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Synthesis of acrylonitrile from propylene and nitric oxide mixtures on PbO_2–ZrO_2 aerogel catalysts

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A series of four PbO_2–ZrO_2 aerogel catalysts, differing by their atomic Pb/Zr ratios, were tested at 420°C in the nitroxidation of propylene into acrylonitrile. All catalysts were active, selective and stable with time on stream. The reactant mixture compositions exerted an influence on the catalytic results; other supports such as MgO, TiO_2, Al_2O_3 and SiO_2 also gave interesting results though not so good as ZrO_2. A redox mechanism fits best the kinetic results which involves again a dissociative chemisorption of NO into a N and an oxygen monoatomic adspecies. N_2O and O_2 give only carbon dioxide through a total degradation reaction under the same experimental conditions.

Keywords: Nitroxidation; nitric oxide; propylene; acrylonitrile; aerogels; lead oxide; zirconia; redox mechanism

1. Introduction

Two recent reviews have shown the interesting results obtained in preparing pure or mixed oxide catalysts by the sol–gel process under the form of aerogels (i.e. dried by evacuation of the liquid phase under supercritical conditions [1]) and especially in the reactions of conversion of hydrocarbons (aliphatic paraffinic and olefinic ones as well as substituted benzenes) into the corresponding nitriles, using nitric oxide instead of the more conventional mixtures of ammonia and oxygen or air, i.e. the ammoxidation mixture [2]. Lead oxide supported aerogel catalysts were recently found active, selective and stable with time in the conversion of aromatics by NO into their nitriles by Abouarnadasse et al. [2–5]. Very few papers have been published concerning propylene and lead containing catalysts and a nitroxidation reactant feed (instead of an ammoxidation one) and it was disclosed in these studies that propylene rich feeds were more performant than nitric oxide rich ones [6–9]. Since the previous nickel oxide supported aerogel catalysts were found interesting catalysts for the nitroxidation of both aliphatic and aromatic hydrocarbons [2], and taking into account the results already published related to the same type of lead oxide containing aerogels for aromatic nitroxidations, it seemed to be of interest to complete the previous studies by evaluating the capabilities of these catalysts towards propylene. Many advantages of the nitroxidation by comparison to the ammoxidation are recalled: less exothermicity (by reducing the ΔH to 2/3 of that when $NH_3 + O_2$ is employed) no free O_2 in the mixture, no HCN formation, the same catalyst formulation can be successfully used to nitroxide aliphatic as well as aromatic hydrocarbons, and finally the nitroxidation catalysts are dispersed single oxides.

2. Experimental results and discussion

The binary aerogel catalysts were prepared as described in a recent paper [10] starting with lead acetate, aluminium sec-butoxide, zirconium or titanium isopropylate, magnesium methylate and silicon tetramethoxide respectively. Their BET specific areas were measured using N_2 at 77 K on samples previously heated in dry O_2 at 450°C for 18 h; table 1 gathers the results.

A pure unsupported PbO xerogel (ex-nitrate) exhibited a surface area of 9 m^2/g. As already mentioned the aerogels show larger specific areas than their xerogel counterparts (compare for instance PbO_2–ZrO_2 and X PbO_2–ZrO_2, table 1).

A microreactor consisting of a pyrex U tube was used to perform the catalytic tests under flow and differential conditions between 400 and 460°C at a total pressure of 1 atm. He was introduced as a diluent, the total flow rate was 60 ml min^{-1} in order to stand in the chemical regime while the amount of catalyst was 50 mg. On line analysis was carried out by two gas chromatographs: a FID and TCD one. The first unit was equipped with a 3 m length column (∅: 1/8) filled with Porapak QS while in the second one two columns were used: a 2 m length (∅: 1/8) filled with Porapak Q, another one 2 m length (∅: 1/4) filled with 13 X molecular sieve. Propylene, acrylonitrile, acetonitrile, nitrous and nitric oxides, carbon dioxide and dinitrogen were easily analyzed and dosed. Water was only detected as well

Table 1
Surface areas of the catalysts

Sample	Pb/M atomic ratio [a]	S (m^2/g)	Remarks
PbO_2–ZrO_2	0.3	169	PbO_2 well crystallized
PbO_2–ZrO_2	0.5	168	PbO_2 well crystallized
PbO_2–ZrO_2	0.75	171	PbO_2 well crystallized
PbO_2–ZrO_2	1	58	PbO_2 well crystallized
X PbO_2–ZrO_2	0.5	43	xerogel
PbO–MgO	0.5	34	PbO litharge
PbO–Al_2O_3	0.5	208	
PbO–TiO_2	0.5	96	

[a] M: cation of the support.

as traces of NH_3 for all runs [11], no HCN was formed even in the form of small quantities.

