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THE LIQUID PHASE REMOVAL OF NO AND H_2S POLLUTANTS USING MEMBRANE SEPARATION OF THE HOMOGENEOUS CATALYST

M.A. FEDOTOV, O.M. ILINICH, L.I. KUZNETSOVA, G.L. SEMIN,
Yu.S. VETCHINOVA and K.I. ZAMARAEV *

Institute of Catalysis, Siberian Branch of the USSR Academy of Sciences, Novosibirsk 630090, USSR

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Using the liquid phase reaction $2NO + H_2S + 2O_2 \rightarrow 2HNO_3 + S$ in the presence of heteropolyanion catalyst $PW_{11}Fe^{II}(H_2O)O_{39}^{5-}$, the potentialities of the membrane method in separation of a homogeneous catalyst from a soluble reaction product have been demonstrated. The use of membranes for this purpose is expected to give a further impact for the search of industrial processes based on homogeneous catalysis.

1. Introduction

The joint use of catalysis and membrane methods of separation opens new perspectives in the design of chemical processes. The membrane separation is better known for processes based on heterogeneous catalysts, the membrane catalysis by metals being the best known example [1]. Heterogeneous catalysis of propylene dehydrodimerisation of the oxide membrane catalyst [2] and electrocatalytic reactions in the presence of oxygen- and proton-conducting inorganic and polymeric membranes [3–16] have been also reported.

The possibilities of combining membrane separation method with homogeneous catalysis have been studied to much less extent. Among the work in this field can be mentioned the use of reverse osmosis (RO) for activating a homogeneous catalyst by selective removal of a triphenylphosphine ligand through the membrane, thus creating the over-equilibrium concentration of catalytically active ligand deficient complex [17]. In refs. [18,19] the membrane distillation method was utilized to increase conversion in equilibrium reactions by removing water which was one of reaction products.

In practical homogeneous catalysis, an important problem is the separation of the catalyst from the reaction products. The present study demonstrates the

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* To whom correspondence should be addressed.

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possibilities of membrane methods in solving this problem. As an example, the liquid phase process of NO and H_2S pollutants removal in the presence of homogeneous catalyst–iron-containing heteropolyanion–was chosen.

Iron(II)-substituted heteropolyanions (HPA) in aqueous solutions interact with NO, forming nitrosyl complexes which are further oxidized by oxygen giving NO_3^- (at pH < 6) or NO_2^- (at pH > 6) [20]. Iron(III)-substituted HPA formed in this reaction can be reduced back to the initial state, e.g. by the action of H_2S [20]. Combination of these stoichiometric reactions taking place at room temperature gives the catalytic cycle

$$2\mathrm{HPA}-\mathrm{Fe^{II}(H_2O)}+2\mathrm{NO} \rightarrow 2\mathrm{HPA}-\mathrm{Fe^{II}(NO)}+2\mathrm{H_2O} \qquad (1)$$

$$2\mathrm{HPA}-\mathrm{Fe^{II}(NO)}+2\mathrm{O_2}+2\mathrm{H_2O} \rightarrow 2\mathrm{HPA}-\mathrm{Fe^{III}(H_2O)}+2\mathrm{NO_3^-} \qquad (2)$$

$$2\mathrm{HPA}-\mathrm{Fe^{III}(H_2O)}+\mathrm{H_2S} \rightarrow 2\mathrm{HPA}-\mathrm{Fe^{II}(H_2O)}+2\mathrm{H^+}+\mathrm{S} \qquad (3)$$

$$2\mathrm{NO}+2\mathrm{O_2}+\mathrm{H_2S} \rightarrow 2\mathrm{HNO_3}+\mathrm{S} \qquad (4)$$

HPA $PW_{11}Fe^{II}(H_2O)O_{39}^{5-}$ (or briefly $PW_{11}Fe^{II}$) was chosen as the catalyst of reaction (4) because pH region of its stability (pH 2–6) allows to oxidize the nitrosyl complex formed in reaction (1), to HNO_3 [20], whose solutions do not evolve NO back, differing in this respect from HNO_2.

2. Experimental

2.1. SYNTHESIS OF HPA

HPA $PW_{11}Fe^{II}$ was synthesized according to ref. [21]. To the initial solution of $H_3PW_{12}O_{40}$, H_3PO_4 was added until the ratio P/W = 11 was achieved; then the solution was heated up to boiling, and Na_2CO_3 was added to obtain pH 4, at which the Na salt of HPA $PW_{11}O_{39}^{7-}$ was formed. HPA $PW_{11}Fe^{II}(H_2O)O_{39}^{5-}$ was obtained by adding $FeSO_4 \cdot 7H_2O$ to the latter solution in the ratio $Fe : PW_{11} = 1 : 1$. Formation of $PW_{11}O_{39}^{7-}$ and $PW_{11}Fe^{II}(H_2O)O_{39}^{5-}$ was controlled by ^{31}P NMR (for $PW_{11}O_{39}^{7-}$, $\delta = -106$ ppm, for $PW_{11}Fe^{II}(H_2O)O_{39}^{5-}$, $\delta = 615$ ppm with respect to H_3PO_4 used as the external reference [21]). Iron (III)-containing HPA was obtained by oxidation of $PW_{11}Fe^{II}(H_2O)O_{39}^{5-}$ with oxygen in the solution.

