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Synthesis and molding of niobium oxynitrides with macropores generation

Reactivity and stability in cyclohexane dehydrogenation

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Abstract

The main objective of this work is to prepare extruded niobium oxynitrides with macropores generation from niobium oxides varying: (i) the pore size distribution, burning polymeric molecules mixed with the precursor oxide before peptization; (ii) the final temperature of nitridation; (iii) the nitridation heating rate. The samples were characterized at different preparation stages. The specific pore volume increased up to five times without any loss of the total specific area. Some of these materials were employed in the cyclohexane dehydrogenation reaction. It was observed that they are active but they are less stable than molybdenum and tungsten oxynitrides when exposed to air. This behavior may be due to a faster superficial oxidation process. ©2000 Elsevier Science B.V. All rights reserved.

Keywords: Niobium oxynitride; Peptization; Cyclohexane dehydrogenation

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1. Introduction

Small atoms, such as carbon, nitrogen or oxygen, dissolved interstitially in the lattices of early transition metals produce a class of compounds with unique physical and chemical properties [1]. These materials are referred to as metal (oxy)nitrides and (oxy)carbides. Their catalytic activities have been compared to those of noble metals like Ir, Pt and Pd [1–4]. Specific surface areas (Sg) higher than $50\,m^2\,g^{-1}$ are generally required for catalytic applications. The group of Boudart developed a new temperature-programmed reaction (TPR) method of preparation [5] which produces high specific surface areas (Sg). The method consists of placing an oxide precursor under flowing NH_3 or CH_4/H_2 [1,6,7] and this has led to higher Sg for molybdenum, tungsten and niobium (oxy)nitrides and (oxy)carbides [8–10].

In the present work extruded niobium oxynitrides were prepared with macropores generation from niobium oxides. In the first-step of the preparations the optimization of niobium oxides molding process was studied with cellulose addition to produce an extruded shape with controlled volume and pore distribution [11–13]. After molding, three materials were selected with different volume and pore distribution, all of them with good mechanical strength. The next step was to prepare oxynitrides from these materials following the

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method of Volpe and Boudart [6]. Oxynitrides were prepared by reaction of the selected niobium pentoxides with flowing ammonia, at atmospheric pressure.

The resulting materials were characterized by X-ray powder diffraction (XRD), physisorption of nitrogen at 77.3 K, mercury porosimetry and the elemental analysis of O, N and Nb was made after nitridation.

The reactivity and stability of these materials were studied in the cyclohexane dehydrogenation and the performance of these catalysts were compared to those of molybdenum and tungsten oxynitrides.

2. Experimental

Nb_2O_5–HY-340 (99.8%), was kindly supplied by CBMM (Companhia Brasileira de Metalurgia e Mineração, Brazil).

The niobium oxide molding process was carried out with acid oxalic as a peptization agent and the meso- and macropores generation occurred from two kinds of burned celluloses: microcel and methocel-J12ms, mixed with the precursor oxide before peptization [11]. The peptized materials were shaped by extrusion into 1 mm×2 mm particles, dried at 393 K for 12 h and calcined at 773 K for 3 h.

After molding, three materials were selected with different volume and pore distribution, all of them with good mechanical strength. Reaction with ammonia was carried out in a tubular quartz reactor.

Gas mixtures were prepared using flowmeters (He, O_2 and NH_3). Linear heating rates were obtained with a Robertshaw temperature programmer. The heating rates were 3.0 and 7.5 K min^{-1}, the final temperatures were 923 and 1023 K and the volumetric space velocity (VSV) was about 3×10^4 h^{-1}. The nitridation was maintained for 6 h at the final temperature. The products were cooled to room temperature under flowing helium, following a treatment with 1 wt.% oxygen in helium called passivation to protect them from pyrophoric oxidation after contact with air.

A gas chromatograph (GC) using a thermal conductivity detector (TCD) and an automatic injection valve was employed to analyze the gas-phase composition at the outlet of the reactor. Nitrogen, ammonia and water were separated on a 2 m, $\frac{1}{8}$ in. Chromossorb 102 column with helium as carrier gas.

