

Synthesis and Catalytic Bifunctional Properties of Tungsten Oxynitrides

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Reaction of ammonia with various tungsten precursors leads, after passivation, to tungsten oxynitrides whose bifunctionality is tested in *n*-heptane isomerization (high selectivity); polyanionic precursors containing phosphorus give oxynitrides with enhanced metallic properties.

In recent years interest has developed in exploring the catalytic properties of transition metal nitrides or carbides for traditional reactions catalysed by noble metals. Little attention has been paid to the catalytic properties of bulk tungsten nitrides. These materials, like molybdenum and vanadium nitrides, exhibit high activity for quinoline hydrodenitrogenation.¹ Several authors have observed that the presence of chemisorbed oxygen affects the catalytic properties of tungsten carbides.^{2–5} Such modifications of tungsten nitrides have not been mentioned. Here we describe the synthesis and characterization of tungsten oxynitrides and an investigation into the activity of bulk tungsten oxynitrides for *n*-heptane cracking or hydrogenolysis/isomerization. We have shown that these new materials exhibit interesting and original catalytic bifunctional properties.

Tungsten oxynitride was prepared using a modification of the standard procedure of Volpe and Boudart.⁶ Two polyanionic compounds (NH₄)₆H₂W₁₂O₄₀ and (NH₄)₆P₂W₁₈O₆₂ (to investigate phosphorus promotion) were used as precursors. The starting material (1 g) was placed in a quartz reactor and

reduced in flowing NH₃ (10 l h⁻¹). The temperature was increased from room temperature to 673 K at 100 K h⁻¹, then to the final temperature (973 K) with a heating rate of 30 K h⁻¹. The temperature was held at 973 K for 4 h, then the reactor was cooled to room temperature in flowing ammonia. The reactor was then flushed with argon and the material passivated by O₂ (1% v/v) in the Ar stream (9 l h⁻¹) for 1 h. The resulting oxynitrides were stored *in vacuo*. The unit cell parameters, the average particle sizes deduced from X-ray line broadening, the BET specific surface area and the chemical analyses of the materials synthesized are listed in Table 1. Before elemental analysis, the oxynitrides were evacuated for 1 h at 673 K and stored at room temperature in sealed tubes. The elemental analyses were performed without any exposure to air. The chemical compositions are in agreement with the structural assumptions postulated by Kiessling and Peterson.⁷ The oxynitrides present a face-centred cubic structure of tungsten atoms with vacancies in the metal atom lattice, the octahedral interstices being occupied by nitrogen or oxygen atoms. Similar observations have been reported for titanium⁸ and molybdenum⁹ oxynitrides. A slight lowering of the specific surface area was observed for the oxynitrides containing phosphorus. The pore volume decreased by 50% in comparison with the oxynitrides, in agreement with the pore diameter distribution data (2 nm for oxynitrides containing phosphorus, 4 and 8 nm for the other oxynitrides).

Transformation of *n*-heptane was carried out in a flow system (fixed bed microreactor; 10 mm i.d.; 70 mg of catalyst) at 623 K, with a total pressure 1 bar, nitrogen/*n*-heptane or hydrogen/*n*-heptane ratio 18:1 and a WHSV (weight of *n*-heptane per hour per unit weight of oxynitride) of 2.36. Before

Table 1 Properties of tungsten oxynitrides

	Precursors	
	(NH ₄) ₆ H ₂ W ₁₂ O ₄₀	(NH ₄) ₆ P ₂ W ₁₈ O ₆₂
Cell parameters/Å	4.153(3)	4.144(6)
X-Ray particle size/Å	47	33
BET specific surface/m ² g ⁻¹	74	64
Pore volume/cm ³ g ⁻¹	0.083	0.042
Chemical composition	WN _{1.34} O _{0.42}	WN _{1.34} O _{0.60} P _{0.12}

Table 2 Steady state selectivity for *n*-heptane reactions over tungsten oxynitrides at 1 bar total pressure^a

	Polyanionic precursor				
	(NH ₄) ₆ H ₂ W ₁₂ O ₄₀		(NH ₄) ₆ P ₂ W ₁₈ O ₆₂		Pt/SiO ₂
	Non-passivated	Passivated	Non-passivated	Passivated	
<i>n</i> -C ₂	—	—	13.54	—	—
<i>n</i> -C ₃	—	3.27	12.17	<0.5	3.93
<i>n</i> -C ₄	5.02	1.75	11.70	2.98	4.84
<i>n</i> -C ₅	4.56	—	12.02	2.54	2.17
<i>n</i> -C ₆	2.21	—	9.25	1.81	1.71
1,2-DMCP ^b	—	5.81	—	2.76	17.95
2,3-DMP ^b	—	—	—	—	4.67
3-EP + ECP ^b	—	—	—	—	21.15
2-MH + 3-MH ^b	76.00	87.89	35.50	83.42	14.87
HEP ^b	12.14	1.28	5.79	6.47	10.08
TOL ^b	—	<0.5	—	<0.5	18.62
Activity/mmol h ⁻¹ g ⁻¹	0.164	0.515	0.383	0.638	0.110
Reaction for 100 mol of <i>n</i> -C ₇ converted (%) ^c					
Hydrogenolysis	4.17	1.23	43.88	2.59	3.94
Isomerization	79.03	96.22	48.25	88.19	61.86
Dehydrogenation	12.62	1.31	7.87	6.62	30.27