2.2. GENERAL SCHEME OF THE PROCESS

The scheme of the process for carrying out reactions (1)–(3) together with membrane regeneration of the HPA catalyst is given in fig. 1. In the first stage NO or its mixture with argon is absorbed by $PW_{11}Fe^{II}$ (reaction (1)); then the nitrosyl complex formed is oxidized by O_2 giving NO_3^- and $PW_{11}Fe^{III}$ (reaction

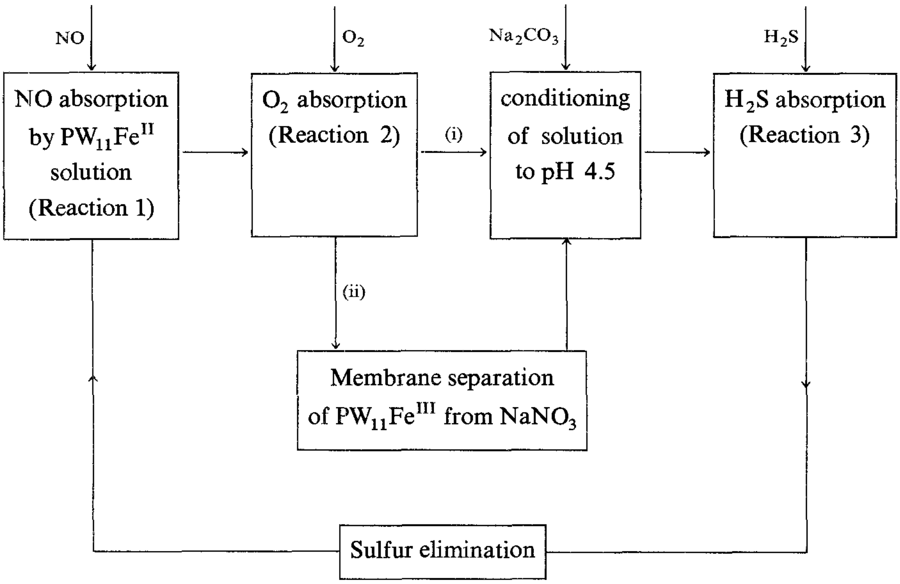

Fig. 1. General scheme of the process of NO and H_2S removal with membrane separation of homogeneous $PW_{11}Fe^{III}$ catalyst.

(2)). After this the solution containing $PW_{11}Fe^{III}$ and NO_3^- can be recycled either by route (i) (if NO_3^- concentration is low) or by route (ii) (if NO_3^- concentration is high). Route (ii) implies the use of membrane apparatus where NO_3^- is separated from HPA by RO. NO_3^- penetrates through the membrane and thus is eliminated from the reaction mixture, while HPA remains there. In the next stage the pH of the reaction mixture is first increased up to 4.5 by adding Na_2CO_3, and then the reaction mixture is reduced with H_2S (reaction (3)). Then sulfur is separated by means of either filtration or centrifugation. After this, further absorption of NO takes place, and so on. Further details of the equipment used to carry out reactions (1)–(3) can be found in ref. [20]. The reactions were carried out at 20 °C at total pressure of 1 at. Contact solutions with pH 2.4–2.8, containing 0.005–0.24 mole/l $Na_5PW_{11}Fe^{II}(H_2O)O_{39}$ and 0.005–0.24 mole/l Na_2SO_4 (obtained as described in section 2.1), were used initially to provide NO absorption via reaction (1). During cyclic performance of reaction sequence (1)–(3), up to 0.8 mole/l of $NaNO_3$ could be accumulated in the contact solution without any noticeable decrease of NO absorption. The reverse osmosis (RO) membrane separation of HPA catalysts was carried out at the same temperature under a pressure of pure argon of 30 at. in a stainless steel cell with a magnetic stirrer. The composite RO membrane with a thin polyamide skin [22] was used.

2.3. ANALYSIS OF PRODUCTS

The concentration of Fe(III)-containing HPA was determined with a Spekord M-40 spectrometer from the intensity of the absorption at 21600 cm^{-1}. Total concentration of iron in solution was determined by means of flame-photometry, while the concentration of NO_3^- by ^{14}N NMR. Signals of ^{14}N and ^{31}P NMR were registered at frequencies of 21.68 and 121.47 MHz. Chemical shifts were measured with respect to external references $NaNO_3$ and H_3PO_4.

Accuracy of the concentration measurements was ±5% for Fe, ±15% for NO_3^- and NO_2^-.

