

Catalytic hydrotreatment on alumina–titania supported NiMo sulphides

J.R. Grzechowiak^{a,*}, J. Rynkowski^b, I. Wereszczako-Zielińska^a

^a *Institute of Chemistry and Technology of Petroleum and Coal, Technical University of Wrocław, 7/9 Gdańska St., 50 344 Wrocław, Poland*

^b *Institute of General and Ecological Chemistry, Technical University of Łódź, 36 Żwirki st., 90-924 Łódź, Poland*

Abstract

MoNi/Al₂O₃ catalysts have been widely used for hydrodesulphurisation of oil fractions. In order to enhance the catalytic activities for HDS and HDN, catalysts supported on titania-modified alumina carriers have been studied. The MoNi/Al₂O₃–TiO₂ catalysts were characterised by benzene sorption, ammonia sorption, temperature programmed reduction, X-ray diffraction and scanning electron microscopy. The supports effect was examined by comparing thiophene conversion and sulphur or nitrogen contents in diesel oil fraction. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

To control diesel emission to the environment many attempts have been made to promote the classical hydrotreating catalysts or to develop new supports. Of these much consideration was given to alumina–titania supported catalysts [1–7]. Therefore it is of great interest to examine the influence of the preparation method on the properties and activity of the catalyst, as well as on the interaction between promoters and Al₂O₃–TiO₂ supports [8].

In our investigations emphasis was focused on studying the effect of the preparation method on the texture, acidity, morphology and hydrotreating activity of Mo–Ni catalysts. Alumina–titania supports were prepared using coprecipitation methods. Titanium was also added by mixing aluminium hydroxide with titanium oxide.

2. Experimental

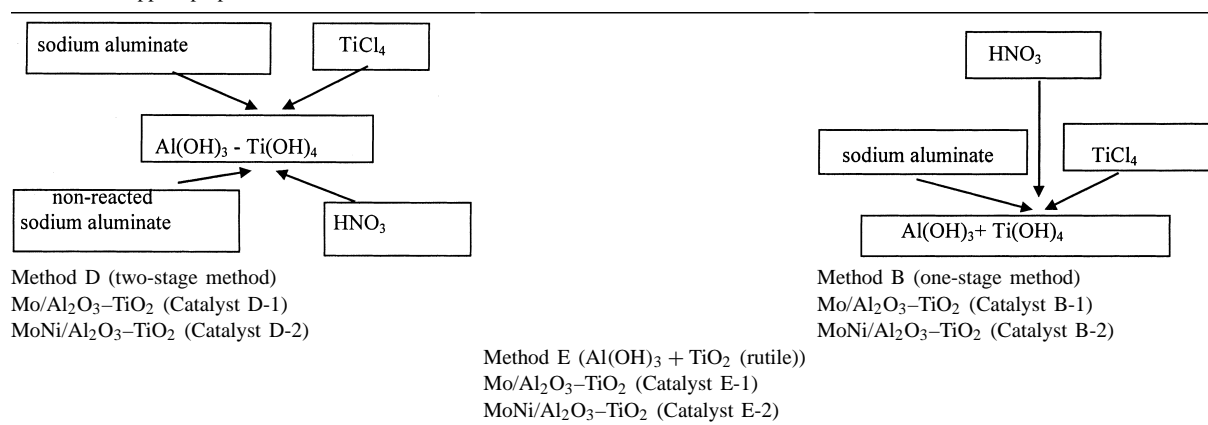
2.1. Preparation of catalysts

A series of supports containing 15 wt.% of TiO₂ were prepared and characterised. Molybdenum (MoO₃) and nickel (NiO) loading was kept constant (12 and 3 wt.%, respectively). Molybdenum was deposited on 1.2 mm diameter alumina–titania extrudates by impregnation (wet method) with heptamolybdate solution. After impregnation of the desired molybdenum loading, the catalysts were dried at 110°C for 12 h and then calcined at 450°C for 3 h. Subsequently, nickel impregnation took place followed by drying and calcining under the same conditions as for Mo/Al₂O₃–TiO₂ catalysts.

Alumina–titania supports (Catalysts B-1, B-2, D-1 and D-2) were prepared by two methods of coprecipitation (Method B and Method D) and by mechanical mixing of Al(OH)₃ and TiO₂ (Method E), which are listed in Table 1.