Blank tests at 420°C were carried out with ZrO_2 (and the other supports) alone, PbO alone and also with the nitroxidation mixture in absence of the aerogel catalyst. On pure zirconia and PbO, a very small activity was recorded and only CO_2 was formed as well as in homogeneous conditions. For all the catalysts tested, the following results are those registered at steady state of activity which lasted over more than 50 h of run, after a transient period of 2 h or less.

2.1. INFLUENCE OF THE ATOMIC RATIO Pb/Zr

A $P_{NO} = 25$ Torr, $P_{C_3H_6} = 350$ Torr and $P_{He} = 385$ Torr mixture was introduced in the reactor at 420°C with a flow rate of 60 ml min^{-1}. The results are collected in table 2. In this table the activities are given with respect to the whole catalyst.

For the high partial pressures of C_3H_6 used in the runs given in table 2, the selectivities were calculated by assuming that the sum of the rates of formation of the three products was equal to the global rate of C_3H_6 disappearance, because in these conditions it was difficult to measure precise values for the conversion of C_3H_6. A check was made in separate runs with much lower C_3H_6 partial pressures (≈ 10 Torr) where the conversions were now accurately measured as well as the yields, and a good carbon balance was always recorded. The values given for the formation of the reaction products in table 2 are expressed as rates of reaction (i.e. allowance being made for the stoichiometry with respect to the C atoms contained in each product and in the reactant).

The values quoted in table 2 show that the atomic ratios exert a significant role only on the total activity of the catalysts, i.e. disappearance of C_3H_6. The global selectivities in nitriles (aceto- and acrylo-nitriles) are 90% at least.

2.2. INFLUENCE OF THE SUPPORTS

Four additional supports were involved in this study and for each of the corre-

Table 2
Catalytic properties as a function of the various Pb/Zr atomic ratios

Pb/Zr atomic ratio	Specific rate (10^{-7} mol g^{-1} s^{-1})				Selectivity (%)		
	C_2H_3N	C_3H_3N	CO_2	disappearance of C_3H_6	C_2H_3N	C_3H_3N	CO_2
0.3	3.84	61.33	7.54	72.71	5.3	84.3	10.4
0.5	4.66	77.5	7.76	89.92	5	86	8.6
0.75	5.36	70.3	8.89	84.55	6.3	83.1	10.5
1	2.4	56	6.36	64.76	3.7	86.4	9.8

sponding mixed aerogel catalysts, the Pb/M atomic ratio was fixed at 0.5 (M = Al, Si, Ti and Mg). The reactant feed contained 267 Torr of C_3H_6, 35 Torr of NO completed by He for all the aerogel catalysts while for the xerogel it contained more propylene (450 Torr) and NO (50 Torr) because this catalyst was not so active as the others. The results obtained at 420°C are given in table 3. The results related to catalyst PbO_2–ZrO_2 show that the selectivities do not vary with the composition of the feed.

Many remarks can be made from the above data. First, as previously mentioned [2] the aerogel form is more attractive than the xerogel one, i.e. compare PbO_2–ZrO_2 and X PbO_2–ZrO_2 for both qualities: specific activities and selectivities. Second, the most active aerogel catalyst, namely PbO–MgO, and the less active one, PbO–SiO_2, are both non-selective towards nitrile formation. Third, the most interesting catalyst of the series is the PbO_2–ZrO_2 aerogel sample. Surprisingly the PbO–SiO_2 sample is not a catalyst contrary to the results published by Arai et al. [6]. One can easily rank the support in decreasing total activity of catalysts with their decreasing basicity as follows:

$$\mathrm{MgO} > \mathrm{ZrO_2} > \mathrm{XrO_2}\ \text{xerogel} > \mathrm{Al_2O_3} > \mathrm{TiO_2} >> \mathrm{SiO_2}\,.$$

Finally the reactant composition exhibits an influence upon the catalytic reactivity of C_3H_6 disappearance as shown for catalyst PbO_2–ZrO_2 (Pb/Zr = 0.5) from tables 2 and 3, where in the first experimental conditions the C_3H_6/NO ratio was 14 (table 2) and in the second case only 7.6 (table 3). The stoichiometry of the nitroxidation reaction for the main product, which is acrylonitrile, is given by

$$\mathrm{C_3H_6} + \tfrac{3}{2}\mathrm{NO} \rightarrow \mathrm{C_3H_3N} + \tfrac{3}{2}\mathrm{H_2O} + \tfrac{1}{4}\mathrm{N_2}\,. \tag{1}$$