3. Results and discussion

The amounts of NO and O_2 absorbed via reactions (1) and (2) by $PW_{11}Fe^{II}$ and $NaNO_3$ containing solutions, do not depend on $NaNO_3$ concentration within the range 0.2–0.8 mole/l (table 1) and correspond to the reaction stoichiometry.

Hence, accumulation of NO_3^- up to the concentration of at least 0.8 mole/l does not suppress the reactions (1) and (2), and there is no need to remove NO_3^- from the reaction mixture after each cycle of reactions (1)–(3). It is sufficient to remove NO_3^- periodically, after its concentration reaches ca. 0.8 mole/l.

Note that NO_3^- is the only product of NO oxidation via reaction (2), as, after its completion, there is no ^{14}N NMR signals from NO_2^-. At the same time, for the reference samples containing 0.2 mole/l $PW_{11}Fe^{III}$ + (0.01–0.1) mole/l $NaNO_2$ + 0.4 mole/l $NaNO_3$ under argon atmosphere, the ^{14}N signals from both NO_3^- ($\delta = 0$ ppm) and NO_2^- ($\delta = 202$ ppm) have been observed.

Retaining ability of a membrane with respect to a solute is characterized by selectivity $S = (1 - C_i/C_i^0) \cdot 100\%$, where C_i^0 and C_i are concentrations of the solute in the initial solution and in the permeate, respectively. For the solution containing HPA $PW_{11}Fe^{III}$ in concentrations ranging between 0.005 and 0.24 mole/l and having pH between 2.4 and 3.6, the selectivity of the membrane with respect to the HPA was found to equal 97–99.5%. After fractionation with the membrane, the HPA composition remained unchanged (in particular, Fe^{III} ion was not lost from $PW_{11}Fe^{III}$), as ascertained by ^{31}P NMR of solution.

For the $NaNO_3$ solution with $[NaNO_3] > 0.2$ mole/l the selectivity S with respect to $NaNO_3^-$ did not exceed 60%. Marked difference between the selectivi-

Table 1
Effect of $NaNO_3$ concentration on the amount of NO absorbed at 20 °C by 10 ml of 0.216 mole/l solution of $PW_{11}Fe^{II}$ with pH 4.5–4.7.

$[NaNO_3]$, (mole/l)	[NO] absorbed (mole/l)	pH after reaction (2)
0.2	0.214	2.4
0.4	0.218	2.5
0.6	0.220	2.3
0.8	0.219	2.3

Table 2
Fractionation of HPA-NO_3 mixture. Three samples of permeate with the volumes 2.8, 2 and 2.6 ml were collected from the mixture with the initial volume 30 ml.

Sample	Volume (ml)	[HPA] (mole/l)	$[NO_3^-]/[HPA]$
Initial mixture	30	0.219	1.74
Permeate: sample 1	2.8	0.0113	62
sample 2	2	0.0321	20
sample 3	2.6	0.0714	9
Nonpermeate	22.6	0.286	0.9

Table 3
Relative amounts of NO absorbed in consecutive runs ($t = 20\,°C$)

Run number	1	2	3	4 *	5	6	7 *
$[NO_3^-]/[HPA]$	0.9	–	0.83	0.89	0.86	0.80	1.03

* Separation of NO_3^- from HPA with the membrane was carried out before runs number 4 and 7.

ties with respect to HPA and nitrate made it possible to eliminate efficiently the nitrate from the reaction mixture retaining the HPA in it (table 2).

The data of table 2 show that NO_3^- and HPA are indeed well separated. The loss of HPA upon a single contact with the membrane does no exceed 3% of its initial quantity. The pH of the permeate solutions was found to range between 2.8 and 3.2, i.e. the exceed slightly pH = 2.8 of the initial solution, thus indicating that Na^+ ions pass through the membrane to permeate more easily than protons.

To elucidate the possibility of multifold reuse of HPA in the NO absorption, a number of runs (1)–(3) with the accumulation of nitrate ions followed by their separation, were carried out. During each run in the course of reactions (1) and (2) pH reaches ca. 2.4. After completing the reaction (2), pH of the solution was adjusted with Na_2CO_3 to 4.5. Under such conditions H_2S reacts with HPA quantitatively by reaction (3), and hence if dosed properly, may be used as a reagent for the HPA absorber regeneration with no environment pollution.

Note that as checked in special experiments, the absorption capacity with respect to NO for HPA, separated by RO, remains unchanged within the accuracy of our measurements (table 3).

4. Conclusions

Thus, using the liquid phase process of NO and H_2S detoxication via the reaction $2NO + H_2S + 2O_2 \rightarrow 2HNO_3 + S$ in the presence of a heteropolyanion catalyst $PW_{11}Fe^{II}(H_2O)_{39}^{5-}$ we have demonstrated the potentialities of the membrane method in separation of a homogeneous catalyst from a soluble reaction product. One may expect that the use of membranes for this purpose will markedly influence the search of industrial processes based on homogeneous catalysis.

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