* Corresponding author.

Table 1
Methods of support preparation



To prepare the support for Catalysts E-1 and E-2, as well that for Catalysts B-1 and B-2, use was made of the one-stage method. Chemicals were added gradually to the solution of ammonium nitrate at constant pH (pH = 9) and temperature (70°C). Nitric acid was also used for lowering of pH adjustment to 7. When use was made of the two-stage method, sodium aluminate was added to the solution of ammonium nitrate successively with TiCl₄ (pH = 9, $T = 70^\circ\text{C}$) and then with nitric acid (pH = 9, $T = 70^\circ\text{C}$). Nitric acid was also used to bring the hydrogel to the desired pH (pH = 7).

2.2. Characterisation of catalysts

Porous volume and porous surface distributions were determined by benzene sorption. The texture of

the catalysts is shown in Table 2 and Figs. 1 and 2. Acidity and acid strength distribution were evaluated by temperature programmed desorption of NH₃ (TPD_{NH₃}). Acid sites were classified as

weak ($T_{\text{des}} < 300^\circ\text{C}$), medium ($300^\circ\text{C} < T_{\text{des}} < 450^\circ\text{C}$) and strong ($450^\circ\text{C} < T_{\text{des}} < 550^\circ\text{C}$).

Titania, molybdenum and nickel distributions were studied by scanning electron microscopy (SEM) with Jeol JSM 5888 LV.

Structure and phase composition were measured with a Siemens D5000 diffractometer using Cu K α radiation. The diffractograms were compared to those of known standards taken from the JCPDS index.

Table 2
Influence of the preparation method on the texture and acidity of the catalysts

Properties	Catalyst		
	D-2	B-2	E-2
Specific surface ($1.5 < r < 100$), m ² /g	291	268	265
Total volume ($1.5 < r < 100$), dm ³ /kg	0.550	0.320	0.440
Volume of mesopores for the of pore radius range			
1.5–3 nm	0.170	0.270	0.200
3–5 nm	0.200	0.030	0.110
5–10 nm	0.090	0.004	0.050
10–100 nm, dm ³ /kg	0.100	0.020	0.080
Average pore radius, nm	3.8	2.4	3.3
Total acidity, mmol NH ₃ /g	0.96	0.75	0.76

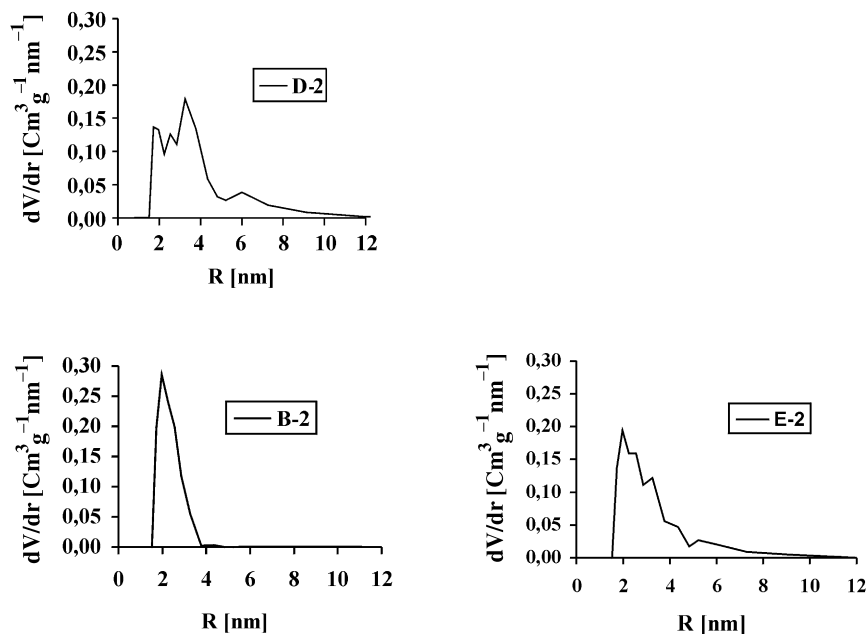


Fig. 1. Effect of the TiO_2 incorporating method on the distribution of mesopore volume.