Therefore, both reactant mixtures can be considered as rich in olefin and lean in NO. The richer the feed, the greater the catalytic activities, the different selectivities remaining similar no matter the richness of the feed. This trend has also been confirmed by the measurements of the activation energies in the temperature range 400–460°C: the richer the feed, the smaller the activation energies, as indicated in

Table 3
Catalytic properties for different lead oxide supported catalysts with a fixed Pb/M atomic ratio of 0.5

Catalyst	Specific activity for C_3H_6 disappearance (10^{-7} mol g^{-1} s^{-1})	Conversion of C_3H_6 (%)	Selectivities (%)		
			C_2H_3N	C_3H_3N	CO_2
PbO_2–ZrO_2	66.5	2.3	4.7	86	10
PbO–Al_2O_3	16	0.5	0	84	16
PbO–TiO_2	5	0.1	0	75	25
PbO–MgO	103	1.3	9	0	91
PbO–SiO_2	quite nil	quite nil	0	0	100
XPbO_2–ZrO_2	57	0.9	3	79	18

Table 4
Apparent activation energies as a function of the reactant mixture

C_3H_6/NO values	Apparent activation energies (kcal/mol)			
	disappearance of C_3H_6	C_2H_3N	C_3H_3N	CO_2
14	17	13	19	12
4	34	39	33	36

table 4 where two mixtures were tested $C_3H_6/NO = 14 : 1$ and $4 : 1$ respectively, for PbO_2–ZrO_2 catalyst $Pb/Zr = 0.5$.

The results described above are in good agreement with the proposed reaction mechanism which is of the redox type as discussed below.

2.3. KINETIC STUDY AND REACTION MECHANISM

A complete study was carried out at 420°C with catalyst PbO_2–ZrO_2 ($Pb/Zr = 0.5$) using feed mixtures containing different fixed partial pressure of one reactant, the other one being variable, as illustrated in figs. 1 and 2 which show the rates of formation of acrylonitrile for a set of fixed partial pressures of NO and variable partial pressures of C_3H_6 (fig. 1) and the same rates for variable partial pressures of NO and fixed partial pressures of C_3H_6 (fig. 2). A similar set of figures was obtained for the rates of disappearance of propylene as a function of $P_{C_3H_6}$ or P_{NO} (not shown here) [11]. It can be seen from fig. 1 that for a given P_{NO} the higher $P_{C_3H_6}$, the higher the activities, and vice-versa. The same remarks given for fig. 1 are valid for fig. 2 again. A common conclusion for both figures is that the partial orders with respect to NO and C_3H_6 depend more or less on the range of pressures used in the kinetic study. In particular the order with respect to C_3H_6 is close to unity while that of NO decreases from a value close to unity to near zero with P_{NO}. Three main reaction models were successively tested: Langmuir–Hinshelwood with and without competitive adsorption, Rideal–Eley with NO adsorbed with and without competitive adsorption of an unreactive C_3H_6 species and finally the Mars and van Krevelen redox model. The mathematical treatment (developed in ref. [11]) led to the possibility to choose between either the Langmuir–Hinshelwood model without competitive adsorption or the Mars and van Krevelen one. A closer look at the activation energies as a function of the reactant partial pressures helps to decide whether one mechanism fits the results better than the other one. Three reactant mixtures were tried and the results are shown in table 5.

For mixture 1, no reactant saturates the surface (see figs. 1 and 2) so the Langmuir–Hinshelwood model leads to a rate expression,

$$A_s = k' P_{C_3H_6} P_{NO}, \quad k' = k K_{C_3H_6} K_{NO}, \tag{2}$$

where k is the rate constant and $K_{C_3H_6}$ and K_{NO} are the equilibrium constants for

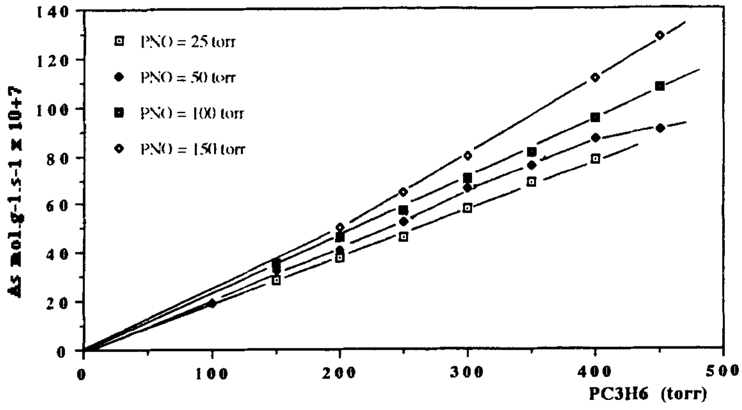


Fig. 1. Rates of formation of acrylonitrile versus $P_{C_3H_6}$ for four fixed P_{NO}.