Specific surface areas (Sg) of precursors and final materials were determined by physisorption of nitrogen at 77.3 K and calculated using the BET method. The pore-size distribution was obtained from Quantachrome-Autoscan 33 mercury porosimeter.

Mechanical resistance measures were obtained employing a special device.

A Philips PW1830 diffractometer was used for the XRD patterns using a Cu Kα radiation. The identification of the different phases was made using the JCPDS library for Nb_2O_5 (No. 28-0317) and NbN (No. 25-1360).

The elemental analysis in O, N and Nb after nitridation was performed using a combustion method.

After treatment under hydrogen flow (20 cm^3 min^{-1}) at 673 K, during 2 h, the catalytic tests were performed in a tubular glass dynamic-differential reactor at 623 K and atmospheric pressure, under C_6H_{12} (5.4 kPa) and helium flow.

A gas chromatograph (GC) using a flame ionization detector (FID) was used to analyze the gas-phase composition at the outlet of the reactor. Cyclohexane and benzene were separated on a 4 m, $\frac{1}{8}$ in. 10% dinonilfthalate column with helium as carrier gas.

3. Results and discussion

3.1. Molding of niobium oxide and synthesis and characterization of niobium oxynitrides

According to XRD the niobium oxide molding process and the cellulose addition do not change the hexagonal oxide crystallographic structure after thermal treatment at 773 K for 3 h. Table 1 shows the

Table 1
Cellulose contents in molding process

Samples	Celluloses (% (w/w))
AC-1	15% methocel-J12ms
AC-2	15% microcel
AC-3	5% methocel-J12ms
AC-4	5% microcel
AC-5	3% microcel+2% methocel-J12ms
AC-6	3% methocel J12ms+2% microcel
AC-7	Without cellulose
AC-8	10% methocel-J12ms
AC-9	10% microcel
AC-10	5% methocel-J12ms+5% microcel

Table 2
Characteristics of the molded oxides after calcination at 673 K

Samples	Mechanical strength (a.u.)	$60<Dp<10^2$ Å (%)	$10^2<Dp<10^3$ Å (%)	$10^3<Dp<10^4$ Å (%)	$10^4<Dp<2\times10^4$ Å (%)	$2\times10^4<Dp<5\times10^4$ Å (%)	Total volume ($cm^3\,g^{-1}$)	Sg ($m^2\,g^{-1}$)
AC-1	1	1.3	25.1	50.8	11.9	10.9	0.311	27
AC-2	1	3.5	12.1	40.4	12.1	31.9	0.282	36
AC-3	2	9.5	36.0	28.0	15.3	11.1	0.189	32
AC-4	2	3.9	7.9	68.4	19.7	0.0	0.076	30
AC-5	2	20.3	16.3	34.1	25.2	4.1	0.123	26
AC-6	2	12.0	23.0	29.7	11.0	24.4	0.209	44
AC-7	3	3.3	53.3	43.3	0.0	0.0	0.060	29
AC-8	2	9.3	39.0	30.8	8.1	12.8	0.172	43
AC-9	2	11.4	7.3	39.9	24.4	17.1	0.193	40
AC-10	2	8.3	18.7	34.0	12.9	26.1	0.241	36

cellulose addition conditions during the niobium oxide molding process. The Table 2 shows the results obtained for mechanical strength, Sg and the pore-size distribution. It can be observed:

- cellulose contents higher than 10 wt.% decrease mechanical strength of the extruded materials;
- the higher the cellulose content the higher the pore volume obtained. This increase is concentrated for diameters superior to 1000 Å.

Oxynitrides were synthesized by reaction of the selected molded niobium pentoxides (AC-7, AC-8 and AC-10) in flowing ammonia, at atmospheric pressure. The reduction/nitridation of Nb_2O_5 starts near 900 K and a gas chromatograph (GC) were used to analyze the gas-phase composition of NH_3, N_2 and H_2 (Fig. 1). The decomposition rate of ammonia increases with the reaction time. This decomposition was not complete maybe because the VSV was very high ($3\times10^4\,h^{-1}$) decreasing the contact time between the gas and the precursor. This VSV was chosen because the water formation occurs during the nitridation/reduction of the Nb_2O_5 and it must be evacuated to avoid the sintering of the final products.