Temperature programmed reduction (TPR) measurements were carried out in an AMI-1 catalyst characterisation system (Altamira Instruments). Use was made of a 90 vol.% Ar and 10 vol.% H_2 mixture, a gas flow rate of $50 \text{ cm}^3/\text{s}$, and a linear temperature increase of $10^\circ/\text{min}$.

Catalytic activity was examined by two methods: in a continuous-flow high-pressure microreactor system using oil fractions (S: 0.85 wt.%, N: 321 ppm, density: 0.8560 g/cm^3 , IBP: 236°C , T_{90} : 360°C) as feed-stock, and by thiophene conversion (400°C , 4.5 vol.% $\text{C}_4\text{H}_4\text{S}$).

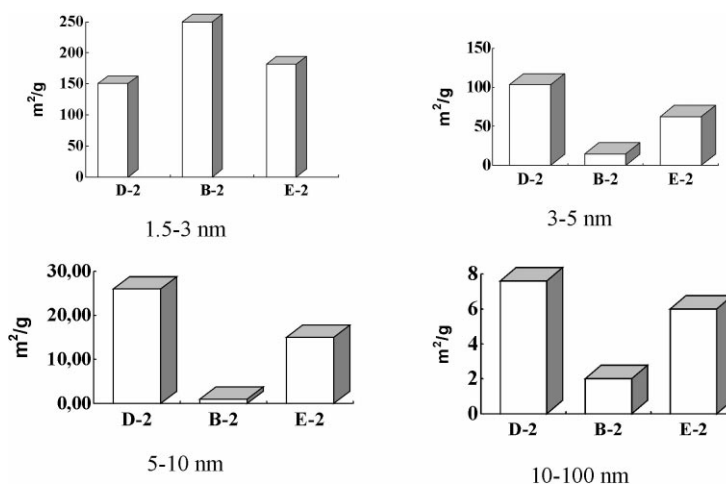


Fig. 2. Effect of the TiO_2 incorporating method on the distribution of mesopore surface.

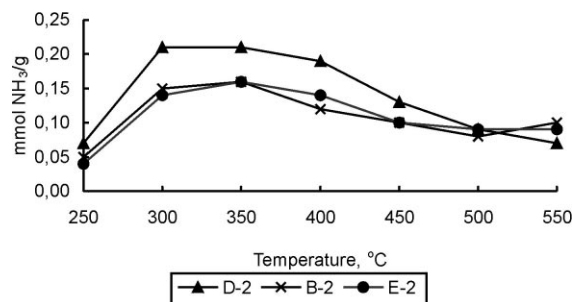


Fig. 3. Acid strength distribution of the catalysts.

3. Results

It was found that the coprecipitation method exerted a markedly different effect on the mesopore surface and mesopore volume distributions (Table 2, Figs. 1 and 2).

Compared to the one-stage coprecipitation method and mechanical mixing, the two-stage coprecipitation method of preparing $\text{Al}_2\text{O}_3\text{--TiO}_2$ supports brings about an increase of the specific surface area and the volume of mesopores. When TiO_2 was incorporated using Method B (Catalyst B-2), the catalyst had a monomodal structure (Fig. 1).

Examination of surface distribution (Fig. 2) showed that surface in the pore radius range of 1.5–3.0 nm was noticeably larger (250 m^2/g) for Catalyst B-2 (prepared by the one-stage method). When the two-stage coprecipitation method was applied (Catalyst D-2), the mesopore surface value of 250 m^2/g was reached for the pore radius range of 1.5–5 nm.

Of the catalysts examined, Catalyst D-2 was characterised by the highest acidity. The greatest differences in acidity were observed at the NH_3 desorbing acid sites in the temperature of 300–450 °C (i.e. medium acid sites) (Fig. 3).

X-ray diffraction (XRD) patterns for Catalysts B-2 and E-2 after TPR to 900 °C confirmed that the promoting influence of TiO_2 on the reduction of the molybdenum oxide phase depended on the preparation method (Fig. 4). Thus, for Catalyst B-2, which was obtained by the one-stage coprecipitation method, there are metallic molybdenum lines. When use was made of the Al_2O_3 and TiO_2 mixture as a support (Catalyst E-2), susceptibility to reduction of molybdenum oxide phase

to Mo^0 was comparatively small. The diffractogram for Catalyst B-2 does not contain lines characteristic of crystalline TiO_2 . The results of XRD measurements encouraged us to formulate the hypothesis that susceptibility to reduction of molybdenum oxide phase depends on the phase composition of the TiO_2 . It was also found that under experimental reduction conditions Catalyst B-2 displayed the poorest alumina stability. As shown in Fig. 4, investigated catalyst showed presence of $\alpha\text{-Al}_2\text{O}_3$.