C_3H_6 and NO adsorption respectively. The apparent activation energy is represented by

$$E_a^1 = E - Q_{C_3H_6} - Q_{NO}, \tag{3}$$

where $Q_{C_3H_6}$ and Q_{NO} are the heats of chemisorption and E the true activation energy.

Discussion of the results of mixture 2 shows that taking into account that now NO is strongly chemisorbed and C_3H_6 only weakly the rate equation becomes now

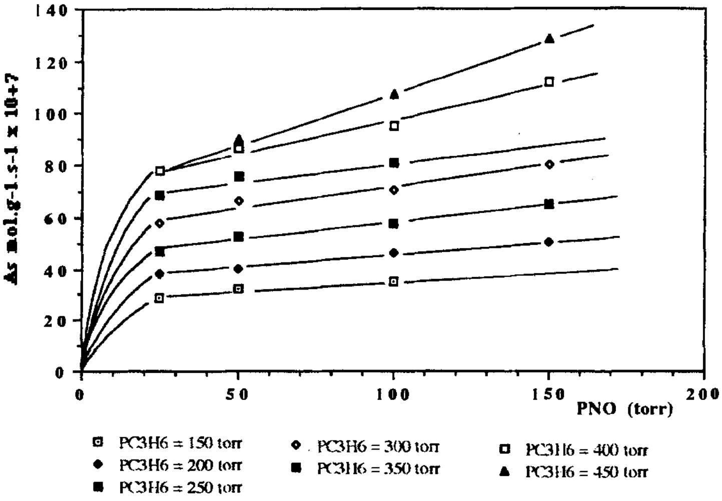


Fig. 2. Rates of formation of acrylonitrile versus P_{NO} for seven fixed $P_{C_3H_6}$.

Table 5
Dependence of the activation energies with the composition of three different feeds

Mixture	Partial pressures (Torr)		E_a (kcal/mol)
	C_3H_6	NO	
1	200	50	33
2	50	400	15
3	400	50	26

$$A_s = k''P_{C_3H_6}, \quad k'' = kK_{C_3H_6}, \tag{4}$$

and the apparent activation energy becomes

$$E_a^2 = E - Q_{C_3H_6}, \tag{5}$$

and in principle one should find $E_a^2 > E_a^1$.

Finally, the third mixture shows that neither of the two reactants is strongly adsorbed, therefore this situation is similar to that observed with mixture 1 so that in principle $E_a^1 = E_a^3$. However, the experimental values given in table 5 clearly indicate that the Langmuir–Hinshelwood model must be discarded in favour of the redox model. According to this conclusion the rate of reaction can be written as

$$\frac{1}{A_s} = \frac{1}{k_o P_{NO}} + \frac{1}{k_r P_{C_3H_6}}, \tag{6}$$

where k_o and k_r are rate constants for oxidation and reduction steps of the catalyst respectively [2,11].

Table 6 gives the values measured for k_o and k_r for the formation of acrylonitrile and propylene consumption; their values being of the same order of magnitude are well consistent with the Mars and van Krevelen model.

As for other nitroxidation catalysts no matter their chemical formulation [2] k_o is always greater than k_r and justifies the necessity of employing reducing reactant mixtures, i.e. containing a large excess of C_3H_6 in order to obtain the best results.

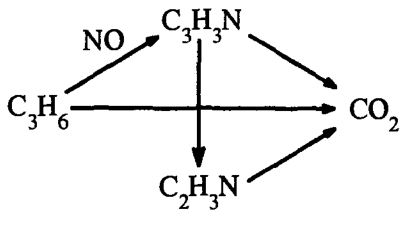
The proposed reaction mechanism is the adsorption of C_3H_6 with subsequent reduction of the catalyst surface and formation of a three times dehydrogenated radical C_3H_3: and the reoxidation of the catalyst O atomic adspecies provided by the dissociative chemisorption of NO into nitrogen and oxygen atomic chemi-

Table 6
Rate constants k_o and k_r for propylene disappearance and acrylonitrile formation

Rate constants	Disappearance of propylene (10^{-7} mol g^{-1} s^{-1} Torr^{-1})	Formation of acrylonitrile (10^{-7} mol g^{-1} s^{-1} Torr^{-1})
k_r	0.4	0.24
k_o	4.8	6.2

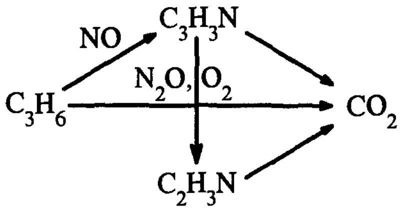
sorbed species. The atomic N: adsorbed atom reacts easily and rapidly with the C_3H_3: radical to yield acrylonitrile (see ref. [2] and references therein).