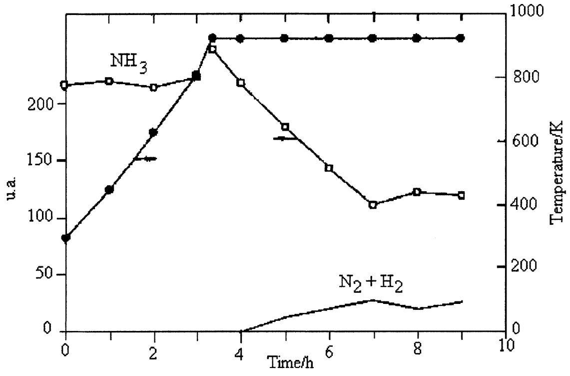

Fig. 1. Ammonia decomposition during the nitridation process.

The synthetized oxynitrides presented the face centered cubic phase and the nitrogen content and unit cell parameters (a_0) depend on the temperature of preparation and the heating rate (Table 3). A

Table 3
Chemical analysis of products obtained by nitridation of molded niobium oxides

Sample	Final temperature (K)	ΔT ($K\,min^{-1}$)	N (wt.%)	O (wt.%)	Composition	a_0 (Å)
N-7A	1023	7.5	14.3 12.1[a]	8.1 9.7[a]	$NbN_{1.22}O_{0.61}$ $NbN_{1.03}O_{0.72}$	4.3333
N-7B	923	7.5	10.5[a]	9.9[a]	$NbN_{0.88}O_{0.72}$	4.2880
N-7C	923	3.0	13.7 9.8[a]	8.6 11.6[a]	$NbN_{1.17}O_{0.65}$ $NbN_{0.82}O_{0.85}$	4.2972
N-10	923	3.0	10.1[a]	10.4[a]	$NbN_{0.84}O_{0.76}$	4.2870

[a] The chemical analysis were carried out after 5 months under air atmosphere.

Table 4
Sg, volume and pore distribution after nitridation

Sample	$60<\mathrm{Dp}$ $<10^2$ Å(%)	$10^2<\mathrm{Dp}$ $<10^3$Å(%)	$10^3<\mathrm{Dp}$ $<10^4$Å(%)	$10^4<\mathrm{Dp}$ $<2\times10^4$Å (%)	$2\times10^4<\mathrm{Dp}$ $<5\times10^4$Å (%)	V_{pTOTAL} ($\mathrm{cm^3/g}$)	Sg ($\mathrm{m^2/g}$)
N-7A	1.8	40.9	39.5	8.4	9.4	0.50	30
N-7B	2.0	31.4	36.4	13.4	0	0.36	45
N-7C	4.1	35.5	49.6	10.7	0	0.29	45
N-10	2.6	27.7	41.8	14.8	13.1	0.43	43

significant shift in the location of peaks (obtained by XRD), by comparison with the standard fcc NbN, was observed. As would be expected, this shift decreases as the temperature of nitridation increases. This is probably due to an increased participation of N in the composition, which approaches to that of NbN standard (fcc). The unit cell parameter a_0 of the oxynitrides was measured as a function of these final reaction temperature and the nitrogen or oxygen contents. For N-7A and N-7B samples with different final temperatures, the percentage of oxygen diminishes as the temperature rises but in all cases always remains oxygen in the bulk. This fact was also observed by Kim [10]. It was also observed that the samples oxidized after long exposition in air. This indicates that such materials are unstable in the presence of oxygen, even though in ambient pressure and temperature. According to Oyama [1], the TPR method produces high surface area materials, with generation of micropores (<30 Å). However, the severe conditions employed in this work probably are the origin of a relative small increase of Sg and of the transformation from micro pores to meso- and macropores (Table 4).