As shown by the results of our study, the influence of the promoter depended on the method, by which TiO_2 had been incorporated, and was more distinct when the support was prepared by Method E (Table 3). The TPR results revealed that the temperature of the maximum of the first TPR peak for Catalyst E-2 was approximately by 115 ° lower than that for the unpromoted sample. When a promoter was introduced into the $\text{Mo}/\text{Al}_2\text{O}_3\text{--TiO}_2$ catalysts on supports which had been prepared by coprecipitation methods (Method D and Method B), the differences in the position of T_{MAX} amounted to 50–60 °.

SEM (Fig. 5) revealed a homogeneous dispersion of TiO_2 for binary oxides obtained by the two-stage coprecipitation method (Catalyst D-2). However, the one-stage coprecipitation method (Catalyst B-2) yielded a non-homogeneous dispersion of TiO_2 at the same loading. The weaker interaction of molybdenum with titania (as compared to Al_2O_3) enhances molybdenum dispersion on the support. Agglomerates of TiO_2 were present, when aluminium hydroxide was mixed with TiO_2 (Catalyst E-2). In the presence of this catalyst, interactions of molybdenum and alumina are predominant.

With regard to the thiophene hydrogenolysis, the conversion over the investigated catalysts increases as follows:

Mo catalysts : D-1 > B-2 > E-2,

and over MoNi catalysts : D-2 > B-2 \cong E-2.

Of the promoted catalysts, the one prepared by the mechanical mixing method (Method E) was affected by the presence of NiO to the greatest extent (Fig. 6).

As shown in Table 4, hydrodesulfurization of oil fraction on the Catalyst E-2 was higher than those on the catalysts B-2 and D-2. The catalyst which was found to be the least active in the HDS process

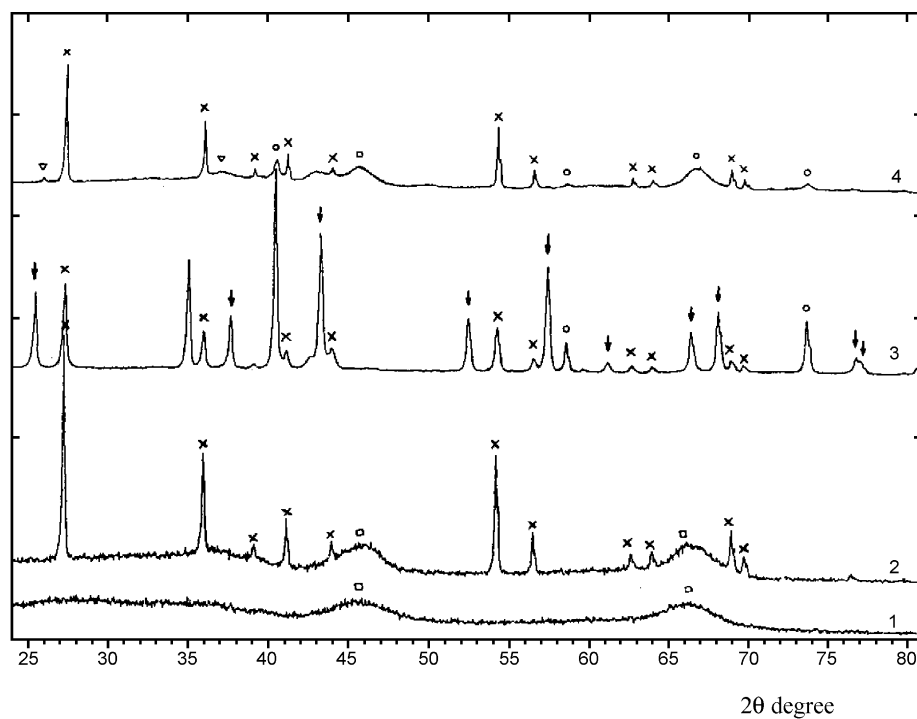


Fig. 4. XRD patterns of the catalysts: B-2, 1 before and 3 after reduction; E-2, 2 before and 4 after reduction. (\square) γ - Al_2O_3 ; (\circ) Mo^0 ; (\times) rutile; (∇) MoO_3 ; (\downarrow) α - Al_2O_3 .