A reaction network can be formulated by the following scheme:



2.4. TENTATIVE EXPLANATION OF THE DEGRADATION REACTION OF C_3H_6

Separate experiments involving NO only, showed that at 420°C the PbO_2–ZrO_2 aerogel catalyst gave stoichiometrically N_2O by the disproportionation reaction (and O_2), therefore it was of interest to replace NO by N_2O into the usual feed containing C_3H_6; only CO_2 was detected under these conditions. When O_2 replaced NO in the feed, again only CO_2 was found. As during the nitroxidation reaction N_2O and O_2 are always more or less present and supplied by the disproportionation of NO, the total oxidation of C_3H_6 at least, into CO_2, can be assumed to be the result of the reactivity of the oxygen species formed from the interaction of the catalyst with N_2O and/or O_2. The above reaction scheme can be more precised now:



Therefore it must be concluded that the oxygen species originating from the interaction of NO with the catalyst is not chemisorbed under the same form as the one produced by the interaction of the catalyst with N_2O or O_2. N_2O is decomposed by the catalyst into N_2 and O_2, which in turn are not chemisorbed at the aerogel surface into N and O monoatomic species, because a feed composed of dinitrogen and hydrogen for NH_3 synthesis was not transformed at all in our conditions while a stoichiometric ammonia synthesis mixture from NO and H_2 effectively yielded ammonia. The last ammonia synthesis reaction obtained from NO and H_2 is in favor of the dissociation of NO into atomic nitrogen species able to react with the

C_3H_3: radicals when they are present at the surface of the catalyst. This reaction is also responsible for the traces of NH_3 which are always detected during the conversion of C_3H_6 by NO into acrylonitrile.

3. Conclusion

The main results described in this paper are in line with those already published concerning nitroxidation reactions carried out on lead oxide supported binary simple aerogel catalysts. The redox mechanism which seems to apply satisfactorily in order to explain the main results of the catalytic study, confirms the nature of the dissociative NO chemisorption into N and O species which, in turn, can be proposed as the pivotal process reaction of the nitroxidation: it is able to discriminate between interesting (or not) nitroxidation catalysts, and between ammoxidation or nitroxidation catalysts since on the first type of catalysts, which are always more complex (ternary systems) nitroxidation reactions cannot be performed because the chemisorptive dissociation of NO does not take place on this type of catalyst [2].

References

[1] G.M. Pajonk, Appl. Catal. 72 (1991) 217.

[2] G.M. Pajonk, J. Chim. Phys. 88 (1991) 547.

[3] S. Abouarnadasse, G.M. Pajonk and S.J. Teichner, *Proc. 10th Ibero-American Symp. on Catalysis*, Venezuela, 2 (1986) 615.

[4] S. Abouarnadasse, G.M. Pajonk and S.J. Teichner, *Proc. 9th Int. Congr. on Catalysis*, Vol. 4, Calgary 1988, eds. M.J. Phillips and M. Ternan (Chem. Inst. of Canada, Ottawa, 1988) p. 1936.

[5] S. Abouarnadasse, G.M. Pajonk and S.J. Teichner, in: *Heterogeneous Catalysis and Fine Chemicals*, Studies in Surface Science and Catalysis, Vol. 41, eds. M. Guisnet, J. Barrault, C. Bouchoule, D. Duprez, C. Montassier and G. Pérot (Elsevier, Amsterdam, 1988) p. 371.

[6] H. Arai, H. Iida and T. Knugi, J. Catal. 17 (1970) 396.

[7] T. Munuji, H. Ose, H. Arai and H. Iida, J. Chem. Soc. Japan 72 (1969) 553.

[8] K. Ayakan, US Patents 3 362 784 (1968), 3 361 519 (1968).

[9] W.H. Manogue, US Patent 3 360 331 (1967).

[10] R. Tleimat-Manzalji, T. Manzalji and G.M. Pajonk, J. Non Cryst. Sol. 147-8 (1992) 744.

[11] T. Manzalji, PhD Dissertation, No. 247-92, Lyon I, France (1992).