3.2. Reactivity and stability of niobium oxynitride in the cyclohexane dehydrogenation

Some of the niobium oxynitrides synthesized were tested in the cyclohexane dehydrogenation under helium flow ($20\,\mathrm{cm^3\,min^{-1}}$) at 623 K, and the cyclohexane partial pressure was 5.4 kPa. The performances of these catalysts were compared to molybdenum and tungsten oxynitrides.

During the reaction, a slow catalyst deactivation was observed for all samples and this behavior has been also verified in benzene or cyclohexene hydrogenation reactions over supported group VIII metals as catalysts [14,15], probably due to a strong benzene adsorption over the metallic active sites. On the other hand, Figueiras et al. [16] did not observed this deactivation in the cyclohexane dehydrogenation over $\mathrm{Pt/SiO_2{-}Al_2O_3}$ maybe because it was carried out with a very strong partial pressure of hydrogen (90.9 kPa). This deactivation obeys a second-order kinetic law, which allowed the determination of the initial conversions (τ).

Table 5 shows the activity of the niobium oxynitrides and Table 3 shows their compositions. Both of

Table 5
Oxynitrides catalytic tests results

Sample	Composition after storage in air	Storage time in air (days)	Initial $\mathrm{C_6H_{12}}$ conversion τ (%)	Initial specific conversion $\tau\,\mathrm{m^{-2}}$ (%, $\mathrm{m^{-2}}$)
	$\mathrm{MoN}_x\mathrm{O}_y$[a]	>730	2.7	0.16
	$\mathrm{WN}_x\mathrm{O}_y$[a]	>730	0.2	0.03
N-7C	$\mathrm{NbN_{0.82}O_{0.85}}$	128	0	0
N-8A[b]	$\mathrm{NbN_{1.07}O_{0.61}}$	16	4.8	1.92
N-8B[b]	$\mathrm{NbN_{0.86}O_{0.69}}$	6	0.1	0.03
N-8C[b]	$\mathrm{NbN_{1.15}O_{0.65}}$	3	1.6	0.41
N-10	$\mathrm{NbN_{0.84}O_{0.76}}$	98	0	0

[a] Materials supplied by J.A.J. Rodrigues.
[b] Materials N-8A, N-8B and N-8C have been prepared in the same conditions of N-7A, N-7B and N-7C.

these parameters depend on the storage time in air. The percentage of nitrogen decreases and the percentage of oxygen increases when the storage time is long, showing that the niobium oxynitrides are very less stable than the molybdenum and tungsten oxynitrides which were stored for 2 years. This behavior is probably due to a superficial oxidation process that blocks the active sites and the micropores, whose rate depends on the pore structure of each material.

4. Conclusions

The niobium oxide molding process with polymer addition led to a meso- and macropore generation. However, contents of cellulose superior to 10 wt.% lead to a loss of mechanical strength of these materials.

The reaction with gaseous ammonia and the molded niobium oxide enabled us to prepare niobium oxynitrides with different volume and pore distribution and good mechanical strength. The specific surface areas of the final products (30 and 45 $m^2 g^{-1}$) were higher than the molded niobium oxides (29 and 36 $m^2 g^{-1}$). These results, when compared with those reported for molybdenum and tungsten oxide nitridation, suggest that the reaction conditions were too severe leading to a partial sintering of the final products. The XRD showed that the Nb_2O_5 hexagonal phase disappeared to give a cubic face centered niobium oxynitride, and the nitrogen content and unit cell parameters depend on the temperature of preparation and the heating rate.

After long time of exposition in air the nitrogen content in the niobium oxynitrides decreases and the oxygen content increases, probably due to a superficial sample oxidation.

The specific activities of niobium oxynitrides in cyclohexane dehydrogenation depend on the storage time in air. The fresh niobium oxynitride was very active but this behavior decreases when the storage time is long, and the kinetics results show that the niobium oxynitrides are very less stable in air than molybdenum and tungsten oxynitrides which were stored for 2 years in this atmosphere.

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