Table 3

TPR data of catalysts: TPR up to 900°C \rightarrow TPO_{700} \rightarrow TPR up to 900°C

Catalyst	T_{MAX} ($^\circ\text{C}$)					
	D-1	D-2	B-1	B-2	E-1	E-2
TPR after calcination at 450°C	451	420	475	422	530	415
TPR after reoxidation at 700°C	445	441	450	445	505	440

Table 4

Hydrotreating efficiency of oil fraction (p : 4 MPa, LHSV: 3 h^{-1} , H_2 :CH = $350:1\text{ Nm}^3/\text{m}^3$)

Catalysts	HDS efficiency (%)				HDN efficiency (%), 370°C
	330°C	340°C	350°C	370°C	
D-2	62	71	77	88	69
B-2	55	66	74	87	73
E-2	69	77	82	92	68

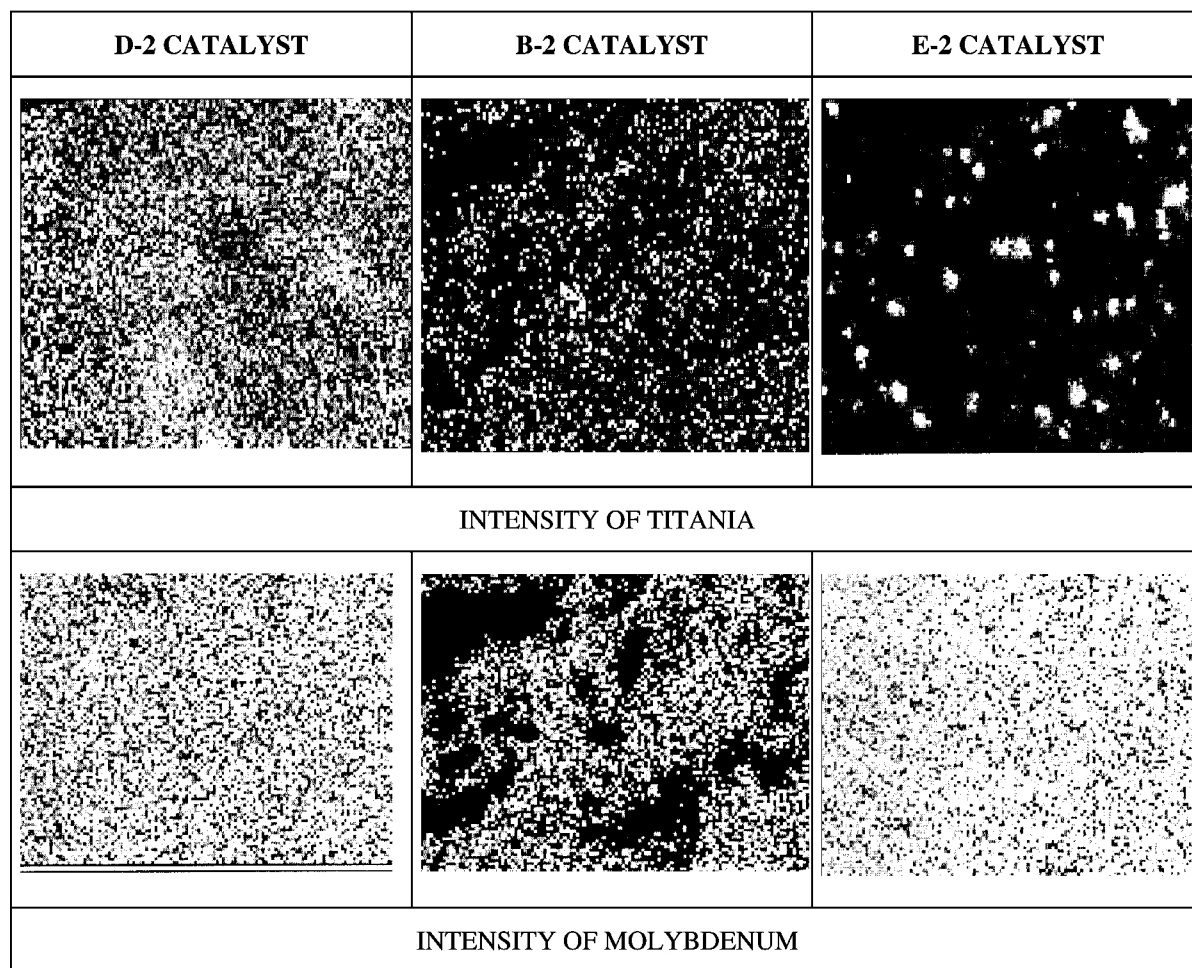


Fig. 5. Titania and molybdenum distribution on the investigated catalysts.

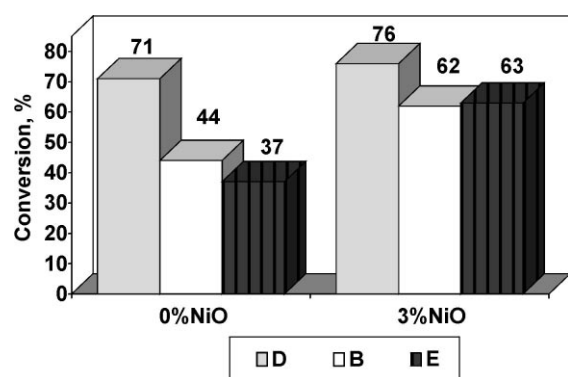


Fig. 6. Effect of NiO content on the hydrogenolysis of thiophene.

(Catalyst B-2) had a surface with a small share of 3–100 nm mesopores. The lack of correlation between the activity determined in the hydrogenolysis of thiophene and that determined in the HDS of the

Table 5
Effect of pressure on hydrodesphurisation process

Catalyst	HDS efficiency (%)								
	$T = 330^{\circ}\text{C}$			$T = 350^{\circ}\text{C}$			$T = 370^{\circ}\text{C}$		
	4 MPa	6 MPa	Δ	4 MPa	6 MPa	Δ	4 MPa	6 MPa	Δ
D-2	62	67	5	77	82	5	88	91	3
B-2	55	56	1	74	76	2	87	89	2
E-2	69	72	3	82	86	4	92	94	2

oil fraction should be attributed to the differences in the porous structure (Figs. 1 and 2).

The effect of pressure on HDS efficiency was also investigated (Table 5). It was found to be small for Catalyst B-2. The influence of pressure increase on the efficiency of HDS was more perceptible in the presence of the catalyst prepared by the two-stage coprecipitation method.

4. Conclusions

