity was observed. The TiN support showed lower hydrogenation activity than the TiO_2 support (fig. 2) which is probably due to the lower surface area of TiN support. In addition, the TiC support gave lower hydrocracking and hydrogenation activities, probably being due to a lower surface area. For the NiO-MoO_3 catalysts, the TiN support gave higher activity for hydrogenation but lower hydrocracking activity. This indicates an increase in the level of hydrogenation active sites and the decrease of hydrocracking active sites on the TiN support by the addition of nickel ions.



HYG (%) : Hydrogenation activity which means the yields of 1-methyltetralene and 5-methyltetralene from 1-methylnaphthalene.

Fig. 2. Hydrogenation on various supports

Though the hydrocracking activity of the NiO-MoO$_3$/TiN catalyst is less than that of the NiO-MoO$_3$/TiO$_2$ catalyst, the TiN support which has a larger surface area will give superior hydrogenation activity than the TiO$_2$ support. This is because highly dispersed states of active ions are necessary for higher hydrogena-

Table 2
Atomic ratio on catalyst surface measured by XPS

Active metal	element	Support		
		TiO$_2$	TiN	TiC
10% MoO$_3$	Mo	16	19	39
	S	33	35	70
2% NiO	Mo	14	12	107
	Ni	26	21	117
7% MoO$_3$	S	35	27	200
10% NiO	Ni	46	70	383
	S	20	22	113

Each atomic ratio was calculated relative to a titanium standard of 100.

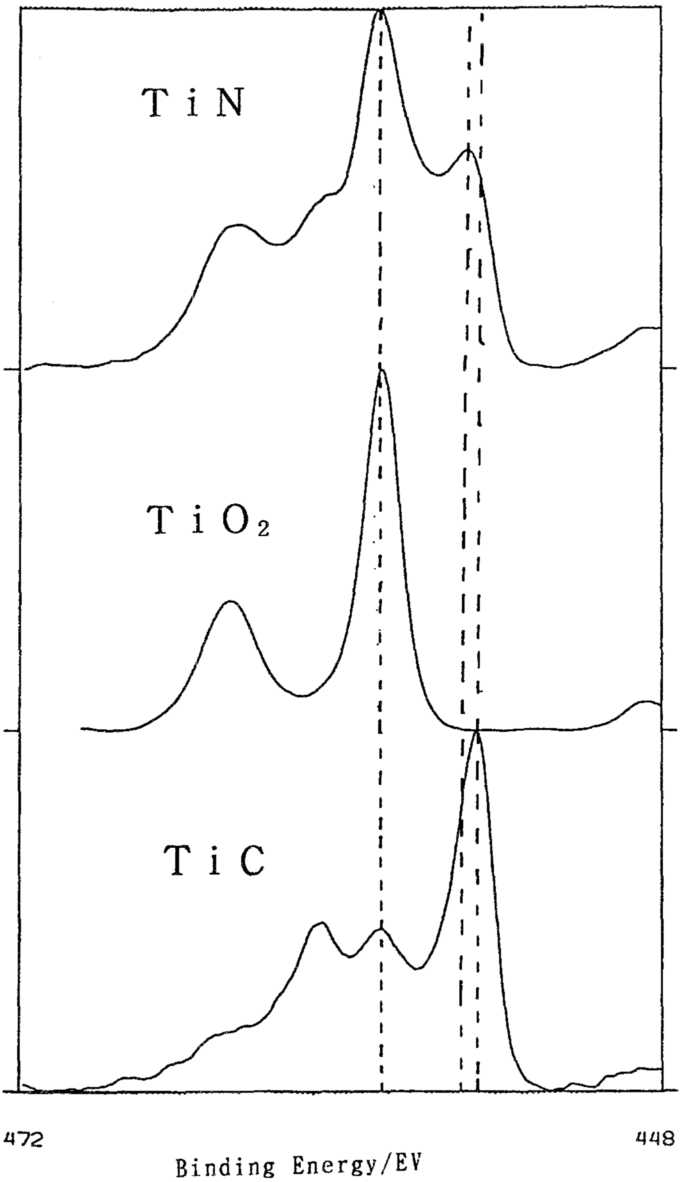


Fig. 3. Ti 2p photoelectron spectra of the titanium based catalysts.

tion activity. These results show that the TiN may be a new generation of catalyst support to control catalyst selectivity and to minimize hydrogen consumption.