^a Conditions: 623 K, H₂: *n*-heptane 18:1, 0.070 g catalyst. ^b 1,2-DMCP = 1,2-dimethylcyclopentane; 2,3-DMP = 2,3-dimethylpentane; TOL = toluene; 3-EP = 3-ethylpentane; ECP = ethylcyclopentane; MH = methylhexane; HEP = heptenes. ^c Fraction of 100 moles of *n*-heptane converted to isoheptanes (isomerization), C₂–C₆ products (hydrogenolysis) or heptene (dehydrogenation).

reaction, the catalysts were pretreated at 773 K for 5 h in flowing hydrogen in order to activate the material. The reaction products were analysed by on-line gas chromatography on a 50 m PLOT capillary column coated with alumina deactivated by KCl, using temperature programming and an FID detector.

Reactions of *n*-heptane over tungsten oxynitrides were performed over non-passivated and passivated tungsten oxynitrides, and compared with a typical metallic catalyst (1% Pt/SiO₂). In Table 2 the selectivity of the products for *n*-heptane reactions over the various materials after 5 h on stream are reported. The *n*-heptane conversion slowly decreased, reaching a similar value after 1 day whatever the precursors, with the catalysts remaining active after 5 days. Isomerization was the major *n*-heptane reaction, methylhexane isomers being predominant, whereas products of cracking/hydrogenolysis (C₁–C₆) or dehydrogenation (heptenes) were always present in small quantities. The oxynitrides were less active without passivation, especially with (NH₄)₆H₂W₁₂O₄₀ as the precursor. When phosphorus was present, isomerization products were observed from 27 to 48 moles for 100 *n*-heptane moles converted, the heptenes being around 6.5%. These results suggest that variable amounts of residual oxygen remaining from incomplete nitridation of the precursors can strongly affect the catalytic behaviour.

The transformation of *n*-heptane over tungsten oxynitrides was also studied in flowing nitrogen. Conversion of *n*-heptane was very low and after 30 min on stream, the tungsten oxynitrides were deactivated. Substituting N₂ with an H₂ stream allows the tungsten oxynitrides to partially restore the activity observed with the H₂/*n*-heptane feed.

The tungsten oxynitrides are active catalysts for the hydrogenation of propene, leading to 100% conversion at 423 K, indicating the presence of a metallic function. All these results are explained by a classical bifunctional mechanism,^{10,11} *n*-heptane dehydrogenating on metallic sites to give heptene which in turn migrates to acid sites in order to isomerize,

presumably by a carbenium ion mechanism. These observations are in agreement with those already observed for oxygen-exposed tungsten carbides.^{2–4}

In conclusion, tungsten oxynitrides are new bifunctional catalytic materials. The bifunctional nature of the catalysts is reflected in the *n*-heptane molecular probe reactions (hydrogenolysis/cracking and isomerization). The activity and selectivity of the catalysts verify the influence of the passivation step by oxygen in terms of a higher isomerization (acidic function). Selectivities are significantly affected by the presence of phosphorus in passivated materials, leading to higher metallic properties.

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References

- 1 H. Abe, T.-K. Cheung and A. T. Bell, *Catal. Lett.*, 1993, **21**, 11.
- 2 F. H. Ribeiro, M. Boudart, R. A. Dalla Betta and E. Iglesia, *J. Catal.*, 1991, **130**, 86.
- 3 F. H. Ribeiro, R. A. Dalla Betta, M. Boudart, J. E. Baumgartner and E. Iglesia, *J. Catal.*, 1991, **130**, 498.
- 4 F. H. Ribeiro, M. Boudart, R. A. Dalla Betta and E. Iglesia, *J. Catal.*, 1991, **131**, 523.
- 5 V. Keller, M. Cheval, M. Vayer, R. Ducros and G. Maire, *Catal. Lett.*, 1991, **10**, 137.
- 6 L. Volpe and M. Boudart, *J. Solid State Chem.*, 1985, **59**, 332.
- 7 R. Kiessling and L. Peterson, *Acta Metallurgica*, 1954, **2**, 676.
- 8 C. H. Shin, G. Bugli and G. Djega-Mariadassou, *J. Solid State Chem.*, 1991, **95**, 155.
- 9 X. Gouin, R. Marchand, P. L'Haridon and Y. Laurent, *J. Solid State Chem.*, 1994, **109**, 175.
- 10 M. Boudart and G. Djega-Mariadassou, *Cinétique des réactions en catalyse hétérogène*, Masson, Paris, 1982, p. 120.
- 11 J. H. Sinfelt, H. Hurwitz and J. C. Rohrer, *J. Phys. Chem.*, 1960, **64**, 892.