Mechanical mixing of $\text{Al}(\text{OH})_3$ and TiO_2 (rutile) can be used to prepare mixed oxide supports for HDS catalysts. The catalyst prepared by the mixing method (Method E) displayed the highest activity (as compared to the catalysts obtained by Method D or Method B). This catalyst was most affected by the presence of the NiO promoter, as shown by the results of activity determination (thiophene conversion) and analysis of the TPR profiles for Mo catalyst (unpromoted) and MoNi catalyst. Susceptibility to the reduction of the molybdenum oxide phase to Mo^0 for $\text{MoNi}/\text{Al}_2\text{O}_3\text{--TiO}_2$ was comparatively small.

The one-stage precipitation method (Method B) brought about a decrease of the total mesopore volume and yielded the monomodal structure of the catalyst. Compared to the two-stage precipitation method, the surface of the pores in the radius range 1.5–3.0 nm was noticeably larger (about 90% of the total mesopore surface). In the XRD pattern for catalyst B-2 after TPR to 900°C metallic molybdenum lines

became more distinct. Under experimental reduction conditions the catalyst displayed the poorest alumina stability. The one-stage coprecipitation method accounted for the non-homogeneous dispersion of titanium and molybdenum. The catalyst was found to be the least active in the HDS of the oil fraction.

The $\text{MoNi}/\text{Al}_2\text{O}_3\text{--TiO}_2$ catalyst on a support prepared by the two-stage precipitation method showed a greater HDS activity than when its support was prepared by the one-stage method. Pressure exerted more perceptible influence on the activity of the catalyst prepared by the two-stage coprecipitation method. SEM revealed a homogeneous dispersion of TiO_2 and molybdenum for binary oxides prepared by Method D.

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