XPS analysis showed that a fraction of the surface titanium of the TiN support is oxidized (fig. 3). This oxide is hypothesized to have formed during the preparation of catalyst.

The titanium on the surface of the TiO_2 of the TiC supports remain in their original state. The binding energy of the Mo $3d_{5/2}$ line for the TiO_2 and the TiC

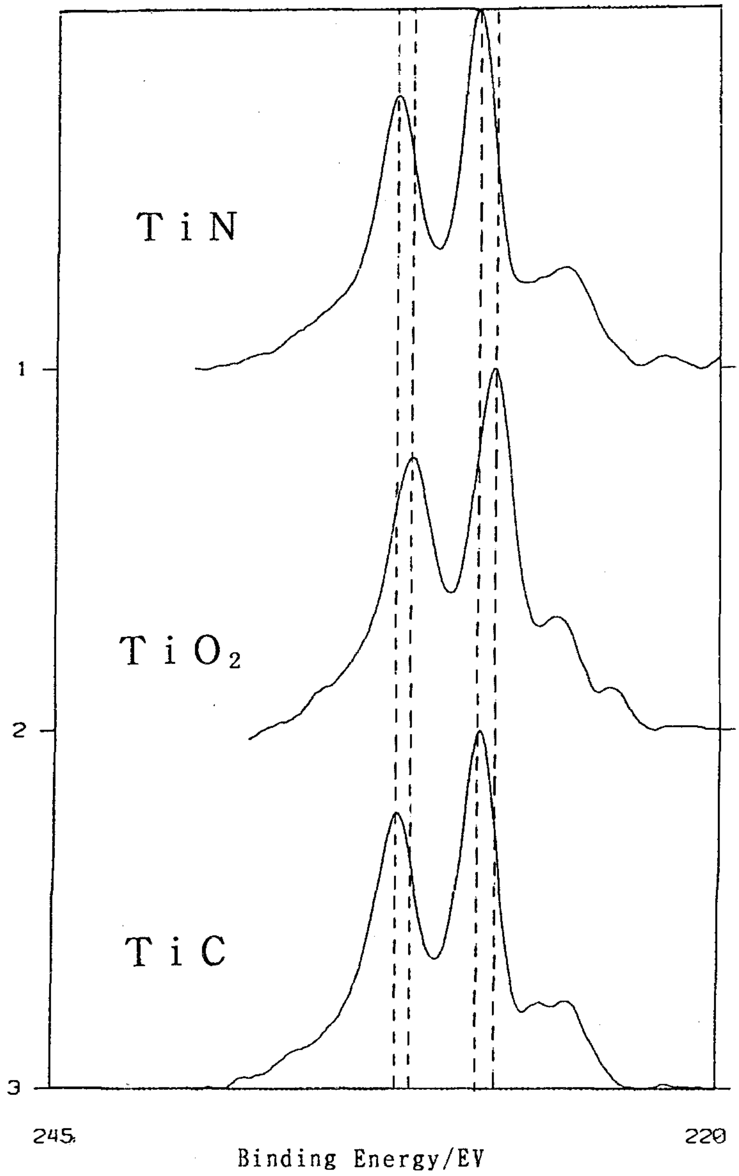


Fig. 4. Mo 3d photoelectron spectra of the titanium based catalysts.

supports were a little lower than that for the TiN supports, indicating the more electronegative state of the molybdenum ion on the TiO_2 or the TiC supports (fig. 4). These results suggest that the TiO_2 and the TiC supports are stable and less interaction occurs between the active metals and support, particularly for the TiO_2 support. Table 2 shows the atomic ratio of the active metal and support on the catalyst measured by XPS. The Mo and S ratio on the TiN support is similar to those on the TiO_2 support, in spite of the difference in their surface areas. On the other hand, this ratio on the TiC support is much higher than those on the TiO_2 support, indicating the agglomeration of molybdate and nickel. It is known that molybdenum catalysts have several different active sites where hydrocracking or hydrogenation is catalyzed. Accordingly, the differences of the catalytic activities are due to different species of molybdate formed on the support. The hydrocracking active site is considered to be formed on the TiN support, while less hydrocracking active sites seem to be formed on the TiC support due to the agglomeration of molybdate. The present study clearly showed that the supports affect the structure of the active component and result in large difference in the catalytic activities. The investigation about the interaction between the support anion and the catalytic activities are now in progress.

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